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100+ Years of Plastics. Leo Baekeland and Beyond

EDITED BY

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Foreword

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Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

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Preface

Historians have the habit of characterizing past ages in terms of materials. We have the Stone Age, the Copper Age, the Bronze Age, and the Iron Age, followed at some remove by the Dark Ages, which couldn't have been a good time to be around. There would be some justification for calling the 20th century the Age of Plastics. The establishment of General Bakelite Corp. in 1910 initiated an age in synthetic polymers that provided plastics, fibers, and elastomers for a multitude of uses. Perhaps the importance and ubiquity of plastics is best demonstrated by the famous scene from the 1967 movie *The Graduate* in which recent college graduate Benjamin is given the following one word of advice by Mr. McGuire, "Plastics" (*1*). McGuire goes on to tell Benjamin there is a great future in plastics. Screenplay writers Calder Willingham and Buck Henry probably intended the audience to believe that Benjamin was being tempted to sell out for mere financial success, but it has always seemed to us that this was good advice for its time and place.

This volume consists of written chapters taken from the presentations at the symposium "100+ Years of Plastics: Leo Baekeland and Beyond", held March 22, 2010, at the 239th ACS National Meeting in San Francisco. This symposium was organized by the ACS History of Chemistry Division (HIST) and cosponsored by the ACS Divisions of Polymer Chemistry (POLY) and Polymeric Materials: Science & Engineering (PMSE). The symposium celebrates the 100th anniversary of the formation of General Bakelite Corp., which was preceded by Leo Baekland's synthesis of Bakelite in 1907 and the unveiling of the Bakelite process in 1909. It is quite reasonable to use the synthesis of Bakelite as the starting point of the Age of Plastics. Indeed, Time magazine in its June 14, 1999, issue on the 100 most influential people of the 20th century chose Leo Baekeland and his Bakelite synthesis as the sole representative of chemistry (*2*). In a previous article detailing the merits of Baekeland's contributions, author Ivan Amato persuasively argued that the invention of this first true plastic transformed the world (*3*). Although a brief sidebar also mentioned Wallace Carothers and Nylon (*3*), Carothers did not make it into the final top 100 (*2*).

Leo Baekeland and Bakelite are the topics of the first four chapters of this volume. The first two chapters come from the perspective of Baekeland family members. Carl Kaufmann is related to the Baekeland family through marriage and is the author of the only full-length biography of Baekeland, published as a master's thesis from the University of Delaware (*4*). As a family member Kaufmann had access to all of Baekeland's papers. This first chapter (*Leo H. Baekeland*) is not only a biographical sketch, but an exploration of Baekeland's effect on the chemical industry. Hugh Karraker is Baekeland's great-grandson, and his chapter (*A Portrait of Leo H. Baekeland*) provides a family picture of the great inventor. Gary Patterson's chapter

(*Materia Polymerica: Bakelite*) goes into the history of Bakelite chemistry, while Burkhard Wagner's contribution (*Leo Baekeland's Legacy—100 Years of Plastics*) covers the history of Bakelite manufacture through time and space, finishing with a description of another Baekeland legacy, the Baekeland Award given through the North Jersey Section of the ACS.

The next chapters branch out somewhat. Les Sperling (*History of Interpenetrating Polymer Networks Starting with Bakelite-Based Compositions*) covers the improvements in interpenetrating networks. James Economy and Z. Parkar (*Historical Perspectives on Phenolic Resins* and *High-Temperature Aromatic Polyesters of p-Hydroxybenzoic Acid and Their Copolyesters*) follow the paths of resoles, novolaks, and related chemicals.

Leo Baekeland's invention brought forth a flowering of polymer products, so the remaining chapters are much more diverse. James Traynham (*In Their Own Words: Plastics Pioneers in the Chemical Heritage Foundation Oral History Archives*) tells the story of two pioneers in innovative fabrication techniques. Mehmet Demirors (*The History of Polyethylene*) tells the tale of probably the most widely used polymer of them all. The diversity of polymers is well illustrated by the fact that they can now be conductors. Remember that polyethylene was first valued as an insulator. However, this view of polymers as insulators changed with the work of Heeger, MacDiarmid, and Shirakawa on the conducting polymer polyacetylene, for which they were given the Nobel Prize for chemistry in 2000 (*5*). Seth Rasmussen describes the work of Weiss and Jozefowicz on the conducting polymers polypyrrole and polyaniline, respectively, which predated the polyacetylene work (*Electrically Conducting Plastics: Revising the History of Conjugated Organic Polymers*). Finally, Wen-Bin Zhang, Stephen Z. D. Cheng, and Mike Yaszemski take polymers well into the 21st century with their chapter (*Polymeric Biomaterials: A History of Use in Musculoskeletal Regenerative and Reconstructive Medicine*).

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While the chapters to follow are clearly a selective rather than a comprehensive survey of polymer history, they show something of the many paths possible after that crucial Bakelite invention. Read and enjoy!

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Chapter 1

Leo H. Baekeland

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Leo H. Baekeland (1863-1944) was a pivotal figure in the history of science and technology. As a chemist, chemical engineer and entrepreneur, he made "game changing" contributions in photography, electrochemistry, and polymer science. Bakelite, the product that made him most famous, provided the foundation for the modern plastics industry. Blending skills in theory and application, Baekeland demonstrated that what chemists had long hoped to be true was, in fact true: It is both possible and practical to create wholly new compositions of matter that will deliver properties that are unduplicated in nature. With Bakelite standing as proof, Baekeland opened new doors for generations of chemists who followed, and led them to discoveries and inventions that made possible today's synthetic polymers industry.

Leo Baekeland was a much-honored man. He was awarded the Perkin Medal (1916) and the Franklin Medal (1940). He was president of The Chemists Club (1904), of AIChE (1912), and of the American Chemical Society (1924). Universities gave him honorary degrees. "Time" magazine put him on its cover. The U.S. Patent Office awarded him 55 patents. He made a considerable fortune through his inventions, first in the field of photography and then, in far greater measure, in plastics. His flagship invention, Bakelite (date of invention: 1907), was not just another composition of matter: It was, instead, a material unlike anything seen before. It offered physical, chemical, and electrical properties not available in any other product, natural or man-made. Bakelite was inexpensive, easy to formulate and fabricate, and versatile in applications. As a result, it found its way into hundreds of products, and the General Bakelite Company grew into a

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large-scale enterprise that was much more than just another producer company in an emerging plastics industry: In effect, for the early decades of the 20th Century, Bakelite was the industry.

How did this come about? What led Leo Baekeland to his multiple successes in research and industrialization? His career story has long been known. Baekeland described his discoveries in numerous public lectures and technical articles, dating from the time of his early successes. However, historians interested in the "how" and "why" questions had to wait until the primary source materials came to light. That happened after his death, when his grandchildren made available all of the personal records that could be found in his home and laboratory. The surviving items include his laboratory notebooks, correspondence, personal day books (diaries), and photographic prints, film negatives, and early glass plates, many showing Baekeland's numerous famous friends. [These primary-source materials were first made available to this author, who used them for a biographical study written as a graduate school thesis in the history of science and technology. The family records have since been donated to the Smithsonian Institution in Washington DC. (See the last paragraph of this chapter for availability of the thesis in CDE format.)]

Extracted from Baekeland's personal records are the characteristics that seem to explain most of his accomplishments. Baekeland emerges from his own archives as a hard-working scientist who was as solidly grounded in chemistry as it was possible to be in his time. He shows himself to have been a disciplined, thorough experimentalist who taught himself to concentrate on carefully selected, limited questions in research. On many occasions, in letters and speeches, he claimed that his ability to focus was the major reason for his success. He was sharp in his criticism of other investigators who, in his judgment, set off on ill-defined missions, wandered off on tangents, and let "chaos" (his word) rule the laboratory.

Throughout his life, Baekeland retained a strong interest in theory. He kept in touch with research in various fields, reading numerous journals and remaining in close touch with compatriots at the Chemists' Club in New York City and in universities. In his own laboratory, however, he was strictly needs-driven: He chose his goal before devising a research strategy. He first convinced himself that the world did need (and would buy) a better photographic printing paper, a better varnish, or a molding material that would not melt. Only then did he ask whether he as a chemist might find a way to fill the need.

Always happiest when at his lab bench, and never pleased to be spending long hours in an office as a business manager, he nonetheless had a strong entrepreneurial drive: Research discoveries were not enough. He also wanted to transform his findings into useful products and processes, and he wanted to do this on his own terms, in his own organization rather than as someone's employee.

On the technical side, he earned success the hard way. He was not just an inspired tinkerer who happened to get lucky, but a chemist trained at the University of Ghent in Belgium, as a disciple of renowned professors. Nor was he a one-shot success, to be remembered for Bakelite alone. Years before Baekeland began his work on condensation polymers, the road that led to Bakelite, he had become a respected, recognized scientist and inventor. He had also become financially independent, by virtue of the invention and development of Velox, a black-and-white photographic printing paper.

Baekeland came to the world of science and technology at an ideal time for a man with his mindset and skills. There was a lot going on in science at the turn of the century, and in the application of knowledge to engineering and industrial technology. Baekeland's time was also the time of Thomas Edison (b. 1847), who ended up with nearly 1100 U.S. patents to his name. This was the time of the Wright brothers, who came up with their one big invention. It was a time when George Eastman was turning photography into a mass market. It was a time when inventors, entrepreneurs, and a new breed called industrialists were finding ways to mass-produce all sorts of basic materials and consumer products.

Before the beginning of the 20th Century, it was clear that the U.S. would be the largest industrial power and economic machine in the world. Its climb to the top was largely a reflection of America's ability to bring together diverse technical advances (some domestic in origin, some foreign), and merge them into large-scale manufactures. The auto industry is a case in point. The ingredients came forward one by one. Charles Goodyear showed how to vulcanize rubber (1840's) – remove sulfur, add heat, and you have a durable, waterproof product much more useful than natural rubber. The pneumatic tire became available, thanks to John Dunlop. High-quality steel was being mass-produced, largely because of the Bessemer process (1855). Charles Martin Hall and others had found a practical way to make a lot of aluminum, using electricity to extract it from bauxite ore (1889).

There was a cascade of results. If you have steel at a reasonable price, if you know how to make rubber tires that will hold air, if you can find someone who can build an internal combustion engine that will start when you turn the crank, and if the notion of an assembly line has come into view, then imaginative fellows such as Henry Ford have the tools they need to build automobiles for the masses. A mass-production industry came into being, and in the process changed the U.S. economy and the social structure of the nation.

The Road To Velox

Baekeland was a perfect fit for such a dynamic world, with the entrepreneurial spirit to capitalize on his technological abilities. Born in Belgium, he made it to the University of Ghent on a scholarship ---his family had no money – where he showed so much potential that he drew the personal attention of the senior professor of chemistry at the university, Theodore Swarts, himself one of Friedrich Kekule's students. Baekeland got a Ph.D *maxima cum laude ,* in 1884. The track to a Ph.D. is longer today than it was in Europe then, but even so, it is remarkable that Baekeland had his doctorate before he reached his 21st birthday.

Almost immediately, he turned his attention to making useful products. The first effort was in photochemistry. Baekeland as a teen-ager had been interested in photography, and as a freshly minted Ph.D. and instructor, he used his spare time to work on the dry-plate process for photographic negatives. These plates carried both a light-sensitive material and a coating of developer in dry form, plus a protective layer to prevent oxidation. After the plate was exposed, the photographer dunked it in water to activate the developer. That meant that there were no more hassles with plates that had to be coated wet just before exposure. Baekeland got a few patents and started a company to manufacture his plates (1887).

It failed. Unfortunately for Baekeland, the world of flat-plate photography, wet or dry, was ending. Baekeland learned the price of selecting the wrong target, a lesson he never forgot. Flexible-backed negative materials were coming into use. Film wrapped on a spool was "the next big thing" because it permitted cameras to be made smaller and more portable. In the United States, a plate maker named George Eastman read the trend line correctly and converted his business to flexible films. The rest, as they say, is history. Baekeland's little company in Belgium did not make that switch, and went belly up.

(As a point in passing, it should be noted that there was nothing unusual about an academic chemist like Baekeland turning his attention to commercial products. It is sometimes claimed that serious scientists disdain "mere applications" and wish to concern themselves only with theory. If that is true for some disciplines, at some times, it surely does not apply to the physical sciences in Baekeland's time. It was commonplace in the 19th Century, and well before, for academics to work on practical, everyday projects. To pick two of many examples, in chemistry Joseph Black, the famous professor at Glasgow, spent much of his time working with linen manufacturers to improve bleaching processes. Black was also a co-worker and mentor to James Watt. Watt had no formal education, and Black guided him in the study of heat and gases. Without Black's help, it is doubtful that Watt would have come up with the condensing steam engine. Going back a generation, Black's own teacher was a man named William Cullen, a physician [as was Black] and professor of anatomy. Cullen was also deeply involved in textile industry chemistry, to the point where some historians label him as a pioneer in what might be called industrial science. Thus Baekeland, in trying to make money in a venture outside academe, was following a well-worn path. Further, he never looked down his nose at people who got dirt under their fingernails. He respected competence, not academic degrees or social status.)

The failure of Baekeland's photo-plate company was a minor set back. At that point Baekeland had two other things on his mind: One was Celine Swarts, the professor's daughter. He married her. Then, with some money he had won as a prize, he took a trip to the United States, which he saw as the land of opportunity beyond anything available in his homeland. The move became permanent.

In the U.S., happily for Baekeland, his interest in photography quickly provided useful contacts, and got him a job. In New York City, Baekeland joined a camera club and made friends with the Anthony brothers. They made photographic materials (later, the Anthonys and Scovill joined forces to create the Ansco Company). The Anthonys introduced Baekeland to one of their consultants, a chemistry professor at Columbia, Charles F. Chandler.

Leo could not have found better company. Chandler seems to have known everybody connected to chemistry at the time. He was an organizer of the ACS and its president twice (1881 and 1889). He founded The Chemists Club in New York City. Chandler and his brother started what is said to be the first chemical journal in the U.S., "The American Chemist." Chandler and Baekeland hit it off immediately. Though there was a big age difference –- Chandler was senior by 27 years – Chandler saw young Leo as an exceptional talent. He took this young immigrant under his wing, and he and Baekeland remained close friends until Chandler's death (1925).

Chandler also happened to be an enthusiastic amateur photographer, and probably was responsible for the Anthonys offering a job to Baekeland. Leo certainly needed the work. He had arrived in the United States with little money to spare. The Anthonys put him to work in their lab, on both film emulsions and printing papers. He stayed there for about two years, and then left to set forth on his own as a consulting chemist. While that was no surprise, given Baekeland's independent streak, the loss proved expensive to the Anthonys. Had Leo stayed with the Anthonys for a few more years, Ansco might have become the owner of Baekeland's Velox printing paper. As it turned out, the company that ended up with that printing paper, and all the technology behind it, was Eastman Kodak -- after George Eastman came up with enough money to make Baekeland financially independent.

To a chemist, Velox may be as good a story as Bakelite. Velox wasn't just another black-and-white printing paper: Like Bakelite, it was a game-changer. Further, the creation of Velox shows Leo's habits of mind at work: Identify a need; figure out why earlier research has not filled it; find a better way to frame the questions; and ask them one by one.

At this point in time, the 1890s, photography had moved half way down the road to a popular, mass market. Flexible films, as noted, had made small cameras practical. Even an amateur could make pictures – or "attempts," as they were often called, successful outcomes being far from certainties. George Eastman had made it simple. Always a pitchman, Eastman came up with the slogan: "You push the button; we do the rest" (1888). When this slogan first came out, it meant that the customer made the exposures, and then sent the whole camera back to Eastman. The prints came back in the U.S. mail, along with a reloaded camera.

Photography then progressed to the point where customers reloaded cameras themselves, sending just the film out for processing. However, there remained the problem of making suitable prints. There were some fine printing processes available. Platinum prints had been around since the 1840s. Prints of this kind are durable and can be beautiful, but they were expensive and time consuming to make. (That is still the case.) There were more economical printing processes on the market -- costing less than 10 percent of the price of platinum prints -- but the papers used in each of them had severe shortcomings. The finished prints had poor tonal gradation; or the prints faded; or they were grainy, or streaky, or were marred by what were called "comets" running across the pictures.

Baekeland saw his chance: A better printing paper. He chose to try to do so via the silver chloride route. Though his past experience in plate making had been with bromide emulsions, he decided that for printing papers the chlorides would be a better bet. Bromide emulsions offered more speed – more light sensitivity -- but with the chlorides the sensitivity could be varied, and tonal qualities could be manipulated to give hard or soft prints – "flat" or "contrasty" in modern parlance.

Either route presented many hurdles. It took Baekeland many months of work, and many failures, before he came up with what he regarded as an acceptable result. As his laboratory notebooks show, on the way to the product he labeled Velox (1894), Baekeland prepared more than 50 formulas of the chloride type. Meticulously, he evaluated each end result for numerous variables – coatability, sensitivity, tonal qualities, shelf life, and permanence of image.

Even when he settled on the recipe that worked best, and was ready to produce paper in quantity, he was plagued by engineering problems. A key problem was humidity in the workplace. In the summer months, the Hudson River valley where he was working is sometimes hot and humid. Photo emulsions become sticky in those conditions., and there were days or weeks in which it was impossible to apply coatings properly. Baekeland's solution was to invent his own air conditioner: Outside air was passed over ice to precipitate out the moisture. Then the dry air was run through a heat exchange, to bring it up to the room temperature of the production area. This was not an energy-efficient process, but it worked. Baekeland found out later that this was an invention with many fathers. Other people in other industries had come up with similar solutions, but Baekeland did not know that at the time.

Baekeland started the Nepera Chemical Company to make Velox (1893). He found a financial backer, Leonard Jacobi, a scrap metal dealer from San Francisco. No one yet knows how Jacobi and Baekeland came together, but with Jacobi's backing, Baekeland was able to build a plant in Yonkers, NY. In a few years, Velox papers had earned a large market. Velox prints offered excellent tonal range with rich blue-blacks. There were no "comets." The prints were durable. Velox was offered in different grades, so that photo finishers could make acceptable prints from negatives that were thinner or heavier than normal.

Best of all, Velox was user-friendly and delivered predictable results. With most other printing papers of the time, the negative and paper were put in printing frames and exposed to daylight (contact prints: the enlarger was yet to come). That is a bit of a guessing game. How bright, exactly, is daylight? How long, exactly, should the printing frame be faced to the sun? Velox, by contrast, is what was called a "gaslight paper." It was designed to be exposed to an artificial light source, a source of known, constant intensity.

It was easy for technicians to use, for papers in the Velox family are relatively insensitive to the frequencies that came to be known as darkroom "safe lights." That was a huge plus, as the exposed printing paper no longer had to be processed in near-total darkness. Instead a technician could work in amber light, loading and exposing the printing paper, and then watching the image emerge in the developer, deciding whether further prints should be given longer or shorter exposure times.

Velox made it possible to set up a darkroom in the back of a drug store, and hire a teenager to come in after school to develop pictures and get them processed locally. Photography was not just for professionals anymore. It could be a hobby for Everyman. Millions of people responded, with Eastman pushing them on. Credit George Eastman for leading the way, but give a big assist to Baekeland for making the photofinishing business practical.

After Nepera turned the corner financially, Baekeland came to a decision point. He could expand the plant – the market told him to do that – and battle for market share with competitors and imitators, or he could sell out and go back to research. He elected to sell, hoping to get enough money to tide him over while he did research and consulting. Eastman was ready to buy. He paid well –reportedly $750,000 – but he got his money's worth: Velox made profits for Kodak for decades.

Baekeland did well, too. He netted enough from the sale to assure his independence. At age 36, he had enough money to buy a larger Victorian house overlooking the Hudson River in Yonkers, and to set up a laboratory in an outbuilding on the property. He returned to consulting. The outbuilding became his research headquarters and eventually the birthplace of Bakelite.

Electrochemistry

Baekeland's work in electrochemistry came on the heels of Velox. From the limited records on this period in Baekeland's life, it is clear that when he came into this field to consult, he concluded that it was in turmoil and he thus proceeded with caution. He chose able people to work with, and, characteristically, limited himself to well-defined problems where his skills could be used to good effect.

He first spent some months in Europe, visiting labs and conferring with others interested in electrochemistry. Then, returning to the United States, he elected to work on improvements in processes for making caustic soda and chlorine. Both had wide potential uses in industry. Baekeland teamed up with Elon Hooker and with the inventors of the Townsend cell, Clinton Townsend and Elmer Sperry (of gyroscope fame). It was the Townsend diaphragm cell that put the Hooker Chemical Company in business.

In principle the Townsend cell is not complicated. It is a tank in which brine is subjected to an electrical current to yield chlorine and caustic soda. Hydrogen is liberated in the process. The problems were that the early cells needed huge amounts of electric power (Townsend's first commercial cell pulled 2000 to 2300 amps); and the separated materials tended to recombine into materials that were not only unwanted, but that also ate the anode material at a fierce rate. Townsend had put a diaphragm between the anode and cathode, added a perforated, kerosene-filled jacket around the cell, and found a way to keep the chlorine, caustic, and hydrogen separate. Baekeland devised an improved diaphragm, cut down the corrosion losses, and improved the electrical efficiency.

Baekeland displayed here the wisdom of building a pilot plant: The conventional wisdom among chemical engineers is to avoid scaling up new technologies straight from the laboratory to the factory floor. Take a small step first. Build a pilot plant and then, as the saying goes, you can make your mistakes on a small scale, so that later you will make profits on a big scale. Utilizing Baekeland's improvements, a pilot plant was built in Brooklyn NY, and the improved Townsend process was debugged before a full -scale production unit was built in Niagara Falls (1905).

It was on this project that Baekeland also struck a blow for improved industrial health and safety practices. The early Townsend cells leaked catastrophic amounts of chlorine, to the point where workers were gagging. Baekeland insisted that emissions had to be reduced to tolerable levels. Several years later, when still a consultant to Hooker, Baekeland confided the following words to his diary:

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"…(T)he labor inspector should intervene and compel to obtain proper conditions, or shut down…. What's the use of having cheap bleach and cheap caustic at such a price? …What harm would it do if bleach was somewhat more expensive so as to observe proper sanitary conditions? Ten dollars a ton would accomplish great things and nobody would feel it." Protests like that did bring action. Over time, industrial safety and health practices got better, though in hindsight, it is fair to ask why it took so long.

The Road to Bakelite

Lots of other things interested Baekeland in his years as a consultant – the effect of X-rays and ultraviolet light on organic compounds, soybeans as a possible chemical feedstock, and the need for better ways to make nitrocellulose base for film. It is not clear when or why he elected to turn his attention away from those fields and concentrate on the phenols and aldehydes, the basic materials in Bakelite. It is known that Baekeland was familiar with work that had been done with these materials in Europe years before. Further, from his correspondence and diaries, we know that he saw a growing demand for better coating materials, to supplant shellac and tung-oil varnishes, and for improved plastic-like materials. He saw that phenols and aldehydes might be candidates for new products in those fields, but he was also aware that the European investigators going down that path had failed to find any useful formulations.

Plastics as a class of materials were not new, Cellulosic films and fibers (rayon) had existed for decades. Casting materials were available, notably celluloid. However, all such products had severe shortcomings. Even the inventor of celluloid, John Wesley Hyatt, admitted its deficiencies. (Hyatt won a $10,000 prize for celluloid, in a contest to find a material to make a better billiard ball, though it is not clear that he ever collected the money.)

Here again, Baekeland's first look at the field told him that there were obvious needs but that the research approach was chaotic. In Europe at least 10 investigators had worked on phenol-aldehyde combinations, including such eminent men as Adolf von Baeyer and his student Werner Kleeberg. Baekeland respected them but concluded that, at least in this case, their research approach was undisciplined and doomed to fail. In Baekeland's personal records, he was blunt in his criticism, speaking of other chemists almost as though they were alchemists throwing random ingredients into a cauldron, hoping to come up with gold. What emerged from the cauldron in question here, with phenol and aldehydes in the mix, was, by Baekeland's measure, just useless gunk.

To do better, Baekeland concluded that he would have to go back to Square One, and do research that met his own high standard. That is what he did. The great physicist, Richard Feynman, said something that applies here. Speaking at Caltech in 1971, Feynman set forth what is quoted to this day as Feynman's Dictum. He said that in science, the easiest person in the world to fool is yourself. Thus, he counseled, when an investigator launches a research project with an idea, the first thing he or she must do is to run the experiment that could prove the idea wrong. That is the intellectually honest thing to do, Feynman said, and it is also the way to avoid wasting everybody's time. Feynman put it well, but he was only recording what scientists such as Baekeland already knew. As the Bakelite chronicle shows, three quarters of a century before Feynman, Baekeland knew how to do research without fooling anybody, least of all himself.

Baekeland's first step was to repeat the phenol-aldehyde experiments done before. Where other scientists had failed to get usable products, Baekeland also failed, but he expected that, and began to isolate the pieces of the puzzle. With his lab assistants (he usually had one or two, but never a large number) he set up procedures for testing the raw materials, to be sure of their purity and consistency. (He had done the same on the way to Velox.) Then he set about the business of changing the variables and altering the recipes. He substituted cresol for phenol, and replaced formaldehyde with various relatives such as methylene acetate and a compound of formaldehyde and ammonia. He added bases. He took out the bases and put in acids instead, He changed heat, then pressure, then both. He made the changes not all at once but one at a time, so that whatever the result, he could relate cause and effect. This deliberate research approach finally led to HHthe "better answer" Baekeland sought, a condensation polymer he named "Bakelite." He created it by combining phenol and formaldehyde at precise temperatures and pressures.

Baekeland did not immediately run into the streets shouting "Eureka." He spent almost two years working out applications, and letting other people evaluate Bakelite. He wanted to be sure that this new material really was as useful, as manageable, and as versatile as it seemed to be. Only then, when he had investigated dozens of potential applications and had considerable field data in hand, did he make his formal announcement. He did that in 1909, in a technical paper delivered, appropriately, at his old stamping grounds, The Chemists' Club.

Three qualities made Bakelite special, and account for its claim to be the foundation stone of today's world of plastics. First, Bakelite had properties no earlier materials could match. Contrast it to the cellulosics. While celluloid can be molded and cellophane cast in sheets, the cellulosics are not tough or strong or naturally moisture resistant. They will not tolerate heat. They are attacked by many solvents. They catch fire easily. (There were disastrous episodes to prove that, including a nightclub with cellophane decorations that caught fire.) Bakelite, by contrast, is tough, stable and fire resistant. It is indifferent to most solvents. Once phenol and formaldehyde react to produce Bakelite, the final product will take heat up to more than 300 Fahrenheit. Cellulosics are thermoplastic: Heat Hyatt's billiard ball and it will soften like butter.. Bakelite is thermosetting. It stays solid until it is hot enough to char. It is an excellent electrical insulator. Products in the mold don't shrink or crack as they harden, and the material doesn't give off foul odors for hours or weeks, as some of the early plastics did. When Bakelite came along, it was clear that no other material in the world, natural or man-made, could match it.

The second reason for Bakelite's impact on the market comes from the ease in which it can be handled, and its versatility. It can be loaded with additives to yield products with different properties and colors, and the basic chemical reaction can be carried out in stages. These are big advantages. Kleeberg and others in Europe had come up with infusible resins, but they were produced in a single, direct reaction. With Bakelite, it is possible to start the reaction, stop in midstream, ship the material across the country and then later pack the Bakelite into a mold to finish the reaction --- with the end product being a camera body, distributor cap, lamp base, electrical insulator, telephone handset, or piece of costume jewelry.

Third, and perhaps most important to the long-term chain of history, Baekeland's Bakelite was the first to show that molecules can be successfully put together in ways that nature has never tried, to create compositions of matter never seen before, often with useful, unique properties.

Bakelite was not an end point for such synthetics: It was just the beginning. Following Leo Baekeland's example, scientists set out to make new materials for fibers, finishes, and molded products. In the decades that followed Bakelite's launching, scientists learned that they could accomplish still more, and design molecular structures to order, to deliver predictable chemical, biological and physical properties.

That brought a new sense of confidence to materials science, a sense of control, a belief not only in the analytical possibilities of science at the molecular level but the creative potential as well. This helped lead chemists to the other "polys" that have become so prominent in today's markets – the polyamides, polyethylenes, polyesters, polyacrylics, polypropylenes, polyurethanes, and so on.

Baekeland made a lot of money, both when he ran his company and when he sold it to Union Carbide (in 1939, by which time General Bakelite had merged, diversified, and grown into what was named the Bakelite Corporation). He used his wealth (a yacht, an estate in Florida, a camp in the Adirondacks [which his wife and family used, but which he visited only once], but he was not one to bask in luxury. At heart, he remained a research man, and he never stopped thinking about the next main chance. In the late years of his life, looking at the world of science, he was not thinking about condensation polymers or his other accomplishments at all. His mind went in other directions, to the ways he thought science might improve the human condition.

In 1934, 10 years before his death, from his estate in Coconut Grove, he wrote a letter to a friend, a lawyer in New York. In it, Baekeland said this: "If I had my life to life over again…. I would not hesitate to devote my best endeavors to biochemical research. The future of mankind depends on this subject."

He had a dark view of the world around him, saying in that letter that he despaired "… of the helter-skelter methods of our vaunted *homo sapiens*, misguided by … ignorance and … politicians. If we continue our ways… the human race may follow the road of former living races of animals whose fossils proclaim that they were not fit to continue."

But he did see a light at the end of the tunnel. The closing words in the letter are these: "Religion …laws …morals… not enough. We need more. Science can help us."

Note: A more extensive profile of Baekeland is available in the author's graduate school thesis, written in 1968. This is an unpublished manuscript, but single copies can be obtained in CD format, from the author.

Chapter 2

A Portrait of Leo H. Baekeland

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This chapter originates from a talk given at the History Symposium held at the 2010 spring meeting of ACS in San Francisco. It describes the L. H. Baekeland Project and reveals the progression of events and the exceptional qualities, which led Baekeland to become “the father of modern plastics.” The chapter continues with the acknowledgment of Baekeland’s achievements and concludes with a brief view of his descendants.

The Inspiration

At the 2010 spring meeting of the ACS in San Francisco, I gave a presentation on my great grandfather, Dr. Leo H. Baekeland. I began by showing a short sample of a documentary film I am producing called, “All Things Bakelite”. The following pages are based on the presentation and include noteworthy additions.

My mother, Céline Baekeland Karraker was one of Baekeland’s grandchildren. She inspired me to embark on a project to celebrate his life and work. She was very close to “Grand Papa” and his wife, Céline, known affectionately as “Bon Bon.” She told me stories of how her grandfather amused her by performing elementary chemical reactions in his laboratory. He imbued in her his love of nature (Figure 1) (*1*). He showed her how to collect sponges from his boat in Florida. She emulated his simple lifestyle.

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Figure 1. Baekeland at the Berlin Zoo (circa 1935).

From 1907 to 1932, Baekeland kept journals (now in the Smithsonian Institute) and my mother made extensive notes while reading all 62 of them. She intended to write a book based on these notes, but died before being able to do so. I read her notes and assured her I would try, in my own way, to honor our family's patriarch.

The L. H. Baekeland Project

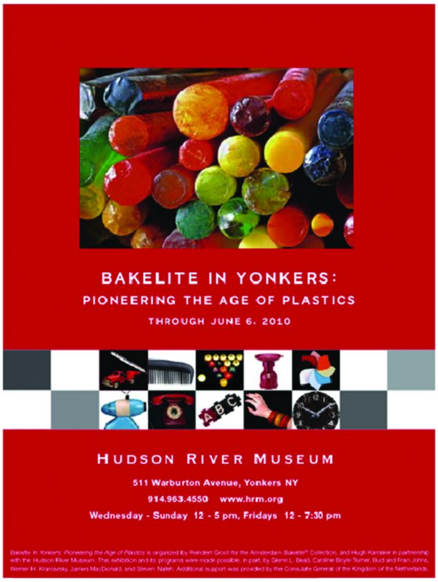
The 100th anniversary of the invention of Bakelite was being celebrated in 2007 in Ghent, Belgium, Baekeland's birthplace. The celebration organizers from The University of Ghent, Baekeland's alma mater, graciously hosted me. While in Ghent, I met Iwan Röpcke, the great grandson of a life-long friend of Baekeland's. Iwan and I co-founded the L. H. Baekeland Project. We collaborated on a script for a documentary film about Baekeland and his friend. After some failed attempts to produce the film, we put the script on the shelf. In 2009, Belgian producers accepted a script by a notable Belgian screenwriter. At present a production team is in place and partial funding has been obtained.

As I mentioned above, I am producing my own film about Baekeland and Bakelite in this country. I intend to make a one-hour version of the film to be shown on television – PBS or the Discovery Channel. The film would also be suitable for showing at chemical and plastics industry meetings and as part of high school and university curricula.

Reindert Groot, a Dutch film producer/director, who is also the founder/curator of the Amsterdam Bakelite Collection (*2*), is working on a documentary in the Netherlands with a working title of "Transatlantic Chemistry: Baekeland the Inventor of Bakelite".

The L. H. Baekeland Project includes a touring exhibition. The original exhibition was composed of Baekeland family artifacts and more than 350 items made of Bakelite selected from the Amsterdam Bakelite Collection (*2*). Most items from the past and some from the present included automobile and electrical parts, home appliances and office equipment, smoking and drinking paraphernalia and jewelry and toys. Advertisements on display billed Bakelite as “The material of a thousand uses”. Archival film, photos and other printed materials illustrated the history and chemistry of Bakelite, as well as the life and work of its inventor. For the past 2 years, the exhibition was shown in Redding, Connecticut, Saginaw, Michigan and Yonkers, New York (Figure 2). During the exhibition’s run in Redding and Yonkers, The New York Times gave it glowing reviews. The Smithsonian Institute in Washington, DC is considering an expanded and newly designed exhibition.

Also, integral to the Project, are presentations and “Talks with the Experts”. I have had the opportunity to give presentations at national and international chemical and plastics industry symposia. I have designed my talks to suit schools, museums and historical societies. In November 2009, I gave a presentation at the North Jersey Section of the American Chemical Society’s 2009 Baekeland Awards Symposium at Rutgers University. Later that month, I participated in the second bi-annual Baekeland Thermoset Symposium held in Antalya, Turkey. On that same trip, I was a guest at the 100th anniversary celebration of the founding of the first plant to manufacture Bakelite, in Erkner, Germany, in 1909.



Bakelite In Yonkers: *Pioneering the Age of Plastics* is organized by Reindert Groot for the Amsterdam Bakelite® Collection, and Hugh Karraker in partnership with the Hudson River Museum. This exhibition and its programs were made possible, in part, by Glenn L. Beall, Caroline Boyle-Turner, Bud and Fran Johns, Werner H. Kramarsky, James MacDonald, and Steven Nafeh. Additional support was provided by the Consulate General of the Kingdom of the Netherlands.

Figure 2. Poster used for the Bakelite exhibition in Yonkers, New York (2010).

Iwan Ropcke, Reindert Groot and I agree that the L. H. Baekeland Project appears, thus far, to be achieving its objectives – entertaining, enlightening and inspiring a wide and varied audience.

The Father of Modern Plastics Revealed

My greatest discovery about my great grandfather, linking him with other inventors and industrialists who stand out in history, was his courage to think outside the box, to take risks and to follow his passion. And these traits plus exceptional perseverance were formed at an early age.

In 1863, Leo Baekeland, son of Karel and Rosalia Baekeland (Figure 3), was born into the working class in a suburb of Ghent, Belgium. He was expected to continue in his father's trade as a shoe repairman, but his mother saw his potential and urged her husband to allow him a complete education. As a young student, he was passionate about photochemistry, working on glass plate emulsions. According to one story, he acquired silver nitrate by melting down the chain from the watch his father had given him. Another story tells how he put silver nitrate in the holy water receptacle at his family's church. Parishioners were shocked to find indelible black marks on their foreheads.

At the University of Ghent, Baekeland continued to exercise his rebel spirit by joining a student/faculty club, which scorned the predominant Catholic influences of the time and instead, espoused liberal policies and freethinking. Later in life, he became more conservative, but retained an open-mind. The club is still active today.

It is an accepted notion that a biography of Benjamin Franklin inspired Baekeland when he was a young student. Also, it is likely he dreamt of going to America – the land of opportunity.

After graduating the University of Ghent with the Belgian equivalent of magna cum laude, he had the audacity to marry his chemistry professor's beautiful daughter, Céline (Figure 4). Within the same year, he gave up what would have been a well-paid and respected academic career in Belgium, offered to him by his father-in-law, and took his young bride to America. Almost immediately, he sent her back to Ghent to be with her parents for the birth of their first child, Jenny.

Figure 3. Karel and Rosalia Baekeland.

Baekeland struggled in his career as a photo chemist and became bogged down with too many unfulfilling endeavors. Céline complained of being abandoned and he brought her back to America. But, after her fifth birthday, Jenny died of influenza. Shortly after this tragedy, the couple produced George and then, Nina. Later on in their marriage, the couple came to peace with each other – Baekeland achieving his potential and Céline becoming a success in her own right as a distinguished painter and a social activist.

Figure 4. Céline Swarts Baekeland and Leo H. Baekeland (1889).

As an example of risk taking, during the economic recession in the early 1890s, Baekeland teamed up with a wealthy financier to establish the Nepera Chemical Company in Yonkers, New York. Here, he perfected a photographic printing paper, which became Velox. In 1899, the company was sold to George Eastman of Eastman Kodak for $750,000. With his share of the profits, Baekeland bought Snug Rock, a mansion overlooking the Hudson River in Yonkers, and converted a barn on the property into his laboratory (Figure 5). Here he began experiments on phenol and formaldehyde.

Figure 5. Snug Rock.

As an example of Baekeland's foresight, soon after discovering Bakelite, he envisioned its many applications. This trait – vision – set him apart from other chemists working on similar experiments (Figure 6).

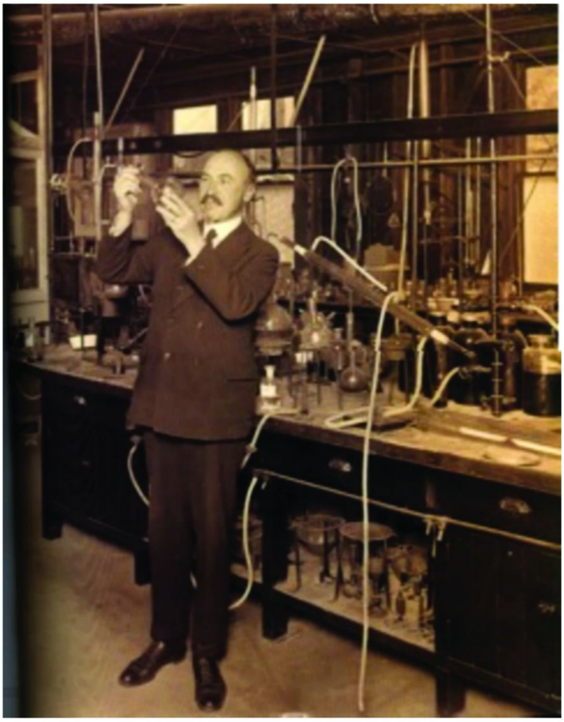


Figure 6. Baekeland in his laboratory.

Baekeland also developed a passion for motor cars (Figure 7). In 1905, one of his daring feats was to take his own car and his wife and children on a tour of Europe. They motored from Edinburgh, Scotland to Naples, Italy. He wrote a fascinating book about it called, “A Family Motor Tour Through Europe” published by the Horseless Age Press.

During the market crash of 1929, with a clear vision of the future of Bakelite, he took a huge financial risk, and began building the flagship Bakelite plant at Bound Brook, New Jersey.

Baekeland’s persistence and his willingness to take risks eventually brought him to Velox and Bakelite, and to his ultimate success as an industrialist. However, his journals reveal that he had mixed feelings about being the CEO of an international enterprise. For example, shortly after announcing his invention of Bakelite in 1909, he was compelled to fight numerous patent infringement cases. After winning one particular case, instead of penalizing his opponents, he offered to merge his company, the General Bakelite Company, with theirs, forming the Bakelite Corporation in 1923. He was a good businessman, but he preferred “the simple life” and shunned the trappings of fame and fortune.

Figure 7. The Baekeland Family at Snug Rock (circa 1900).

As Baekeland was nearing his eighties, his son, George, declined to take charge of the business. So the company was sold to the Union Carbide and Carbon Corporation in 1939. Union Carbide is now a subsidiary of the Dow Chemical Company.

Baekeland's Achievements and Associations

Baekeland was active in patent system reform, and at the request of President Woodrow Wilson, served on the US Naval Consulting Board. He was awarded hundreds of patents, and received many prestigious chemical industry awards and medals. He wrote and delivered hundreds of scientific papers and addresses. He was honorary professor of several universities. He was co-founder and an early president of The Chemists' Club and, in 1924 he was president of the American Chemical Society. That same year he was featured on the cover of Time Magazine (Figure 8). Baekeland became rich and powerful, but he never forgot his humble beginnings and throughout his life he was grateful for the advantages he was given in America.

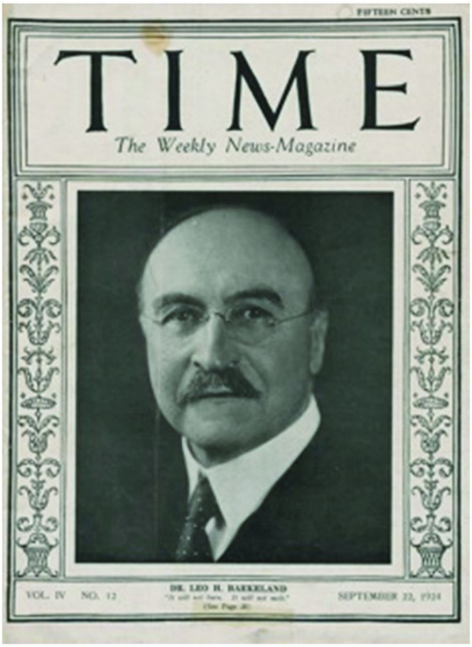


Figure 8. Time Magazine (1924).

The American Chemical Society gave its first National Chemical Landmark status to the "Bakelizer", Baekeland's early Bakelite-producing reactor. The "Bakelizer", the designation plaque, Baekeland's lab books, journals, photos and letters are all housed in the Smithsonian Institute's archives located at the National Museum of American History in Washington, DC. Also, biannually, since 1945, the American Chemical Society has awarded the Baekeland medal and a monetary prize to a promising chemist under the age of 40.

Baekeland's Descendants and His Later Years

Céline and Leo Baekeland's descendants through their son George and daughter, Nina, include 10 grandchildren and 21 great grandchildren. Some have achieved success in the arts, finance, education and healthcare. In the field of science, so far, a grandson was a psychiatrist and two of his great great grandsons are a marine biologist and a biochemist.

Biochemistry became of particular interest to Baekeland. In a letter written in 1934, he stated: "If I had to live my life over again, with free choice of work…I would not hesitate to devote my best endeavors to biochemical research. The future of mankind depends on this subject." In fact, Baekeland's dim view of mankind's future led him to become a proponent of eugenics before its brutal use by the Nazis.

Most of Baekeland's later years were spent in Coconut Grove, Florida (Figure 9) where he raised fruit trees and cruised the coastal waters on his yacht, "Ion". He died in 1944 and is buried in Sleepy Hollow Cemetery in Tarrytown, New York.

Figure 9. In retirement in Coconut Grove Florida with his motor sailer "Ion".

Acknowledgments

I want to thank Dr. E. Thomas Strom, Dr. Seth C. Rasmussen, and the American Chemical Society's Division of the History of Chemistry for inviting me to participate in the 2010 Spring ACS meeting and for inclusion in this distinguished publication.

References

1. Photos 1 and 3–9 are courtesy of the Baekeland Family archives.
2. Amsterdam Bakelite Collection, www.amsterdambakelitecollection.com.

Chapter 3

Materia Polymerica: Bakelite

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One of the most remarkable materials known to humankind was created from simple, inexpensive industrial chemicals: Bakelite. The present paper details the history of the invention of Bakelite and focuses on the attempts to elucidate its chemical structure.

Introduction

While some of the early paradigmatic polymeric materials were natural products, such as natural rubber, and some were chemical modifications of natural products, such as gun cotton (nitrocellulose), there was one material that was entirely synthesized from readily available small molecules and when fully processed had chemical and physical properties that were unknown for an organic material: Bakelite. The present paper will examine the creation of a coherent picture of the chemical structure of this remarkable material. Limitations of space and purpose restrict attention to a few main themes on the road to the current paradigm. Excellent monographs exist that explore the many scientific byways and dead ends associated with Bakelite.

The earth contains many interesting artifacts. One class of solid objects that have been known since antiquity is amber. It is very old tree resin and often contains embedded objects such as insects. It is constituted of carbon, hydrogen and oxygen in the ratio $C_{10}H_{16}O$. The composition is variable and depends on the age and thermal and pressure history of the resin. Heated amber will soften, but above 200° C it will burn. It is highly prized as a solid gemstone.

Younger tree resin deposits are called copal. These materials are often reacted with glycerol and suspended in oil and organic solvents to make a varnish. The highly heterogeneous nature of natural copals and their uncertain quality and availability provided motivation to create pure and consistent materials for use as varnishes or molding materials. The story of Bakelite is part of the larger tale of

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
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the search for better materials. A classic treatise on this subject is "The Chemistry of the Natural and Synthetic Resins" by T. Hedley Barry, Alan A. Drummond and R.S. Morrell (1926) (*1*).

Historical Chemistry before Baekeland

Phenol(hydroxybenzene) (C_6H_5OH) was discovered as a component of coal tar in 1834. However, many natural products exist that are modifications of phenol, such as resorcinol, catechol, hydroquinone, cresol and pyrogallol. In the 1870's Adolph von Baeyer (1835-1917, Nobel 1905) carried out systematic studies of the reactions of the phenol type molecules with aldehydes, such as acetaldehyde and benzaldehyde (*2*). The reactions were catalyzed by the addition of strong acids. Viscous solutions were obtained.

The generality of the reaction between phenols and aldehydes is now taken for granted, but Baeyer established it in the laboratory and was rewarded with his Chair at Munich.

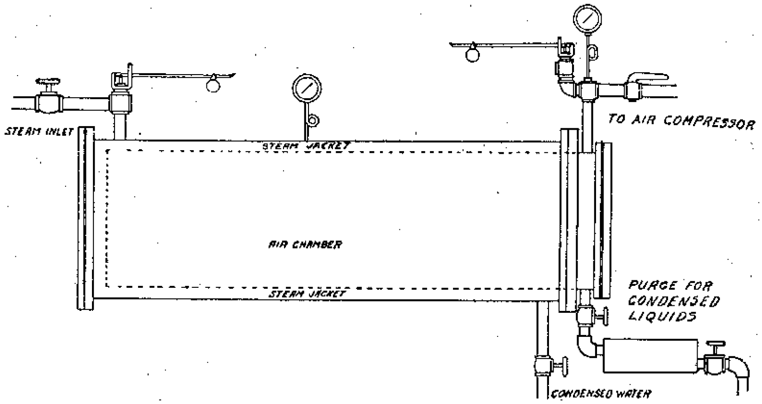
In the 1880's Arthur Michael (1853-1942) continued the study of these reactions and demonstrated the amorphous character of the resinous products. He also showed that the reactions could be catalyzed by base as well as acid (*3*). Eventually this work resulted in his election to the National Academy of Sciences (1889) and to appointment to Harvard University (1912). Michael is best remembered for his work on enolate ions, a subject central to the formation of Bakelite.

By 1890 formaldehyde could be obtained commercially as a 40% aqueous solution. Research in the laboratory of Emil Fischer was instituted by W. Kleeberg on the reactions of formaldehyde and phenol. When hydrochloric acid was used as a catalyst, a resinous product was obtained which carbonized upon heating without obvious melting. It was insoluble in most solvents and could not be analyzed into pure components of low molecular weight (*4*). A true polymeric solid had been formed, but little understanding was yet available.

An attempt to gain some understanding of the intermediate products in the reaction of phenol and formaldehyde was made by O. Manasse (*5*) and independently by L. Lederer (*6*). In this case, the catalyst was basic and could be caustic soda or other strong bases. The initial product was isolated and purified. It was found to be saligenin (o-hydroxybenzyl alcohol). Further work also isolated p-hydroxybenzyl alcohol. When saligenin was reacted in the presence of acid, it oligomerized into saliretin, a mixture of many substances. This pathway was known to Leo H. Baekeland (1863-1944).

Historical Industrial Chemistry before Baekeland

Although either added acid or base can catalyze the reaction of phenol and formaldehyde, the application of heat and pressure also produces a chemical reaction. W.H. Story devised a heated pressure reactor shown in Figure 1.



Courtesy Bakelite Corporation

Figure 1. High temperature and pressure reactor of Story.

The system was charged with commercial carbolic acid (phenol) and 40% formaldehyde solution. It was heated to 100^{0}C and stirred for 8 hours. The highly viscous solution was then drawn off and concentrated at temperatures high enough to drive off as much water as possible (> 100^{0}C). After the water was removed, further heating led to a solid product that was clear, tough and a good electrical insulator (*7*).

A classic reference for this story is “The Chemistry of Synthetic Resins” by Carleton Ellis (1935) (*8*). It is both encyclopedic and insightful with respect to scientific as well as industrial issues. Six chapters are devoted to phenol-aldehyde resins.

Baekeland Surveys the Field and Sells It

With substantial fundamental organic chemistry in print on the reactions of phenol and formaldehyde, Leo H. Baekeland set out to reproduce and extend this work with an eye to actual industrial production. He verified that saligenin could be synthesized and then polymerized to higher oligomers. He also explored the reactions between saligenin and phenol itself. This reaction produces substances of the diphenylol methane type.

Baekeland was especially interested in the infusible and insoluble resin produced by the method of Story. He did a more careful chemical engineering analysis of the process and showed that during the long “drying” stage, both water and phenol were expelled from the mass. The heterogeneous nature of this procedure produced a product with large stresses and distortions. The process is also so slow that no money would ever be made!

After surveying both acid and base catalysts, he concluded that acids lead to soluble, fusible resins of the Novolak type. These have important uses of their own, but Baekeland was more interested in producing insoluble and infusible products. Base catalysts were found to lead to these substances. While some recipes called for equimolar amounts of strong base to produce phenolate ions, Baekeland showed that using only catalytic amounts of ammonia produced the best product and the ammonia was far easier to remove than water or acids.

Baekeland organized his discussion of the reaction into three phases: an initial condensation product (dubbed A); an intermediate condensation product (dubbed B) and a final condensation product (dubbed C). The first two phases involved condensation and removal of water. The final product was almost pure oxy-hydrocarbon ($(C_{43}H_{38}O_7)_n$) with no remaining water or free phenol. The initial phase includes the range of viscosities from low to high, but is demarcated by the final formation of a brittle solid which melts when heated. The second phase involves the formation of an insoluble, but swellable, network. It can be molded under pressure. The final phase produces an entirely infusible and insoluble solid that is insensitive to all solvents. It can be heated to high temperatures (300^0C) without melting or charring, but it can be degraded by boiling concentrated sulfuric acid. It is a great insulator. The reactor is charged with equal amounts of phenol and formaldehyde and a small amount of alkaline catalyst. During the initial phase, the solution separates into a resinous phase and a dilute aqueous phase. If the resinous phase is then separated and heated at temperatures above 100^0C, it transforms into a porous spongy mass. This substance is of little or no commercial importance. Instead, the aqueous phase is drawn off and the reaction is continued at elevated temperature and pressure by the introduction of a chemically inert gas. The A phase can also be poured into a mold and then processed at elevated temperature and pressure in the “Bakelizer.” (The original Bakelizer is now at the Smithsonian Institution, but a good replica can be seen at the Chemical Heritage Foundation.) The specific gravity of the product is about 1.25 and is very hard. These outstanding properties are coupled with a very low price!

This story is well told in the classic report of Baekeland’s 1909 presentation to the New York Section of the American Chemical Society published in the initial volume of the Journal of Industrial and Engineering Chemistry (p.149) (*9*).

Baekeland on the Structure of Bakelite

Careful studies on the best stoichiometry for the production of Bakelite revealed that 7 moles of formaldehyde were needed for every 6 moles of phenol. The initial intermediates were ortho and para-hydroxybenzyl alcohol. Baekeland subjected his final product to elemental analysis and found the empirical formula given above. He traced the formation of various anhydrides as water was eliminated and removed.

His notion of the chemical structure of phase B in 1909 was consistent with general notions of the time, promulgated by chemists such as Fischer and Beilstein. Baekeland thought that the structure was a cyclic oligomer. The fascination with cyclic oligomers has persisted into the 21st century. The main argument seemed to be the absence of detectable hydroxyl groups and the measured empirical formula.

Baekeland continued his fundamental studies of Bakelite, even as he successfully brought the product to market. His efforts were rewarded in 1913 with the Willard Gibbs Medal of the Chicago Section of the American

Chemical Society. His acceptance address detailed his current understanding of the chemistry and structure of Bakelite and was published in the 5th volume of Industrial and Engineering Chemistry (p. 506) (*10*).

Baekeland continued to read all the available literature on phenol and formaldehyde reactions. The period before the First World War was the great age of speculation about Bakelite. One of the leading speculators was F. Raschig (*11*). Baekeland was careful to point out that when phenol is present in excess and acid catalysis is used, a very wide range of saliretin isomers are produced. These Novolak type resins remain soluble and fusible. He seemed to be aware that these were all oligomers of saligenin and that since phenol can react at three different positions on the benzene ring, a great multiplicity of products are possible for even low oligomers. Since the linkages between phenyl units are variable, the linear oligomers are incapable of crystallization. Since the actual mixtures obtained in the reaction are so heterogeneous, the resins remain amorphous.

The enormous amount of fundamental work carried out by Baekeland and his employees in the period from 1909-1913 led him to become very cautious in his assertions. He summarized all this work as follows:

"First: That these bodies are phenolic condensation products of formaldehyde, this condensation process having for result a corresponding enlargement of the so-called carbon nucleus of the molecule.

Furthermore, it is a well accepted fact that in these reactions, formaldehyde can be replaced by its many equivalents.

Second: That after the so-called condensation has taken place polymerization sets in, with the result that the molecules of condensation product form by aggregation or regrouping, so-called polymerized molecules of much higher molecule weight. This at once explains the higher specific gravity and contraction of the polymerized product.

If we go beyond these mere general theoretical conceptions and try to interpret the intimate chemical constitution of these bodies in about the same way as we are able to do with the relatively much simpler crystalline or volatile organic compounds, then our flights of fancy are justified to take as well one direction as another. If beginners in organic chemistry may be impressed to a certain extent by the proposed formulae, which try to represent the molecular structure of these refractory bodies, the experienced organic chemist will only consider them as a matter of very subordinate interest, and merely as a crude attempt to show one of the many ways in which the constitution of these interesting products might be explained, according to our rather insecure theoretical notions."

Baekeland praises Raschig for the ingenuity of his analysis of saliretin oligomers, but cautions against taking the highly specific cyclic structures too seriously. He also calls attention to the possibility of rearrangements of the substituted benzene core molecules during the reaction at high temperatures. While saliretin oligomers can produce interesting substances, only when excess formaldehyde is present is the ultimate insoluble and infusible Bakelite produced.

In order to produce a deeper study of the fundamental organic chemistry, Baekeland supported a graduate fellowship at Columbia carried out by H.L.Bender. The published version of the thesis appeared in the usual Journal in 1925 (*12*). The emphasis was on isolating and characterizing all the initial products of the reaction. Saligenin is crystallizable and was easily demonstrated. However, the mechanism of the formation of the benzyl alcohols was further elucidated by proposing phenoxymethylalcohol as the actual initial product. This substance undergoes rapid rearrangement to the benzyl alcohol. This is an example of a Claisen rearrangement. Either saligenin or the para-hydroxybenzylalcohol then reacts with phenol to produce phenoxy-p-hydroxyphenylmethane. This compound can, and occasionally does, rearrange to di-hydroxyphenylmethane. It can be crystallized and was isolated by Baekeland. The mixed product remains in the amorphous state. The measured molecular weight of both substances was 200 Daltons.

Baekeland then considered the further reaction in the presence of more formaldehyde and under basic conditions. Where could the reaction come from? He proposed that the formaldehyde attacked the methane carbon to produce an unsaturated molecule, a substituted ethylene. The vinyl monomer can then polymerize under the application of heat to produce high polymer. It is notable that in 1925 Baekeland is discussing seriously the polymerization of an organic compound. Work by Staudinger and by Carothers was only in its infancy. Perhaps the macromolecular paradigm was more widespread in the United States than in Europe!

Magnificent Studies of Megson

Soon after the publication of the monograph on natural and synthetic resins cited above, A.A. Drummond recruited N.J.L.Megson of the British Government Department of Scientific and Industrial Research to study the detailed pathways of the phenol-formaldehyde reaction. The basic philosophy was that if the proposed intermediates could be synthesized by rational organic methods, a clearer picture could be constructed. Megson was present at the birth of Polymer Science at the Faraday Discussion of 1936 and talked on phenolic resins. He followed the field avidly his whole career and published “Phenolic Resin Chemistry” in 1958. He was awarded the Gold Medal of the Plastics Institute.

One of the products of Megson’s research was an actual three dimensional model of the structure of Bakelite (*13*). He emphasized the importance of using true bond angles in full Cartesian space to gain an understanding of the highly contorted molecules. The picture is shown in Figure 2.

The course of the phenol-formaldehyde reaction depends on both the composition and the pH of the reaction mixture. H.S. Lilley studied the reactions of pure saligenin under acidic conditions (*14*). He proposed the formation of a benzyl cation by protonation of the alcohol and elimination of water. This highly reactive species then attacks the benzyl alcohol to form an ether. In mixtures of saligenin and phenol, the carbocation can attack phenol itself to produce a dihydroxyphenylmethane. The scheme is shown in Figure 3.

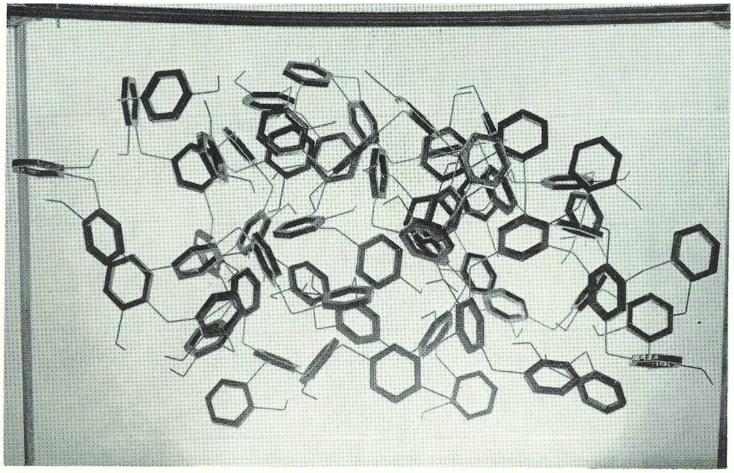
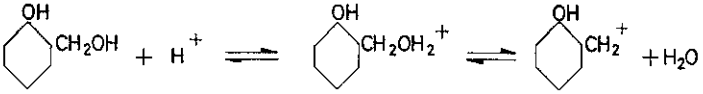


PLATE 3. *Model of phenolic resin* (*Reproduced by permission of Mr. E. G. K. Pritchett.*)

Figure 2. Three dimensional model of Bakelite due to Megson. Reproduced by permission of Mr. E. G. K. Pritchett.

Lilley first formulates the ionic mechanism thus:



followed by the reactions 1 and 2 below:

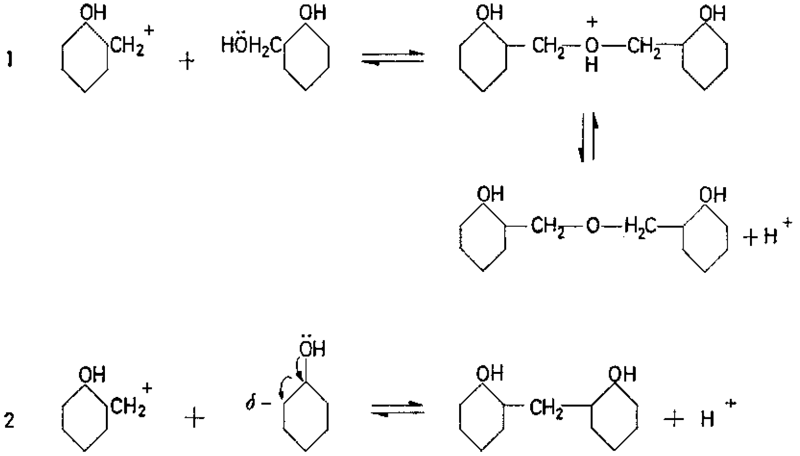


Figure 3. Reaction scheme of Lilley.

This route to the methylene bridged compound differs from that suggested by Baekeland. However, the importance of methylene bridged polyphenols in the structure of Bakelite was further strengthened by this work.

One of the crowning achievements celebrated in "Phenolic Resin Chemistry" was the kinetic study of Freeman and Lewis (*15*). The conditions were changed to strong base and the reaction was carried out with a large excess of formaldehyde. The actual concentrations of the reactants and products were measured during the reaction. The resulting graph shown in Figure 4 was very illuminating.

Under basic conditions, all the phenol is used up. The formation of the substituted phenols at the 2,4 and 6 positions proceed at varying rates, but the trisubstituted phenol achieves quantitative concentration after 40 hours. The reaction does not stop at this stage but continues with oligomerization of the polyfunctional phenols. Pairs of methylol substituents combine to produce a methylene bridge and a molecule of formaldehyde. This process can continue until all the possible sites are consumed and excess formaldehyde is expelled. The product is then a highly crosslinked network.

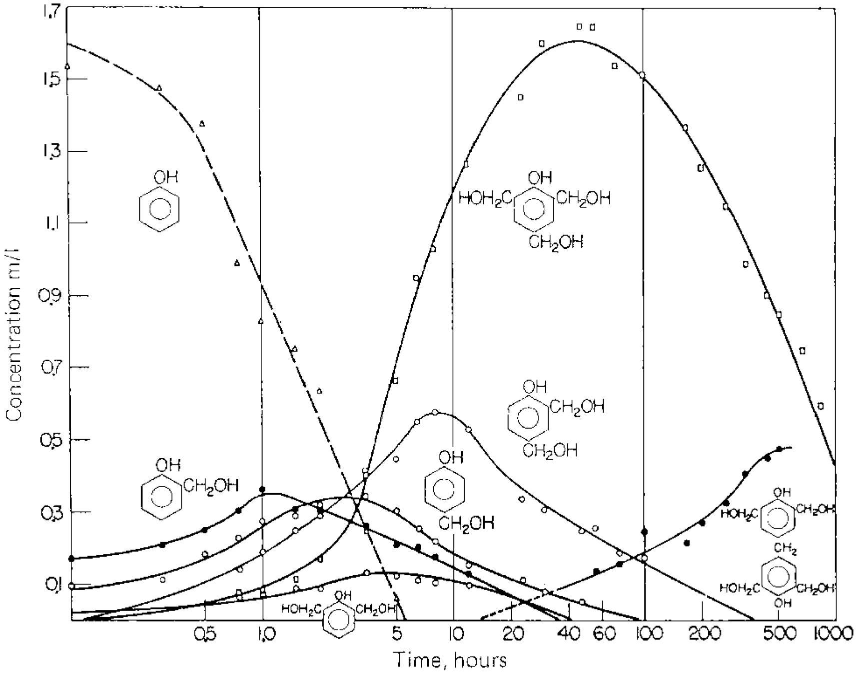


Fig. 3.2. Change in concentration of phenol and methylol phenols with time[31] (formaldehyde and phenol at 30 °C with NaOH catalyst)

Figure 4. Kinetic results of Freeman and Lewis (15).

Bakelite in Germany and New Jersey

The first actual plant to manufacture Bakelite under the Baekeland patent was in Germany (1910). When Baekeland sold his company, it was acquired by Union Carbide in Bound Brook, New Jersey. In 1985, Andre Knop (Frankfort, Germany) and Louis Pilato (Bound Brook) published a 75th Anniversary monograph on "Phenolic Resins" (*16*).

The themes introduced above are summarized nicely in this volume. When phenol rich mixtures are reacted under highly acidic conditions (pH=1-4), linear or slightly branched resins are produced with methylene bridges: these are called Novolaks. Molecular weights in the range of 200-2000 are included. Novolaks are soluble and fusible resins, but they can be hardened by reaction with formaldehyde under basic conditions, usually by the addition of hexamethylenetetramine. Resols are produced by reactions that are formaldehyde rich under basic conditions (ph>7). They can be hardened by heat and pressure into classic Bakelite.

The fact that fully cured Bakelite is insoluble and infusible allows a wide range of applications where both thermal and mechanical stability are important. It is still used in the manufacture of insulators and increasingly in expensive art and jewelry. The best Bakelite competes with rare and expensive amber in the gem market. But because it is synthesized from inexpensive ingredients, Bakelite remains affordable and available. It is truly part of the Materia Polymerica.

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In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Chapter 4

Leo Baekeland's Legacy – 100 Years of Plastics

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Leo Hendrik Baekeland (1863-1944) was one of the icons of the American Industrial Age, and a source of inspiration for later entrepreneurs in industry and academe. After uprooting his academic career at the University of Ghent at age 35, he emigrated to the United States to reinvent himself in a host of diverse roles. We can list him as industrial researcher, successful inventor, CEO and proprietor of a large commercial enterprise, President of numerous technical societies including the ACS (1924), member of governmental commissions, educator, and founder of the modern plastics industry. His legacy spans multiple dimensions. The invention of Velox and Bakelite contributed to the formation of the 20th century consumer society. His success encouraged competitors to develop other commodity plastics (polyethylene, nylon, polyurethanes) within a short time. The resin production processes and extrusion, blending, and lamination technologies developed at the Bound Brook Bakelite plant were adopted by competitors for other plastics. As founder of the Bakelite company he instituted a successful discovery and commercialization methodology that would still be recognizable in the invention of novel polymers at Bound Brook throughout the next 80 years. Finally, the Baekeland Award established in 1944 after his death continues to inspire young researchers to emulate his accomplishments in fundamental and applied research.

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Introduction

Few inventions have captured the public's imagination as much as plastics, and few inventors have faded from public memory as thoroughly as Leo Hendrik Baekeland. A cursory googling yielded 32,000,000 hits for 'plastics' and 14,000,000 for 'Bakelite', versus a paltry 68,000 hits for Leo Baekeland. In contrast, contemporaneous industrial giants such as Thomas Edison (1,960,000 hits) and George Eastman (664,000 hits) have remained in public memory to a much greater extent. Unlike Henry Ford, the DuPonts, or Herbert Dow, Leo Baekeland did not continue to guide the enterprise through his descendants, who have chosen instead to lead anonymous lives (*1*, *2*). A member of the extended family did write an outstanding historical monograph on the inventive process and the detailed technical steps leading to Velox and Bakelite (*3*, *4*). This 1968 graduate thesis project has not received wide dissemination. A great-grandson on the maternal side has recently begun to revive public interest in Leo Baekeland through the Baekeland Project, a series of lectures (*5*), a documentary film (*6*), and a traveling exhibit illustrating the historical significance of Leo Baekeland's accomplishments and the far-ranging diversity of Bakelite objects (*7*, *8*). Both of these family members participated in this special symposium on 100 Years of Plastics.

Leo Baekeland would not have minded that his name has faded from public consciousness. Biographies (*1*, *3*, *9–14*) paint the picture of an obsessed inventor, an outsider glorying in his differences but still eager to socialize with his scientific and business peers, a genius in science and technology so obsessed with his work that he temporarily shipped his young wife back from New York to her parents in Belgium while he worked out his first invention, and later expressed his appreciation that she took on the load of running the family for the rest of her life. This prototypical, far-seeing founder of a new industry soon resented the commitment of time required by business life, which kept him away from the many other activities that he deemed more important. In later life he would become a near recluse.

Legacies

Iconic photographs depict Leo Baekeland in the garb of a 19th century professor, as a prosperous but clearly tired businessman, and as a 20th century inventor (unencumbered by 21st century OSHA regulations). There is no doubt from his writings which of these roles he relished the most, and which the least (Figure 1).

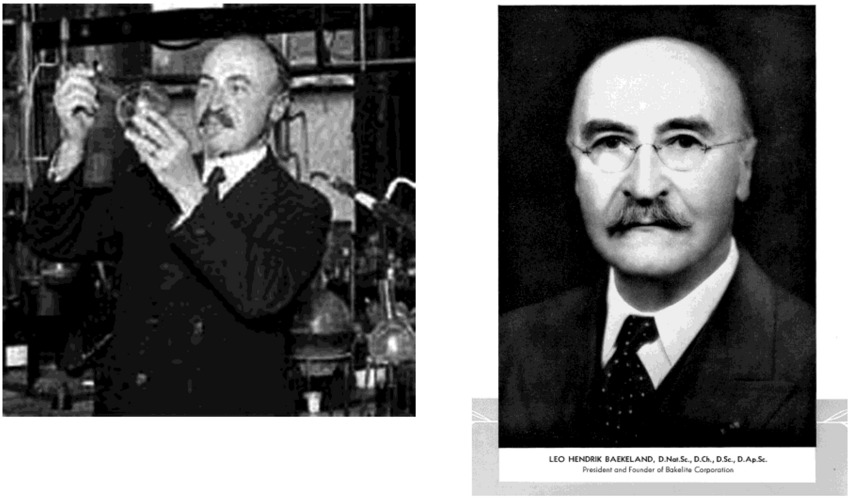


Figure 1. Leo Baekeland as scientist (without protective equipment) and as well-credentialed businessman / founder. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

But we in the early 21st century are indebted to Leo Baekeland's undertakings in all three roles. His scientific insights, technical breakthroughs, educational endeavors, and world-scale commercialization of the first man-made plastic all contributed to the world in which we live. We are indebted to Leo Baekeland when we pick up an old family photograph depicting great-grandparents that we never met, when we enjoy the music coming from our radio or iPod, and when we tinker with the electrical system of our car engine. The integrated circuits in our camcorder might have been laid down using phenolic resists. A piece of Bakelite, a component in the heat shield of the Galileo spacecraft, now rests on the planet Jupiter; two more are leaving the solar system on board of the Voyager space crafts. And Bakelite was in the first atomic bomb.

Middle Class Lifestyle

Leo Baekeland's legacy spans several dimensions. We in academe or industry pay tribute to Leo Baekeland as one of the founders of the second industrial revolution whose work initiated waves of technological developments that are still spreading, and have turned into tsunamis. As far as the public was concerned, his enabling contributions to the new middle-class lifestyle of the 20th century were so important as to rate a cover story in *Time Magazine* (*15*), and a listing in the more recent Time 100 The Great Minds of the Century ("transformed the world") (*16*).

Figure 2. A Midwestern family snapshot (early 1950ies), with Velox trademark still in use. Courtesy and with permission of Dr. Marie Borzo.

Velox

Sociologists point to the seminal importance of George Eastman's camera (*17*). Baekeland's contribution was Velox paper, a combination of paper backing and applied coating that allowed processing and copying of photographic images in dark rooms on large scale, at high quality, and low cost (*3*, *14*). Before the advent of the camera, only the rich or powerful elite sitting for painters had the privilege of being immortalized.

I am in the process of digitizing untold hundreds of photographs from family albums and personal scrap books dating back to before World War I. Although the people depicted in these photographs were poor by modern standards, they could afford to snap seemingly innumerable pictures that documented births, deaths, and intervening private joys and pains within their family. At Christmas time, many copies of photos were sent out to far-away relatives and friends that one did not expect to see ever again. Descendants admire pictures of little girls that the mind remembers only dimly as very aged great-grandparents. Many of the prints up to the early1960ies are stamped on the back with the 'Velox' trademark (Figure 2), even though the chemical formulation had changed since Baekeland's day (*18*).

Together, Baekeland and Eastman have helped us to document our lives. The photographic prints we owe to them serve as memorials to the continuity of our families throughout time and space. No wonder George Eastman was willing to pay Leo Baekeland a fortune for the rights to Velox paper (*3*, *4*, *9*). 'Preserve your memories' (*19*), indeed.

World of Plastics

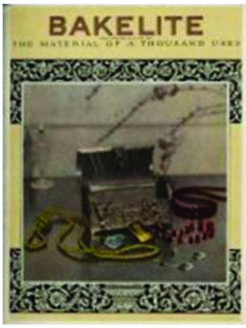
While the upper classes were already sneering at '*cheaplastics*' during the roaring 20ies, the average American was eagerly reaching for the fruits of technological breakthroughs that these new raw materials made feasible (*20–22*). The emerging electrical industry was furnished materials which were easy to mold, heat-stable, insulating, long-lived, and inexpensive, so that the generation and universal distribution of electrical power became feasible. Electrical lines strung to apartment houses fed radios, refrigerators, toasters, telephones, and later the first TV sets – all of which were molded from Bakelite resin. Carving these objects laboriously out of wood at an industrial scale was simply not an option. The versatile Bakelite materials combined some of the most important positive features of wood, ceramics, or metals in a lightweight and readily moldable form that could be mass-produced as quickly as applications could be dreamed up, and sold for less than anyone could have imagined. The host of industries that arose to serve the new consumers began to develop and produce a never-ending torrent of products made from the 'material of a thousand uses'. A walk through the traveling exhibit of Bakelite objects makes us marvel at the dizzying range of objects that could now be produced on large scale and at low cost (Figure 3,4) (*22*). And the upper classes were right, there were indeed deplorable lapses in taste brought on by an emphasis on function and cost over aesthetics. But industrial designers and artists were soon drawn to the possibilities inherent in these new plastic materials (*23*). The results of their endeavors are all around us, perhaps appreciated only when our attention turns to them in museum exhibitions (*7*, *24*), art books (*25*), or craft fairs (*26*). For the first time in the history of the world, the common man could enjoy the lifestyle of a king, as shown in the infomercial "To Shape Tomorrow", produced by the British Bakelite Limited sometime in the 1930ies (*27*).

20th Century Industrial Revolution

Plastics Industry

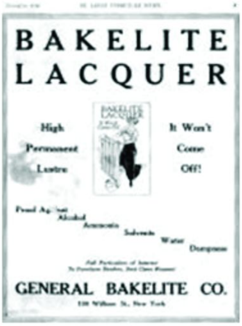
For the industrialist, Baekeland's legacy lies in the opening of the doorway leading to the modern plastics industry. Once the commercial success of the Bakelite technology was demonstrated, world class corporate competitors could justify their own gambles on divergent technologies despite the ravages of the Great Depression. Examples such as high pressure polyethylene (1933, ICI), nylon (1935, DuPont) and the various polyurethanes (1937, Bayer) readily come to mind.

Figure 3. Some examples from the cornucopia of middle-class objects made from Bakelite. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

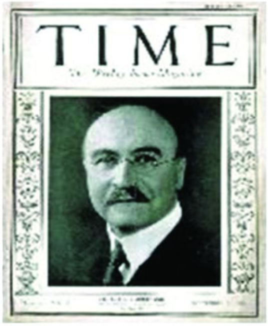


Bakelite catalogue
1920ies, USA

Advertisement for a propeller
made of Bakelite-Micarta
USA 1920



Advertisement for wood
lacquers USA 1912



Time cover
September 22, 1924

Bakelite advertisement
1920ies, USA

Figure 4. Early ads for various Bakelite products. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Plastics Process Engineering

Engineers within the Bakelite Company held with the thesis that Baekeland's true legacy should be found in polymer process technology rather than polymer science or chemistry. Combinations of phenol and formaldehyde were after all well-known curiosities when Baekeland began his experimentation (*28*). It was process technology, specifically high pressure reactions combined with controlled heat removal on an industrial scale, that led to commercial production of Bakelite resins. Hence the iconic Bakelizer (*29*), now in the Smithsonian collection. In their opinion, the host of process technologies developed to prepare these varied resins and varnishes were the truly inventive steps. At this point, molding and extrusion engineers as well as materials scientists would protest that the truly inventive step for which Baekeland should be remembered lay in the technologies that had to be perfected in order to turn raw resin into the final molded articles, sheets, laminates, and composites (*20*). All these advances in production technology leading to the final articles of commerce were proudly shown to the world by the Bakelite Company in the film documentary *The Fourth Kingdom,* which was narrated by the famous Mr. Lowell Thomas himself (Figure 5) (*27*).

Industrial Management

As with the initial commercialization of Velox (*3*, *4*), Baekeland quickly realized that contemporaneous production practices and doctrines were not up to the demands of the Bakelite process. Molding and extrusion skills required to convert resin into articles of commerce were also lacking in the outside world. Although he had wisely planned to step back, license Bakelite manufacture to other companies, and continue his work in the role of the R&D resource (a role befitting the former professor), general incompetence all around him forced him to undertake resin manufacture himself- first in his garage, and later in loaned quarters in Perth Amboy, New Jersey (Figure 6) (*30*). Valuable research time was being usurped by plant issues and the need to deal with the competitors that were springing up around the world, seemingly just to violate the patents which he had wisely obtained all along the path of his research. He dealt with these competitors by co-opting them in various ways and by assembling his management team from among the best of them (*9*). He was not encumbered by an ego that sought to vanquish others, so that his firm was not driven into the ground by issues of pride or jealousy that destroyed so many other founders.

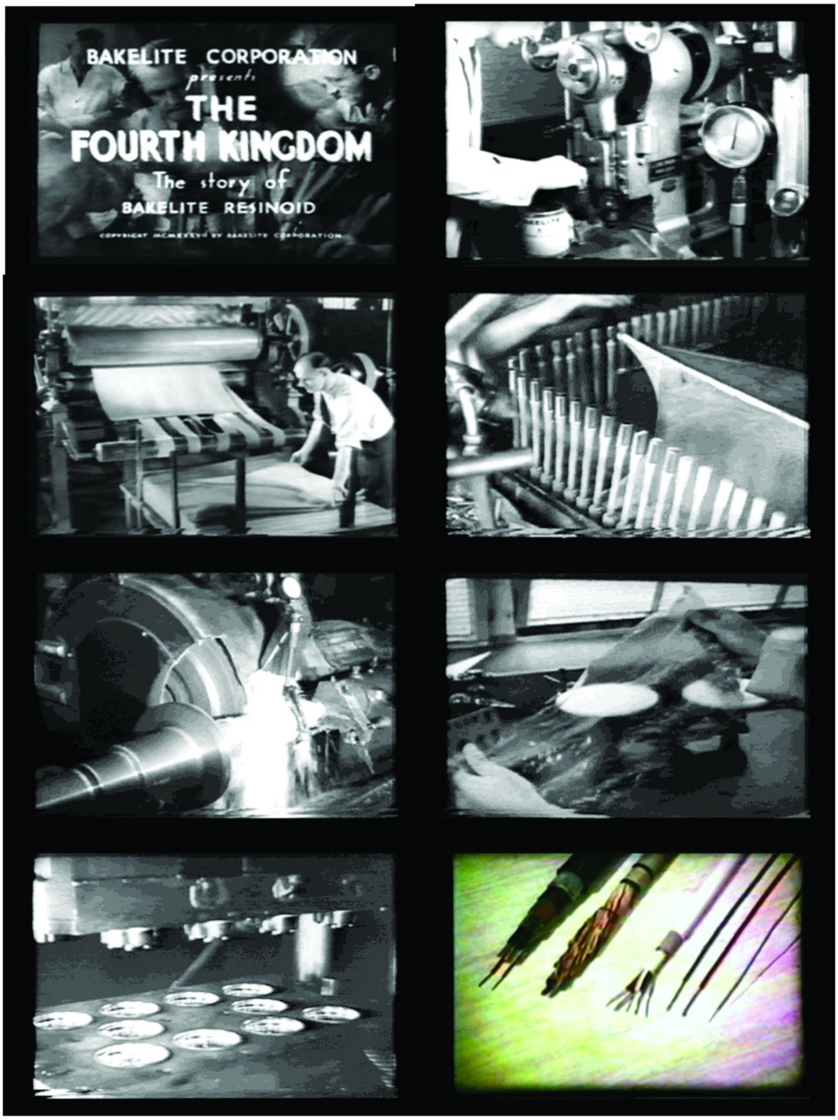
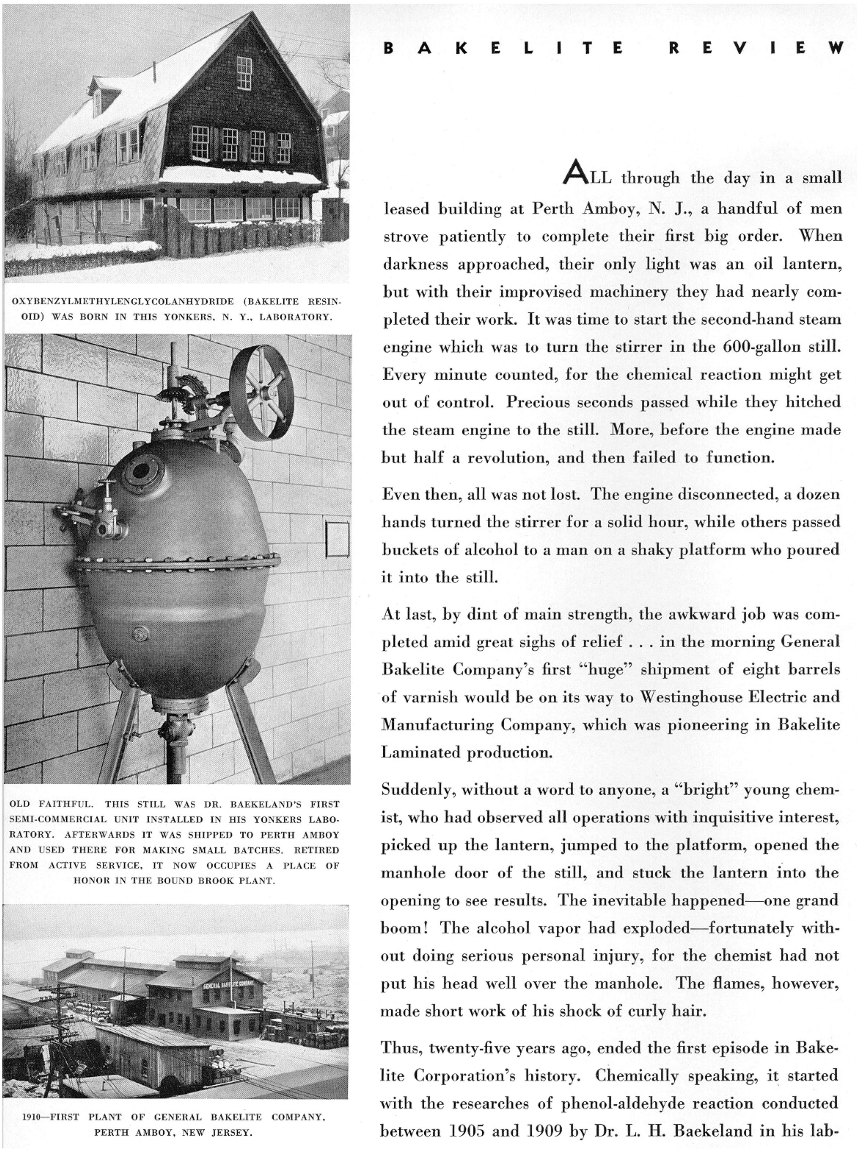


Figure 5. Some stills from "The Fourth Kingdom" and "To Shape Tomorrow", describing industrial processes and product applications. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.



BAKELITE REVIEW

OXYBENZYLMETHYLENGLYCOLANHYDRIDE (BAKELITE RESINOID) WAS BORN IN THIS YONKERS, N. Y., LABORATORY.

OLD FAITHFUL. THIS STILL WAS DR. BAEKELAND'S FIRST SEMI-COMMERCIAL UNIT INSTALLED IN HIS YONKERS LABORATORY. AFTERWARDS IT WAS SHIPPED TO PERTH AMBOY AND USED THERE FOR MAKING SMALL BATCHES. RETIRED FROM ACTIVE SERVICE, IT NOW OCCUPIES A PLACE OF HONOR IN THE BOUND BROOK PLANT.

1910—FIRST PLANT OF GENERAL BAKELITE COMPANY, PERTH AMBOY, NEW JERSEY.

ALL through the day in a small leased building at Perth Amboy, N. J., a handful of men strove patiently to complete their first big order. When darkness approached, their only light was an oil lantern, but with their improvised machinery they had nearly completed their work. It was time to start the second-hand steam engine which was to turn the stirrer in the 600-gallon still. Every minute counted, for the chemical reaction might get out of control. Precious seconds passed while they hitched the steam engine to the still. More, before the engine made but half a revolution, and then failed to function.

Even then, all was not lost. The engine disconnected, a dozen hands turned the stirrer for a solid hour, while others passed buckets of alcohol to a man on a shaky platform who poured it into the still.

At last, by dint of main strength, the awkward job was completed amid great sighs of relief . . . in the morning General Bakelite Company's first "huge" shipment of eight barrels of varnish would be on its way to Westinghouse Electric and Manufacturing Company, which was pioneering in Bakelite Laminated production.

Suddenly, without a word to anyone, a "bright" young chemist, who had observed all operations with inquisitive interest, picked up the lantern, jumped to the platform, opened the manhole door of the still, and stuck the lantern into the opening to see results. The inevitable happened—one grand boom! The alcohol vapor had exploded—fortunately without doing serious personal injury, for the chemist had not put his head well over the manhole. The flames, however, made short work of his shock of curly hair.

Thus, twenty-five years ago, ended the first episode in Bakelite Corporation's history. Chemically speaking, it started with the researches of phenol-aldehyde reaction conducted between 1905 and 1909 by Dr. L. H. Baekeland in his lab-

Figure 6. History of Bakelite production at the first plant (Perth Amboy, NJ). Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Physical Legacy – The Bound Brook Bakelite Plant

Construction and Expansion of the Bound Brook Bakelite Plant (*31–34*)

The first expansion into larger, untested quarters has been the doom of many a young business. Despite continuing merger and licensing activities that increased supply, the Perth Amboy production facilities were becoming inadequate as demand for Bakelite surged in the Roaring Twenties. Baekeland finally had to make an all-or-nothing gamble on a large-scale production plant and R&D center, and chose to build a grass-roots facility in the isolated orchard country just outside of Bound Brook, New Jersey. The 80 acre Bakelite plant taking shape in 1930 near the banks of the Raritan River had been envisioned in the exploding markets of the 1920ies at a scale that could supply the entire US with a large spectrum of Bakelite resins and molded products, with a power plant and transportation hub to match (Figure 7, 8). However, the construction of the plant (*35*) began just as demand for plastics appeared to be collapsing along with the rest of the US economy during the early Depression years (*3*). The rushed redesign of the plant (*36*) allowed the enterprise to survive, and to flourish (with further redesigns and multiple expansions) as the economy began to improve in the mid-1930ies (*37*) before dipping back into Depression. From a startup with 270 workers ("three times as many as initially needed" (*34*)), an expansion of the work force to 745 workers was required by 1938, when production reached a record with total sales of the Bakelite Company exceeding 50 million pounds for the first time. Profitability however lagged behind, initially due to the depression, and later due to the inevitable slide of the Bakelite product line from a specialty material to a commodity product even as new production records were being set. Pictures of the plant were disseminated all over the world, and probably became the starting point for the design of plants by competitors who reemerged once Bakelite patents began to expire. The design of the plant was versatile enough to permit a huge increase in production of phenolic, styrenic and vinyl resins by the time the Second World War broke out. The Bakelite subdivision of Union Carbide was reported to be the largest plastics organization in the world by 1941.

Business appears to have continued in unbroken continuity after the takeover by Union Carbide (itself assembled from diverse chemical and material science companies) (*38*). Union Carbide had been the key supplier of petrochemical raw materials to the Bakelite company. Other reasons for the purchase were the close business relationship between the two companies throughout the existence of the Bakelite plant, the obvious need for consolidation of the industry, and truly synergistic possibilities for future developments and business growth. The chemical arm of Union Carbide (*38*) was centered on the Kanawha Valley in West Virginia, where the company had pioneered in the development of the petrochemical industry, and was pioneering in the commercialization of other resins (vinyls, polyethylene) (*39*). Historical sources unanimously considered the integration of the Bakelite Company into the Union Carbide fold to be highly beneficial, and truly synergistic (*40*). Expansion of the plant into new polymer areas continued throughout WW II (Figure 9), with some 2,900 employees working at Bound Brook by 1947.

The Swayze orchard farm (early 1930).

Plant about to open while construction continues (Winter 1930/31).

Bakelite plant at time of sale to Union Carbide (1938). Facing Northeast. Ready for WW II. Note absence of Suburbia.

Figure 7. The Bound Brook Bakelite Plant. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

George Baekeland (left) with visiting Leo Baekeland (center).

Left: Visiting Nippon Bakelite delegation

Below Left:
Plaque for the boss from the "Old-Timers Organization" (1938!).
Below Right:
"Jack, Union President 1940ies".

GREETINGS TO DR. LEO HENDRIK BAEKELAND

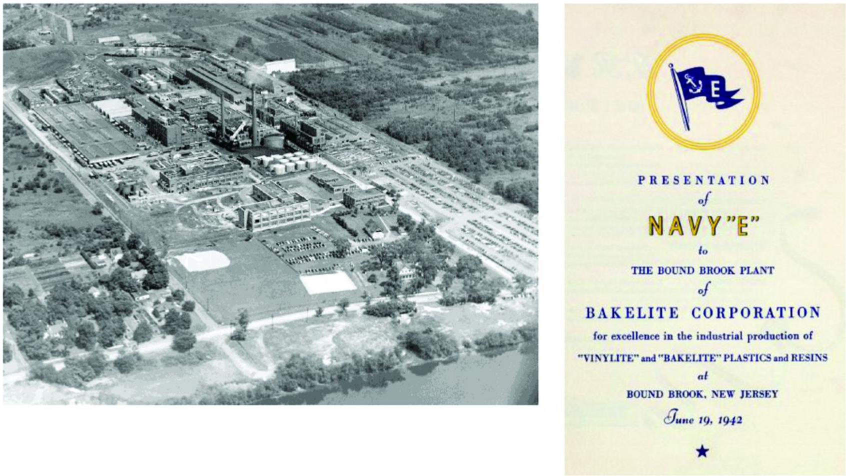
THE MEMBERS OF THE OLD TIMERS ORGANIZATION, CELEBRATING THEIR FIFTH ANNUAL REUNION, SEND THEIR GREETINGS TO OLD TIMER NUMBER ONE.... THE FOUNDER OF OUR CORPORATION.

TO YOUR LEADERSHIP WE ATTRIBUTE THE SPIRIT OF LOYALTY AND SERVICE WHICH HAS BECOME AN INHERENT CHARACTERISTIC OF BAKELITE EMPLOYEES.

WE EXTEND OUR SINCERE APPRECIATION AND BEST WISHES FOR YOUR CONTINUED HEALTH AND HAPPINESS.

THE OLD TIMERS OF BAKELITE CORPORATION
MAY 1938

Figure 8. People of the Bakelite Company. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.



PRESENTATION
of
NAVY "E"
to
THE BOUND BROOK PLANT
of
BAKELITE CORPORATION
for excellence in the industrial production of
"VINYLITE" and "BAKELITE" PLASTICS and RESINS
at
BOUND BROOK, NEW JERSEY
June 19, 1942

Figure 9. Union Carbide Plant after WW II. Facing Southeast. Navy Excellence Award for Bakelite Plant wartime production record (1942). Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

With Bakelite resins losing in importance after World War II, vinyl and styrenic resins became more dominant, and the R&D facilities expanded until it became necessary to build a large R&D center (*41*) adjacent to the existing plant in the late 1950ies (Figure 10). There was some controversy because expensive last-minute changes in plans (*42*) called for the extravagance of a hood with external exhaust in every research bay of every floor – a luxury which allowed the buildings to survive as OSHA-compliant R&D labs for 60 more years.

The 40th anniversary celebration of the North Jersey chapter of the ACS in 1965 featured a press release (*43*) that pointed to the "tremendous expansion of chemical research and manufacturing industry in New Jersey since World War I " (Figure 11). There were 900 manufacturers, 81,000 employees, 1.7 Billion dollars (1965 value) of chemical production per year, and membership in the North Jersey ACS Section had increased to some 7,000 members. The list of chemical companies with headquarters or major R&D facilities in Northern New Jersey took up a long paragraph in the following page of the article.

While the growth of the chemical industry in New Jersey extended over some sixty years, the collapse would be much more rapid. While advances in R&D would continue unabated, the majority of chemical plants in New Jersey including the Bakelite plant began to lose viability from the 1960ies on due to the rapid urbanization of the area, not to mention an increasingly more unfavorable tax policy in New Jersey. The Last Hurrah for the Bakelite plant was the conversion of some production facilities to a polymer recycle plant, but even that proved uneconomical given the high built-in cost structure. The plant itself stood empty by 2000, just before the merger with Dow (Figure 12).

The production part of the plant was fully razed by 2010, some 80 years after its construction, and only the footprint remains. The Bakelite plant, now surrounded on all sides by dense suburbia, an interstate highway, and harried New Jersey commuter traffic, had outlived its usefulness (Figure 13). Baekeland's most prized physical legacy was gone.

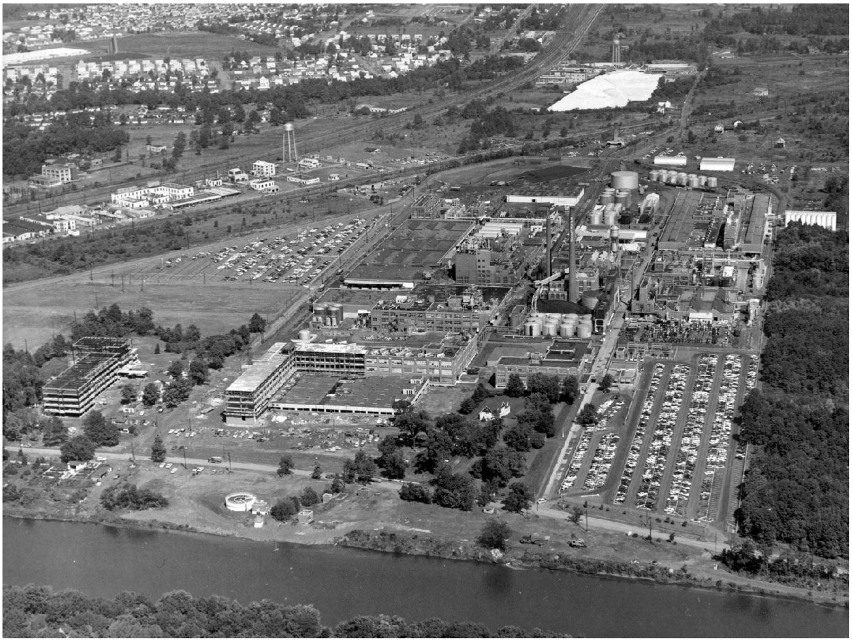


Figure 10. High water mark for the Bakelite plant 1957. Two R&D buildings under construction at lower left. Facing East. Plant employee parking lots (right front, left rear) are full. But Suburbia is approaching from North. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

GLASS WONDERLAND—Compounds are prepared on a large scale for testing at the Merck Sharp & Dohme Research Laboratories, a division of Merck & Co., Rahway.

CHAIRMAN-ELECT — W. Lincoln Hawkins oxidation test on polyethylene at Bell Teleph

Chemical Industry Celebrates

Party to Mark 40th Anniversary of N.J. Society

By ALBERT M. SKEA

The explosive growth of the chemical industry in New Jersey will be celebrated at a special birthday party tomorrow night at Seton Hall University, South Orange.

The affair will mark the 40th anniversary of the founding of the North Jersey Section of the American Chemical Society. With nearly 7,000 members the group has been the largest ACS section in the nation since 1960.

The growth of the section reflects the tremendous expansion of the chemical research and manufacturing industry in the state since the end of World War I.

Today New Jersey leads the nation in the production of chemicals. The some 900 man-

more often, at Rutgers. The official historian, Delmer L. Cottle of Esso Research and Engineering Co. in Linden, comments on those outings:

"The membership expected to be informed, which must have led the wives to think that chemistry was pretty stuffy business."

Not that this is so, but the section has revised the format of its monthly meeting only slightly to permit the anniversary celebration.

Members are being asked to meet at 5:30 p.m. for topical group discussion. A complimentary cocktail party will follow. But a serious note is anticipated at the dinner to follow.

Scientist to Speak

The speaker will be Dr. Charles C. Price, president of the ACS, and a scientist of international reputation. The 52-year-old native of Passaic will talk on "Chemistry and Public Affairs."

Only 11 of 100 invited chemists had attended the organization meeting of the section in 1918 at Newark Technical School, which later became Newark College of Engineering.

Decision to form the New Jersey Chemical Society, as it was then known, had been reached by three faculty members of the school.

During World War I, cut off from the vast chemical re-

ments. Income is from ACS allotments, profits from its Indicator bulletins, lecture series surplus and capital investment.

The section history is vague about the latter. It notes: "In April of 1937 Dr. David Wesson called the members' attention to the endowment fund and this is all that is known about it."

In addition to lecture series, the section seeks to promote interest in chemistry among high school students, awards and supervises the award of industrial scholarships, maintains a speakers' bureau and honors accomplishments in pure or industrial chemistry.

Three past chairmen of the section have gone on to become presidents of ACS. Dr.

Figure 11. Newark News write-up of the 40th anniversary of the North Jersey ACS Section. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Figure 12. Decommissioned plant lies behind the R&D Center (2000). Plant employee parking lot (left rear) is empty. Facing South. Suburbia is marching forward from the South as well. The two landmark chimneys still stand. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Legacy of Leo Baekeland as CEO and Businessman

Legacy as CEO

Our inquiries among old-timers (*44*) concerning the legacy of Leo Baekeland as 20th century CEO did not receive strong responses. It is puzzling why workers of later times would remember Baekeland with reverence and nostalgia as the founder of the Bakelite enterprise, but insisted that he had no impact on their current activities. It appears that Baekeland was not considered inspirational as a CEO because the business was handled in such a smooth way that heroics by a leader on a white horse were simply not required. It was also acknowledged as his rightful privilege that his interests had moved on to issues beyond his business enterprise. He began to give more of his keen mind to Government commissions and boards, and more and more of his time to scientific societies, issues of education, and not to forget, his yacht *Ion* (*10*). After the Bakelite plant was built in 1930, he seemed to have acted more as major stockholder than as hands-on CEO. Many of those questioned revealed shyly that their affection and dedication instead lay with the plant itself. The facility was still sometimes called ‘The Bakelite Plant’ some 70 years after the sale of the company to Union Carbide. In the first decade of the 21st century, after ownership had passed to the Dow Chemical Company, management correctly anticipated enraged protests in 2002 when the iconic dual smokestacks featuring the vertical BAKELITE inscription had to be torn down for safety reasons (Figure 14) (*22*). Tellingly, activists could not come up with a good reason why the stacks should be rebuilt.

A large number of the bricks were carved up and mounted on commemorative plaques, where the white bricks coming from the white BAKELITE inscription on the brown smokestacks were especially prized. This despite the undisputed fact that no Bakelite had been produced at the plant for more than 40 years.

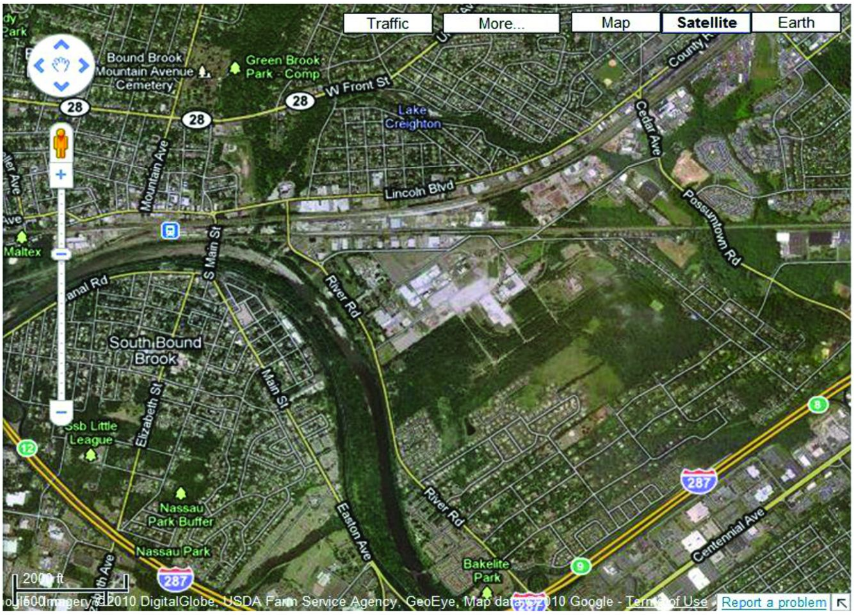


Figure 13. Google Earth satellite map of the Bakelite plant and environs (2010). Facing North. Only the R&D buildings are still active (at "Rd." mark of "River Road" caption near bend of the Raritan River). Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Figure 14. Landmark Bakelite chimneys slated for demolition in 2002. View from main plant entrance, facing East. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Legacy as Businessman

The businessman Leo Baekeland took a laboratory curiosity from the garage stage to a successful, world-wide enterprise; protected his intellectual property adequately; assembled a well-functioning management team; and was successful in his gamble on the future of plastics by moving his production facilities to a newly designed, untested, continent-scale plant at a time when his first patents were beginning to expire, and when the world economy seemed to be collapsing. His paternal leadership style instilled in his workers an esprit de corps and a love of the new plant that was unequalled. This dedication to the plant nourished the workers through the Depression and would invigorate them for the huge demands on the plant in the Second World War. In 1938, when he was 76 and infirm, the business was sold to Union Carbide by his son who saw himself as an engineer, not as a CEO (*45*, *46*). Multiple generations of workers had found gainful employment through the fifty years of Bakelite production, especially in the dark days of the Depression. Finally, the proceeds of the sale of the Bakelite Company to Union Carbide brought in enough money (some $200,000,000 in today's value (*3*)) to assure the financial stability of several generations of his descendants as well. Quite a set of achievements, despite the fact that the business could no longer flourish on its own, and despite the fact that his private dynastic dream had remained unfulfilled.

R&D Management

While the Bakelite plant can be considered his most tangible legacy, the corporate culture he engendered provided the intellectual DNA for the rest of the 20th century. The intellectual steps that led Baekeland to two world-class technological breakthroughs while untold others had failed were subsumed in his motto “Furthering Chemistry in the Service of Humanity”. The operational approach (*47*) consisted of the following new precepts, which have become commonplace for industrial R&D in our time:

- There is new chemistry and material science out beyond the horizon that can address the emerging needs of a new 20th century consumer society.
- First clearly identify the need, and then the chemical principles that could potentially fulfill this need.
- Intensive and focused basic research is the key to harnessing this chemistry, which in turn must lead to rapid implementation, and a total focus on the final commercial objective.
- Move on to other objectives as soon as the current target has been reached, as proven by successful commercialization.
- Use technology licensing as multiplier of profits, and encourage cooperative ventures and mergers to avoid debilitating battles with competitors.

It is part of Baekeland’s legacy that Ph.D. recruits coming to Bound Brook for site visits in the late 1970s would still receive an orientation folder that featured the Baekeland Award medal on the cover, and a synopsis of Baekeland’s achievements as the first page of the booklet. The tab “Recent Technological Advancements” proudly featured polymer discoveries and commercializations of novel materials such as Polysulfone™, Parylene™, Polyox™ (Polyethylene oxide), and the Unipol™ process and catalysts for gas phase olefin polymerization. This gas phase process, a combination of coupled advances in polymerization process, catalyst, and extrusion technology, was described with only minor exaggeration to be the biggest breakthrough is the field of plastics since Bakelite. All of these polymer innovations had followed the developmental pattern thoroughly familiar to Leo Baekeland, and all were also exploited through world-wide licensing.

Unipol as Business Legacy

The Unipol saga presents a beautiful example of how innate biases in corporate cultures can shape scientific development and commercial success. Several companies (including Union Carbide) licensed ICI’s high pressure polyethylene in the 1930ies, and developed or licensed the emerging new low pressure catalyst technology in the 1950ies. In contrast to high pressure products, the final properties of the low pressure materials were seemingly infinitely adjustable by the combination of process and catalyst technologies, and plants were considerably cheaper to build than high pressure plants. A race ensued in the 1960ies and 1970ies to exploit the new product space made possible by new catalyst (*48*), process (*49*), and product technologies (*50*). Union Carbide followed the path that had been institutionalized since the days of Baekeland, and invested heavily in fundamental R&D and new process technology (the fluid bed, unproven for the production of sticky polymers) (*51*). The intention was to have first-mover advantage, and to satisfy the emerging needs of the world for the new polymers via an aggressive licensing program (*50*). There was no serious opposition to this strategy within the organization, since it followed past practices dating back to Baekeland's time. The initially hesitant push of technology by the process R&D arm of the Corporation was quickly met with a determined, enthusiastic pull by top management, which rejected a cautious probe approach. Instead, top management called for rapid implementation of options brought out by basic research, and immediate exploitation of the new technology through an aggressive licensing program. These licenses promised process capabilities and product properties that would hopefully be available two years down the road, just when the licensed plant was ready to start up, rather than the more limited capabilities that were firmly in hand at the time the licensing agreement was initialed.

Union Carbide was not the first in the field (*52*). Another company had already been out in the marketplace for some years with an aggressive licensing program utilizing a different process technology and a restricted set of catalysts, but appeared to be locked into their technology. Other competitors were following the diverse pathways they were most comfortable with. A second company, with a similar process technology as the aforementioned one, was determined to make the absolutely best (and most expensive to produce) polymer on the market, and so garnered a small (but reasonably profitable) niche in the polymer and licensing marketplace. A third company was not about to share its own in-house technology with potential competitors and so built a few small-scale plants that made profits on polymer sales alone. A fourth world-scale company saw the advantages of the gas phase process, and was still exhaustively studying the specific details of the intricate catalyst/process/product technology space while Union Carbide was rushing into the marketplace to sign up key potential licensees. Yet another company, finally, was a very able and competent competitor to Union Carbide, with a rich in-house catalyst technology that dwarfed that of all their competitors. Alas, a senior technical expert claimed (after his retirement) that their considerable commercial success in the outside world would have been even greater if their own top management had not been such an obstacle to success. Leo Baekeland would have smiled over Union Carbide's achievement.

Technology Development as Key Driver

As part of the Baekeland legacy, the motto "Furthering Chemistry in the Service of Humanity" would still be a good characterization of the business enterprise for more than a generation after the sale of the Bakelite Company to Union Carbide. Product innovation followed product innovation, and the Plastics arm of Union Carbide was strongly represented in open publications as well as in world-wide patents. But this inherited value system also has a dark side. A review of articles in *The Trefoil*, the internal news publication of the Bound Brook site, uncovered innumerable articles throughout the 1930ies to the 1970ies describing scientific awards, product breakthroughs, production accomplishments, and licenses issued to other companies, but was essentially silent on profit targets, return on investments, and meeting of profit rather than production quotas. Concerted attempts to change the corporate culture away from that inherited from the Bakelite Company did not gain a footing until the 1980ies. Only then was it pointed out to employees that while “Furthering Chemistry in the Service of Humanity” was an admirable objective, it needed to be coupled with “service to the stockholders” if long-term survival of the business was to be one of the goals. The function of R&D in a survivor organization needed to be generation of profits, not just the invention of marvelous new products (*53*).

Modern Science Education

As mentioned previously, Baekeland was devoting more and more of his time to scientific organizations as the Bakelite company was gaining a more secure footing. The cited biographies list service in innumerable technical societies from 1909 on, an extensive publication record, an honorary professorship of chemical engineering at Columbia University in 1917, Presidency of several organizations including the ACS in 1924, and frequent lectures and addresses at Universities and technical meetings. He stressed the importance of basic research for uncovering the laws governing chemical reactions, and the need to apply the thus gained insights for the betterment of daily life. The move from sole proprietorship to industrial corporation, and from impecunious independent researchers to industrial R&D labs with huge budgets and novel modes of operation was well under way world-wide at the time, and Baekeland wanted academe to be both cognizant and to take a larger role in guiding these changes.

The ACS Baekeland Award

Soon after his death on February 23, 1944, Union Carbide and the North Jersey Section of the American Chemical Society jointly announced the establishment of the Leo Hendrik Baekeland Award as a special legacy of Leo Baekeland. The award was to consist of a $1,000 check and a gold medal bearing the image of Leo Baekeland on one side, and the icons of Baekeland’s accomplishment plus the name of the winner on the other side (Figure 15) (*54*).

The award was sponsored and funded by Union Carbide, and administered by the North Jersey section of the American Chemical Society. The Bakelite plant and R&D centers were located in the area overseen by this section of the ACS; the general North Jersey area also was the epicenter of the US chemical industry at the time.

Figure 15. Front and Obverse of the Baekeland Medal. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Award Stipulations and Procedures

While memorial awards honoring a founder figure are quite common, the Baekeland Award contained unusual stipulations. It was to be awarded

"to an American chemist who has not yet reached his 40th year in recognition of accomplishments in pure or industrial chemistry".

The Bound Brook *The Trefoil* added the following amplification as part of its write-up on the establishment of the award (*55*):

"By means of the Baekeland Award, the sponsor and the North Jersey Section of the American Chemical Society seek to encourage emulation of the inspiring career of Dr. Leo Baekeland, much as Dr. Baekeland was stimulated by receiving a similar award, when teaching chemistry and physics ...at Bruges, Belgium."

We do not know if he had planned this award himself in earlier times, or whether the conditions of the award were framed after his death. There is no dispute that Baekeland considered the award which allowed him to come to the United States as the seminal point of his life. Likewise, he was grateful to the United States for allowing him to work to the fullest of his capabilities, and for rewarding his success. The award criteria certainly reflected his value system.

Nominations are solicited via an announcement in C&E News and in ACS Section publications such as the North Jersey *The Indicator* (Figure 16). Winners are also publicized in C&E News, and given prominent display in internal Union Carbide/Dow new publication/web sites.

The membership of the jury, headed by the chairman of the North Jersey ACS Section, reflects the nature of the award. By common consent, the sponsor (Union Carbide/Dow) is not involved in either the solicitation for the award nor in the selection of the winner. The jury, headed by the chairman of the Section, consists of a mix of academic and industrial researchers, where the expertise of the industrial members is complementing that of the academic members of the jury. The nomination write-up is even more important for the Baekeland Award than for other awards, since the award does not just reflect past accomplishments by the recipient, but also predicts future achievements. The nominator is in the best position to see whether the nominee has this required potential for future exceptional accomplishments along the lines exemplified by Leo Baekeland.

CALL FOR NOMINATIONS FOR BAEKELAND AWARD

THE ACS NORTH JERSEY Section is soliciting nominations for the 2009 Leo Hendrik Baekeland Award, sponsored by Union Carbide.

The award consists of a gold medal and $5,000, and it is presented every two years to an American chemist in recognition of accomplishments in pure or industrial chemistry, as characterized by the initiative, creativity, leadership, and perseverance of the individual and indicated by published or unpublished evidence. To be eligible for the award, individuals must be under the age of 40 as of Jan. 1, 2009.

Nominations should include a letter describing the nominee's achievements, a brief biography, and a list of the nominee's more important publications. Two or three recommendation letters are encouraged. Individuals can be renominated, provided they still meet the age requirement.

Materials are due by Dec. 31 to Michael M. Miller, Baekeland Award Committee, 2008 Section Chair, North Jersey ACS, Bristol-Myers Squibb, 311 Pennington-Rocky Hill Rd., Pennington, N.J. 08534. For more information, visit njacs.org/baekeland.html.

Mirkin Receives Baekeland Award

THE ACS NORTH JERSEY SECTION recently presented its 2001 Leo Hendrik Baekeland Award to Chad A. Mirkin, George B. Rathmann Professor of Chemistry and director of the Institute for Nanotechnology at Northwestern University. The Baekeland Award was established in 1944 by the section and has been continuously sponsored by Union Carbide, now a division of Dow. The award commemorates the technical and industrial achievements of Leo Baekeland and attempts to encourage younger chemists to emulate his example. The biennial award is conferred upon a U.S. citizen under 40 years of age in recognition of accomplishments in pure or industrial chemistry.

Mirkin was recognized for invention and development of dip-pen nanolithography and development of a fundamental understanding of the structure versus function relationships for nanoparticle-based architectures formed from biological constructs. He was also recognized for developing the "weak-line synthetic approach" in inorganic supramolecular structures, which comprises a general set of high-yielding reactions for preparing flexible macrocycles, cylinder, and other three-dimensional nanometer-scale objects.

Mirkin received a B.S. in chemistry from Dickinson College in Carlisle, Pa., in 1986 and a Ph.D. in chemistry from Pennsylvania State University in 1989. He is the founder and a member of the board of directors of Nanosphere Inc. and NanoInk Inc.

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Figure 16. Call for Baekeland Award Nominations, and announcement of the Award winner in C&E News. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Evolution of the Baekeland Award

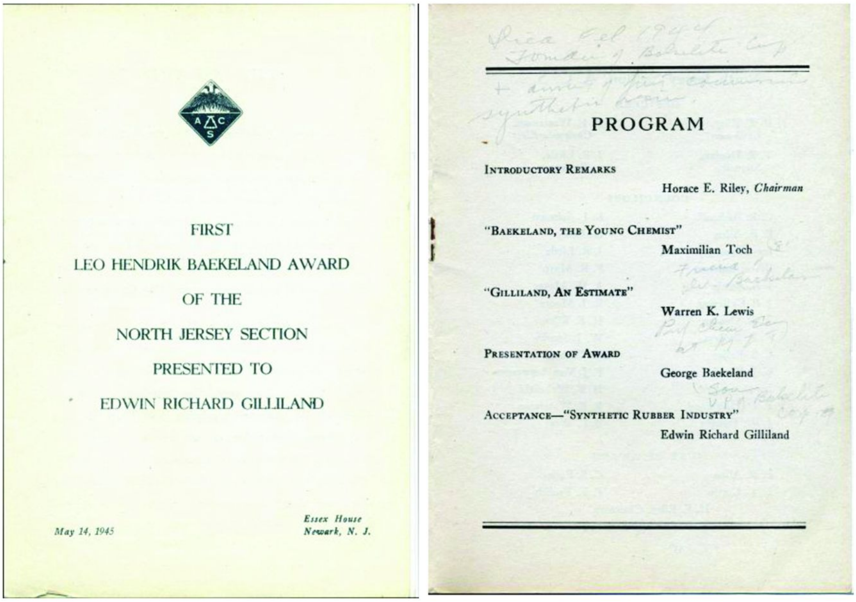
Early ACS Jury committees (*56*) advised potential nominators that "accomplishments" should be measured in terms of what an outstanding researcher could reasonably have accomplished before the age of 40. These accomplishments however should be predictive of stellar future accomplishments if the recipient is encouraged to stay on the current trajectory by winning the Baekeland Award and (consequently more likely) subsequent awards. The criterion of 'pure *or* industrial' accomplishments was soon merged with the criterion of 'emulation of the inspiring career of Dr. Leo Baekeland'.

As time went on, it became easier and easier to find nominees from academe who fit the requirements of the Baekeland Award, since the combination of basic research plus engagement with the outside world has become almost compulsory for young professors (*57*). It has become progressively harder to obtain nominations from industrial labs, where the practice of cooperative teamwork makes selection of an individual nominee both difficult and politically inappropriate, and where increasing secrecy requirements and lack of outside visibility make a fair assessment of individual achievements very difficult for the jury.

When the scientific enterprise became more international in the 1980ies, the stipulation of "an American chemist" also became an issue. Does work done in the United States by a researcher with a British passport qualify? Work by an American researcher in Cambridge, England rather than in Cambridge, Massachusetts? What about a researcher from mainland China who comes to the West Coast as refugee, and sets up an outstanding research group at a local State University, and whose graduate students come from all over the world? The jury, with additional feedback from the sponsor of the award, ruled that there must be a strong American connection of either the awardee or the location where this seminal work was accomplished. The specifics of Leo Baekeland's own life were used to interpret the intent of this stipulation.

Past Award Winners

The first award was given out in 1945, and demonstrated both the high standards and sagacity of the jury committee. The award went to Dr. Edwin Gilliland (*58*) for basic mathematical and experimental work on fluid catalytic cracking, and for his industrial leadership as Assistant Rubber Director for the War Production Board between 1942 and 1944 (Figure 17).



FIRST
LEO HENDRIK BAEKELAND AWARD
OF THE
NORTH JERSEY SECTION
PRESENTED TO
EDWIN RICHARD GILLILAND

May 14, 1945

Essex House
Newark, N. J.

Pres. Gel 1944
Founder of Bakelite Corp
+ author of first commercial
synthetic resin.

PROGRAM

INTRODUCTORY REMARKS
Horace E. Riley, *Chairman*

"BAEKELAND, THE YOUNG CHEMIST"
Maximilian Toch
Friend of L. Baekeland

"GILLILAND, AN ESTIMATE"
Warren K. Lewis
Prof Chem Eng at MIT

PRESENTATION OF AWARD
George Baekeland
(Son
V.P. of Bakelite Corp.)

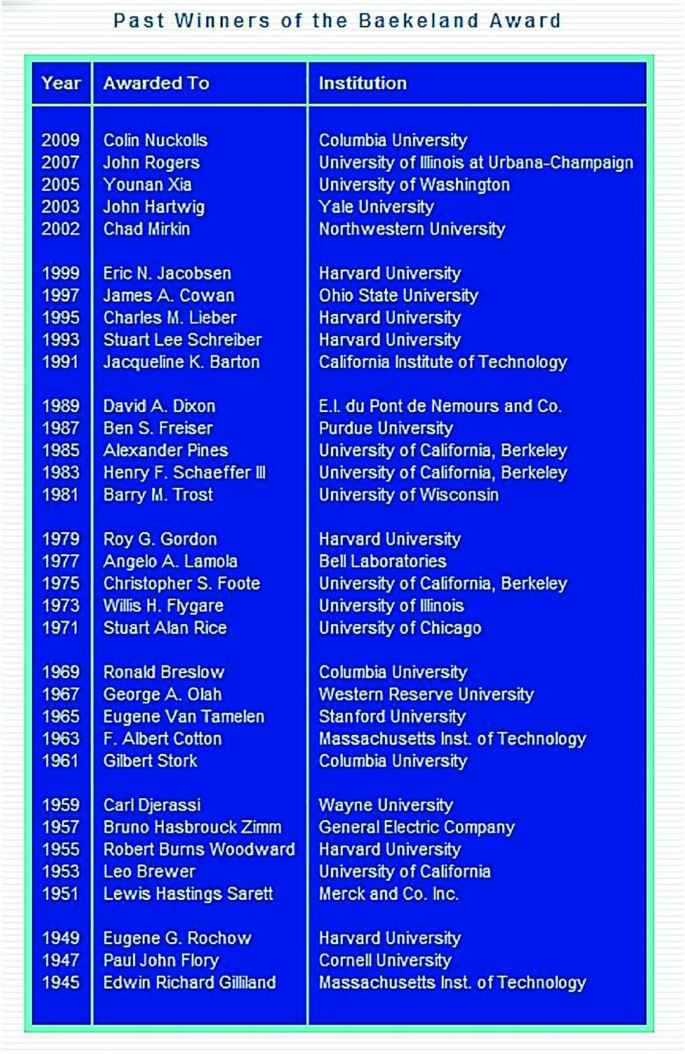
ACCEPTANCE—"SYNTHETIC RUBBER INDUSTRY"
Edwin Richard Gilliland

Figure 17. Program of the first Baekeland Award in 1945. George Baekeland presented the award to Edwin Gilliland. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Gilliland went on to confirm the wisdom of the jury by becoming Institute Professor at MIT, and serving as Deputy Chairman of the President's Science Advisory Committee under Presidents Kennedy and Johnson.

The Baekeland Award winners from 1945 to 2009 are listed below (*59*) (Figure 18).

Three Baekeland Award winners would subsequently win the Nobel prize (Flory, Woodward, Olah), and presumably there are several more to come. One winner would later be elected to the Board of Directors of the Dow Chemical Company (Prof. Jacqueline Barton). Alas, she is also the only woman to have won the award so far. The changes in research areas over the years reflect the changes in the frontiers of chemistry. The dominance of nanotechnology over the last ten years is particularly striking. This area appears to be the new 'Plastics' of Dustin Hoffman fame. One of Leo Baekeland's prescient pronouncements was that the life sciences would be the next frontier where Chemistry would make the greatest contributions. It however appears that nanotechnology has become a more accessible field in which young individual researchers can leave their mark on the world more rapidly than through the life sciences.



Past Winners of the Baekeland Award

Year	Awarded To	Institution
2009	Colin Nuckolls	Columbia University
2007	John Rogers	University of Illinois at Urbana-Champaign
2005	Younan Xia	University of Washington
2003	John Hartwig	Yale University
2002	Chad Mirkin	Northwestern University
1999	Eric N. Jacobsen	Harvard University
1997	James A. Cowan	Ohio State University
1995	Charles M. Lieber	Harvard University
1993	Stuart Lee Schreiber	Harvard University
1991	Jacqueline K. Barton	California Institute of Technology
1989	David A. Dixon	E.I. du Pont de Nemours and Co.
1987	Ben S. Freiser	Purdue University
1985	Alexander Pines	University of California, Berkeley
1983	Henry F. Schaeffer III	University of California, Berkeley
1981	Barry M. Trost	University of Wisconsin
1979	Roy G. Gordon	Harvard University
1977	Angelo A. Lamola	Bell Laboratories
1975	Christopher S. Foote	University of California, Berkeley
1973	Willis H. Flygare	University of Illinois
1971	Stuart Alan Rice	University of Chicago
1969	Ronald Breslow	Columbia University
1967	George A. Olah	Western Reserve University
1965	Eugene Van Tamelen	Stanford University
1963	F. Albert Cotton	Massachusetts Inst. of Technology
1961	Gilbert Stork	Columbia University
1959	Carl Djerassi	Wayne University
1957	Bruno Hasbrouck Zimm	General Electric Company
1955	Robert Burns Woodward	Harvard University
1953	Leo Brewer	University of California
1951	Lewis Hastings Sarett	Merck and Co. Inc.
1949	Eugene G. Rochow	Harvard University
1947	Paul John Flory	Cornell University
1945	Edwin Richard Gilliland	Massachusetts Inst. of Technology

Figure 18. Past Winners of the Baekeland Award. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

The Award Presentation

The changes in the award presentation reflected changes in the administration of the award, and changes in fortune of the chemical industry following World War II. The first award in 1945 was presented by the son George Baekeland, with much of the top leadership of Union Carbide in attendance. Based on the documents in the Baekeland Award Committee files, the arrangements for this first and the next few award dinners were handled from within Union Carbide.

The Award presentations consisted of a welcome, a presentation introducing the winner, and an award presentation by the winner. The location for the first few award presentation, the Essex House (known then as Newark's "smartest hotel" (*60*)) also attests to the corporate flavor of the event. The next two awards were presented by senior Union Carbide managers. George Baekeland, "Union Carbide VP" is listed for the last time as presenter in 1951, ending the connection of the award with the Baekeland family. The presenter for the next 30 years would be the Vice President of R&D, Union Carbide (Figure 19), and later leadership personnel from the Bound Brook R&D Center (Director of the site, or the senior Corporate Research Fellow). After the merger of Union Carbide with Dow Chemical, the Dow NJ Site Operations Leader demonstrated Dow's commitment to the award by continuing this tradition (Figure 20, 23).

Figure 19. The dais of the 1985 Baekeland Award Celebration. Prof. Alex Pines to the left of the Award presenter, Dr. L.M. Baker, VP of R&D of Union Carbide. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Figure 20. Award picture from the NJACS web site. Award committee members watch as Alan Fowler, NJ Operations Leader, Dow Chemical, presents the 2002 Award to Prof. Chad Mirkin, with ACS President Eli Pierce in attendance. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

The first few Baekeland Award presentations thus had been highly exclusive affairs attended by high Union Carbide officials, the head of the ACS, officers of the local and neighboring ACS sections, and by a few individuals from within Union Carbide that the company wanted to honor. By the late 1950ies, Union Carbide felt assured that the launch of the Baekeland Award had been successful, and turned responsibility for the award ceremony over to the North Jersey ACS so that more of the academic community could be drawn into the process.

With the administration of the award ceremony fully transferred to the North Jersey ACS, the venue was changed away from the hotel used by Union Carbide for important banquet events. From then on, Award ceremonies were shifted between industrial and academic locations to highlight the importance of both types of institutions to the chemical enterprise in New Jersey, then the center of the chemical industry in the US. New Jersey universities in turn were expanding rapidly due to the increased emphasis on science education in the post-Sputnik years, and due to the wave of baby boomers that were beginning to flood these universities.

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

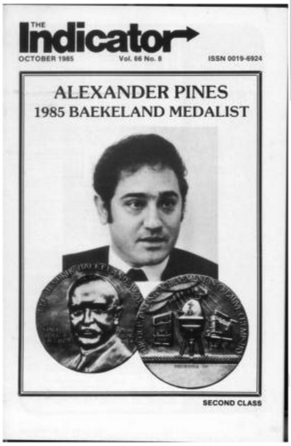
The Baekeland Symposium

The 1961 Award presentation at Seaton Hall University was grafted onto a routine monthly ACS Section meeting, and followed unrelated lecture presentation of the various Topical Groups earlier in the afternoon. Attendees were simply invited to stay for the Award presentation. Within the following few years, the unrelated afternoon presentations morphed into the Baekeland Symposium, which became an increasingly more important part of the Award ceremonies. The symposium became focused around the topic of expertise of the Award winner, so that the audience would gain an overview of the current status and future potential of this field of chemistry at the outer frontiers of science. The symposium presentations have remained an integral part of the Baekeland Award, with the Award winner sometimes having to strive mightily not to be overshadowed by the scope and intellectual wealth of the preceding Symposium presentations. Other presenters occasionally delight in reminding the Awardee in a friendly way that there were other people capable of doing outstanding research in the area as well.

The high stature of the Symposium was not explicitly recognized until the 1985 Award Symposium for Prof. Alex Pines, who received the award for the development and applications of zero field NMR (Figure 21).

Prof. John Waugh, the developer of solid state NMR, went off-topic in his introduction of the winner to declare that in his entire career he had never been together at any one time and place with so many academic and industrial luminaries in the field of NMR as at this symposium. He congratulated the Celanese symposium chair on corralling these speakers, and hoped the audience was appreciative of the value of the event. Prof. Richard Ernst, the first speaker at the afternoon's symposium, would in fact win the Nobel prize in Chemistry a few years hence.

Much had changed by the time of the 2002 "Award Presentation and Symposium" at the Fiber Optics Auditorium at Rutgers University, the first Baekeland Award of the 21st century. The Award itself had been postponed from 2001 to 2002 on account of the cataclysmic events of 9/11, which had been visible on the horizon from the symposium site. The role of the chemical industry in New Jersey had diminished considerably by the turn of the millennium, as most of the chemical companies listed in the 1965 ACS press release had disappeared, merged with other companies, or left the state. Employment in all types of manufacturing in New Jersey had decreased to about half that of 1965. Chemical production at the former Bound Brook Bakelite plant had essentially ceased except for a plastics recycling facility. Union Carbide had already shrunk from 100,000 to 10,000 employees world-wide, and had been merged into the Dow Chemical Company the previous year. Chemists now were considered valued support staff in many different industrial fields, no longer core employees in a thriving chemical industry. Chemistry had become "the enabling science", and the field in New Jersey now belonged to the rapidly expanding Pharma industry. On more cheerful notes, the universities were stronger than ever, and the monetary component of the Baekeland Award had been increased to $5,000 to take account of inflation.



THE **Indicator**
OCTOBER 1985 Vol. 66 No. 8 ISSN 0019-6924

ALEXANDER PINES
1985 BAEKELAND MEDALIST

SECOND CLASS

BAEKELAND AWARD SYMPOSIUM & DINNER
HONORING ALEXANDER PINES

Recent Applications of NMR in Chemical, Biochemical, and Materials Research

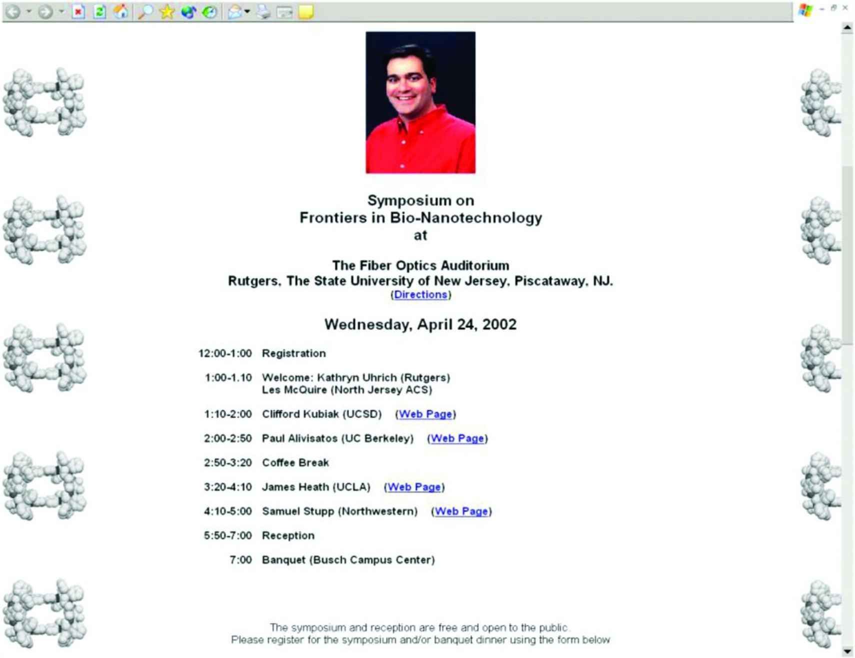
Presiding — Dr. Marie Borzo, Celanese Corporation

1:00 PM	Prof. Dr. Richard R. Ernst, ETH, Zurich Chemical Structure and Dynamic Processes Visualized by Two-Dimensional NMR
1:55 PM	Dr. Jacob Schaefer, Monsanto Company Double Cross — Polarization NMR Studies of Carbon and Nitrogen Metabolism
2:50 PM	Break
3:10 PM	Prof. Charles P. Slichter, U. of Illinois NMR — A New Method to Probe Real Catalysts
4:05 PM	Prof. Alexander Pines, U. of California, Berkeley Development and Applications of Zero Field NMR
	SOCIAL HOUR — DINNER
5:30 PM	Social Hour
6:30 PM	Dinner
7:30 PM	Presentation of the Baekeland Medal
8:00 PM	Medalist's Award Address

Figure 21. Announcement of the Baekeland Award winner for 1985, Prof. Alex Pines. Program for the Award Symposium. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

At this first Baekeland Award of the 21st century, Leo Baekeland would have been mystified by 'electronic registration' on the 'North Jersey ACS web site' and by complaints by members that 'credit cards' could not yet be used on line for prepayment. Equally puzzling would be references to 'group web pages' during the presentations, not to mention the presence of 'hyperlinks' in presentation abstracts that seemed to point to a host of further information accessible by clicking with a 'mouse', of all things (Fig. 22). The symposium topic "Frontiers in Bio-Nanotechnology" itself would have intrigued him, and he would have been delighted at the presented interplay of fundamental studies and concrete applications at the outer frontiers of chemistry. He also would have nodded in sympathy when the award recipient, Prof. Chad Mirkin, mentioned the chores involved in securing intellectual property, the difficulties in obtain funding for the companies he had founded to exploit his discoveries, and the challenges in finding the best path through an essentially unexplored field of interdisciplinary science and technology.

Leo Baekeland would certainly have been delighted and even more mystified at the 2007 Award Presentation by Prof. Richard Rogers, which did not deal centrally with chemicals at all but with solar panels, LCD screens, chemical constructs for quantum-based electronics, and social issues such as novel methods of energy conservation, and countering global warming. In retrospect he would have been reassured by the realization that new basic chemistry still played a key role in the described innovations in material science.



Symposium on
Frontiers in Bio-Nanotechnology
at

The Fiber Optics Auditorium
Rutgers, The State University of New Jersey, Piscataway, NJ.
(Directions)

Wednesday, April 24, 2002

12:00-1:00	Registration
1:00-1.10	Welcome: Kathryn Uhrich (Rutgers) Les McQuire (North Jersey ACS)
1:10-2:00	Clifford Kubiak (UCSD) (Web Page)
2:00-2:50	Paul Alivisatos (UC Berkeley) (Web Page)
2:50-3:20	Coffee Break
3:20-4:10	James Heath (UCLA) (Web Page)
4:10-5:00	Samuel Stupp (Northwestern) (Web Page)
5:50-7:00	Reception
7:00	Banquet (Busch Campus Center)

The symposium and reception are free and open to the public.
Please register for the symposium and/or banquet dinner using the form below

Figure 22. Announcement of the 2002 Baekeland Award Symposium on the NJACS web site. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Baekeland Symposium Poster Session

The last decades also brought deep changes in science education, and to the nature of the student population. Science and technology education is seen as the road for advancement in the emerging economies, while the perceived lack of career opportunities within the US has driven native students into other fields of endeavor. The large number of foreign students flocking to the US for a science education were quite receptive to Leo Baekeland's philosophies on education, and in agreement with the crucial importance of fundamental studies and the need for rapid application of the gained understanding to raise the lifestyle of their own people. They were eager to learn at the Symposium how these concepts were being put into practice. To encourage attendance, symposium fees for students have been subsidized to accommodate their budgets. The Baekeland Award Symposium has turned into a popular forum for listening to and for discourse with the world-class presenters. In order to draw these student audiences even more into the process, a very popular poster session has been instituted where the role of the presenter and audience are reversed, so that the Baekelands of the future can proudly describe their own innovations to the current luminaries in the field (Figure 23).

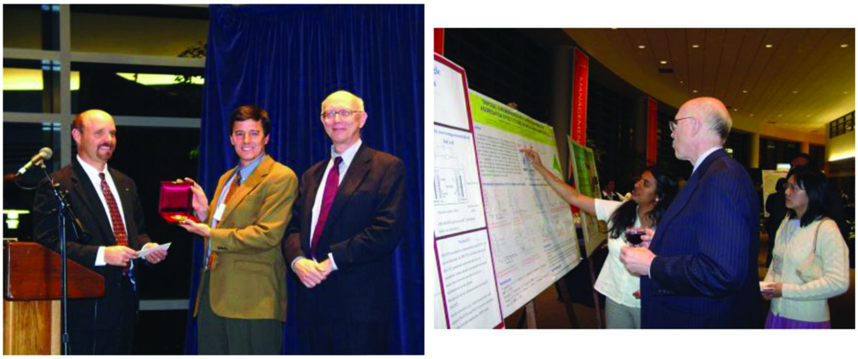


Figure 23. Left: Brian Maurer, NJ Operations Director, Dow Chemical, asking Prof. George Whitesides, the nominator, to join him in presenting the 2007 Baekeland Award to Prof. Richard Rogers at the NJIT celebration. Right: Prof. George Whitesides listening to two future Baekelands describing their 21^st^ century research. Courtesy of the Leo Hendrik Baekeland Award Collection, North Jersey Section of the American Chemical Society.

Continued Relevance of the Baekeland Award

In his debriefing after the award ceremony, one of the winners expressed his thanks for receiving the award, and explained how much it meant to him. He thought that the Award itself was working exactly as Leo Baekeland intended. A young investigator entering the system as Assistant Professor would receive starter grants from his University, and could apply for a host of Young Investigator awards from the NSF, NIH, and from Industry (such as Union Carbide's and Dow's own Young Investigator Awards). His grant applications would be reviewed with his status as young investigator in mind. After about 10 years of building and establishing a career and an area of research of his own, there came a dry spell when he was merely one of a host of faceless researchers, all with bright ideas and good track records, all applying for the same limited grant money and competing for the same bright graduate students. Other ACS awards targeted lifetime achievements, for which he was (for better or worse) not yet eligible. Winning this first high-profile award in the early middle of his career put him on a special pathway reserved for those recognized as having the potential for exceptional contributions; a path travelled before him by the previous illustrious winners of the Award, and leading back to the young Leo Baekeland himself. The spotlight on his work brought on by the Baekeland Award should allow him to further expand the scope of his activities, and ensure more rapid breakthroughs in his field.

Acknowledgments

Helpful discussions with Dr. George. L. Goeke, Dr. Walter T. Reichle, Dr. Marie Borzo and Hugh Karraker are gratefully acknowledged. I express my deepest thanks to Carol Patton, Barbara Mellish, and many anonymous office professionals of the Bakelite Company and Union Carbide Corporation (1930 – 2000) for the preservation, collection, and retrieval of historical Baekeland documents.

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Chapter 5

History of Interpenetrating Polymer Networks Starting with Bakelite-Based Compositions

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Interpenetrating polymer networks, IPNs, are combinations of two polymers, both of which are crosslinked. Bakelite, a densely crosslinked polymer network, was invented by L. H. Baekeland in 1909. The original material was a very brittle plastic. As such, it was used by Thomas Edison in his early phonograph records, which needed to be very thick to prevent fracture in handling. Shortly thereafter, in 1914, Jonas Aylsworth added natural rubber and sulfur, creating the first IPN. With the improved material, Edison's photograph records were made much thinner. IPNs were invented and reinvented many times, according to the patent literature. Early research workers in the field included K. Frisch at U. Detroit, Yu. Lipatov of Kiev, and the current author at Lehigh University, all of whom began their work in the 1960s. Besides tough plastics, current applications of IPNs include sound and vibration damping, false teeth, and medical applications.

Introduction

The history of polymers is a long one, with natural polymers such as wood, animal skins, wool, silk, and cotton being used since the dawn of civilization. Semi-synthetics, such as cellulose nitrate, were made in the 19th century, and used today as an explosive. Synthetic polymers, accidently made during early organic chemistry experiments, were often ignored. The first man to make a successful commercial synthetic polymer was Leo Baekeland, who synthesized and manufactured Bakelite. This was a crosslinked, or thermoset, plastic. Almost immediately, Jonas Aylsworth synthesized the first interpenetrating polymer

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

network, IPN, which was used by no other than Thomas Edison in making his phonograph records, making them much tougher, and allowing the phonograph records to be made much thinner. The idea of an IPN was invented and re-invented several times, each time lost in history, but recorded in patents. This paper will describe what happened during this time.

History of IPNs in a Nutshell

The first patent of interest was the famous patent by Charles Goodyear in 1844 (*1*). He added sulfur to natural rubber, and cooked it up to vulcanize, or crosslink it. Technically, he made a polymer single network. Rubber tires made the material famous.

Baekeland mixed phenol and formaldehyde and cooked them up to make the first successful entirely synthetic plastic (*2*), which he named Bakelite. He already had rich record of past accomplishments. He was born and educated in Belgium, he had done early experiments there. Then, he immigrated to the United States, and developed a laboratory in his home in Yonkers, NY. When he went into the manufacturing mode, he built a plant in New Jersey. The initial material was excellent in many ways, opening doors for a range of manufacturing. Then and now, Bakelite is used for electrical connectors and a range of home and business applications as a stiff, long lasting plastic.

In his patent (*2*), claim 5, Baekeland wrote: “The method which consists in reacting on a phenolic body with formaldehyde in presence of a base serving as a condensing agent, the proportion of base in the product being less than one-fifth of the equimolar proportion of the phenolic body used, separating water from the resulting product, and then hardening the same by application of heat and pressure.” This of course, was the heart of the new material which Baekeland called Bakelite.

One such manufacturing area was the making of phonograph platters (records) by Thomas Edison in his plant in West Orange, NJ, when he switched from spools to platters (*3*). The initial such records were very thick, because the Bakelite material was brittle. Edison had a fellow inventor by the name of Jonas Aylsworth, Figure 1 (*4*), who variously worked together with Edison, and also independently. Aylsworth undertook the task of improving the toughness of the Bakelite, adding various components, as listed in several patents in his name at that time. The composition that worked was the addition of natural rubber and sulfur, which forms a crosslinked material. In his patent, Aylsworth wrote (*5*): “My invention relates to an improved soft or hard rubber composition and methods for preparing same. It comprises the incorporation with masses of India rubber or cautchouc, or of gutta purcha (all names of natural rubber), compounded with sulfur or other vulcanizing agent, of a powdered infusible condensation product of phenol or its homologues or derivatives and formaldehyde or other substance containing the methylene radical CH_2, which will react with the phenol on application of sufficient heat to form a final condensation product.” The reader should note that in neither the Baekeland patent nor the Aylsworth patent was the word “polymer” used, because it was not invented until 1926 by Staudinger (*6*, *7*).

Figure 1. Jonas W. Aylsworth, Edison's chief chemist (4).

Several items should be noted: First, while Baekeland had a Ph.D. from Belgium, Edison only had a grade school education, and Aylsworth, although called "Doctor" by Edison, had only one year of college. Second, the three men were working within a relatively few miles of one another, and they knew each other. Together, the three men did much to transform America and the world into a modern industrialized society.

Some Polymer Structures in a Nutshell

Polymers, as first defined by Staudinger, are long chain compounds, frequently containing hundreds or even thousands of repeating groups. There are several methods of preparing polymer mixtures. Figure 2 (*8*) describes some of these, including the IPNs. In (a), the polymers are mixed without reacting with one another, called a blend. In (b), the second polymer is attached to the side of the first, called a graft copolymer. (In a complex mix of mostly (a) with a bit of (b), where the major polymer, (a), is polystyrene and the minor polymer is polybutadiene grafted onto polystyrene, making (b), makes up the slightly cloudy cover on many soda drinks sold in fast food chains.) In (c), the two polymers are attached end-on-end, called a block copolymer. (A famous such composition is a triblock copolymer of polystyrene-polybutadiene-polystyrene, which forms the rubbery soles of most modern shoes, making for slip resistant, long life materials.) (d) Is called an AB-graft copolymer, used in forming tough polymers. (e) Is an IPN, where the second monomer is swelled into the first network, and polymerized with crosslinking (bonding together), indicated by the black dots. Composition (f) is a semi-IPN, where one polymer is crosslinked, and the other is linear. Thus, the definition of an IPN is a combination of two or more polymer networks, at least one of which is synthesized and/or crosslinked in the immediate presence of the other(s). Applications for IPNs will be given below. Compositions (a), (b), and (c) are themoplastics, which means they will flow on heating. Compositions (d), (e), and (f) are called thermosets, because they do not flow when heated.

There are two general methods of synthesizing the IPNs, see Figure 3 (*8*). In part A, the two polymers are polymerized sequentially. In part B, the two polymers are synthesized simultaneously via stepwise and chain polymerization kinetics, which usually don't interfere with one another.

Multiple Inventions of the IPN Structure

While the Aylsworth patent was certainly used in the manufacture of Edison's patents, with the passage of time it was largely forgotten. The IPN structure was re-invented several times. Staudinger and Hutchinson (*9*) used the idea in 1951 to create thick sheets of clear, void-free materials suitable for optical use, filling the voids and uneven surfaces by swelling in more of the same monomer and crosslinker, and carrying out a second polymerization in situ. This composition is known today as a homo-IPN because both polymers are the same.

In 1955, Solt (*10*) prepared a new type of ion exchange resin by polymerizing one network with anionic groups and the other with cationic groups. Up until then, for complete purification of water, the two networks were polymerized separately and mixed afterwards. Millar, in 1960 (*11*), made undersized suspension particles bigger by a second polymerization with the same polymer and crosslinker, also a homo-IPN. Millar coined the term "Interpenetrating Polymer Networks." Of course, all of these patents were valid; the applications were unique. However, lack of any cross-referencing indicates an absence of realizing the relationship of the structures employed.

In the late 1960's, four academic groups independently arrived at the same basic idea for IPNs, but with different objectives. These were the groups led by Shibayama (*12*), Lipatov (*13*), K. C. Frisch (*14*), and Sperling (*15*). All four groups had a variety of research interests in IPNs. Shibayama and coworkers emphasized dynamic mechanical behavior and ultraviolet polymerization. Frisch and coworkers polymerized two different polymers in latex form, and blended and crosslinked them. Lipatov and coworkers emphasized thermodynamics and mechanical behavior. Sperling and coworkers investigated sound and vibration damping in IPNs. Over the years, all four teams had a variety of interests. And, in a few years, a number of other investigators joined the field.

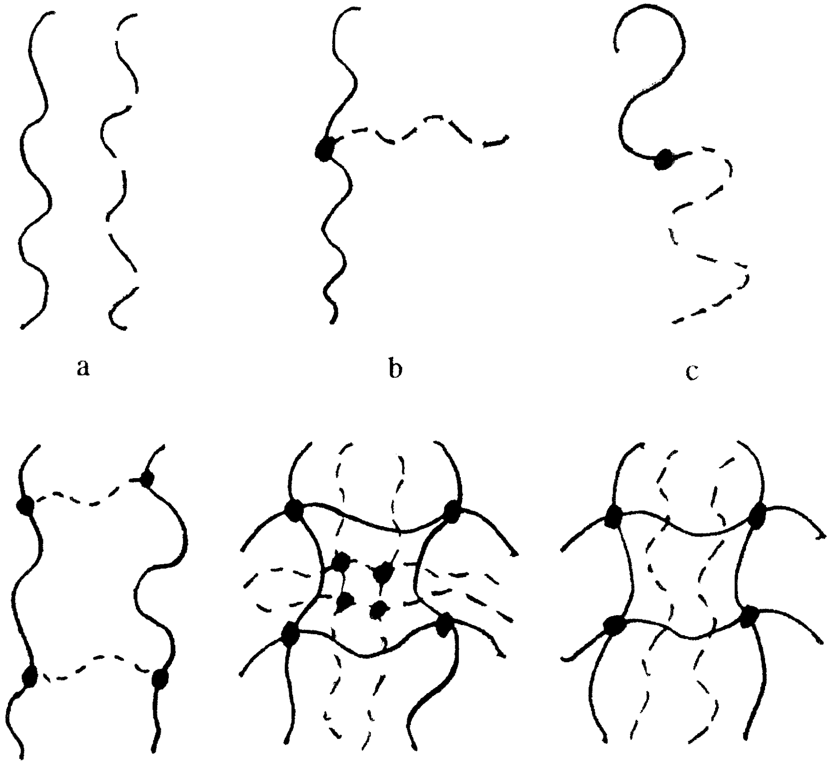

Figure 2. Six basic combinations of two polymers, showing the relationship between polymer blends, grafts, and IPNs. a, a polymer blend; b, a graft copolymer, c, a block copolymer, d, an AB-graft copolymer, e, an IPN, f, a semi-IPN (8).

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

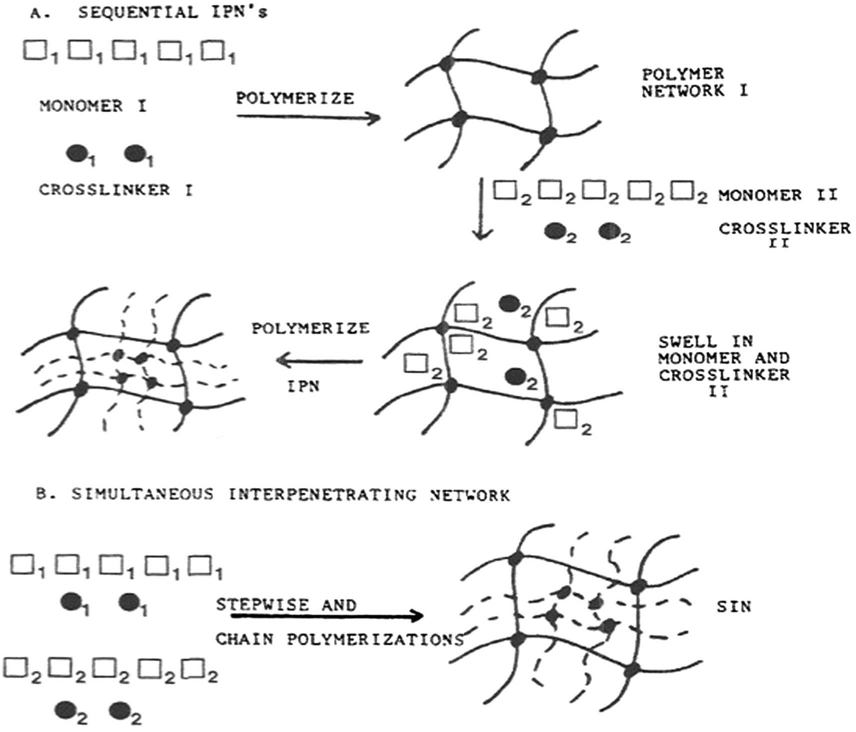

Figure 3. Two methods of IPN synthesis: A, Sequential, and B, Simultaneous (8).

A few words to describe how Sperling arrived at the structure: When he was first hired by Lehigh University in 1967, he was without equipment, but given some money by the university to get started. Besides two graduate students, he was given four seniors. Sperling started the four on different projects. Dave Friedman's task was to build a small U.V. polymerization box, including sheets of glass of 4"x4", with suitable gaskets and clamps, and install a sun lamp. In short order, he did same, and after a few trials was ready for real work. At that time, polymer blends were "hot stuff", and Sperling wanted to try his hand at making the new tough materials. The new polymerization box would have to serve instead of much more expensive heavy mixing equipment. First, Friedman polymerized poly(ethyl acrylate) and crosslinker, (creating an elastomeric network sheet.) Into that he swelled some styrene and its crosslinker, and polymerized same (adding a plastic component). The sheet he made was flexible, and was bent and twisted many times, but unbroken. What a tough material, made on the first try (*15*)!

Shortly afterwards, Sperling, co-investigator Thomas, and graduate students discovered that other combinations, particularly based on ethyl acrylate and methyl methacrylate made sound and vibration damping materials that would cover a very broad temperature range (*16*, *17*),. Figure 4 (*16*) shows tan δ, a measure of damping, as a function of temperature. Note that composition E4 covers the range from approximately -20 C to beyond 100 C, almost constant. A few weeks after Volker Huelck showed Sperling and Thomas his data resulting in Fig. 4, there was a seminar from a man from du Pont, who described their new damping material to damp automobile doors on closing, etc. His data had a sharp peak near room temperature. Huelck's E4 composition, Fig. 4, was not as high, but covered a much broader temperature range. This fruitful area of research resulted in the basis for a number of papers and patents, as well as serving as the basis for a number of Ph.D. students and post-doctoral research efforts, etc. As a major point of the history of invention and discovery, serendipity plays a key role!

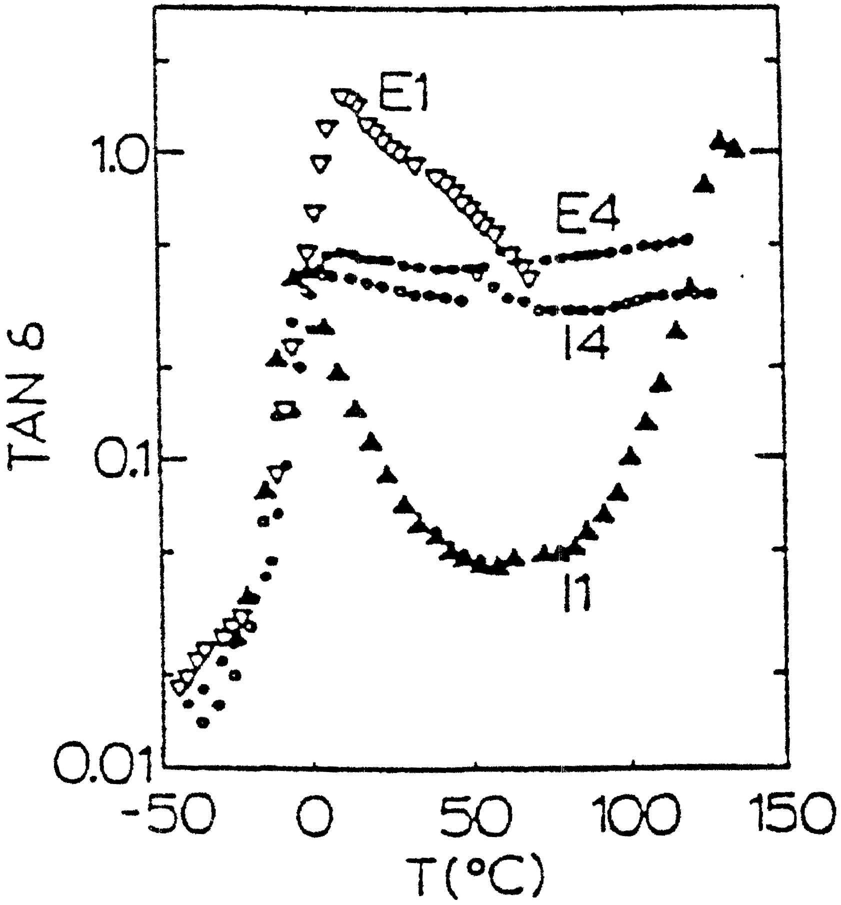

Figure 4. Damping of four cross-poly(ethyl acrylate)-inter-cross-poly(methyl methacrylate). Tanδ = E''/E', where E'' is the loss modulus, a measure of the energy lost as heart during motions, and E' is the storage modulus, providing a measure of stiffness, storing the energy elastically. A high value of either tanδ or E'' indicates good damping (16).

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History of the Understanding of Phase Separation, Cause, Control, and Importance in IPNs

The early patents, as described above, do not mention phase separation. While phase separation was understood for small molecules, such as occurs on cooling many saturated aqueous systems, it could not be effectively studied in polymers. However, one strong hint was that many such materials were cloudy to some extent. Note the soda drink caps mentioned above.

Except for the homo-IPNs, substantially all of the IPNs undergo phase separation. This is important in the development of good properties. However, the type of phase separation, in terms of phase size, which is the continuous phase, and the frequent bonding between the different kinds of chains differs widely. One of the earliest, and still probably best for many phase identification experiments is transmission electron microscopy. In the following paragraphs, a brief study of the development of the morphology of IPNs and related materials will be given.

Figure 5 (*18*) describes six different combinations of polystyrene and polybutadiene. These are “salami” slices of about 600 Angstroms thick. The dark material is the polybutadiene, stained dark with osmium tetroxide. The light material is the polystyrene. The upper left material is prepared by dissolving about 5% of polybutadiene in styrene monomer, and polymerizing with stirring, undergoing both phase separation, and then phase inversion during the polymerization of the styrene. This makes the commercial high impact polystyrene. Note it has a phase-within-a-phase-within-a-phase. This is caused by the droplets of polybutadiene, the dispersed phase, being swollen with styrene, which subsequently polymerizes and phase separates within the droplets. There is significant grafting of the two polymers, especially in the inner phase.

The upper right material has substantially the same composition of monomers and polymers to start, but is polymerized without stirring. It undergoes a relatively coarse phase separation, with the polystyrene remaining in relatively large droplets, and has relatively poor properties. The middle left has the polybutadiene crosslinked before the addition of the styrene (without crosslinker), making a semi-1 IPN of moderate toughness. The middle right has the polystyrene only crosslinked during the polymerization, looking and behaving like the upper right composition, making it a semi-2 composition.

The lower left material is an IPN with light crosslinking in both phases, and is the toughest of the six compositions. Note the very small sizes of the phases. Below, the shape of these phases will be elucidated. On doubling the crosslinking level, lower right, the IPN material is still tough, but not as good as the lower left.

After studying many compositions and cross-sections of the polybutadiene-polystyrene IPN materials, stopping the polymerization and evaporating the remaining monomer, cut at various extents of the polymerization, the development of the morphology of these materials became clearer, see Figure 6 (*8*). Note that the dark material is polystyrene as drawn in Fig. 7, undergoing the polymerization and simultaneously phase separating, and the white material here is the polybutadiene.

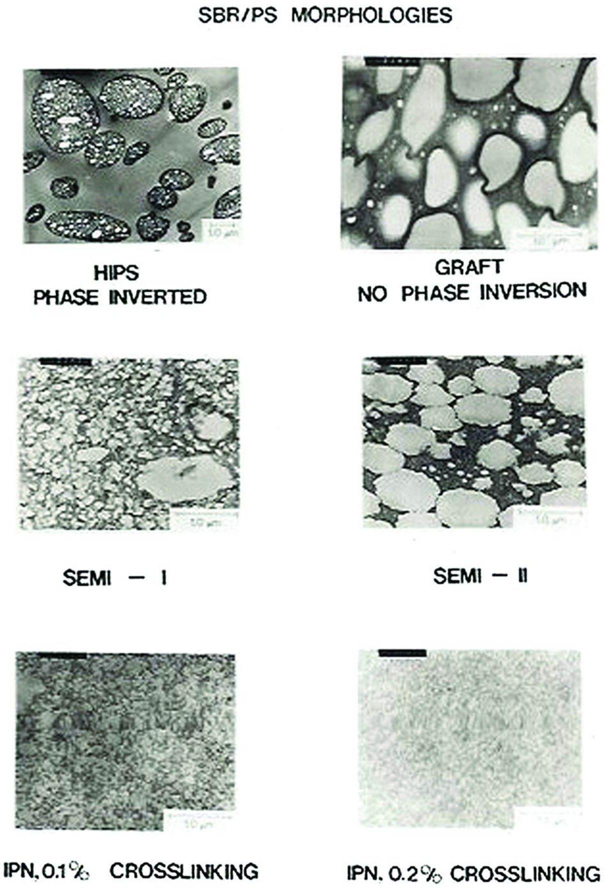

Figure 5. Characteristic morphologies of polymer blends, semi-IPNs, and IPNs based on polybutadiene or SBR (95% butadiene) and polystyrene via transmission electron microscopy. The dark phase is the diene double bond portion stained with OsO_4. The samples are effectively "salami slices" several hundred Angstroms thick (18).

The reader should note that there are two major mechanisms of phase separation: Nucleation and Growth, and Spinodal Decomposition (*19*, *20*). The nucleation and growth mechanism is associated with metastability, implying the existence of an energy barrier and the occurrence of large composition fluctuations. Nucleation and growth mechanisms are the usual mechanisms of phase separation of salts from supersaturated aqueous solutions, for example. The nucleation and growth mechanism results in domain sizes increasing with time. The domains tend to be spheroidal in nature. Spinodal decomposition refers to phase separation under conditions where the energy barrier is very small, so even small fluctuations in composition can grow. Spinodal decomposition tends to form interconnected cylinders; in this case it is the component just polymerizing that forms the cylinders. At the time that Sperling and his students were starting to do electron microscopy, the idea of spinodal decomposition in polymer blends was just taking hold.

The diagrams sketched in Figure 7, can be illustrated in the phase diagram in Figure 8 (*21*), where first there is only one phase, the styrene monomer and crosslinker dissolved in the polystyrene, followed by a small region where nucleation and growth dominate, see the spheres in the first drawing in Figure 6, followed by spinodal decomposition, illustrated by the dark, thick lines shown in Figure 7, actually cylinders, leading to the final composition shown at the bottom of Figure 8.

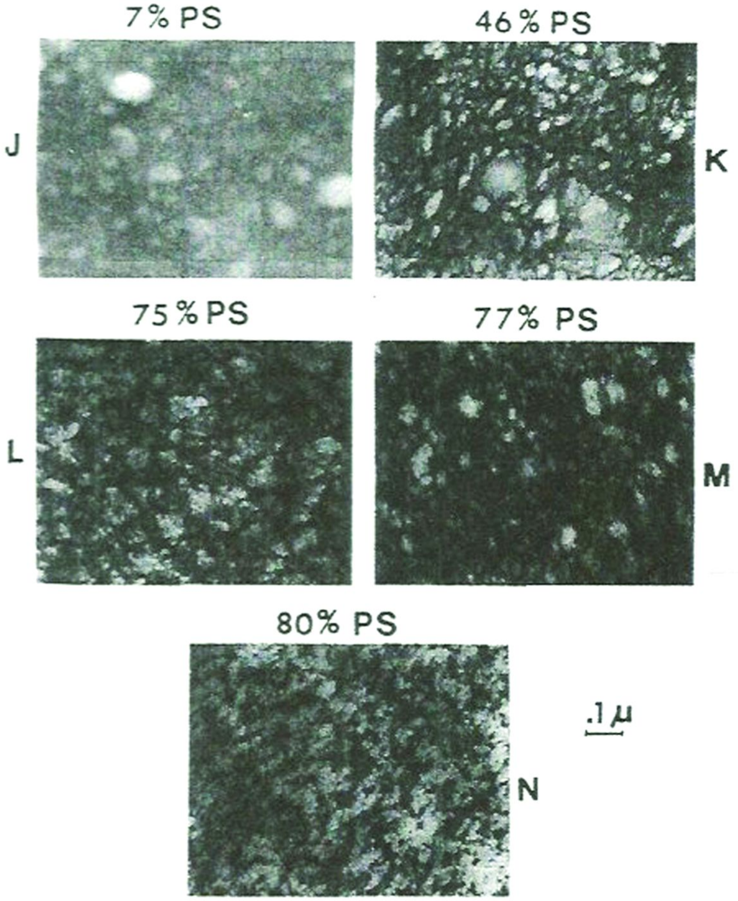

Figure 6. Morphology development in polybutadiene-polystyrene IPNs of variable composition as marked. The polybutadiene phase is stained dark with OsO_4. Again, salami slices. Part of the styrene was evaporated, interrupting the polymerization. Note two kinds of phases: round structures, and oblong structures. Interpretation below (8).

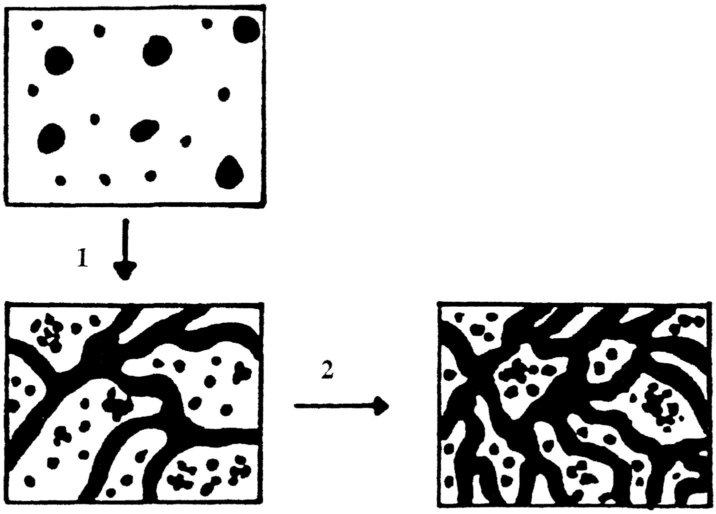

Figure 7. Interpretation of many photos such as shown in Figure 6. The round portions of polystyrene were shown to be roughly spherical, and the oblong structures were cylinders. This indicates that first phase separation is via nucleation and growth kinetics yielding spheres, followed by spinodal decomposition yielding cylinders (8).

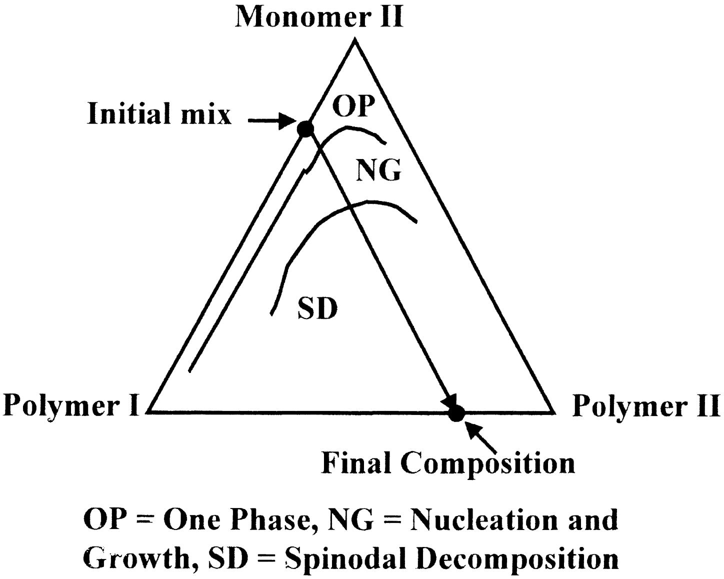

Figure 8. The morphology development path of an IPN. The general path of phase separation in sequential IPNs follows the same general path that polymer blends follow (21).

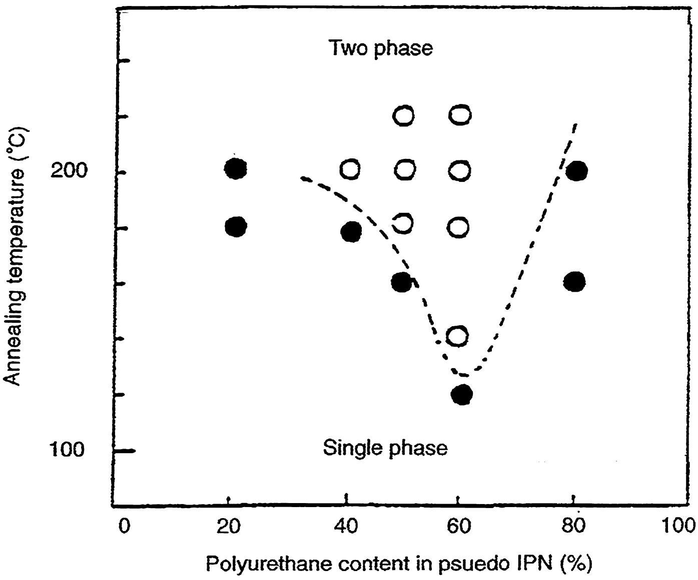

Figure 9. Phase diagram of a semi-IPN of polyurethane and poly(ε-caprolactone diol), PCL, and poly(vinyl chloride, PVC (21).

Table 1. Poly(dimethyl siloxane)/polytetrafloroethylene) IPN films for burn dressings (*23*)

Silicone and PTFE IPNs *M. E. Dillon - BioMed Sciences* *Films for Burn Dressings*	
Property	40/60 PDMS/PTFE
Moisture vapor trans.	720 g/m^2 per day
Hydrostatic resistance	630 kPa
Tensile strength	4825 kPa
Elongation at break	200 %
Porosity	34 %
Transparency	65 %

The Frisch group showed another critical view of phase separation of a fully polymerized IPN as a function of temperature, see Figure 9 (*21*). While most materials become more miscible on raising the temperature, polymer blends and IPNs become less soluble. This is caused by the very small entropy of mixing very large molecules. Note that the Frisch team calls semi-IPNs pseudo-IPNs.

Current rate of publication in the area of IPNs world-wide is approaching 100 papers a year. A relatively large fraction of these papers now are concerned with applications (*22*). And, a surprising number of these papers and patents have a biomedical application. There are a significant number of commercial materials as well. For example, in 1994, Dillon (*23*) published information on “Silon”, an IPN based on silicone rubber and poly(tetrafluoroethylene) which made thin, transparent, moisture conducting, and highly flexible sheets for covering large wounds, especially massive burns, see Table 1 (*23*).

Another material, commercially known as Bioform IPN 20^0 Posteriors, are false teeth based on poly(methyl methacrylate) homo-IPNs (*24*), described by Craig and Powers (*25*), as being teeth that don’t swell in salad oil, can be ground easily to fit, and shrinkage on polymerization is reduced from 21% to 3-6% by using the suspension particles plus monomer mix method selected of preparation. Besides those listed above, commercial applications include wire and cable insulation, ultra high impact resistant plastics, tough automotive bumpers, and belts (*8*).

Where is the Field of IPNs Going?

While IPNs are being investigated in a number of laboratories around the world, some of the most active IPN research developments are coming out of France. Their “hot” area seems to be concentrated about electrical behavior of IPNs. For example, Plesse, et al. (*26*) synthesized conducting IPNs for actuators. The IPNs were synthesized from poly(ethylene oxide) and polybutadiene networks, into which a conducting polymer, poly(3,4-ethylenedioxythiophene) is gradually dispersed. IPNs for electrochromic devices are described by Traqn-Van, et al. (*27*). These conducting films combined linear poly(3,4-ethylenedioxythiophene) and crosslinked poly(ethylene oxide) to make semi-IPNs. Shaplov, et al. (*28*) synthesized a series ofr ionic IPNs for conducting polymers based on imidazliumased monomers. Darras, et al. (*29*) combined polysiloxane with poly(fluorinated acrylates) to make highly transparent materials.

There are also patents of recent interest: IPNs for anion-exchange materials, P. Stevens, et. al (*30*) describe such materials based on IPN and semi-IPN structures. Other applications of interest include fuel cell membranes (*31*), and medical uses such as wound and surgical dressings (*32*).

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Chapter 6

Historical Perspectives of Phenolic Resins

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In the early 1900's, Baekeland first disclosed the successful synthesis of polymers derived from the reaction of phenol and formaldehyde. He was able to commercialize this discovery initially as a Resol and shortly thereafter as a Novolac Resin both as Bakelite products manufactured and sold in Germany and in the USA. In the early stages of this work, Baekeland focused on the commercial development and manufacturing starting in 1910. He suggested the ring structure including phenol and formaldehyde consistent with perhaps Ostwald's concept of the colloid theory for polymers. These two polymers found early use in the abrasives industry – Resoles for bonding the coated abrasives and Novolacs for bonded abrasives.

In the ensuing years, use of phenolic has grown to over 3 billion lbs/year with a critical area of use in the late 1950's to the early 1960's as the matrix of ablative shields for re-entry vehicles. In this chapter, we outline the early history by Baekeland followed by the development of heat shields. We then discuss some more recent work on commercialization of phenolic fibers for use as flame resistant clothing starting in 1969, and subsequent work on development of activated carbon fibers and ion exchange fibers using phenolic fiber precursors.

Introduction

Work on phenolic-like resins was first reported in the early 1870's by Baeyer (*1*) when he described the reaction of resorcinol and methylal : CH2-$(OMe)_2$. Some insight into the nature of the reaction was provided by ter Meer in 1874 (*2*) who isolated dimethoxydiphenylmethane from the reaction of anisole and

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methylal. Initial attempts to polymerize the monomers led to problems of foaming due to evolution of formaldehyde at the latter stages of polymerization. One of the major innovations of Baekeland, pictured in Figure 1, was the use of pressure and filler to eliminate the foaming (*3*, *4*). He shared his findings first at an Americal Chemical Society meeting in February 5, 1909 (*5*). He called the resin Baekelite and described it as “valuable for electrical insulation where a high voltage current is used to greatly reduces the liability of burning out under overload”. Baekeland also proposed a ring structure (I) of the resin (Figure 2), consistent with Ostwald’s colloid theory. At that time, Ostwald argued that polymer did not exist but rather, chains were in the form of cyclic structures which tended to associate to give polymer-like behavior. The issue of the Colloid Theory versus the chain view of polymer was not clarified until 20 years later during a major confrontation between Ostwald and Staudinger in Frankfurt in 1930. It seems that by this time support for the Ostwald interpretation had diminished sharply and other scientists like Mark and Meyer in Germany and Carothers in the USA were making important progress on the structure determination of Cellulose and the new condensation polymers such as the polyesters and more particularly the polyamides based on the Nylon 6,6 composition.

Baekeland patented his process in 1907 and in 1910 formed two companies- The Bakelite Gesellechaft in Germany and the General Bakelite Company in the USA. Baekeland proceeded with the commercialization of two product forms, namely the Resoles and Novolak. Apart from electrical insulation, Baekeland suggested other uses for the resin including lining for metallic pipes, billiard balls and phonograph records.

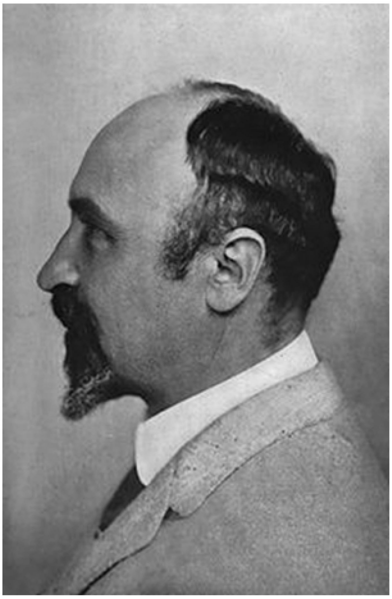
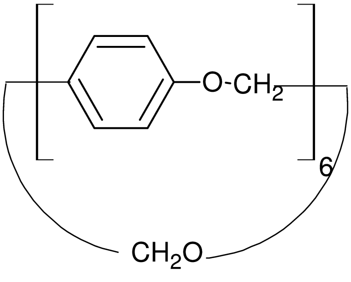


Figure 1. Leo Hendrik Baekeland (1863-1944).



(I)

Figure 2. Structure consistent with Oswald colloid theory.

In this chapter we will discuss the different application areas that emerged for this new polymer system over the ensuing years, and then proceed to describe other areas of use including ablation shields and flame resistant fibers.

Sandpaper

The reaction of phenol with an excess of formaldehyde to form a resole was usually catalyzed with base (*6*). In the manufacture of sandpaper based on Al_2O_3, the abrasive was coated onto a paper backing using the resole as a binder. The coated paper was then draped onto a series of wooden festoons which entered a large oven to initiate the drying process to remove the solvent. As the first step in the reaction from 50-70°C the methylol group condensed with another methylol group to form a dibenzyl ether link (II). As the temperature of reaction increased to 80-100°C the dibenzyl ether link broke down to a more stable methylene bridge (III) plus formaldehyde as a by-product (Figure 3). In this way a 3-dimensional network will form as a coating on the paper. Abrasive grains such as Al_2O_3, diamond grits or silicon carbide were incorporated into the resole during the coating step.

Baekeland certainly deserves much of the credit for demonstrating the utility of the resoles for this application as well as their use in preparing thin film laminates.

Grinding Wheels

Baekeland also successfully developed the Novolac with hexamethylene tetramine $(CH_2)_6$-N_4 as the curing agent. The Novolac (IV) was prepared by the acid catalyzed reaction of phenol with formaldehyde (Figure 4) to yield three distinct oligomeric systems with a low molecular weight of 600, 700 and 800 (*6*). The acid catalyst used more frequently is sulfuric acid, although oxalic acid has found use to reduce problems arising from the more corrosive nature of H_2SO_4. Thus a wide variety of grinding wheels were made available commercially for use in finishing and stock removal in shaping a wide variety of metal products. Companies such as Carborundum and Norton played a leading role in the development and commercialization of these and related fields. Both companies were more recently acquired by St. Gobain Co.

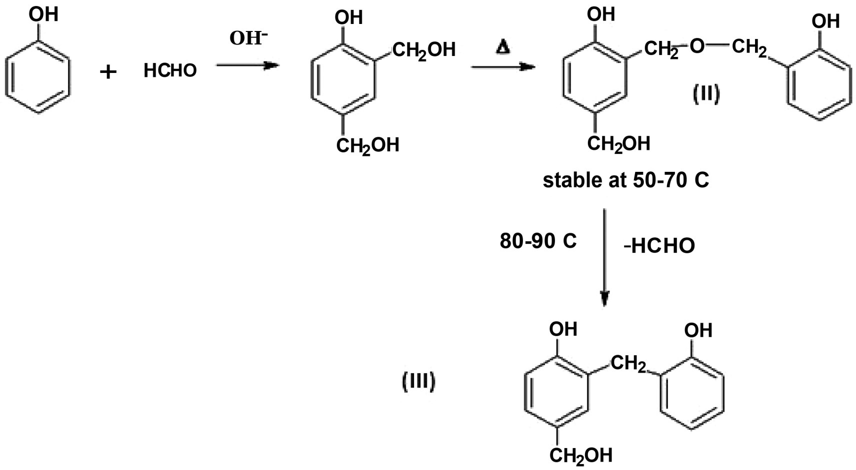


Figure 3. Synthesis of Resol.

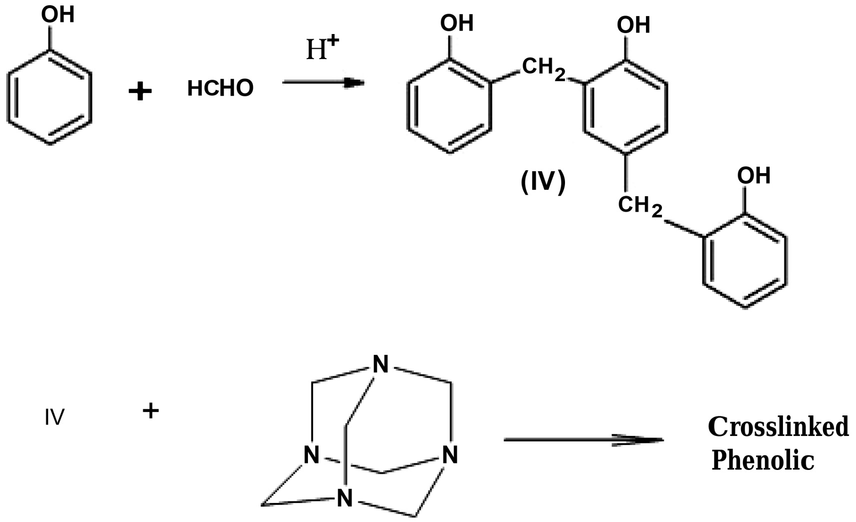


Figure 4. Synthesis of Novolak.

Ablative TPS

Another area where phenolic resins played an enabling role was for use as ablative shields for use in reentry vehicles. In World War II, during the German development of the V2 missiles, it was found that these missiles on reentering the atmosphere of the earth tended to overheat (*7*). Thus the high friction resulting from the outer air atmosphere and the missile travelling at high velocities highly refractory materials could melt, causing major damage to the structure of the missile. This problem was further exacerbated when the USA undertook to design the Apollo in 1961, the manned lunar exploration, program. One of the most difficult tasks here was to design a heat shield that would withstand the reentry into earth's atmosphere. The major innovation facilitating the future missions was the ablative thermal protective systems (TPS).

Ablative TPS protected the space vehicle through (a) an ablation process forming low molecular weight gas molecules that thicken the boundary layers and interfere with the convective heat transfer to the surface, providing a cooling effect (also called blowing) (b) the displacement of the shock layer away from the surface (c) char formed due to burning of the binder that forms an effective insulating layer (*8*). Phenolic resins were found to be great ablative materials because of their high char yield (~55%) and ability to form large fraction of low molecular weight gases.

The ablative TPS research was at its peak from the early 1960's to mid-1970's due to the nuclear missiles programs and the Apollo lunar missions. Phenolic resin impregnated carbon or silica based materials have been used for various missions. The first successful ablative heat protection material was invented by Dr. George Sutton and consisted of refractory fibers in a thermosetting polymer such that the fibers were randomly oriented to hold the resin in place as it pyrolized and charred. His invention was used for ICBM nose cones and made possible the reconnaissance system Corona through its Satellite Recovery Vehicle, and this material was also successfully used for the heat shield of the Mercury manned space vehicle. The development of high strength carbon fibers allowed them to replace the refractory oxide fibers (i.e. glass, silica) that melted when exposed.

NASA selected the Avcoat ablator system for the Orion crew module. Avcoat was used for the Apollo capsule heat shield and on select regions of the space shuttle orbiter in its earliest flights. It was put back into production for the study. It is made of silica fibers with an epoxy-phenolic resin filled in a fiberglass-phenolic honeycomb and is manufactured directly onto the heat shield substructure and attached as a unit to the crew module during spacecraft assembly. Dense carbon-phenolic composites that were developed by the United States Air force for ballistic applications were subsequently used in the Galileo, 1989 and Pioneer-Venus (August 1978) missions. Low density composite, PICA-phenolic impregnated carbon ablator, has been used in the Stardust sample return mission, February 1999 (*9*).

After the 1980's, focus was shifted to development of reusable thermal protective systems, like foamed SiO_2 in the form of tiles, owing to the Space Shuttle program. For future missions requiring more aggressive environments, it appears that NASA will return to an ablative system with superior ablative features compared to phenolic/carbon fiber composites. One such system may consist of carbon fibers embedded in the aromatic thermosetting copolyester (ATSP) matrix. The coauthors have recently developed an aromatic thermosetting copolyester with carbon fibers, which show much lower recession rates and low back face temperatures.

Phenolic Fibers

Use of phenolic resins in the form of crosslinked fine fibers was announced in 1969 for use as low cost flame resistant fibers (*10*, *11*). These fibers were prepared by melt spinning from a stainless steel bushing (3000 tip) which provided a very low cost replacement for the platinum spinneret. These fibers were collected as a 100’ tow cut from the take-up roll in a spiral cut (typically the tow weighed 25 lb). The tow was then cured by contacting with an HCl and formaldehyde solution either as a batch or continuously. The crimped, 2” staple prepared from the tow was readily processable on a cotton card and fabrics could be dyed to light stable colors including olive green, red, brown and black (*12*). A white fiber could be prepared by acetylating the gold fiber which could then be dyed to a full range of light stable colors. The flame resistance of phenolic fiber (tradenamed as Kynol) was outstanding with an LOI of 0.36 (*13*).

A major facility for spinning phenolic fibers using a Pt spinneret was installed in Osaka by Nippon Kynol (a joint venture company between the Carborundum Co, Mitsubishi Chemical and Kanebo) in the early 1970’s. This approach precluded the potential for a much lower cost fiber that would result from using a stainless steel bushing. The large reduction in capital cost resulting from use of an electrically heated steel bushing has apparently never been tested to determine whether a lower cost phenolic fiber would create numerous solutions to problems associated with flammability.

Conditions for curing the fibers involved heating in the presence of a solution of formaldehyde and hydrochloric acid. As the time and temperature of curing is increased from room temperature to 90°C, there is a tendency to introduce significant concentration of non-crosslinked methylol groups or possibly chloromethyl groups. This excess concentration can be controlled by heating in absence of HCl + CH_2O to remove the excess formaldehyde. In the initial polymerization of the phenol and formaldehyde there is a tendency to yield extended chains followed by crosslinking. This is most likely the mechanism by which most Novolac resins undergo curing.

Control of fibers cross-section is an important aspect of the mechanical properties (*14*). Thus, fibers with diameter greater than 20 μ tend to be more brittle. Use of a small amount of an elastomeric finish such as Neoprene can greatly enhance the wear resistance without compromising the flame resistance.

One of the key features of the phenolic fiber (Kynol) is its outstanding flame resistance. Thus the Kynol fiber displays an LOI (Limiting Oxygen Index) of 0.36. See Table I for a comparison to several other carbonaceous material which display in some cases even higher LOI values. As a point of comparison most textile fibers have LOI values of 0.21 which means they will burn on exposure to flame in air. For example, flame resistant fibers such as the Aramids, Nomex and Kevlar, both display an LOI of 0.28 which means that they require a concentration of 28% oxygen to burn with a candle-like flame. Of course if the external temperature is higher (e.g. using a Bunsen burner) then the Nomex will appear to melt and burn. On the other hand the phenolic fibers do not burn even when exposed to an oxyacetylene torch. In a flame the fiber gave off minimal smoke or toxic gases. It tended to form a stable char of carbonaceous fibers in 60% yield which continued to provide protection even in an oxyacetylene torch. In contrast, fabrics of Nomex will melt and burn over a Bunsen flame within 7-10 seconds and after several minutes may begin to generate highly toxic byproducts such as isophthalonitrile.

Activated Carbon Fibers (ACF)

Another area where phenol formaldehyde resins have potential for the future is the synthesis of activated carbon fibers (ACF). We have found that the phenolic fibers can be heated under inert conditions to about 600 °C to yield a carbonaceous fiber with a surface area of 600 m^2/g in 60% yield. Such fibers have far improved contact efficiency with media containing trace impurities to well below 1 ppb compared to 5-20 ppm removed using activated carbon granules, the standard workhouse for water and air purification.

A comparison of the ACG Vs ACF for removal of benzene with an EPA maximum contaminant level (MCL) value of 5 ppb is shown in Figure 5.

An important advance in the use of ACF was made with the discovery that the ACF could be made on a glass fiber substrate which not only simplified the cost of manufacture of the fibers but greatly improved the durability of the carbon coated glass fiber (*15*). Another important innovation was the discovery of the chemical activation process (*16*, *17*) where selected additives such as $ZnCl_2$, H_3PO_4 and other system were incorporated into the resin coated glass fibers e.g. PAN, Phenolic, PVA and Cellulose to achieve high surface areas from 1000-2500m^2/g in much higher yields of upto 35-90%.

The chemical activation could be carried out at temperatures as low as 250-400 °C. This should be contrasted to yields of 10-20% typically obtained in activation carried out with air, steam and CO_2 at temperatures of 750-800 °C.

Table I. LOI of different materials

Material	*LOI*
Activated coconut charcoal	19-25
Carbon fabric (0.28% ash)	32
Phenolic fiber	36
Carbon fabric (350-750 m^2/g)	34-41
Carbon fabric	74-81

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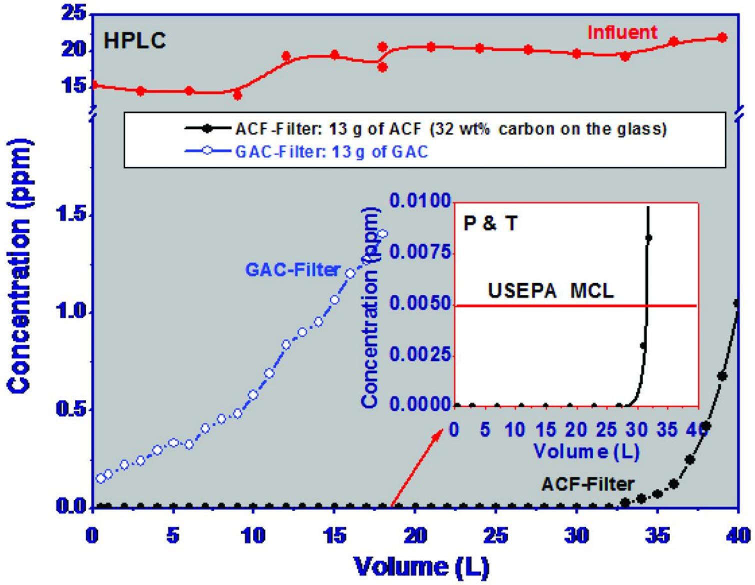

Figure 5. Removal of Benzene using granular activated carbon Vs ACF filter. HPLC stands for High Pressure Liquid Chromatography; P & T stands for Purge and Trap Technique.

Ion Exchange Fibers

The final topic to be discussed briefly is the use of phenolic fibers to prepare ion exchange fibers. This was accomplished in the early 1970's (*18*) and then published in the late 1970's. Subsequently, in the late 1990's it was shown that an improved product could be made by chemically treating the chloromethylated polystyrene fiber on a glass fiber substrate with alkyl amines to yield an anionic fiber or by sulfonating the partially crosslinked polystyrene using divinyl benzene as the crosslink agent (*19*, *20*). As with the ACF, the ion exchange coated on a glass fiber substrate exhibited far superior breakthrough properties to numbers well below 1 ppb and well below the standard set by EPA for impurities such as Pb, AsO_4^{3-}.

Conclusions

The original discovery of the phenolic resins by Baekeland in the early 1900's was pivotal to the field of polymer chemistry. Even though the correct structure was not recognized immediately, it did not interfere with the rapid commericial development of these resins, particularly as binders for coated abrasives and bonded abrasives. The value of these early discoveries of Baekeland is attested to by the subsequent industries that emerged such as the laminating resins, the ablation shields for rocket, flame resistant fibers, activated carbon fibers and ion exchange fibers which will definitely impact fields such as water and air purification.

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Chapter 7

High-Temperature Aromatic Polyesters of p-Hydroxybenzoic Acid and Their Copolyesters

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The polymerization of the p-hydroxybenzoic acid (PHBA) homopolymer was first accomplished in 1963 and then commercialized in early 1970 as Ekonol. In the mid 1960's we successfully prepared melt processable copolymer of PHBA and biphenol terephthalate and proceeded to commercialize it as Ekkcel I-2000 and C-1000 in early 1971. This was followed shortly thereafter with high the discovery of a high strength/modulus fiber (patented in 1974 and based on the I-2000 composition). Important progress was made in the 1980's on the role of interchange transesterification, ITR, leading to randomization and ordering of copolyester chains. As part of ITR we were able to demonstrate development of strong adhesive character between two coatings of copolyesters. Finally we were successfully able to prepare a new kind of thermosetting aromatic copolyester (ATSP), which provides a number of solutions to critical problems including greatly improved ablative shields, far superior matrices for greatly improved fiber reinforced composites and wear resistant coatings consisting of fluorocarbon polymer as blends with ATSP.

Introduction and Background

Work on the polyesters of p-hydroxybenzoic acid (PHBA) represents some of the earliest reports on polymeric materials. Thus, in 1883, Klepl reported on isolating a dimer and trimer of PHBA, along with a residue which he described as

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p-oxybenzid (*1*). On further heating of the residue he observed a sublimate which formed in copious quantities. He further characterized it as a material which on further heating yielded a sublimate of phenyl ester of p-phenoxybenzoic acid. One year later, Schiff (*2*) reported on forming a similar polymer by reacting the acid chloride of PHBA with itself.

In 1909, Emil Fischer, the famous organic chemist in Germany undertook to confirm Klepl's work by unambiguously preparing the dimer and trimer and confirming that Klepl in 1883 had indeed prepared these oligomeric structures. This work was published in 1909 (*3*), one year before Ostwald proposed his colloid theory (*4*) as an alternative explaination for polymer-like materials. It is noteworthy that Fischer had also reported a polypeptide chain of 18 units in 1906 (*5*). Subsequently, little work was done on the PHBA family of polymers until the 1950's when Gilkey and Caldwell (*6*) apparently unaware of the earlier work of Klepl studied the polymerization of the p-acetoxybenzoic acid and m-acetoxybenzoic acid. In the latter case they reported that the ester melted at ~175 °C while in the case of the para ester they isolated a product which didn't melt, but on heating at 350 °C yielded a sublimate. From these results they concluded that the PHBA polymer was unstable and didn't merit any further work. It was this publication and a review talk presented by Fred Wallenberger in the early 1960's that prompted us to re-examine this material, since it seemed that the polymer of PHBA should be more thermally stable based on its molecular structure. Clearly in both Klepl's work and Gilkey and Caldwell's approach, they had carried out their polymerizations in the melt and as the molecular weight increased to 3-6 units, the polymer set up and there was no mechanism to dissipate the heat. Such reactions can show a tendency for a runaway reaction leading to degradation. For example, in this case the temperatures got out of control allowing formation of the phenyl ester of p-phenoxybenzoic acid by an acid catalyzed condensation of two phenolic hydroxyls or two acetoxy units to form an ether. After repeating the work of Gilkey et al and observing the phenyl ester of p-phenoxy benzoic acid, we successfully prepared the homopolymer of PHBA in the Spring of 1963 by capping the carboxylic acid with a phenyl ester and controlling the reaction temperature through use of a heat exchange medium such as Therminol 66. A thermally stable product was isolated that was highly crystalline, stable in air at 350 °C (Figure 1) and was fabricable by metal forming techniques such as plasma spray (Figure 2) and high energy rate forging (HERF) (Figure 3). This product was commercialized in early 1970 as "Ekonol" (*7*). We had already shown that the Ekonol powder could be used as a plasma spray and by the late 1970's the Metco Co was marketing the product as a plasma spray coating for use as an abradable seal in high speed jet engines for aircraft. The Ekonol powder was made available originally at $15/lb, but by the late 1970's, this price was increased to $150/lb with a major increase in the profitability of the Ekonol powder (a market which has persisted up until the last few years). The use of high energy rate forging to fabricate molded samples of the Ekonol was also demonstrated. Thus, by preheating sintered specimens of the Ekonol powder to 300 °C one could insert the samples into the mold used for HERF and in a semi-continuous fashion fabricate fused, highly oriented disks measuring 0.5" in thickness and 3-4” in diameter. This type of equipment at the time was being used to fabricate highly refractory metals such as Titanium and Tungsten.

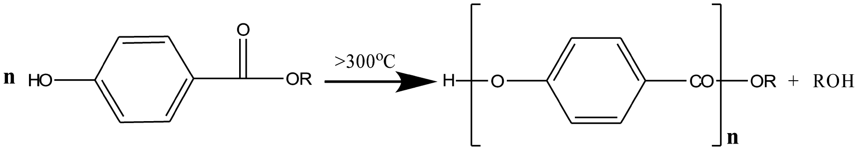

Figure 1. Preparation of Ekonol polyester.

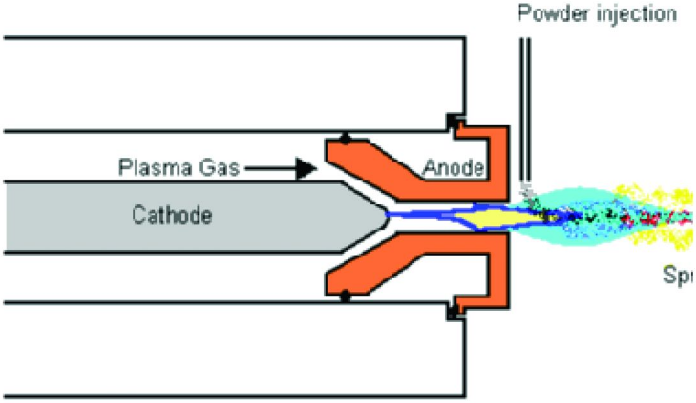

Figure 2. Plasma flame spray for processing ATSP.

In the mid 1960’s some work was initiated to prepare melt processable copolymers of PHBA with biphenol terephthalate (BPT). The hope was that these non-melting rod-like chains would form a eutectic leading to compositions that melted. Very early in this work we observed that the 2:1 PHBA:BPT melted at 408 °C. There were some distinguishing features in the processing, namely under shear in an extruder the melt tended to fibrillate. This problem could be controlled by reducing the shear to yield a more processable melt. The high melting point introduced some concerns, but these were manageable. We also looked at a closely related system namely 1:2 PHBA:BPT which had almost as good high temperature properties but seemed more suitable for compression molding than injection molding. In early 1971, we were able to announce the commercial availability of the Ekkcel family of polymers namely the C-1000 compression molding grade and the I-2000 (an injection molding grade). The properties of these two copolymers are summarized in Table 1.

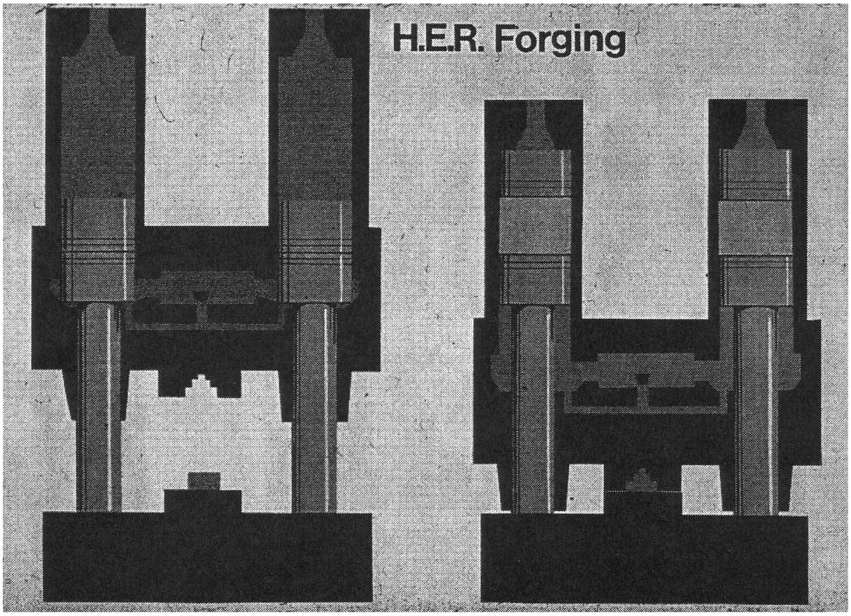

Figure 3. High Energy Rate Forging.

Table 1. Properties of Copolymers based on PHBA and BPT

	Ekkcel I 2000 PHBA:BPT (2:1)	**Ekkcel C 1000 PHBA:BPT (1:2)**
Tensile Strength, PSI (MPa)	14,000 (96.5)	10,000 (68.9)
Tensile Modulus, PSI (GPa)	350,000 (2.4)	190,000(1.3)
Elongation (%)	8	7-9
Flexural Strength @73ºF, PSI (MPa)	17,000 (117.2)	15,000 (103.4)
Flexural Strength @500ºF, PSI (MPa)	4,000 (27.6)	5,000 (34.5)
Flexural Modulus @73ºF, PSI (GPa)	700,000 (4.8)	450,000 (3.1)
Flexural Modulus @500ºF, PSI (GPa)	235,000 (1.6)	125,000 (0.86)
Impact Strength – Unnotched, Ft.lb/in (J/m)	3 (160.2)	2 (106.8)
Heat Distortion @264 PSI, ºF (°C)	560 (293)	572 (300)
Coefficient of Thermal Expansion, in/in/ºF (µm/m-°C)	1.6 x 10^{-5}(2.88)	2.87 x 10^{-5} (5.17)
Specific Gravity	1.40	1.35

One goal that we had for both systems was to design a copolymer that could be processed in the temperature range of 400 °C and retained useful properties up to 300 °C. The quest for melt processable polymers with useful properties at high temperatures was realized with this development. The work on the high modulus/strength fiber merits some discussion from a historical point of view. *In early 1971, Dr. Economy was in England to present a lecture at a major polymer meeting to announce the development of the new family of Ekkcel polymers. A mutual friend invited him to meet with several high level R & D personnel from ICI for lunch. Their interest was primarily to assess our interest in preparing fibers of the Ekkcel family of polymers, since Du Pont was just getting ready to announce the development of benzamide fibers and shortly thereafter the Kevlar fiber, the polyphenyleneterephthalamide composition. They wanted to know whether we had recognized the similarity in structure between the aramid fibers and aromatic polyesters and the potential for these new polymer systems to form similar fibers. During the discussions, Dr.Economy quickly realized the similarity in the structure between the two families of polymer and the possibility of making and commercializing a fiber based on the aromatic polyesters. When Dr.Economy returned to the Carborundum Lab in Niagara Falls, he started a small effort to make fibers of the I-2000 grade of polymer. To facilitate the process we prepared a lower molecular weight version of the I-2000 which could be melt spun into filaments at lower temperatures of ~330 °C. These could be further drawn at elevated temperatures in excess of 400 °C to further orient the crystalline structure and sharply increase the molecular weight and the strength and modulus of the fiber into the range of Kevlar fiber.* In Table 2 is a comparison of properties of the Kevlar fiber vs those of the Ekonol fiber (a name ascribed by the Sumitomo Chemical, former partners of the Carborundum Co. from the early 1970's to the late 1970's). Several key features of the Ekonol fiber included (i) the low moisture pick-up of the Ekonol vs the Kevlar fiber (ii) the slightly lower density of the Ekonol fiber and (iii) not indicated but perhaps most important that the Ekonol fiber was formed by a melt spinning process vs the use of a sulfuric acid solution spinning of the Kevlar with all its concomitant problems of subsequent clean-up.

It is noteworthy that Carborundum management attempted to withdraw the Ekonol powder from the market, but Metco Co. threatened to sue, since an agreement had been made earlier that Carborundum would continue to supply the Ekonol powder to Metco.

Carborundum Co. had established a joint program with Sumitomo Chemical on the aromatic polyesters from the early 1970's when they started to sell the Ekonol as a plasma spray powder for use as an abradable seal. In the late 1970's Carborundum Co. was sold by the Mellon family to Kennecott Copper and then subsequently to Sohio, Amoco, BP and then to Saint Gobain.

Table 2. Properties of Ekonol fiber vs Kevlar. Properties of Ekonol were optimized by Sumitomo chemical research (1987)

	Kevlar 49	Ekonol Fiber
Density (g/cc)	1.45	1.40
Tensile Strength, PSI (MPa)	400,000 (2757)	550,000 (3792)
Tensile Modulus, PSI (GPa)	20 x 10^6 (137.9)	24 x 10^6 (165.5)
Elongation (%)	2.7	3.0
Moisture Absorption (%)	2.0	0.01

In the mid-1970's, Eastman Kodak announced the commercial development of the 60/40 copolyester of p-hydroxybenzoate and ethylene terephthalate (*8*). This product was subsequently withdrawn from the market place undoubtedly because of several drawbacks like its tendency to degrade at temperatures in excess of 300 °C (*10*). An important contribution of the Eastman Kodak work was the demonstration of the shear sensitivity of this copolyester using a melt rheometer. (See Figure 4). Then by 1980, Celanese announced the commercialization of Vectra, a family of polyesters based on 2,6-hydroxynaphthoic acid and PHBA (30/70) (*9*). The advantage of this family of polymers was the ease of processing into molded shapes and into fibers. The drawbacks include the cost of 2,6-hydroxynaphthoic acid which is somewhat more expensive than the PHBA monomer. Also the 70/30 copolymer of PHBA/HNA has a Tg of ~150 °C which sharply reduces the high temperature properties of the copolymer to that temperature range. Another shortcoming is the potential for crosslinking of the naphthalene rings during annealing of the product at 310 °C.

Interchain Transesterification Reactions (ITR)

In the mid 1980's we started a systematic study to explore the nature of the ITR reactions of the aromatic polyesters. The high temperature stability of the aromatic ester units permitted studies of reactions in the temperature range of up to 450 °C for short contact times. For example, reaction of the 50/50 mixture of single-crystal polymers of PHBA with PHNA during compression sintering at 460 °C rapidly yielded the random copolymer as an extrudate with a m.p. of 260°C. In a different example of PHBA/BPT copolymer (commercially available as Xydar, m.p. 408 °C), ITR can be used to improve processibility. It was concluded that the Xydar known earlier as Ekkcel I-2000 was a blocky system which incorporated random strings of the copolymer from the earlier stages of the polymerization. The blockiness arose during the latter stages of solid state polymerization in a therminol solvent. By heating the Xydar (m.p. 408 °C) at 450 °C we obtained a more random structure with a m.p. of 350 °C.

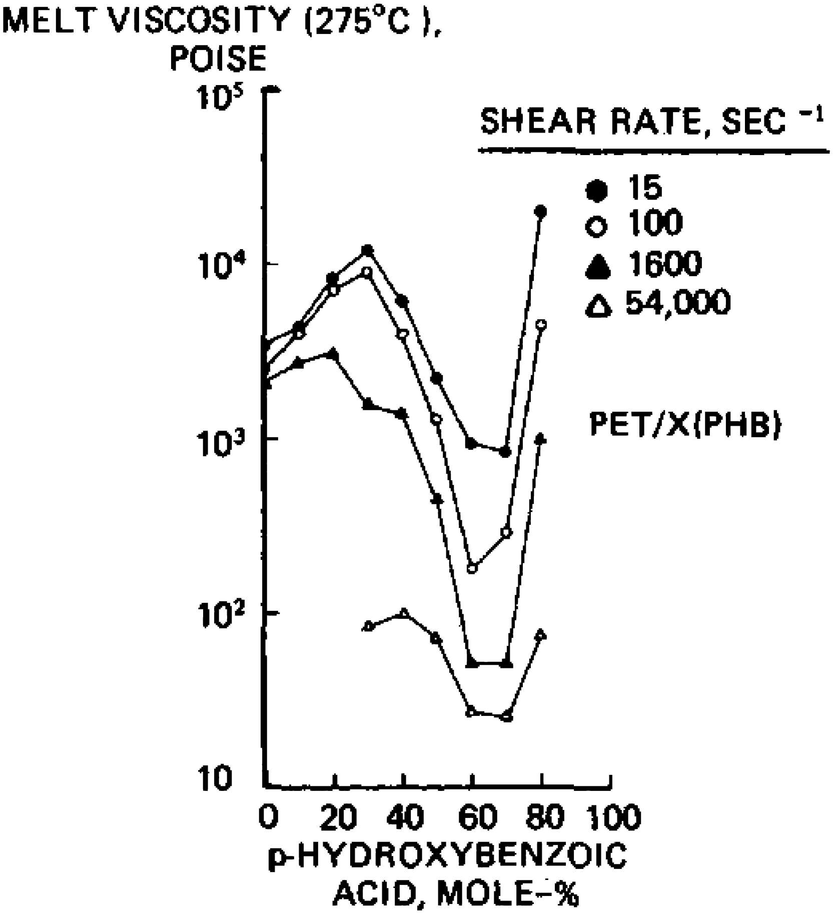

Figure 4. Shear sensitivity of the PHBA/PET copolyester (8).

An important variation on the ITR process was the ability to induce sequence ordering by annealing just below the melting point. For example, the Vectra copolymer with 73/27 PHBA/HNA when prepared in a melt polymerization at 350 °C would yield a random copolymer with a m.p. of 283 °C. On the other hand, annealing the 73/27 Vectra at ~20 °C below the m.p. (~263 °C) the m.p. increased by 20-25 °C as illustrated in Figure 5 which describes both ordering and randomization over the composition range – 20/80 PHBA/HNA to 73/27 PHBA/HNA. Interestingly, attempts to further increase the melting point of Vectra by carrying out a second annealing step led to a degradation reaction which appeared to be specific to the presence of naphthalene (*11*). As far as we were able to determine, the reaction involved dimerization of two naphthalene rings resulting in a degradative coupling with loss of crystalline order. This kind of process was not observed in the Xydar system were the random copolymer with a m.p. of 350 °C could be annealed at 330 °C to increase the m.p. up to 400 °C. A second annealing at 380 °C further ordered the copolymer to reach a m. p. of

450 °C. This kind of ordering when it was first proposed engendered considerable opposition on the part of a number of polymer scientists including Wunderlich, Yoon, Lenz and Geil (*12*).The matter was finally put to rest when Economy et.al. (*13*) carried out NMR studies to show that this was indeed a chemical process based on ITR and not some physical process as proposed by these scientists.

Aromatic Thermosetting Copolyesters (ATSP)

Starting in the early 1990's, the Economy group at Illinois undertook to see if they could design a thermosetting system based on rigid rod-like units (See Figure 6). There were some formidable arguments against such an undertaking. For instance, such a material would set up into a non-melting system that could no longer react after an initial reaction. Another concern was that the acetic acid by-product of polymerization would be trapped in the growing polymer and could lead to local depolymerization. The first approach that we selected is illustrated in Figure 6. where we prepared two oligomers, the first one with carboxylic acid end groups and the second with acetoxy end groups (*14*, *15*). Properties of a number of these oligomers are summarized in Table 3 where the softening points and molecular weights are indicated. Mixtures of the two oligomers were found to coat various substrates and then continued to further react with heat to achieve a highly thermally stable coating or matrix that in a large measure fulfilled our original goal. A second approach involved simultaneously reacting all the monomers used in preparing the two oligomers in order to produce a finely divided crosslinked powder containing relatively high concentrations of readily accessible acetoxy and carboxylic acid groups on the surface of the particles. These particles could then be further reacted by ITR at the respective surfaces to yield an additional level of crosslinking.

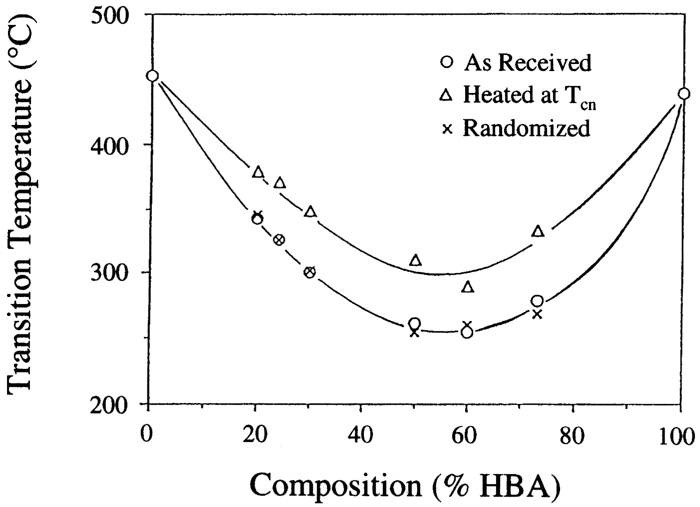

Figure 5. Sequence ordering in Vectra copolymer.

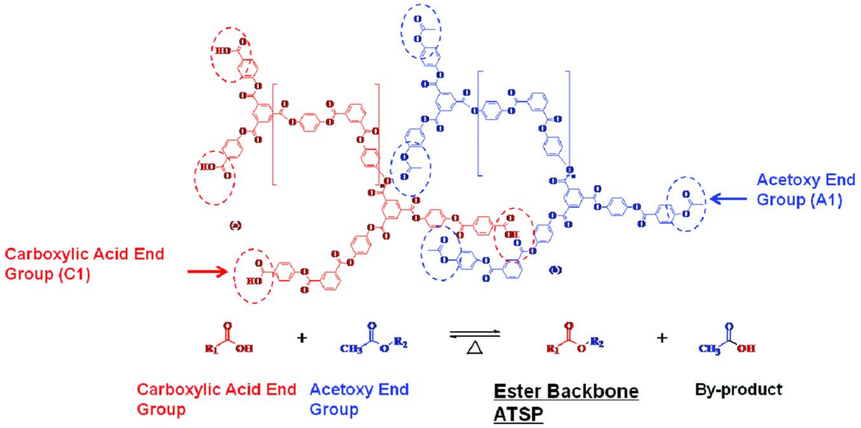

Figure 6. Synthesis of ATSP.

Table 3. Properties of ATSP oligomers, oligomers marked with * exhibit liquid crystallinity in melt

oligomer	molar feed ratio of monomer					MW_{av} (g/mol)	functionality	softening point (°C)
	TM	TAB	ABA	IPA	HQDA			
C-1	2		6	3	4	1934	4	172
C-2*	1		6	4	4	1890	3	143
C-3	2		4	2	3	1454	4	189
C-4	2		5	1	2	1334	4	188
C-5*	1		5	2	2	1290	3	161
C-6	2		3	1	2	1094	4	162
C-7	2		3		1	854	4	148
C-8	1		3	1	1	810	3	136
A-1	2		2	2	7	1750	4	128
A-2*	1		5	2	5	1692	3	130
A-3*	1		5	1	4	1452	3	160
A-4		2	4	2	1	1270	4	128
A-5		2	2	2	1	1030	4	107
A-6		2	3	1		910	4	105
A-7		1	2	1	1	732	3	81

Table 4. Key properties of ATSP

- Stable in air up to 350 ^{0}C and in nitrogen till 425 ^{0}C with T_g up to 285 ^{0}C
- Can process on standard equipment to very low void in the composite
- Interchain Transesterification Reactions (**ITR**) permits further densification, high temperature repair, healing, adhesive bonding to itself and other polymers and various metals – Al, Steel, Titanium, Cu
- **Liquid Crystalline Character** minimizes interfacial stresses associated with CTE mismatch
  - Potentially high mechanical properties with high σ/E carbon fibers
  - Thermal fatigue resistance
- Outstanding **flame resistance**
  - LOI of 0.4 of ATSP and >0.8 for the ATSP/C composite
- Easy to manufacture resin – highly reproducible

To illustrate the anticipated advantage offered by this new system , some groups have used resins such as PEEK or ethynyl and maleimide terminated polyimides as high temperature matrices or precursors thereof. Each of these systems have clear drawbacks, e.g. PEEK is not only difficult to process but its use temperature is limited by its relatively low Tg of 150 °C. In the case of the ethynyl terminated or maleimide terminated groups, the cross-linking of these end groups leads to units which can oxidatively degrade at 250°C and below.

Key properties of the ATSP are summarized in Table 4. Noteworthy among these properties are the ability to continue to further consolidate composites by the ease with which these polymers undergo ITR achieving T_g values as high as 285 °C (*16*). Another impressive feature is the ability of some of these oligomers to display liquid crystalline character which can persist into the cured state. This solves one of the most critical problems in the use of high-modulus carbon fibers which lead to high levels of stress at the fiber-matrix interface due to a mismatch in the coefficient of thermal expansion (CTE). Use of the ATSP solves this problem by yielding a low-stress interface between the C fiber and the ATSP matrix (*17*). Another novel feature is the outstanding flame resistance of the ATSP illustrated by the high limiting oxygen index (LOI) which in combination with appropriate carbon fibers has yielded unparalleled ablation results with very low recession rates. Another area of opportunity for the ATSP is its ability to form blends with Teflon at very high temperatures of 350-400 °C. These composites display very low wear characteristics (*18*, *19*).

Conclusions

The aromatic homopolyesters have been studied as far back as the earliest reported polymers in 1883. It wasn't until 1971-72 that the homopolyesters and copolyesters of PHBA were first successfully commercialized. During the 1980's, important progress was made in understanding the melt processibility of these polymers with the understanding of how these systems could be made into high strength/modulus fibers and how using ITR could further order or randomize the chain sequence. More recently, work on developing a thermosetting ATSP has been successfully carried out. This new thermoset permits design of far more thermally stable matrices for aircraft structures as well as ablation shields with far better recession rates and cooling efficiencies than anything available to date. Blends of ATSP with fluoropolymers have yielded wear resistant surfaces unavailable with any other materials.

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Chapter 8

In Their Own Words: *Plastic Pioneers* in the Chemical Heritage Foundation Oral History Archives

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The oral history archive at the Chemical Hersitage Foundation includes recordings of interviews with several persons who have been designated *plastics pioneers* because of their significant contributions to the development of the plastic industry. The transcripts of the interviews of two *plastics pioneers*, Irvin I. Rubin and John L. Hull, are the basis of this chapter. Extensive quotations of the actual comments of the interviewees capture their personal qualities as well as an account of their contributions, primarily innovative fabrication techniques, to the developing industry.

Introduction

From its early days in the 1980s one of the programs of the Chemical Heritage Foundation (CHF) has been the recording, transcribing, and archiving of oral history interviews of award-winning chemists and chemical engineers. This archive (*1*), which is available to interested scholars, added a dimension to the reporting on the history of chemistry – namely, recording the recollections of the persons who actually created that history. The archive includes interviews with several *Plastics Pioneers* (*2*) who developed successful fabrication techniques without which plastics would not be so ubiquitous in all our lives.

These oral histories provide fascinating, unexpected information about the interviewee that would be unlikely to appear in most biographical accounts. An autobiographical account – an oral history – significantly supplements, but not

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supplants, other accounts of chemical achievements by providing the achiever's own perspective on the pathway to that achievement, a personal perspective related in a conversational setting. Word playing with the acronym CHF, I term these oral histories *Chemical History Firsthand*.

For this chapter I have selected excerpts from two of the *Plastics Pioneers* interviews, selected not so much to inform you about operating details of fabrication processes in the plastics industry as to inform you about self-revealed personal details of the fabricators in their careers.

Irvin I. Rubin (*3*)

Irvin I. Rubin is credited with initiating the idea of recording the autobiographical accounts of the careers of Plastic Pioneers. He had a long, illustrious career in the plastics industry, specializing in injection molding, though his entry job in the industry was not at all promising. His account of his childhood experiences and his family background, however, leads one to high expectations.

Rubin was born in Brooklyn, NY, in 1919. His father was a Russian immigrant who was a dry goods wholesaler, and his mother "came from a long tradition of highly distinguished scholars." He had, he said, "a very good childhood. Every Saturday morning my father would go to the synagogue and when I was about five he took me with him. After lunch he would read to me from *The Swiss Family Robinson, Treasure Island*, and the like, but after ten minutes he'd fall asleep. So I complained to my mother, and she said, 'Then learn how to read.' So at five I was reading *The Swiss Family Robinson* and books like that. To me, it was easy. Well, my mother, who taught in public school, was a great teacher. If I came home with a 99 percent average, she said, 'That's terrible! You didn't get 100 percent.' She was right. There was always the push for excellence. Do the best you can."

Rubin attended public school and, for high school, a preparatory school for CCNY from which he graduated in 1938 with a B.S. degree in chemistry and a speaking knowledge of French, which figured humorously later. "The first time I went to Europe on business I went on Air France, and the stewardess, a very nice young lady, saw me reading a French newspaper. She asked me questions in French and I answered in English. She asked me why, and I said I was too embarrassed [to speak French]. She said, 'If you speak French to me, I'll give you a big hug and a kiss when you get off.' So I spoke French."

After college graduation, he expected to be a chemist, but he couldn't get a job. A man at an employment agency told him that as a Jew he would "never be hired as a chemist, because in those days they just didn't hire Jews. He said, 'Take any job.'" His uncle, a recent immigrant from Austria, was the largest importer of lampshades and lamp parts in the U.S. until World War II cut off the supplies of lamp parts from Europe. He turned to molding the parts himself, with advice and help from Bakelite, among others, in dealing with persistent manufacturing problems. Advised by other injection molders in the New York area to switch to Plexiglas as the injection molding feed stock and to "hire somebody who had a really good technical background because there's no place to learn molding except by doing it…they would be glad to train the new hire if Mr. Robinson [the uncle] wanted."

First Job

"Mr. Robinson knew I was looking for a job, and asked me if I wanted it. I said, "How much?' He said, 'Twelve dollars a week.' That was the minimum wage, thirty cents an hour. I said, 'Look, I've got almost two college degrees. I'm good with my hands. I'm honest, I'm hard working, et cetera.' He said, 'What do you know about lamp parts?' I said, 'Nothing.' He said, 'What do you know about plastics?' I said, 'I never heard the word.' 'Well, if you don't know the industry and you don't know the process, you're not even worth the minimum.' Needless to say he was correct. But he gave it to me anyway. And that's how my great insight got me into the plastics industry."

Rubin became adept at adapting the machinery to solve various problems in plastics fabrication by injection molding for the lamp industry and the Robinson business grew steadily. Rubin also revealed an impressive sense of winning customer relations. He traveled extensively for the company, and "wherever I went I would ask my customers if there were any new lamp manufacturers near by. When in Florida I was told that the Cuban exiles…were making lamps. The first Cuban exile I visited was using my parts…in a small garage…I asked him where he got my parts. He said from a local lamp part store. I asked why he did not buy from us. His answer was he had no credit. I told him that he did. Anybody who came to our country like he did was certainly credit worthy. I gave him a $200 line of credit (more than he needed for the size of his lamp operation) and told him that I would do the same for any of his friends…we became good friends. He placed my parts with all his friends, most of whom became very large and successful. My competitors in the lamp part business could never understand why they could never sell them parts."

On the matter of appreciation of patents, Rubin was ahead of Robinson, who found that the label "patent pending" without any application for a patent seemed to work. But Rubin was able to persuade a reluctant Robinson to apply for some patents, five of which were approved. "All that was needed was the $35 government fee. He did not think it was worth it. Since that was two weeks salary for me, I didn't go ahead – a decision that I still regret. When I was a lad, I had five ambitions: to sleep with a girl, get married, have children, write a book, and get a patent. I still have not gotten a patent though I have had a number of patentable ideas including magnetic coupling of motors and pumps."

Consulting

Rubin was permitted to consult with other companies and his ability to listen carefully to his customers and to solve their problems led to numerous interesting adventures. Describing his entry into consulting, he said, "I lost the first three jobs that I quoted. I asked the purchasing agent on the last job why I was not selected, since the consultant they chose really didn't know that much. He replied that I was much better qualified than his choice… [but] that in case the consultant failed, his boss would ask him why he didn't get the 'best.' By the 'best' his boss meant the most expensive. On my next quote I quadrupled my price and got the job. I rapidly became the most expensive consultant in the injection molding field." His consulting led to participating in legal challenges and court testimony. "In testifying a lawyer will tell you that the jury will only believe what they understand. The more they understand the more credible your testimony will be. An example of this was in a jury trial where the question of density was basic. The opposing side called as its witness a dean of a Midwestern engineering college. He had charts and correctly and fully defined terms in all their mathematical beauty. Our attorney couldn't understand him. When I was used as a rebuttal witness the judge asked me to define density. I said that if you have a liquid and you drop something into it, if it sinks, it is more dense than the liquid, if it floats, it is less dense than the liquid, and if it stays where you put it, it is the same density as the liquid. The jury applauded. We won the case. I found that in similar experiences…this practice was very helpful in testifying."

Rubin together with a few others started a seminar program in the plastics industry. Lectures were offered to inform workers in the industry about what they were doing, and the program was highly successful. Rubin lectured on injection molding and his experience with the seminar program "did two very important things for me. It made me realize how little I and most every one else knew about the injection molding process. I could not answer some of the questions posed to me. It forced me to stop, think, and evaluate what the process actually was. I did a lot of experimental work in my plant to find out how things worked and the effects of varying…conditions." His seminar lectures led him to write his first book, *Injection Molding: Theory and Practice* (*4*). "It was a difficult job because when you start to write you have to answer a lot of questions, many of which you never previously considered. Who will be my audience? I decided that the book should be written at the level of a high school graduate… written in a way that people could understand…I wrote the book as a businessman, because the purpose of molding is to make money, it is not a theoretical exercise. Finally I wrote it from a safety point of view. I would have written a totally different book, which would not have been too successful, had I not been lecturing to people in industry…It was a runaway bestseller. The royalties it gave to my children are in six figures. [It was] published in 1972; this is 2002, and royalties are still coming in…It really put me on the plastics map."

Management Style

He sometimes engaged in a blunt management style. Since his first job he had followed a practice instilled by his employer uncle: Pay your workers more than the competition does, and they won't leave. In the 1960s, he dealt with some molding problems in his plant by asking his operators to brainstorm about the problems and possible solutions, and as they participated they received a pay increase. After a few months, he was challenged by the union for not following the union contract – even though he was paying the union members more than the contract specified. The dispute went to arbitration. The union, which had two of the three representatives for the arbitration panel, usually always won against small companies. Rubin walked into the arbitration meeting, found both union representatives white, and said: "'Look, gentlemen, let's make this very short. I have a statement to make. Here you are a white Jew and a white Italian, and my people are black. I am doing everything to advance them, and I am giving them more money. You're raising objections because of power. You're raising objections because you're white and they're black – just exactly what President Johnson is against. If I don't win this arbitration, I'm going to take a full-page ad in the *New York Post*. I'm going to name you by name; I'm going to name the union by name; I'm going to state my case; and if you don't like it, you can sue me.' I got up and walked out. They knew that I meant it. That was the last I ever heard of it."

Reflections

Near the end of the interview, Rubin was asked what he thought was his chief contribution to the development of the plastics industry. He responded, "I was honored by being elected to the Plastics Hall of Fame in June 1994. This is the most prestigious award in the plastics industry. Since so many people have made huge contributions to the plastic industry, it is very hard for me to understand why I had been selected. An honor such as this forces one to ask what one did to deserve it. It took me quite some time to sort that out….After … eight or nine years of thinking about it and receiving comments from others, I think the most important thing that I did was that I established a theory of injection molding based on scientific principles. Before it was a black box operation – you tried this, you tried that, and by experience you learned what to do, but you never understood why. I was able to explain that in my book and in my lectures."

He wanted to close with some reflections on the plastics industry. "The plastic industry was made up of men who never asked, 'Can you make a part?' They asked, 'How can you make the part?' They did what is really unimaginable. The plastic industry started to become important during World War II. Returning GIs found this brand new industry intriguing and full of promise. They had no money, but brains and vision….They started with one easily financed machine in their garage, ran it with family and friends, expanded to two machines and grew to provide this country with one of its most remarkable growth industries….There's been no fifty-year period in history compared to the fifty years from 1950 to 2000 where the way we live has changed so drastically. Essentially, it happened because of plastic even though you might not easily recognize it." He then cited several examples to illustrate that view. Then: "I have been most fortunate in that within fifty years I have been able to see an industry grow from nothing to the second largest user of material and the fourth largest employer in the United States. The sense of discovery, the newness of the problems every day, the exhilaration of doing things and making things that no one ever thought about before has made my business career an absolutely engaging and fascinating experience. I cannot imagine any other occupation that would have come close to it."

John L. Hull (*5*)

John L. Hull was born in Danville, PA, in 1924. Like Rubin, he had a privileged start in childhood, but his path to the plastics industry was not so direct as Rubin's. Hull's father was a trust lawyer, and his mother, whom he described as "a very intelligent lady," was a Bryn Mawr College graduate who had been a teacher and had traveled in Europe after graduation. After attending a public school through 9th grade, Hull attended Philllips Exeter Academy, in New Hampshire, of which his father and two older brothers as well as several other relatives were alumni.

Upon graduation he enrolled at Massachusetts Institute of Technology (MIT) in aeronautical engineering in fall 1941. After the attack on Pearl Harbor near the end of that year, Hull joined the Navy V-12 program, continued at MIT, graduated in 1944, and started active duty in the Navy. He was quickly sent to Guam, where "I spent a year… running an aircraft repair and overhaul unit for the Navy planes that got banged up and needed fixing…I was pleased that I had picked the Navy. It was interesting because my girl at the time told me I'd look better in the Navy uniform than an Army uniform."

Early International Career Path

A question about his career path when the war was over brought an unexpected answer. "I guess I kind of hedged the decision of a career path for a while. I was in Guam when the war ended, and stayed another year when my points accumulated enough to allow me to go back to the United States. But instead of going back…a friend and I bummed a ride [on a military aircraft] to Shanghai, China. I had in mind that we would sort of work our way around the world the long way on our way home." In Shanghai, they tried unsuccessfully to get jobs with oil and automotive companies, but "they weren't hiring….the one that was hiring was United Nations Relief and Rehabilitation Administration….They seem pleased to get a couple of former Navy officers and sent us to a town in the interior of China…and assigned us to a transportation group. The whole purpose of UNRRA was to offer relief and rehabilitation to the Chinese people and help rebuild the infrastructure of the country…We moved coal and people and foodstuffs, whatever, around….We got our direction and our salaries from United Nations headquarters in Shanghai…it was fascinating work."

While in China, he married a woman from Australia. They returned to the U. S. at the end of 1947, and then Hull accepted a job offer from the United Nations (UN) International Refugee Organization in mid-1948 to work in Germany for two years. What were his language skills for these jobs in foreign locales? "Well, in China I had not studied Chinese. Because my staff, the drivers and mechanics that I had were Chinese, I had to learn enough to get by….I had studied both German and French. I had had three years of French and was able to speak it fluently. German I'd had only one year, but I developed that. So I now feel comfortable with either French or German in my travels."

With his wife, Hull then went to Australia to meet his wife's family and stayed for two years working intensely on design with the Commonwealth Aircraft Corporation. On their return to the US in 1952, he took his first job in US industry – as technical writer, later advertising manager with the Fischer Importer Company. In 1955, 11 years after graduating from MIT, he joined his older brother in a newly founded company, Hull Corporation, which manufactured equipment for pharmaceutical and plastics companies. That was still his employment home 47 years later when the oral history interview was conducted.

U.S. Employment

He spoke about his new job responsibilities, not all of which his round-the-world decade had prepared him to do. "At the time I joined, we had acquired the plastics molding machinery business from the Standard Machinery Company of Mystic, CT, in early 1955….It was actually the plastics-molding business, compression and transfer molding, principally thermosetting materials. We were building [the machinery] with a contract manufacturer…Butterworth Company in a near-by town. We gave them all of the drawings and bills of materials, and they did a very good job of constructing the machines…One amusing situation: Our very first customer was …Shaw Insulator Company…a custom molding company with great expertise in transfer molding. We were making transfer presses and compression presses [and] they gave us one of our very first orders…a two-hundred-ton compression molding press. The system was built at the contract manufacturing plant that we used. We shipped it to Shaw Insulator in New Jersey. I went up the following week for start-up – we probably hadn't run it at the contract manufacturing plant. When we fired up the machine, we found that there were a lot of boil leaks. It didn't take us long to realize that all of the fittings on the hydraulic piping had not been of the high-pressure type. They had cracked and disintegrated fairly promptly under the 2,000 psi that we were working…I had not even thought of it – I didn't even know that there were high-pressure fittings and standard fittings…So we did a complete replacement of every single fitting on the hydraulic system of the press…I think I spent the better part of a week up there swinging wrenches with a couple of our people. But we did get it right…the customer took it in very good graces, and they subsequently purchased quite a few additional presses over the decade or so."

Bell Laboratories was having problems insulating a critical junction in semiconductors; some were successful, but many were failures. They asked Hull to help. He and his fellow workers took Bell Labs knowledge and specifications about the process, refined the molding process by extensive experimentation, and turned out product that had few failures. Bell Labs then gave an order for a machine based on Hull's production mold. That work "led us to working with semiconductor elements and developing the materials that had low enough viscosity and obviously good enough electrical properties to handle other diodes,

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other rectifiers, and on into integrated circuits and so forth. That whole process, direct encapsulation by transfer molding, put us on the map. We had incredible success worldwide."

Hull mentioned that the new machine was never patented, but he escaped competition from rival companies. "Well, I think we lucked out. We never even thought of a patent because to us it was just insert molding, which had been practiced long before Hull Corporation….We were making changes…[and] every stock lot would have improvements from the last stock lot because we'd find things in the control system itself, things mechanically different, methods of mold measuring, and so forth. So competitors who would copy what they saw would always be a little bit behind where we were. I did a lot of technical papers and presentations at technical societies. So we just got the reputation of being the place to go….All of the semiconductor people all over the world…used our machines… Competition ultimately became pretty good, especially offshore…, [when] improvements were fewer and further between…so [machines for semiconductors] is not a major part of our business today."

Hull described several developments in various applications and then offered some overall views. "We make injection-molding machinery for thermoplastics as well as for thermosetting materials. Injection molding is very popular. It's a good automatic way to mold whatever you're molding….Occasionally our ability to come up with better solutions on how to do it efficiently for a given application is known by the industry. So we will get business in injection molding. I enjoy that. A number of companies make very fine machinery, but they don't get involved in the application engineering to come up with the optimum press for something. So that gives us an area of opportunity."

Concluding Reflections

Hull commented on the appeal of an oral history project for Plastics Pioneers: to record "the thinking processes he went through to come up with some of his skills." One of his friends, William Willard, had died a year or so before Hull's interview, but "we never did get his bio. From his widow we've gotten historical information about it. But what was the guy thinking about? What prompted him to approach the need of plasticizing the material and getting it to the right temperature for optimum flow into the mold, and minimizing bypass in the barrel, keeping the temperatures where you need them so that you wouldn't freeze up the material in the barrel? All of these aspects of it that he found solutions to. His patent is used by many subsequently, and long beyond the 17-year life of a typical patent. But we don't have his thinking processes that went into that."

He concluded the interview with some personal comments. "If you are a major in chem engineering or chemistry or aeronautical engineering or plastics, you are exposed to many, many influences, and you end up whatever you are. Some of that may be in the DNA that got us going. But I have enjoyed people. When I was at MIT, I was president of my class for the junior and senior years….I enjoy the reunions. I've always liked people, and I've always liked challenges. It's fun to see youngsters come into the company or into my life in some way, and try to get them to see the opportunities of the future, whether it's plastics industry or anything else they may be in. I helped found a symphony orchestra many years ago, and for 35 years I played clarinet in it. And I've watched a lot of young people get into music, some of them staying in it and some dropping it as many do after they finish high school. It's fun to see people find a niche where they enjoy themselves and, in the case of business, you put bread on the table. The symphony didn't put any bread on the table for me, but it certainly gave me a lot of fulfillment."

CHF Archives

This chapter has presented a small sampling of the CHF oral history archives with the hope of enhancing your acquaintance with and interest in some of the Plastics Pioneers. For most fields of chemistry, the archives are a rich resource for chemical history studies. They are there, available to nurture your curiosity about others in your own niche in the chemical sciences.

References

1. The CHF oral history archive contains several hundred entries. An alphabetical list of the interviewees is accessible at the CHF website, http://www.chemheritage.org/exhibits/ex-nav2.html.
2. *Plastics Pioneer* designates a member of the Plastics Pioneer Association.
3. All of the facts and quotations in this section are found in the volume: Irvin I. Rubin, interview by James G. Traynham at Rubin's home in Brooklyn, NY, 26 February 2002 (Philadelphia: Chemical Heritage Foundation, Oral History Transcript #239).
4. Rubin, I. I. *Injection Molding: Theory and Practice*; Wiley-VCH: New York, 1973.
5. All of the facts and quotations in this section are found in the volume: John L. Hull, interview by James G. Traynham at Hull Corporation in Warminster, PA, 19 June 2002 (Philadelphia: Chemical Heritage Foundation, Oral History incomplete unnumbered transcript).

Chapter 9

The History of Polyethylene

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Polyethylene is the largest volume polymer produced globally, with a total over 90 million metric tons per annum. Since its accidental discovery in 1933 it has evolved into a material critical to modern life. The first product commercialized was low density polyethylene (LDPE) based on free radical polymerization. Shortly thereafter new polymerization chemistries based on chromium catalysis and Ziegler Natta catalysis expanded the product space. Improved polymer performance based on new catalyst and application technologies have made it possible to have the diversity of use we see today. It is an essential material to power transmission, food packaging, consumer goods, electronics, household goods, industrial storage, transportation industries. Developments in technology continues to improve its functionality making polyethylene the most efficient use of natural resources petroleum and natural gas.

The Discovery of Polyethylene

It is hard to imagine modern life without polyethylene. As the largest volume polymer, polyethylene is critical to every aspect of our daily life today. From electricity transmission lines to natural gas transport, from food packaging and preservation to construction, from infra structure to agriculture. Its low cost, highly desirable functional attributes and ease of processing into films, pipes, molded articles of different forms and shapes has enabled it to become what it is today.

The first known synthesis of polyethylene occurred accidentally in 1894 by Hans von Peckmann (*1*). Accidental decomposition of diazomethane yielded

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a white powder, analysis of which indicated that it was made up of hydrogen and carbon atoms with long sequences of methylenes, -CH2-. They called it polymethylene. In 1929 Friedrick and Marvil made low molecular weight polyethylene by heating ethylene with BuLi (*2*) while they were investigating reactions between alkali metal alkyls and quaternary arsonium salts. In 1933 two researchers at Imperial Chemical Industries (ICI) in England, Eric Fawcett and Reginald Gibson studying ethylene and benzaldehyde mixture at very high temperatures, noticed a sudden loss of pressure in the vessel. Fearing a leak, upon opening the reactor they noticed a white waxy solid and realized that they just made polyethylene (*3*). This was the first polymerization of ethylene monomer by a free radical mechanism caused by dissolved oxygen in the system. Fawcett and Gibson, not knowing it was the oxygen impurity that caused the polymerization, were unable to repeat their work in a controlled fashion. The work continued in ICI and eventually in 1935 Michael Perrin was able to produce larger quantities of new polymer. Extensive research into the high pressure polymerization of ethylene eventually culminated in the first commercial production of LDPE in 1939 by ICI in England.

The newly developed material was of great interest as an insulation material to the defense industries during World War II. Indeed the first industrial application was for the development of air born radar and as an insulator for the underwater cables. Polyethylene enabled such a reduction in the weight of the radar equipment that it could be placed in the aircraft. This was particularly valuable for locating enemy aircraft in adverse weather conditions and was one of the big secrets of World War II. DuPont in the USA was collaborating with ICI from early days and was receiving samples regularly. DuPont's collaboration with ICI enabled DuPont to develop a tubular process for the manufacture of LDPE. Even though the tubular process had significant blockage issues, it eventually became one of the two key processes for the manufacture of LDPE. The production of LDPE first started in the US in 1943 subsidized by the US Government for the war effort. Shortly after Union Carbide started production of LDPE by a tubular process. By end of 1947 both DuPont and Union Carbide were commercially supplying LDPE and the annual sales reached 10 million lbs. In the early 50's Dow Chemical Company joined the ranks of new producers of LDPE and licensed the ICI autoclave process.

Structure and Properties of Polyethylene

From a chemical structure perspective polyethylene looks to be the simplest of all the structures. Just repeating units of methylene with occasional comonomer inserted into the backbone of the molecule. Yet this simple structure provides the largest diversity of products, mostly obtained by changes to the molecular structure.

The three fundamental molecular features of polyethylene namely, the molecular weight and its distribution, comonomer content and its distribution; the so called short chain branching coupled with the long chain branching define the performance of the products.

Structure of Polyethylene

The critical morphological structure that determines most of the properties is the semi crystalline structure of polyethylene. The molecular connectivity between the amorphous phase and crystalline phase and the interconnected nature of crystalline network defines most of the physical properties as given in Figure 1.

Development of the tie chain concept has been very helpful in understanding the system (*4*, *5*). A tie chain is defined as a molecule that has parts of it embedded in the core of two or more crystals (*6*, *7*).

This connectivity ensures that any stress applied gets distributed in the system and portioned both in the amorphous phase as well as the crystalline phase. This concept also explains reasonably well the impact of changing molecular weight, density and comonomer content on the properties. In general high molecular weight molecules of a given comonomer content are more capable of forming tie chains as their end to end distance is long enough to participate in two or more crystals. If molecules are not long enough then they cannot function as tie chains. The optimum physical strength is obtained when the tie chain concentration is at its maximum. This requires that the crystal size is in a certain range where a balance between crystal strength and tie chain concentration is attained. This optimum is attained around a density of 0.905 g/cc to 0.915 g/ cc range. The tie chain concentration also depends on the comonomer type used. The longer the short chain branch, the more tie chains occur (*8*). In this respect the butene copolymers generally have the lowest tie chain concentration at a given density followed by the hexene polymers and octene polymers. After octene the effect of increasing short chain branching size on tie chain concentration decreases. In Figure 2 below the tie chain concentration vs. density is given for the most common alpha olefins.

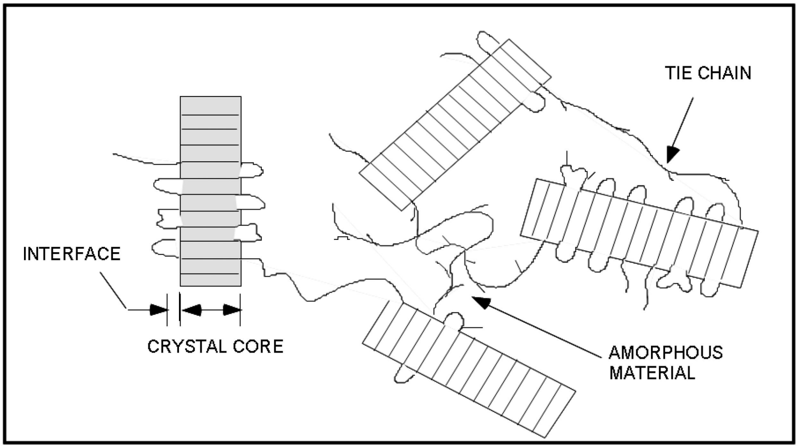

Figure 1. Graphical description of tie chains.

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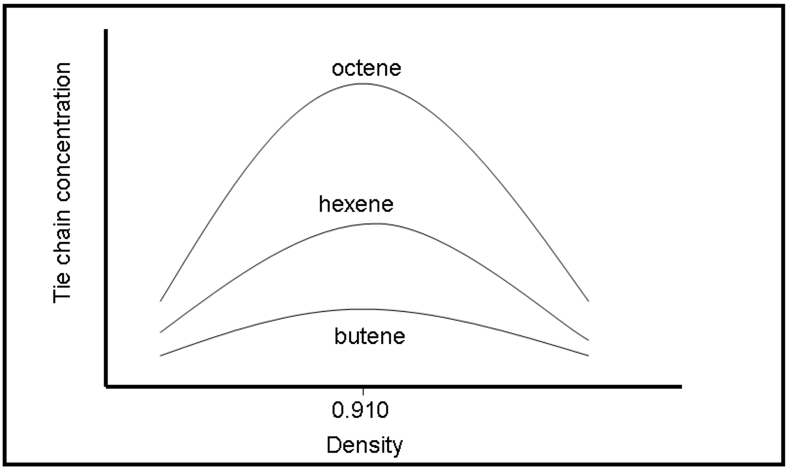

Figure 2. Tie chain concentration vs. density for common alpha olefin comonomers.

Tie chain concentration at a given density has a significant bearing on the physical properties of polyethylene (*9*). Abuse properties such as dart impact, tear and puncture mirror the tie chain concentration and as a result the octene resins have the best abuse properties and the butene resins will have the least. For this reason higher alpha olefin resins are more often used for more demanding applications commanding a premium versus lower alpha olefin polymers such as butene.

Density

Density plays a critical role in defining solid state properties of polyethylene to the extent that polyethylene resins are generally classified depending on their density. In Table 1 below generally accepted classifications of polyethylenes based on density are given.

While the melt index (i.e. the molecular weight) has a minor impact on density at a given comonomer content (*10*), it is rather small in comparison to the effect of the comonomer level. The principle means to control the density of the polyethylene is by incorporation of an alpha olefin co-monomer such as propylene, butene, hexene or octene . Butene, hexene and octene copolymers make up the great majority of resins commercially available. In the case of LDPE the density is controlled by in situ formed short chain branching through the radical "back biting" mechanism of a growing polymer chain.

Table 1. Classification of polyethylenes by density

Resin family	*Lower density limit g/cc*	*Higher density limit g/cc*
High Density Polyethylene (HDPE)	0.941	0.975
Medium Density Polyethylene (MDP)	0.928	0.941
Linear Low Density Polyethylene(LLDPE/LDPE)	0.915	0.928
Very Low Density Polyethylene (VLDPE)	0.900	0.915
Elastomers/Plastomers	0.865	0.900

Polyethylene is a semi crystalline composite material with amorphous and crystalline region. The totally amorphous region has a density of around 0.865 g/cc while the pure crystal structure has a density of 1.00. Even in the case of pure homopolymer 100% crystalinity is not reached as some amorphous material exists in between crystals, even in the absence of any copolymer as well as chain end effects.

The predominant crystalline form of polyethylene is orthorhombic even though both hexagonal and monoclinic forms (*11*) exist. The detailed studies revealed that branches larger than a methyl groups are exluded from the crystal structure (*12*, *13*). Thus addition of comonomer prevents the folding of the back bone to form the crystal structure. This in turn prevents a portion of the polymer from participating in the crystallization process. The portion excluded from the crystal structure remains amorphous. This is the mechanism by which the density vs mole % comonomer relationship as given in Figure 3 is established as well as the actual crystal structure (*14*).

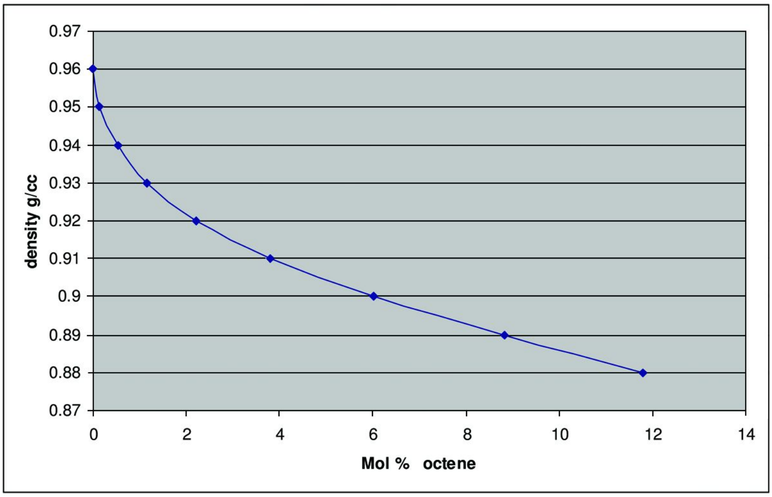

Figure 3. Mole % Octene vs density for metallocene based LLDPE.

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Tensile Properties of Polyethylene

Tensile properties of polyethylene are the most critical properties for a large number of applications. Tensile properties provide a guide to how the material will respond to an external deformation in terms of resistance to deformation, load bearing characteristics as well as ability to accommodate deformation (*15*, *16*). The typical methods utilized in measuring tensile properties of polyethylene are given in the following Table 2.

Tensile properties are determined by subjecting a dog bone type test specimen to extension and recording the response of the material as a stress strain curve. A typical tensile curve is given below in Figure 4.

Table 2. Test methods for tensile properties of polyethylene

Tensile Property	*Test Method*
Tensile modulus	ASTM D638
Tensile yield stress	ASTM D638
Tensile break stress	ASTM D638
Ultimate tensile elongation	ASTM D638
Density	ASTM D972
Melt Index I_2 and I_{10}	ASTM D1238 Conditions E, N
Dart Impact	ASTM D1709
Tear Resistance	ASTM D1922

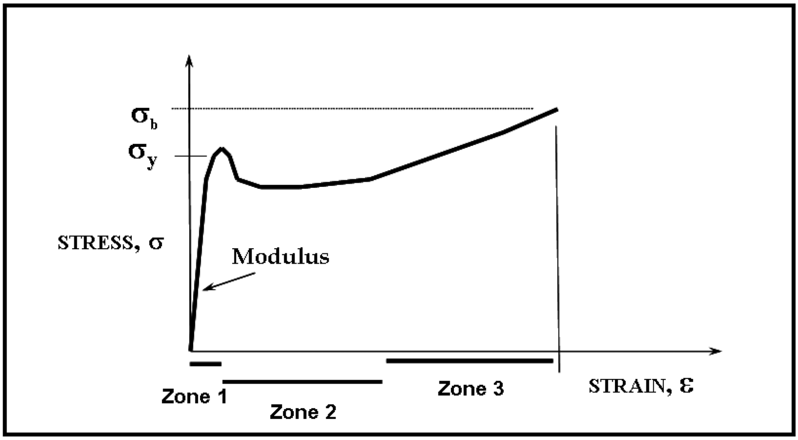

Figure 4. Stress-Strain curve for polyethylene.

As the sample is subjected to strain, the stress required to sustain the strain goes up in a linear and reversible fashion until the tensile yield point. The slope of the very early part of this curve is used to calculate the tensile modulus, and it primarily depends on the density of the polymer (*17*). If the test is stopped before the tensile yield point, then the sample will snap back to its original shape with no permanent deformation. At the yield point the permanent deformation starts. The stress at this point is taken as tensile yield stress. Typically elongations required to reach yield point are in the order of 5 to 15 % depending on the density of the resin. For higher densities the elongation is low while for lower densities it is high. If the density is really low (elastomer) there may be no yield point.

Recent studies whereby real time crystal structure data was obtained while the polymer was undergoing tensile deformation revealed new information as to what happens in each zone (*18*). Zone 1 in Figure 4 is the area where the molecular deformations are primarily in the amorphous phase with little or no deformation taking place in the crystalline phase. At the yield point the sample starts to go through permanent deformation through a “necking” process which is the start of zone II, known as the post yield drawing zone. At this point two distinct processes take place. First the crystals start to orient and align in the direction of extension. As the extension continues the crystals go through a deformation known as “fine slip”, whereby the crystals get tilted like a deck of cards. Towards end of zone 2 smaller crystals which require less energy for deformation starts to break apart through a process called “coarse slip”, whereby crystal planes start to separate. In the final zone, as the larger crystals start to break apart and chains become oriented parallel to the principle strain direction, the material starts to show strain hardening and becomes stronger. If the process of extension continues, eventually catastrophic failure takes place.

Dart and Tear Properties of Polyethylene

Dart and tear are two key abuse resistance properties of polyethylene. Those properties are especially important for film applications such as food packaging. Dart impact strength represents the high speed impact environment such as dropping a package from a certain height and is an indication of the capacity of the resin to survive such an impact and continue to protect the contents of packaging. Dart impact generally depends on density and the molecular weight of the resin and peaks around 0.905 g/cc density for a given melt index. There is a high degree of correlation between tie chains and dart impact of the resin. Presence of long chain branching is usually detrimental to dart impact strength.

Tear resistance is measure of the energy needed to generate certain length of tear in a thin film normalized to a 25 micron thickness. It is a critical property for films. Tear resistance like other properties greatly depends on the molecular structure and the crystalline structure of the polymer (*19*). In general tear resistance tends to be different in different directions. In machine direction (in the direction a film is extruded) the tear resistance is usually lower than in the cross direction. This is mostly a consequence of the orientation levels being higher in machine direction (*20*). As most of the crystals are parallel to machine direction, energy needed to propagate the film in machine direction tends to be less as only a small

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portion of crystals are in the direct path of the propagating crack tip. Things that increase the anisotropy tends to increase disparity of tear in different directions such as long chain branching. Like other abuse properties of polyethylene, tear strength is also highest in the 0.905 g/cc to 0.923 range. In the general Ziegler Natta catalyzed solution process based on octene products have the highest tear, followed by hexene products.

Seal Properties of Polyethylene

An area where polyethylene is unique is in the sealant applications. A large number of applications for films require a material that can be sealed at relatively low temperatures by applications of heat through a metal seal bar to join two films to form a closure (*21*). Such application include food packaging, industrial packaging as well as many other packages. Generally ideal materials for this application have the desirable combination of low heat seal initiation temperature and high hot tack strength. Heat seal initiation temperature is determined through a series of seal experiments at different temperatures whereby the seal strength is measured as Newtons of force needed for a 1 inch seal length. Normally this temperature is defined as temperature at which 2-4 N of seal strength is achieved. The temperature at which the required seal strength is achieved is usually called heat seal initiation temperature (HSIT) as given in Figure 5. The most desirable resins have a low heat HSIT and a high maximum seal strength, the highest point in Figure 5. In general a lower HSIT leads to increased output as it takes less time to heat the polymer to a lower temperature then a higher temperature. Additionally a broad heat seal window is desirable, not requiring precise temperature control at the seal bars. A high heat seal strength enables production of larger and heavier packages. As most converters use a range of package sizes, they prefer a resin that is capable of producing the most demanding packages. This in turn reduces the logistic cost of using multiple resins. There are no standard test methods for this test and most producers and converters have their internal test methods based on the same basic principles.

The molecular make up for ideal sealant resins is complicated as there are opposing requirements of very low melting point necessary for low HSIT and ability to sustain higher loads at the seal point at higher temperatures.

Thermal Properties

The melting point of polyethylene depends on the type of polyethylene. For homogeneous polyethylenes made by metallocene or other types of single site catalyst the melting point is basically determined by the density or mole % alpha olefin in the polymer. This is because single site catalysts make a homogeneous polymer where the longest crystallizable ethylene sequence has a normal distribution and rather a narrow one. The relationship with comonomer content and the melting point and the glass transition temperature is given in Figure 6 below. In the case of heterogeneous polymers made by the Ziegler Natta catalyzed process the melting point has a more complex dependence on density, in general due to the fact that for a broad range of densities such polymers always have a high density component and the melting temperature is greatly influenced by this component. As a result the melting point tends to be rather flat for differing comonomer contents. The melting point is a critical consideration for intended applications. Where structural integrity is required, the melting point of the polymer must be well above the intended use temperature.

While melting point is determined by the crystalline phase of the polymer, the glass transition temperature is a property of the amorphous phase. As can be seen from Figure 6 below it follows a trend similar to the melting point of the homogeneous polymers. As the concentration of the comonomer increases in the chain, the backbone becomes more mobile showing segmental motion at successively lower temperatures. Knowledge of the glass transition temperature is also very important and depends on the application under consideration. Polymers generally become very brittle near or below the glass transition temperature as the segmental motions of polymer chains are restricted and the structure is unable to accommodate external stress or strain.

Rheology of Polyethylene

Polymer rheology deals with the response of molten polymers to externally applied stress and strain. As all polymers must be converted to a final article before they can be made used, they must first be made molten, then shaped into the desired article. The polymer rheology defines the particulars of this conversion process. The conversion process is a significant contributor to the final quality and cost of the article made. For this reason a lot of consideration is given to the design of the polymer to satisfy the requirements of the final article as well as the conversion process.

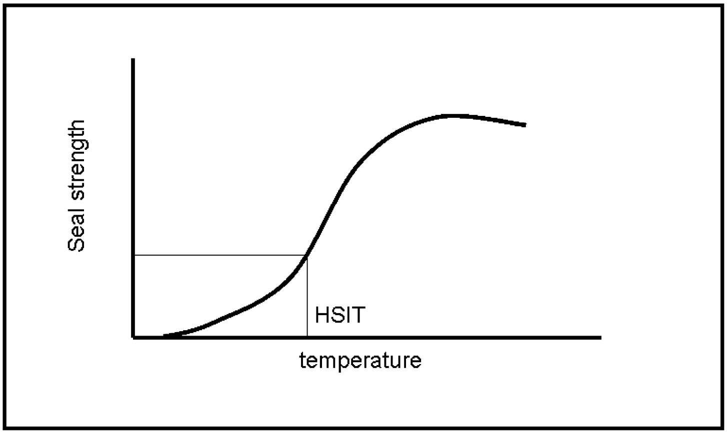

Figure 5. Typical heat seal curve for polyethylene.

The polymer rheology is defined mostly by the molecular weight, molecular weight distribution and long chain branching (not considering additives). Molecular weight is probably the most critical of all the molecular parameters defining polymer rheology. Higher molecular weight polymers have higher viscosities. In practice melt index is used as an indicator of polymer viscosity, and it reflects the flowability of the polymer at a specific temperature, stress and geometry. While melt index is a general indicator of viscosity of the polymer, two polymers with identical melt indices can have vastly different flow characteristics. The following Figure 7 is a good illustration of this. While both polymers have same MI their molecular make up is very different. The LDPE has a broader molecular weight distribution and much higher levels of long chain branching mLLDPE is by a metallocene catalyst.

The metallocene LLDPE rheology curve in Figure 7 is a typical of a polymer with relatively narrow molecular weight distribution and little or no long chain branching (*22*). These polymers have very low shear thinning behaviors. In general polymers with low shear thinning behavior require higher energy to process and have lower melt strength requiring addition of some LDPE in most processes to improve processability. On the other hand LDPE in Figure 7 has a very broad molecular weight distribution with a lot of long chain branching. LDPE shows very high levels of shear thinning vs. the metallocene based LLDPE. Since typical extrusion or injection molding process takes place at much higher shear rates then given in Figure 7, the LDPE resin will be much easier to process than LLDPE resin. Narrow molecular weight resins with no long chain branching has the lowest amount of shear thinning followed by medium molecular weight distribution resins. Broad molecular weight distribution resins are the most shear thinning resins in the absence of long chain branching. Long chain branching has a dramatic impact on the shear thinning behavior. Addition of LDPE resins to HDPE or LLDPE significantly improves the processing aspects and as such is utilized very extensively. The following Figure 8 shows the typical shear curves for resins with different molecular weight distribution. The shear thinning is most critical at the relevant shear rates for a given process. Degree of shear thinning is usually expressed by a single number known as viscosity ratio. One such number is I_{10}/I_2 . This is the ratio of viscosity corresponding to two different shear rates as shown in Figure 8. The larger the number more shear thinning is in the resin. In addition to I_{10}/I_2 other ratios are also employed.

In addition to shear thinning another important aspect of polymer rheology is melt strength. The melt strength is an indication of the ability of the unassisted melt to support its own weight. It is a very critical property for many areas such as blown films, blow molded articles as well as thermo forming processes. The three basic resin attributes that impact the polymer rheology are the key contributors to melt strength; the molecular weight and its distribution and long chain branching. In general higher molecular weight polymers have higher melt strength. Also the presence of long chain branching is the most effective way to achieve melt strength. For this reason LDPE polymers will have anywhere from 3 to 5 times the melt strength of a LLDPE resins at the same MI.

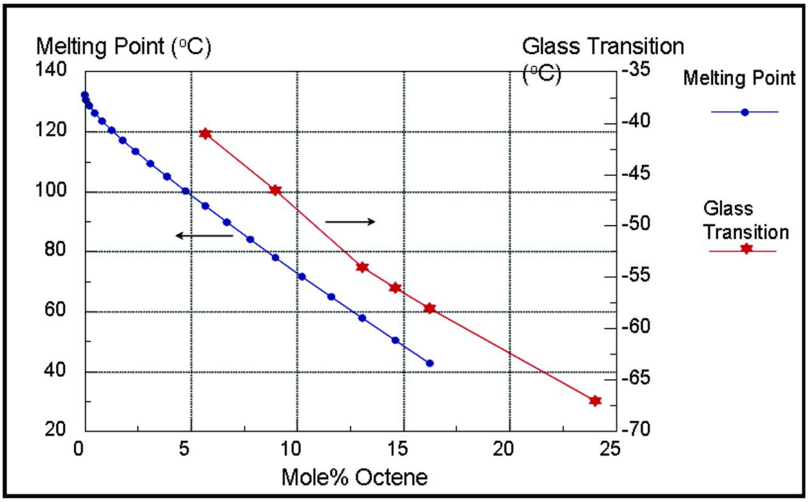

Figure 6. Dependence of glass transition temperature and melting point on comonomer content of homogeneous polyethylene.

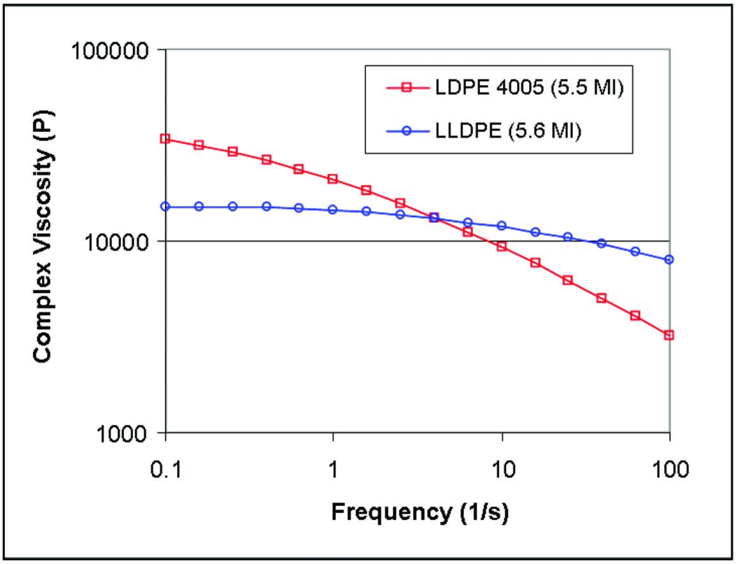

Figure 7. Rheology curves for mLLDPE and LDPE at same MI.

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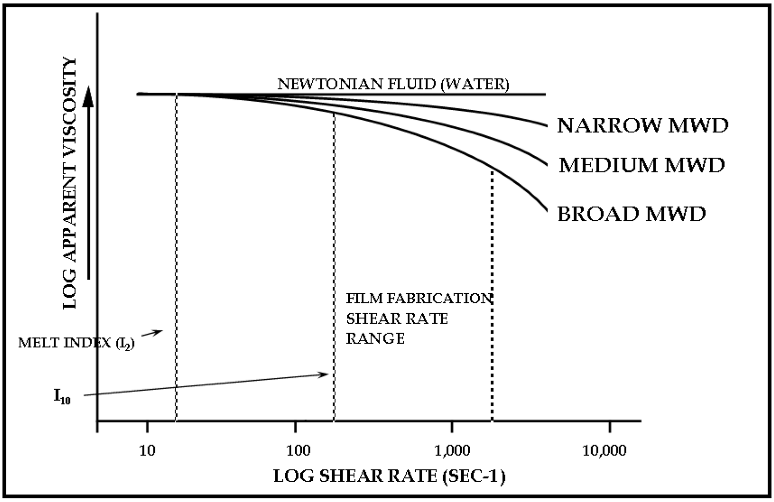

Figure 8. Shear thinning and molecular weight distribution.

Polyethylene Types, Chemistry, and Production Processes

Polyethylene comes in many different forms. In general they are classed into three basic classes.

Low Density Polyethylene (LDPE)

LDPE was the first polyethylene commercially used. It is the only one made utilizing free radical chemistry under high temperatures and pressures. Its unique structure contains long chain branching which makes it highly desirable in the manufacture of thin films either by itself or blends with other types of polyethylenes. Its long chain branching is a consequence of the high pressure process where intermolecular hydrogen abstraction by a growing chain end from another polyethylene is the source of this highly desirable properties especially in melt processing.

Manufacturing Process for LDPE

LDPE is manufactured principally by two different process, the autoclave process and the tubular process.

The Autoclave Process

The autoclave process was the first commercial process for the manufacture of LDPE developed by ICI. Most of the early trains that were built used ICI technology. Some of those trains are still operational today. The autoclave process consists of several unit operations dealing with the pressurization of ethylene to the required pressure usually carried out with multiple stage compressors, an autoclave reactor with internal mixing elements to achieve good mixing, a separation unit consisting of a high pressure separator and a low pressure separator and a recycling unit which recycles the unreacted ethylene back to the compressors. A schematic drawing is given in Figure 9 of a typical autoclave reactor. The initiators, chain transfer agents (commonly referred to as telogens) are added either into the ethylene stream before the reactor or added to the inlet side of one of the compressors for good mixing.

The compressor compresses the industrial grade ethylene to a medium pressure range to be fed into the second compressor. Into the inlet of the first compressor the ethylene coming from the low pressure separator is also fed. The second compressor further compresses the ethylene to the required pressure. The recycled ethylene from the high pressure separator is usually fed into the second compressor as the pressure of this recycle stream is high enough.

The autoclave reactor is a specially constructed reactor that can withstand the temperatures and pressures required for the ethylene polymerization. It has a very high agitation capability to prevent any fouling of the reactor. It typically has a L/D ratio of 15 to 25. The compressed ethylene is fed from the top of the reactor with the telomers and peroxides. Choice of peroxides depend on the reaction temperatures. The choice must be made in such a way that most of the peroxide is reacted in the residence time given.

As the autoclave reactors have very limited heat removal capacity, the incoming ethylene feed is at a relatively low temperature to take up the heat of polymerization. The incoming ethylene feed can be from about 16,000 psi to about 38,000 psi. Typically the average reactor temperatures are in the range of 160 °C to 280 °C. If the reactor temperature is too low, fouling of the reactors might be an issue, especially for higher density and higher molecular weight products. If the reactor temperatures are too high, it may lead to reactor instabilities and ultimately to what is commonly referred to as “decomp”. A “decomp” is the decomposition of ethylene to methane, carbon and hydrogen with high pressure and temperature generation. For this reason all LDPE reactors are built with proper release designs to handle such uncontrolled heat and pressure releases. In a certain temperature and pressure range ethylene is a single phase liquid. If the temperature or pressure is outside this range it can be a two phase medium with a liquid and a vapor phase. Even though autoclaves can be operated in two phases, most of the time they are operated under conditions where ethylene is in a state of single phase. The autoclave reactors usually have multiple zones. Each zone may be fitted with a peroxide injection system to maintain the rate of polymerization across the reactor.

The autoclave process is one of the least efficient processes for the manufacture of polyethylene. Depending on density and melt flow requirements, the autoclave process operates from about 15 to 20% conversion of ethylene. Energy associated with compressing ethylene to such high pressures and only converting up to 20% into polyethylene makes this process fairly expensive. In addition the autoclave process has a relatively low capacity further reducing its ability to compete with the tubular process.

The molecular weight control is provided by process parameters and addition of telogens (*23–26*). Typically telogens are low molecular weight materials, such as butene, propylene, propylene aldehyde or butane. The telogens are added to reduce the molecular weight and obtain a desired melt index.

Unique Features of LDPE Products and Production Processes

For coordination chemistry catalyzed polyethylene resins the density is adjusted by means of adding an alpha olefin such as butene, hexene or octene as a comonomer. The comonomer disrupts the sequences of ethylene and excludes a portion of the chain participating in the crystalline structure, hence reducing overall density. In the case of LDPE no such comonomer is added. Instead through a back biting mechanism, the growing polymer radical intramolecularly abstracts a hydrogen atom usually 3 to 6 carbon atoms from the radical centre forming an in situ short chain branching (SCB). The back biting mechanim is given in Figure 10 below (*27*). The process of back biting can be controlled by reaction conditions such as pressure and temperature providing the ability to target the required densities through changes to the process conditions. This provides a relatively limited room for density variation leading to a small density range for LDPE from about 0.915 g/cm^3 to 0.935 g/cm^3. The effect of temperature and pressure on the density of LDPE is given in Figure 11 below for 28,000 psi. At higher pressures the density vs. temperature line moves up while at lower pressures the line moves down.

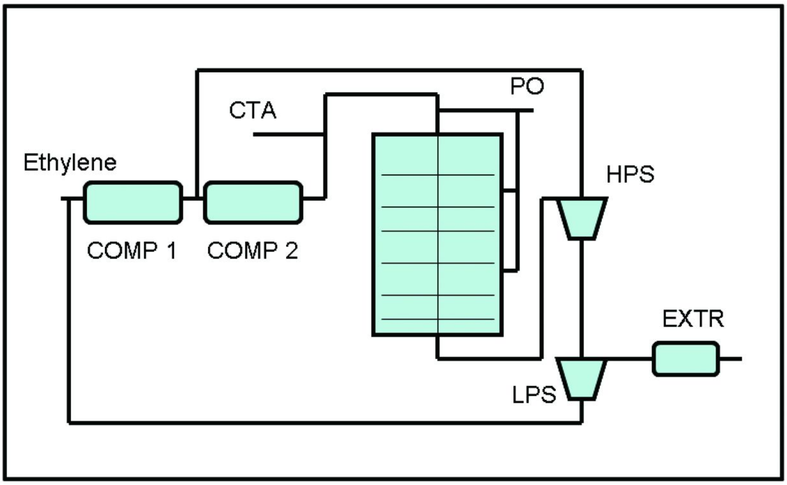

Figure 9. Schematic drawing of an autoclave type LDPE process.

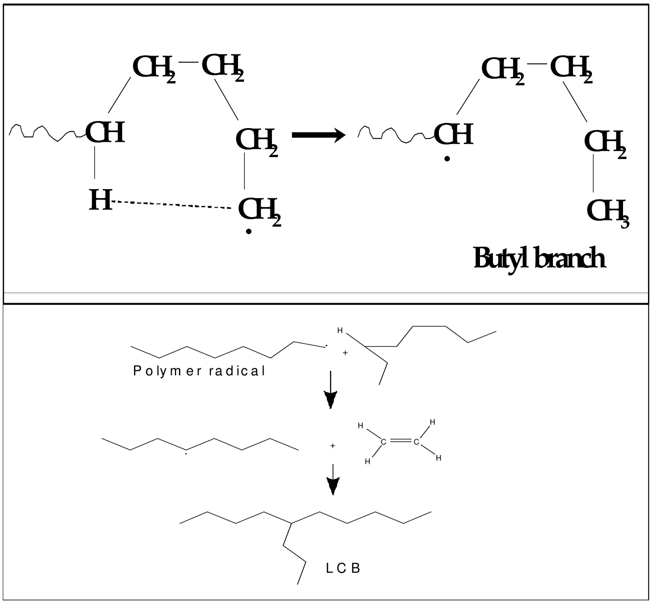

Figure 10. Mechanism of SCB and LCB formation in LDPE process.

While HDPE and LLDPE might have some long chain branching (LCB)(usually less than 0.2 long chain branches per 1000 carbon atoms), LDPE has the highest level of LCB in polyethylene family. Especially the autoclave process provides high levels of LCB. In addition to LCB level differences, the topological features of LCB are also different between the tubular and the autoclave products. The mechanism of LCB formation for LDPE is primarily through intermolecular hydrogen abstraction. In addition the branch lengths and tology of autoclave reactors are different than the tubular reactors.

The presence of LCB has a significant impact on the rheology of LDPE. Presence LCB increases the shear thinning of the polymer, meaning at high shear rates the polymer has lower viscosity than expected while at low shear rates the polymer has higher viscosity than expected. The low viscosity at high shear rates makes the processing of film easier, increasing the output of the extruders as lower pressures are needed to extrude the resin. Lower viscosity at higher shear rates also helps to reduce the energy required to process the resin. On the other hand the increased viscosity at lower shear rates improves the melt strength of the resin. This increase in melt strength is beneficial in making large bubble films as it enables the film to have sufficient strength to hold its weight. Also higher melt strength is critical for the formation of a uniform film with good gauge control in comparison to a resin with little or no LCB. Figure 7 above provides the comparative shear viscosity curve for two types of resins at the same melt index. One resin is an LDPE containing high levels of LCB while the other one is an LLDPE containing low levels of LCB. Where the two points intersect corresponds to the shear rate at which the melt index is measured.

High Density and Linear Low Density Polyethylene

Unlike low density polyethylene which utilizes free radical chemistry, high density polyethylene and linear low density polyethylene are produced through catalysis utilizing coordination chemistry. Three basic chemistries are used for the production of coordination chemistry based HDPE and LLDPE. Those are chromium catalysis, principally used in slurry and gas phase processes, Ziegler Natta catalysts principally used in gas phase and solution processes and metallocene chemistry which can be used in all processes including solution processes.

Development of Chromium Catalyst for Slurry and Gas Phase Processes

By early 1950's LDPE has become available with a number of manufacturers in US and Europe making products. The new plastics was starting to make inroads into new applications, especially films. The major issue remained the fact that the LDPE process required such a high pressures to operate. Thus the race was on to develop an alternative way to polymerize ethylene at lower pressures and temperatures. This would make production of polyethylene much less challenging from an engineering perspective.

The first major breakthrough in low pressure polymerization came about in 1951. Two chemist working for Phillips Petroleum. Robert Banks and J. P. Hagen discovered a catalyst based on chromium trioxide that could polymerize ethylene at 80 to 110 °C and at pressures less than 1000 psi (*28*). The new catalyst system required development of a new process as well. Phillips Petroleum initially had difficulty with its slurry process and filled warehouses with off-spec product. In 1957 the introduction of a new toy, the hula hoop gave a much needed push and HDPE was born. The new HDPE was sold under the trade name Marlex®.

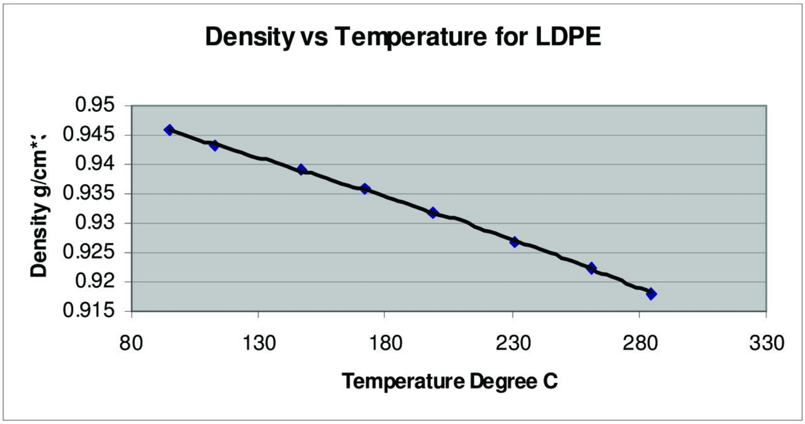

Figure 11. Density vs reactor temperature for LDPE at 28,000 psi.

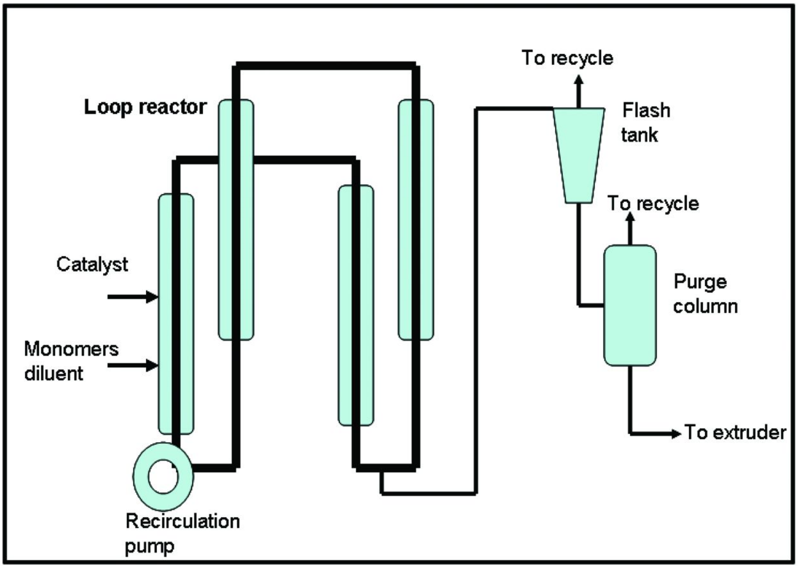

Figure 12. Phillips Petroleum Slurry Process (29, 30).

The chromium catalyst based slurry process uses a hydrocarbon solvent as the medium to conduct the polymerization process (*29*). The process is carried out well below the melting point of the HDPE to maintain a slurry system. The temperature is usually between 85 to 110 C. Ethylene and comonomer (if needed) circulate in a loop reactor at relatively high speeds. As the catalyst comes into contact with ethylene the polymerization leads to formation of the granules of polyethylene. The inert solvent is used to dissipate the heat of the reaction. The typical reactor consists of a folded loop containing four long runs of fairly large pipe (in excess of 1 m), connected by short horizontal lengths of 5m. The slurry of catalyst particles and HDPE circulates through the loop at very high velocities of 5 to 12 m/s to prevent sticking of the slurry to the reactor walls (*30*). In general the lower the density of the polymer the more the chances of reactor fouling as the resin of lower density tends to stick to the reactor walls more easily. The polymer content of the slurry is relatively high reaching 25% by weight. The Phillips slurry process uses a higher pressure than the Ziegler Natta process and this can lead to higher densities as high ethylene pressure reduces the number of short chain branches (usually one or less per molecule). The polymer is recovered and the solvent is recycled. The ethylene conversion is relatively high versus other processes (above 95%). The granular polymer is extruded into pellets with anti oxidants and other additives as needed. The molecular weight control is provided either by reactor conditions or by introduction of hydrogen as a chain transfer agent.

The chromium catalyst is made with the reaction of a chromate, usually chromium trioxide with a supported silica containing siloxanes and absorbed water. First part of the process for the manufacture of chromium catalyst involves the treatment of the silica with the chromium compound in aqueous solution. In the second step the solvent is removed. This step is then followed by calcination of chromium containing silica at very high temperatures of up to 900 °C. The exact mechanism of the polymerization process of ethylene with the chromium catalyst is not known but is believed to involve oxidation-reduction reactions in which chromium (II) is generated as the active centre. The chromium catalyst has gone through several generations starting with the first generation in 1959 (*31*). The first generation catalyst had a longer induction period and was not capable of making higher flow materials (lower molecular weight). The second generation catalyst family introduced in 1975 was developed through the modification of the support surface and was able to generate lower molecular weight resins with a higher melt index. The third generation catalyst family was introduced in 1983 through use of the co-catalyst technology bringing a broader molecular weight distribution capability by increasing the lower molecular weight components for improved processing. The fourth generation catalyst was introduced in 1990s mostly through alternative supports and enabled increased hydrogen response, even broader molecular weight distribution (up to 50 Mw/Mn) further improving the product enhancement characteristics (*32*).

The supported chromium catalysts were also developed by Union Carbide Corporation in 1970s. These were different from the Phillips catalyst in that they utilized different supports and precursors. They also differed in other aspects such as greatly reduced induction period (a major shortcoming of Phillips chromium catalyst, especially early generations), very good hydrogen response and great kinetic profile. These catalysts are used in the Unipol Gas Phase process for the production of both LLDPE and HDPE.

Ziegler Natta Polymerization and Gas Phase Process

Karl Ziegler of Germany and Giulio Natta of Italy were awarded the Nobel prize in Chemistry in 1963 for their work on catalysis of polyolefins. Karl Ziegler spent most of his early career studying metal alkyl chemistry from the 1920s to the 1940s. In the 1940's he discovered the ability of triethylaluminium (TEAL) to produce higher alkyl adducts of ethylene with even numbers of carbon atoms. Through beta hydrate elimination this reaction then leads to the formation of higher alpha olefins. This is in fact one of his most significant discoveries that led to the development of processes to produce comonomers commonly used in the production of LLDPE such as butene hexene and octene. In fact he discovered an economical way to produce the comonomers that would be essential for his later discovery of the Ziegler Natta catalyst system to copolymerize these alpha olefins with ethylene to make LLDPE. Higher alpha olefins are further used to make higher alcohols, another industrially important class of chemicals.

In common with a lot of early discoveries in chemistry, the discovery of the transition metal halides as a component of the Ziegler Natta catalyst system came about by accident. Ziegler and his coworkers working in Max Plank Institute in Mulheim were trying to further expand the TEAL catalyzed ethylene reaction. They discovered by accident that when nickel is present the TEAL reaction with ethylene produces 1-butene. The source of nickel in early experiments was later found out to be the surface of the stainless steel equipment used in the experimental set up. After this Ziegler decided to carry out a systematic study of transition metal compounds and aluminum alkyls on ethylene. Heinz Breil, then a graduate student working with Ziegler for the first time, was able to make a linear polyethylene in the form of a white powder by combining zirconium acetyl acetonate with triethylaluminum. The Ziegler group continued to expand their activities to other compounds and eventually Heinz Martin combined titanium tetra chloride with triethylaluminum to make polyethylene under very mild conditions of temperature and pressure in 1953. Many good descriptions of Ziegler Natta developments have been published (*33*, *34*).

Ziegler wanted to duplicate his success in the polymerization of ethylene in the polymerization of propylene. At this point no good technology existed for the polymerization of propylene to polypropylene. Unlike ethylene propylene does not undergo free radical polymerization to make high molecular weight polymers so the free radical route was not available to propylene to make polypropylene. His repeated attempts were not successful in polymerizing propylene. However Guilio Natta, Professor of Chemistry at the Institute of Industrial Chemistry at Milan Polytechnic was aware of Ziegler's work. As a consultant to Italian Chemical Company Montecatini (a distant relative of current Italian polyethylene producer Polymeri), Natta organized a cooperative development effort and learned the details of Ziegler's success in ethylene polymerization. Natta was able to develop the right catalyst formulation based of $TiCl_4$ to polymerize propylene to polypropylene in 1954.

The early Ziegler Natta catalysts were not supported. Most of the active centers were quickly buried in the growing polymer mass around the catalyst particle and unavailable to further polymerization. This meant that the catalyst activity was relatively low. A major break through took place in 1970's when supported catalyst systems were developed. These systems dispersed the active centers on the support making them available and accessible to ethylene and comonomers. This yielded dramatic improvements to efficiency (*35*). This was one of the most critical features of the Ziegler Natta catalyst development. The high efficiency meant that the metal concentration in the polymer was so low they no longer needed to be removed, making economics of polymerization process far more favorable. A huge number of materials have been tried as supports but Mg Cl2 supported Ziegler Natta catalysts are the largest group of catalysts used in ethylene polymerization.

The Ziegler Natta catalysts are complex structures with multiple active sites. These systems are insoluble in hydrocarbons and other organic solvents. They are in particulate form. They are air and moisture sensitive and must be kept in an inert environment. An industrially critical aspect of Ziegler Natta catalysts is their ability to duplicate catalyst particle size distribution in the polymer. For this reason the polymer producers keep tight control on particle size distribution. If the particle size distribution contains excessive amounts of small particles, it may translate to excessive fines generation in the polymer produced. This ability to control the polymer particle size and size distribution through catalyst particle size and size distribution makes the process control much easier than it would be, especially in gas phase processes. A simplified diagram of the Univation Gas Phase process is given below in Figure 13 (*36*).

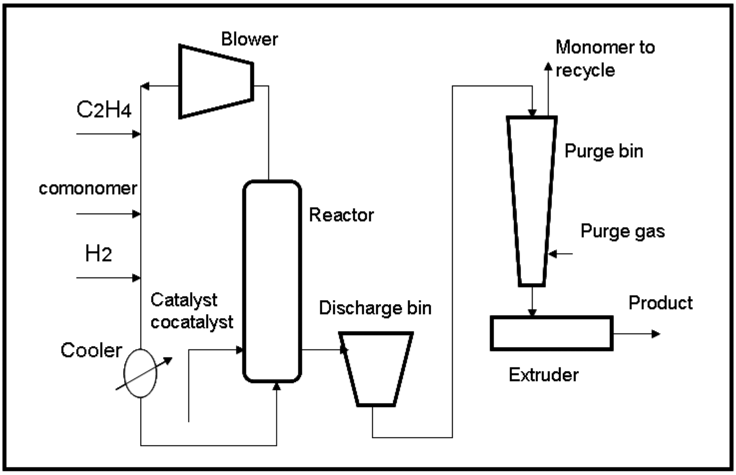

Figure 13. Univation Gas Phase Process.

In the Gas Phase Process reactants and catalyst are fed into a fluidized bed reactor where polymerization takes place. Newly formed polymer particles are fluidized by the incoming reactants. The process takes place at low temperature and pressure. The polymer is withdrawn from the reactor to the discharge bin and from there transferred to the purge bin. In the purge bin unreacted monomer and comonomer is separated and returned to the recycle stream. The granular polymer is then extruded through an extruder with required anti oxidants and other additives and comes out as pellets. The gas phase process is a very versatile process with low capital cost and broad polymer capability. These characteristics has made it the most widely used process for the manufacture of polyethylene especially HDPE (*37*).

Metallocene Polymers

Metallocene polymers represent the newest class of polyethylenes with much higher degrees of control on molecular parameters. They have narrower short chain branching distribution as well as narrower molecular weight distribution. Metallocene polymers were first discovered by Walter Kaminsky and Hansjorg Sinn in Germany in 1976. Unlike Ziegler Natta or chromium catalysts they are molecular catalysts; that is they have a known molecular structure and there is only one active centre. Furthermore they are usually soluble in the polymerization system. The metallocene class of catalysts are characterized in that they have two cyclopentadiene rings sandwitching the active metal structure. In general the active metal can be a number of transition metals. Since in metallocene polymers there is only one active centre, as a result the composition i.e. the copolymerization characteristics, is always the same. The result is a very narrow distribution of comonomers across the polymer backbone, and it is always the same. Metallocene polymers are mostly produced in a gas phase process or in a solution process. Metallocenes as a class have very high efficiency normally running into millions of g of polymer per g of catalyst. In addition new developments in homogeneous catalyst families continue such as Dow's constrained geometry catalysts (CGC) containing no metallocene rings (*38*).

Uses of Polyethylene

Polyethylene is the most widely used polymer by a wide margin. As a result its uses are very widespread. It is almost impossible not to come into contact many times in our daily lives with polyethylene. It powers our electrical grid by insulating power lines, makes electronics possible through insulation of electricity cables. Our houses and factories have many miles of wires protected by polyethylene. A major portion of our food is protected from the elements, their shelf life extended. It protects us from bacteria and other harmful pathogens. Our natural gas is transported by pipes made from polyethylene. Our land fills are lined with polyethylene films to prevent contamination of ground water. A multitude of toys are made from it that entertain and educate our children. Polyethylene enables our high productivity agriculture through green house films, micro irrigation and mulch and silage films. By replacing high energy consuming packaging materials such as glass and metal in food packaging it contributes to sustainability. Its light weight vs. regular packaging materials reduces cost of transport and its carbon foot print. It is an essential element of manufacturing, distribution and retailing industries. Cast stretch films protect contents as secondary or tertiary packaging making transport, handling, warehousing and retail operations more efficient. Polyethylene foams protect us in accidents from the impact in our cars, in helmets and other protective equipment. A thin coat of polyethylene on paper makes it resistant to wetting and makes it possible to use for liquid packaging of milk, juices and other liquids. Our milk and orange juice are served in a polyethylene bottle. Its resistance to acids, alkaline and other corrosive environments make it ideal for household cleaners, detergents, motor oil, gasoline storage and many other applications too numerous to mention. As the new technologies develop, polyethylene is usually the first material considered due to its cost, ease of processing and its properties.

In this section a brief overview of the principle uses of polyethylene will be given.

Polyethylene Films

Polyethylene films are produced by extruding molten polymer through an annular die and at the same time expanding the bubble by applying air pressure. As the melt comes out of the annular die, it is pulled in the machine direction by rollers and expanded with air pressure applied inside the bubble. What makes polyethylene such a good film forming material is the fact that it has sufficient melt strength to sustain its own weight and stretch uniformly through the internal pressure. It can be by itself, in which case it is a monolayer film, or co-extruded with other materials such as a barrier material (ethylene vinyl alcohol, EVOH). It is quite common to have up to 7 or more layers of co-extruded films. Each layer contributes certain functionality. It is even possible to have polymers that are incompatible such as nylons and polyethylene through incorporation of a tie layer between the two polymers.

Films represent the largest use of polyethylene. Typical applications include the following:

- Food packaging covering bread, fresh produce such as lettuce, celery, cereals, cheeses, meat, dry vegetables and cookies. Meats (usually multi layer films), processed meat products such as ham, sausage and cured meats. Portion packaging for condiments. A big application area is institutional food packaging such as hospitals, schools, correctional institutions, retirement houses and armed services. In these institutions food products usually come in large polyethylene bags and are used for the preparation of cooked meals. In recent years bag in box applications like wine, juice and other liquid foods have also become wide spread. Pet foods are another large area of use.
- Agricultural products covering silage film for animal feed, mulch films and fumigation films. In parts of the world where grain elevators are not available, silo bags made out of polyethylene are used for safe storage of grains until they can be transported to the market.
- Industrial applications include cling stretch films for pelletization of manufactured goods and retail items. White goods like fridges, washing machines and other appliances are wrapped in polyethylene film to protect them against accidental damage during transport. Shrink films for water, juice, carbonated drinks, cans, glass jars. In manufacturing granular or powder materials are also packaged in polyethylene films such as palletized resins.
- Home and garden use include storage and sandwich bags, cling film for hand wrapping food and other goods, tissue packaging. Gardening necessities including mulch, fertilize and seed packaging. Gravel and other DIY materials for home use.
- Polyethylene films are also used in construction for house wrap, where the film protects the house against moisture by not letting water to get into house but letting the water vapor to be transported to assist drying. Also most items used in construction such as windows, doors even bricks are protected by polyethylene films from accidental damage.
- Health and hygiene films include diaper back sheets and adult incontinence and convenience items.

Blow Molded Articles

Blow molding is a process by which hollow items can be manufactured. Typically blow molding operation consists of three steps. First the resin is made molten, then extruded into a mold. In the third step vacuum is applied to help the polymer take shape of the mold and uniformly distribute. Melt rheology of polyethylene is very suited to this type of application and as a result polyethylene is the most widely used polymer for this application.

- Small part blow molding including milk bottles, juice and water bottles (typical 1 gallon jugs we see in supermarket shelves). Cosmetic items for creams, powders and others. Home and garden chemicals such as detergents, bleach, pesticides, herbicides and other garden chemicals. Motor oil, anti-freeze other automotive fluids. Gasoline jerry cans.
- Large part blow molding including drums, plastic barrels and larger items for storage and containment.

Pipe

Use of polyethylene in pipe applications is more recent. In the US almost all of the natural gas is transported by polyethylene pipe. This is because of resistance to cracking, chemical components of the natural gas and ease of installation. Another fast developing application for pipe is potable water transport. Again toughness and resistance to cracking coupled with low cost and ease of installation make it an ideal choice. Due to its flexibility it can be installed without digging up inner cities. It is estimated that up to 30% of the potable water in US is lost due to damaged municipal water system. Shortage of water in agriculture has led to development of new irrigation technologies such as drip irrigation. Drip irrigation reduces the water usage up to 80%. Polyethylene is the dominant polymer for this application due to ease of manufacture, excellent flexibility and toughness coupled with its low cost. Polyethylene based pipe structures find wide spread use in under floor heating, geo thermal energy, sewage, water drainage and surge water management.

Industrial pipe is another area for polyethylene. This includes chemical industries, oil industries, power plants and other areas.

Thermoformed Articles

Thermoforming is a process whereby a sheet of polymer is heated to soften, then by application of pressure and/or vacuum formed into a pre defined shape. There are a large number of uses for such items including trays for food packaging, truck beds for protection, shower basins, RV industry, manufacturing industry and others. Good dimensional stability, melt strength and resistance to aggressive environments make polyethylene the material of choice.

Health and Hygiene

Health and hygiene applications for polyethylene include woven and non woven materials for diapers, absorption pads, adult incontinence and other protective uses. Hospital gowns are also used widely. Fibers are a big area of use and include fishing nets. Polyethylene fibers are first spun and then chopped up to make non wovens. They tend to be softer than other materials such as polypropylene.

Rotational Molding

Rotational molding is used for larger parts whereby polymer is first ground to a fine powder, loaded into a mold and slowly rotated while being heated, hence the name rotational molding. Molten polymer forms a thin skin on the mold and after cooling the mold is opened and the item is removed. The environmental stress crack resistance of polyethylene towards aggressive agents, acidic materials and chemicals make it an ideal choice. The uses include large water tanks, chemical storage, industrial intermediates, agricultural chemicals such as pesticides and herbicides.

Injection Molding

Injection molding is a process whereby polymer is first heated to melt, then injected into a mold. The mold is cooled to speed the cooling process hence the productivity.

Wire and Cable

One of the earliest uses of polyethylene was for submarine cables and radar equipment. Polyethylene is the material of choice for wire and cable. High and medium voltage electric transmission lines and electric distribution lines are coated with polyethylene due to its long term stability, ease of manufacture and properties as an insulating product. Modern day information infrastructure relies on polyethylene. Factories, transportation equipment and electrical equipment all use large amounts of polyethylene.

Global Production

At the time of writing this chapter (end of 2010) the total production capacity of polyethylene across the globe was well over 90 million MTs. The explosive growth from the 1960’s had continued till the late 1990s. By the end of the 1990s and early 2000s, the growth rate has slowed down to those of GDP, especially in Europe and North America. The following pages will take a brief look at the changes that are on going in the production capacity and consumption for polyethylene, both geographically as well as production technology (*39*).

In the last 10 to 15 years the polyethylene industry has gone through major transformations in many aspects. One of those has been the consolidation in the industry. This trend is projected to continue as growing economies and the low cost raw material regions will have more of the global share of the production capacity. The following Figure 14 gives the projected top 5 producers in 2009 and 2014 projection.

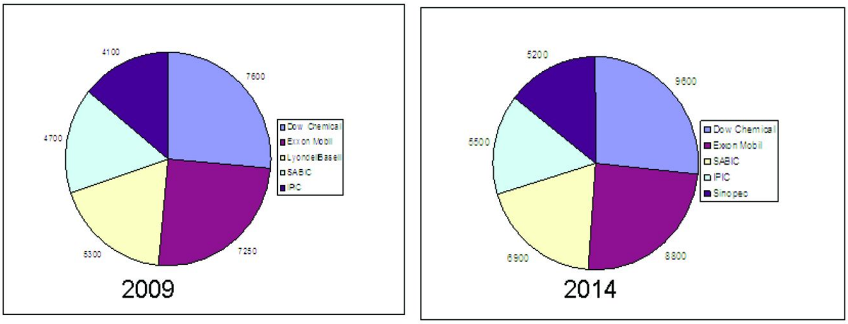

Figure 14. Projected top 5 producers of polyethylene 2009 to 2014 (M mt).

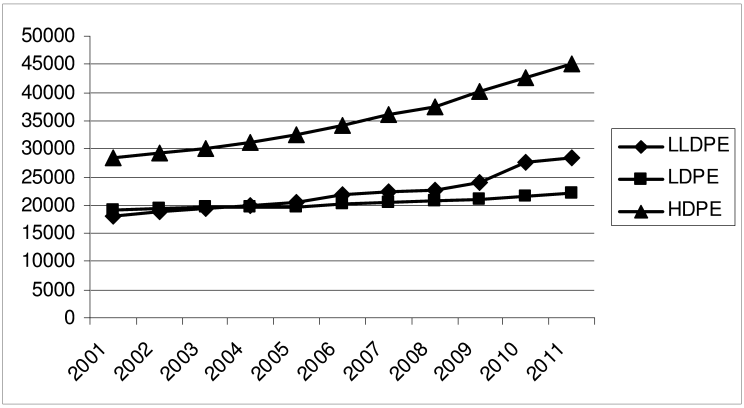

Figure 15. Global production of three main types of polyethylene 2001-2011.

The polyethylene industry is a cyclical industry whereby the investment in new facilities follows a pattern that is somewhat similar to economic growth but out of phase with it. Currently HDPE is the largest volume polyethylene resin followed by the LLDPE. The position of LDPE as the dominant polyethylene has eroded over the years to the extend that today it has become the smallest of the three classes. LLDPE has taken over the second spot after HDPE in early 2004. In the last ten years the growth was primarily driven by HDPE and LLDPE while LDPE capacity remained the same.

The primary growth in the production capacity is driven by two regions: Asia through its needs for raw materials for its growing economy and the Middle East searching for more value added use of its abundant raw materials. This picture emerges time after time for every product family. Figure 15 gives overall growth of each main product line for the last ten years.

LDPE Production

Figure 16 gives the changes during last ten years on geographic distribution of production capacity. Europe still remains the leading producer of LDPE but investments in Asia, especially China have been accelerating. At this rate Asia will become the dominant producer of LDPE globally in a few years. Another area that has been growing at a faster rate than average is the Middle East, especially in the last few years. That trend for the Middle East will most likely be accelerating as a large number of projects are underway to be completed in the next few years. As there is no significant consumption of polyethylene, most of the production is intended for export markets. Globally North America is the only area where the LDPE, production capacity has shrunk over the last ten years primarily due to shut down of the older assets without any new assets to replace them. In the case of LLDPE and HDPE the North American assets are relatively new and benefit from the scale of economies. In the case of the LDPE capacity, especially autoclave LDPE, this is not the case.

LDPE was the first polyethylene to be commercially produced. In 1950’s through 1980’s it fuelled the major part of the expansion. Its major shortcomings in the area of density and mechanical strength accelerated the expansion of HDPE and LLDPE product families. With the advent of chromium, Ziegler Natta and metallocene catalysts the initial thinking was that LDPE would shrink and may be totally replaced by LLDPE. The unique long chain branching structure of LDPE was not duplicated by other technologies. While its overall volume has declined in proportion to other polyethylene families it continued to be used as a blend to impart processing and melt strength characteristics to both LLDPE and HDPE. The two basic technologies for the production of LDPE remain the only technology. The early capacity built was mostly autoclaves while later capacity built is mostly tubular in nature. As the autoclave process is smaller in scale and more costly, it continues to lose ground even during the last decade. Figure 17 shows the relative global capacity change by the two main processes to produce LDPE.

Figure 17 shows that during the last 10 years the tubular LDPE capacity has increased by almost 50 % while autoclave capacity decreased by 15%. It is expected that this trend will continue as no significant new autoclave capacity is planned. Furthermore most of the existing autoclave reactors are relatively old and smaller then their tubular counterparts. As those plants age they will require more investment to keep them operational further worsening the economics of already non competitive assets.

HDPE Production

HDPE production has undergone a dramatic change in recent years from a geographical perspective. Economic growth in developing countries and the broad range of technology available for licensing has shifted the balance of production to Asia. Figure 18 gives the distribution of global capacity in the last ten years. While the growth has been steady in North America, South America and Europe all of the growth came from new capacity additions in Asia and Middle East. This is a common trend for all the polyethylene families. It is anticipated that this trend will continue moving forward at an accelerated rate as larger integrated facilities with highly efficient new plants will come on stream with raw material and logistics advantages.

The gas phase process continues to dominate in the production of HDPE closely followed by the Phillips slurry process. Ziegler is a collection of other technologies primarily made up of Basell Hostalen, Mitsui process, bimodal Borstar from Borealis and Hoechst process. This group of technologies have not made significant expansion in additional capacity. The solution process continues to have a small portion of the HDPE market with no new capacity addition.

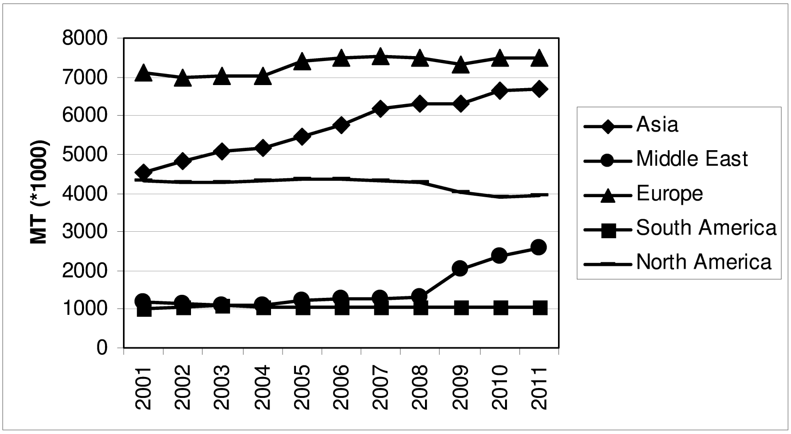

Figure 16. Geographic distribution of polyethylene production capacity.

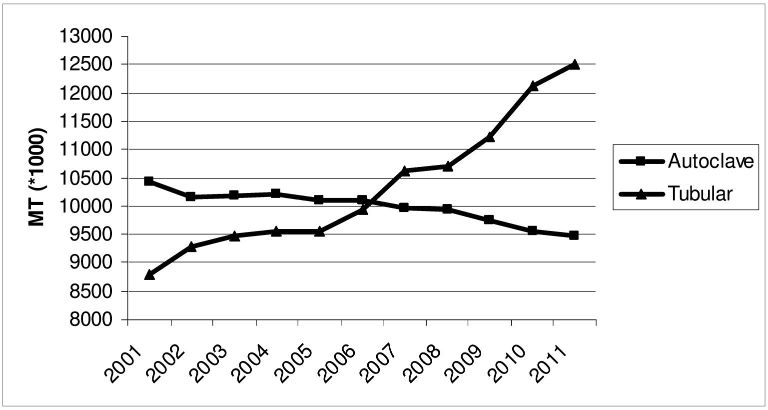

Figure 17. LDPE autoclave vs tubular capacity changes 2001 to 2011.

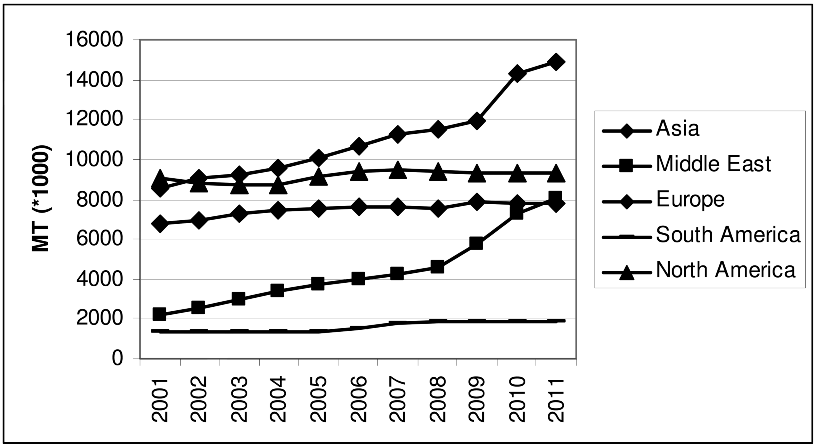

Figure 18. HDPE capacity geographic distribution 2001 to 2011.

The change in selection of technology for the production of HDPE is given in Figure 19 below.

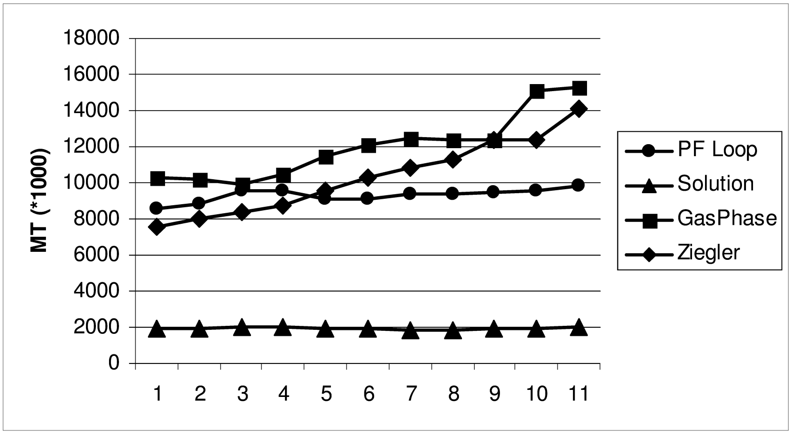

Figure 19. Selection of production technologies for HDPE 2001 to 2011.

LLDPE Production

LLDPE capacity has taken over LDPE in 2003 to 2004 and continues to grow somewhere between the two other products HDPE and LDPE. Figure 20 below gives the geographic production distribution for LLDPE from 2001 to 2011. The geographic changes in new capacity additions are not too dissimilar to other polymers as given in Figure 20 below.

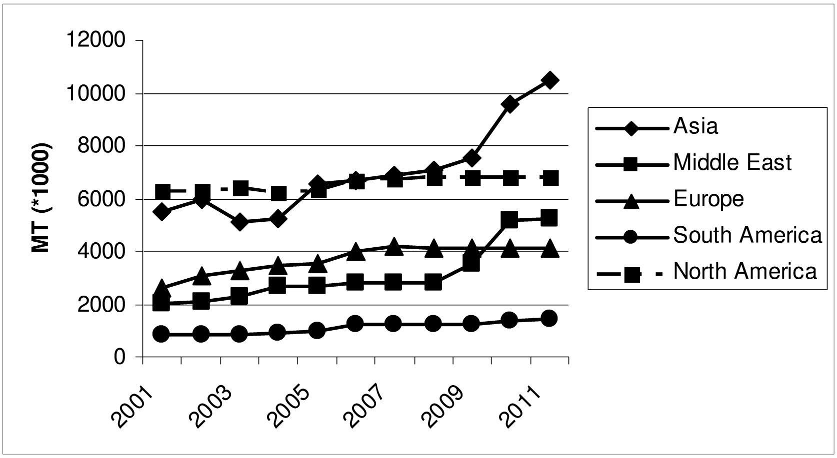

Figure 20. Geographic distribution of LLDPE capacity 2001 to 2011.

Again the biggest increases has taken place in Asia and the Middle East primarily driven by demand in the case of Asia and raw material economics in the case of the Middle East. For the first time in 2009 Asia has taken over the North America as the largest producer of LLDPE. The capacity available for LLDPE has been essentially flat in all other geographies.

The two dominant production technologies as given in Figure 21 below still keep their relative positions in LLDPE production. The gas phase process, especially Unipol Technology from Univation (a joint venture between The Dow Chemical Company and Exxon Mobil Chemical Company) continues to dominate LLDPE production. The solution process has not grown as fast as the gas phase primarily due to the lack of availability of licensing options from especially Dow Chemicals Solution Process technology.

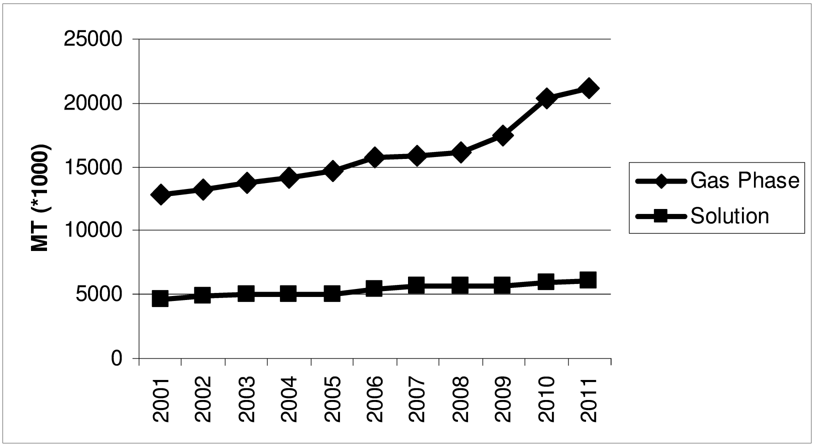

Figure 21. LLDPE production technology capacity period 2001 to 2011.

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ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

Conclusion

Polyethylene has become the number one polymer in the world in a relatively short time from its first production in gram quantities just over 70 years ago. It came into existence mostly by accident but has now grown into a highly sophisticated technology with world class science driving productivity and expanding its functionality. It is unlikely that this position will change any time soon. The developments in conversion equipment continue to expand the market and application space. Ethylene, the simplest of all monomers is readily available as a low cost material further consolidating its position as the largest volume polymer. Perhaps its beauty is in its simplicity.

While polyethylene is currently based on natural gas and oil, one can argue it is perhaps the most efficient use of those resources. It contributes to societal needs greatly in every sphere of human activity. It is usually the best solution in most areas where it is used. As the demand for renewable resources increases, polyethylene producers have also been working on making ethylene from natural resources such as sugar cane and other potential sources of ethanol. The conversion of ethanol to ethylene is a simple mature process.

While it is unlikely that new types of polyethylenes will be coming into existence, continuous improvements will drive utilization. In the last ten to fifteen years the packaging films have gone down in thickness on average 20 to 50%. Compared to it nearest competitors this productivity will open up other opportunities to replace traditional materials such as glass, metal and paper. Not because there is a conscious effort on the part of producers (almost none of them actually make the final article), but because it is the best overall solution to those needs.

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Chapter 10

Electrically Conducting Plastics: Revising the History of Conjugated Organic Polymers

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The discovery that the conductivity of conjugated organic polymers can be controlled through oxidation or reduction led to materials combining the electronic properties of metals with the weight and density of plastics. For this reason, such materials have been studied extensively and their importance recognized with the awarding of the 2000 Nobel Prize in chemistry to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa for their polyacetylene work beginning in the 1970s. While these studies produced the most dramatic results, investigations of electrically conductive conjugated polymers date back to the early 1960s, particularly with the work of Donald Weiss on polypyrrole, as well as that of René Buvet and Marcel Jozefowicz on polyaniline. That these previous studies are overlooked in the history of conjugated polymers is unfortunate and thus many in the field are unaware of these previous contributions. To rectify this, this chapter will attempt to present a more complete picture of the initial history of these important electronic materials.

Introduction

Most organic polymers or plastics are excellent insulators and are often used to isolate metallic conductors from other conducting materials. However, the discovery that the electrical conductivity of conjugated organic polymers (Figure 1) can be controlled through oxidation or reduction has led to the attractive

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

possibility of materials with the conductivity of metals, but with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs (*1–3*). Such materials, often referred to as *synthetic metals* (*4*), are semiconductors in their neutral state and exhibit increased conductivity (quasi-metallic in some cases) in the oxidized or reduced forms. As such, they have received considerable fundamental and technological interest over the last few decades, leading to their current use in such applications as sensors, field effect transistors (FETs), organic photovoltaic (OPV) devices, electrochromic devices, and light emitting-diodes (LEDs) (*1–3*).

The impact and importance of these materials was recognized with the awarding of the 2000 Nobel Prize in chemistry to Professors Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa "*for the discovery and development of conductive polymers*" (*5*). The fact that this field of study had changed the way that one viewed plastics was outlined in the initial press release as follows: "We have been taught that plastics, unlike metals, do *not* conduct electricity. In fact plastic is used as insulation round the copper wires in ordinary electric cables. Yet this year's Nobel Laureates in Chemistry are being rewarded for their revolutionary discovery that plastic can, after certain modifications, be made *electrically conductive*." The scientific contributions recognized by this award was for their collaborative work on conducting polyacetylene beginning in the mid 1970s and as illustrated by the quote above, most discussions of the history of this field begin with these efforts.

While these studies produced quite exciting results and had far-reaching impact on the growth of the fields of conjugated polymers and organic electronics, investigations of electrically conductive conjugated polymers date back to the early 1960s, particularly with the work of Donald Weiss on polypyrrole, as well as that of René Buvet and Marcel Jozefowicz on polyaniline. That these previous studies are overlooked in most discussions of the history of conjugated polymers is unfortunate (*6*) and results in the fact that the majority of researchers in this evergrowing field are unaware of these previous contributions. To rectify this, this chapter will attempt to present a more complete picture of the initial history of these important electronic materials, beginning with efforts in the 1950s and highlighting the contributions of Weiss, Buvet, and Jozefowicz along with the more well-known work of Heeger, McDiarmid, and Shirakawa.

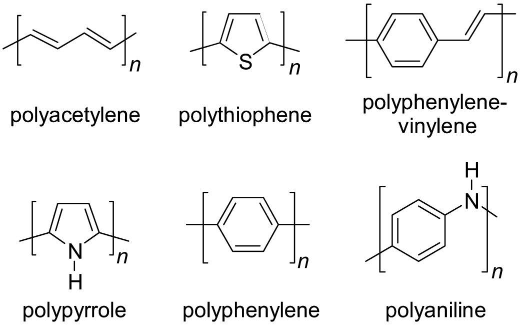

Figure 1. Commonly studied conjugated polymers.

Carbon Blacks and the Start of Conjugated Organic Polymers

Perhaps the oldest known organic materials that exhibit electrical conductivity are the carbon blacks. Carbon black is a generic term for various forms of carbon made from the partial burning or carbonizing of oil, wood, vegetables and other organic matter (*7*). Such carbon blacks are among the oldest polymeric organic substances of commerical importance due to their black color, high electrical conductivity (up to 50 Ω^{-1} cm^{-1}), and high thermal stability (*7*, *8*). The use of carbon blacks as pigments extend back to pre-history and the oldest recorded process for its production was practiced in China as early as 3000 B.C. (*7*).

Although the current description of modern carbon black is that of a particulate, quasigraphitic carbon material (*7*), many earlier studies considered carbon blacks as three-dimensional, crosslinked organic polymers with various structures and elemental constitutions depending on their specific origin (*8*). As these "carbonaceous polymers" (*8*) were considered to have chemical structures that were too complex, ill-defined, and poorly understood, efforts beginning in the 1950s focused on the production of related polymers with more defined and controllable compositions. Such attempts typically utilized either the high temperature pyrolysis of various synthetic organic polymers or the direct polymerization of monomeric precursors using less drastic organic methodologies. Examples of early efforts along these lines include the production of polyvinylenes (i.e. polyacetylenes) through the pyrolysis or chemical elimination of poly(vinyl bromide), poly(vinyl chloride) (*9*, *10*), and poly(vinyl alcohol) (*11*), polyacetylenes via either Ziegler-Natta catalyzed processes (*12*, *13*) or the thermal polymerization of phenylacetylenes (*14*), and polyphenylenes from the coupling of various dihalobenzenes (*11*, *15*, *16*). For the most part, however, these initial attempts produced materials with very high resistivities and could nearly be considered insulators (*8*). The first real successful synthesis of an organic polymer with significant conductivity was reported in 1963 by Donald Weiss and coworkers with the thermal polymerization of tetraiodopyrrole (*17–19*).

Donald Weiss and Polypyrrole

Donald Eric Weiss (Figure 2) was born October 4, 1924 (*20*, *21*) in St. Kilda, a suburb of Melbourne in Victoria, Australia (*22*). The only child of Vernon Weiss and Lillian Le Lievre, he grew up in Adelaide, where he attended Mitcham Primary School and Scotch College (*22*, *23*). In 1942, he started studying industrial chemistry at the South Australia School of Mines and shortly thereafter transferred to the University of Adelaide (*22*, *23*). He received his BSc in 1945 (*20*, *21*), after which he became a shift chemist for Associated Pulp and Paper Mills in Burnie, Tasmania (*21*, *24*). He then moved to Commonwealth Serum Laboratories (CSL, Melbourne) in 1947, trying to improve their new penicillin process (*21–24*).

During his time at CSL, he met Dick Thomas of CSIR’s (Council for Scientific and Industrial Research) Division of Industrial Chemistry at Fishermen’s Bend (another suburb of Melbourne) (*22–24*). As a result, Weiss moved to CSIR (now CSIRO) the following year, working under Dirk Zeidler in the Chemical Engineering Section, Division of Industrial Chemistry (*20–24*). Mutual friends then introduced him to Betty Evans and they were married in 1951, followed by the birth of two sons; Robert in 1952 and Peter in 1956 (*22*). In October of 1958, Weiss submitted a collection of his CSIR research entitled “Adsorbents and Adsorption Processes” (*25*) to the University of Adelaide in support of his candidature for the degree of Doctor of Science (DSc), which was granted by the University in 1960 (*20–23*).

About this same time, he began research on electrically conducting organic polymers as potential electrically-activated and easily regenerated adsorbents (*24*, *26*). This work began in 1959 with the preparation of xanthene polymers via the condensation of hydroquinone with phthalic anhydride and/or pyromellitic dianhydride. The resulting materials were insoluble, black tars that exhibited properties of p-type semiconductors, although the observed conductivity was still fairly low in comparison to activated carbon (*26*).

Observations reported in the older Italian literature of the 1920s, however, suggested a new approach (*17*, *27*). These papers reported that tetraiodopyrrole was thermally unstable and when heated, liberates iodine vapor to produce a black substance that resembled graphite in appearance (*17*). As the electrical properties of these materials were never reported, Weiss and coworkers set out to reproduce such materials in order to characterize the resulting structure and potential conductivity. Thus, they prepared a series of "polypyrroles" by heating tetraiodopyrrole in a rotating flask under a flow of nitrogen to both maintain an inert atmosphere and to transfer iodine vapor away from the reaction (*17*).

Figure 2. Donald E .Weiss (1924-2008). [Courtesy of Robert Weiss.]

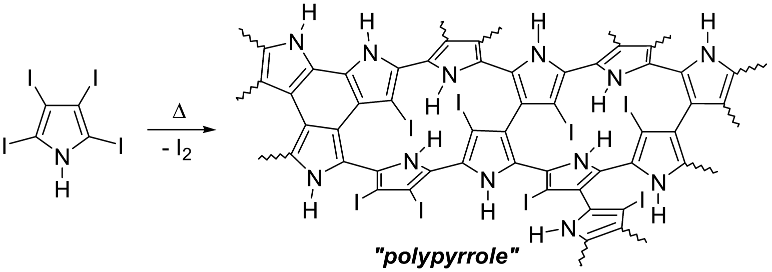

Figure 3. Thermal polymerization of tetraiodopyrrole.

The products of these reactions were reported (*17*) to be insoluble, black powders, which was described as "...a three-dimentional network of pyrrole rings cross-linked in a nonplanar fashion by direct carbon to carbon bonds." In addition, it was found that the products contained both "adsorbed molecular iodine" and nonreactive iodine which was concluded to be "iodine of substitution". Based on the descriptions of Weiss and coworkers, a hypothetical structure for the polymeric material is given in Figure 3.

Characterization of the electronic properties of the polypyrrole products revealed good conductivities, with resistivities of 11-200 Ω cm (*8*, *19*). The nature of this conductivity was described as follows (*19*): "However it is apparent that the polymers are relatively good conductors of electricity. Since no polarization was observed during the measurement of the electrical resistance, even over substantial periods of time, it is assumed that the conductivity is of electronic origin." Perhaps of greatest interest was that it was found that the removal of adsorbed molecular iodine by solvent extraction (*19*), chemical or electrochemical reduction (*17*, *18*), or thermal vacuum treatment (*19*) resulted in a significant increase in resistance.

Further study of this effect led them to find that "...evidence for the formation of a strong charge-transfer complex between polypyrrole and iodine was obtained from e.s.r. studies..." (*18*). This then led to the conclusion (*19*) "Charge-transfer complexes of strength sufficient to cause partial ionization induce extrinsic behaviour by changing the ratio of the number of electrons to the number of holes." Thus, they understood that "...the presence of the oxidant iodine, and in its absence oxygen, facilitates oxidation of the polymer" (*17*). However, Weiss admitted that the full role of this to conductivity was not realised until much later (*27*).

Weiss and coworkers went on to study a few more related polymers (*28*, *29*), but determined that the application of such materials for an electrical desalination process was impractical and by 1967 moved on to other projects (*27*). In 1973, the CSIRO Division of Chemical Technology was formed and Don Weiss became its Chief (*24*). It was during these years that he made his most well-known contributions, particularly the development of magnetic ion exchange resins and SIROFLOC, a large-scale continuous water treatment process (*23*, *27*). Over the years, Weiss earned a number of prestigious awards, cultimating in his being made an Officer (OBE) of the Most Excellent Order of the British Empire in 1976 for his contribution to science (*20–22*). He finally retired from CSIRO in October of 1984 (*22*, *27*) and passed July 30, 2008 due to pneumonia brought on by a battle with lung cancer (*22*, *30*).

Conductive Polyaniline

As Weiss and coworkers were winding down their work on polypyrrole, related work on another conjugated polymer, polyaniline, was on the rise in the laboratory of Rene Buvet at the Ecole Supérieure de Physique et de Chimie Industrielles de la ville de Paris (also known as ESPCI ParisTech). The majority of this work was carried out by Marcel Jozefowicz (b. 1934) (*31*), working under Buvet. Jozefowicz and Buvet initially focused on oligophenylenes (*32–34*), but by 1964 had shifted their efforts to oligo- and polyanilines.

Aniline materials have a very extensive history with observations of colored precipitates resulting from the oxidation of aniline dating back to the mid-1800s (*6*). By the beginning of the 20th century, work performed first by Willstätter and coworkers (*35*, *36*), and then followed up by Green and Woodhead (*37*), proposed such precipitates to be linear octameric species, which were believed to exist in at least four different oxidation states. However, in the early 1900s, most studies on such aniline oligomers focused on studies of the mechanism of oxidative polymerization (*6*).

Initial work by Jozefowicz and coworkers focused on developing reproducible methods for the preparation of aniline oligomers in order to carry out detailed studies of their electronic properties (*38*). This was then followed with detailed studies of the redox reactions of the resulting materials (*39*). By 1966 (*40–42*), they had developed methods for the production of the emeraldine form of polyaniline via the oxidative polymerization of aniline using persulfate (as shown in Figure 4) and began studies of its conductive properties.

It was found that pressed pellets of these materials were indeed quite conductive, stating "La conductivité des polyanilines est très élevée et classe ces composés parmi les meilleurs conducteurs organiques connus. Cette conductivité est, sans contestation possible, électronique" (*trans.* The conductivity of the polyanilines is very high and classifies these compounds among the best known organic conductors. This conductivity is, without possible dispute, electronic) (*41*). Continued studies showed that the conductivity of these materials was dependent on both the pH of the solution used during the polymer preparation (*41*) and the water content of the resulting sample (*42*). Focusing on the pH dependence, it was found that the conductivity increased linearly with decreasing pH to give conductivities that ranged from a low of 10^{-9} S cm^{-1} to a high of 30 S cm^{-1} (*41*). Buvet reviewed the electronic characteristics of polyaniline during a lecture presented at the 18th meeting of CITCE (Comité International de Thermodynamique et Cinétique Electro-chimiques) in April of 1967 (*6*, *43*) and concluded that the conductivity of polyaniline was electronic and not due to any ion transport.

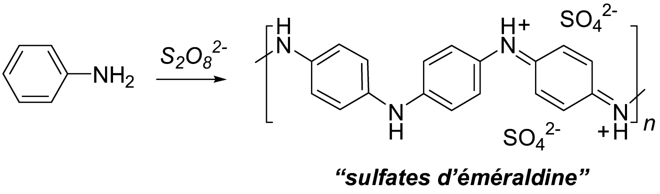

Figure 4. Production of sulfates d'éméraldine.

Jozefowicz went on to join the faculty of Nancy-Universite before becoming Professor at Universite Paris-Nord in 1969. While he and Buvet continued to study polyanilines for a while (*44–46*), Jozefowicz is most well known for his work on the synthesis of polymers for biomedical purposes (*31*).

Hideki Shirakawa and Polyacetylene Films

Hideki Shirakawa (Figure 5) was born in Tokyo, Japan on August 20, 1936 (*47*, *48*) to parents Hatsutarou and Fuyuno, the third of their eventual five childern (*47*). Spending most of his childhood in Takayama, he entered Tokyo Institute of Technology in April of 1957. During his undergraduate years, he studied primarily applied chemistry, although he did work in the area of polymer physics during his final year (*47*). His focus then changed to polymer synthesis for his graduate studies and received the degree of Doctor of Engineering in March of 1966 (*47–49*). That same year he married his wife Chiyoko Shibuya (*47*).

In April of 1966, he joined Prof. Sakuji Ikeda's group as a research associate at the Research Laboratory for Resources Utilization, Tokyo Institute of Technology, where he began investigating acetylene polymerization (*47*, *48*). Following the initial report by Natta and coworkers that polyacetylene could be produced via Ziegler-Natta catalytic processes (*12*), Ikeda and coworkers began studying the mechanism of actylene polymerization by various catalysts. In the process, it was found that in addition to polyacetylene, these methods also produced benzene (Figure 6) and that the ratio of the two products varied with the species of catalyst (*48*, *50*, *51*). Upon joining Ikeda's group, Shirakawa then continued in these ongoing mechanistic investigations.

Figure 5. Hideki Shirakawa (1936-). [Hall, N. Chem. Commun. 2003, 1; Reproduced by permission of the Royal Society of Chemistry.]

In the fall of 1967 (*47*, *51*), a visiting Korean coworker (Dr. Hyung Chick Pyun) working under Shirakawa tried to make polyacetylene by standard methods, but produced ragged pieces of a film, rather than the typical powder (*52*, *53*). [Note: While Shirakawa identifies the coworker in the acknowledgements of reference 45, Dr. Pyun's position at the time of the discovery is uncertain and has been described as a 'visiting scientist' (*47*), 'visiting Korean researcher' (*52*), 'student' (*52*), 'graduate student' (*53*) and 'foreign student' (*54*).] In reviewing the reaction conditions utilized, it was found that the catalyst concentration was the decisive factor for the film formation and the catalyst concentration used had been a thousand times higher than intended (*47*, *48*, *51–53*). Shirakawa explained the mistake as follows (*47*): "I might have missed the "m" for "mmol" in my experimental instructions, or the visitor might have misread it." Interestingly, MacDiarmid gives a different account (*54*), stating "and he [Shirakawa] replied that this occurred because of a misunderstanding between the japanese language and that of a foreign student who had just joined his group." Nevertheless, it appears that the very high catalyst concentration accelerated the polymerization rate so that as the acetylene gas contacted the catalyst solution, it polymerized on the surface as a thin film (*47*). Optimization of these accidental conditions then allowed Shirakawa to reproducibly generate silvery films of polyacetylene (*55–57*) as illustrated in Figure 7.

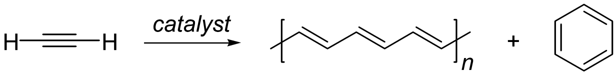

Figure 6. Ziegler-Natta catalyzed polymerization of acetylene.

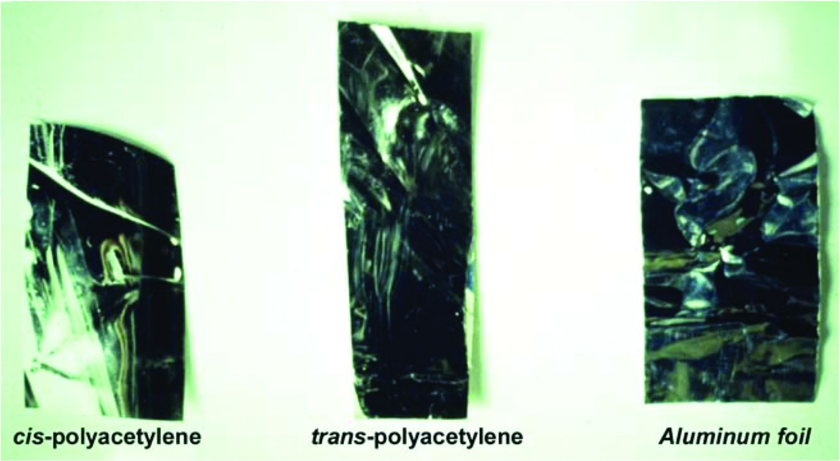

Figure 7. Films of cis- and trans-polyacetylene in comparison to aluminum foil. [Courtesy of Dr. Richard Kaner.]

Further study of the resulting polyacetylene films showed that the double bond configurations of the polymer backbone were strongly temperature dependent (*48*, *55–57*) as illustrated in Figure 8. The trans content of the film increased with polymerization temperature such that films prepared at 150 °C gave 100% *trans* content, while samples prepared at -78 °C consisted of ~98% *cis* content. It was determined that the temperature dependence was due to an irreversible isomerization of the cis to trans forms at temperatures above 145 °C. Samples of (nearly) all-*cis*-polyacetylene are copper in color and exhibit conductivities of 10^{-9}-10^{-8} S cm^{-1}, while the all-*trans* samples are silver-colored with relatively higher conductivites of 10^{-5}-10^{-4} S cm^{-1} (*48*, *51*, *58*).

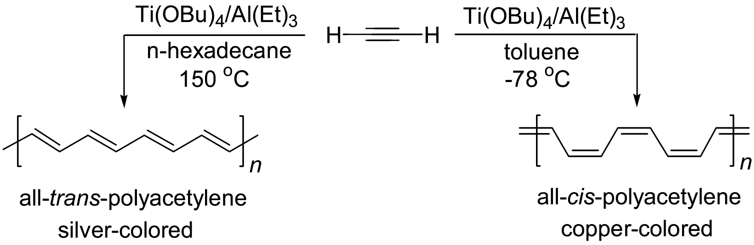

Figure 8. Temperature dependence of polyacetylene polymerization.

MacDiarmid, Heeger, and Poly(sulfurnitride)

Alan Graham MacDiarmid (Figure 9) was born in Masterton, New Zealand on April 14, 1927 (*54*). He came from humble beginnings and when his father retired, he was forced to leave high school at age 16 to take a part-time job as janitor in the chemistry department at Victoria University College. While there, he worked through his B.Sc. and M.Sc. studies as a part-time student. After completing his B.Sc. in 1948 (*59*), he was promoted to the position of demonstrator (*54*). It was during this time that he studied the chemistry of S_4N_4 for his M.Sc. thesis under Mr. A. D. Monro, resulting in his first publication in 1949 (*60*). Completing his M.Sc. in 1950 (*4*, *59*), MacDiarmid received a Fulbright fellowship to attend the University of Wisconsin. There, he studied inorganic chemistry under Prof. Norris F. Hall (*54*), recieving a M.S. in 1952 and his Ph.D. in 1953 (*4*, *61*). While still at Wisconsin, he obtained a New Zealand Shell graduate scholarship to study silicon hydrides at Cambridge University, England under the directorship of Prof. H. J. Emeléus (*54*). After completing his second Ph.D. in 1955 (*4*, *59*), he held a brief appointment as Assistant Lecturer at Queens College of the University of St. Andrews, Scotland, before joining the Department of Chemistry at the University of Pennsylvania (*54*).

Alan Jay Heeger was born in Sioux City, Iowa on January 22, 1936. His early years were spent in Akron, Iowa, but his family moved to Omaha after his father's death when he was only 9 (*62*, *63*). He attended the University of Nebraska with the initial goal of becoming an engineer. However, that changed after his first semester and he pursued a dual major in Physics and Mathematics (*62*, *63*), completing his B.S. in 1957 (*64*). He then began graduate studies in Physics at Berkeley with the goal to do a theoretical thesis under Charles Kittel. Kittel, however, recommended that he consider working with someone who does experimental work in close interaction with theory and thus he joined the research group of Alan Portis (*62*, *63*), receiving his Ph.D. in 1961 (*64*, *65*). After completing his Ph.D., he went directly to join the Physics Department at the University of Pennsylvania in 1962 (*64*), working initially on the metal-physics of TTF-TCNQ (*62*, *63*).

In 1975, reports of a novel metallic polymer poly(sulfurnitride), also called polythiazyl or $(SN)_x$ (*66*, *67*), begain to appear in the literature and quickly caught Heeger's attention (*62*). After learning that his Penn colleague MacDiarmid had some experience with sulfurnitride chemistry, he met with MacDiarmid to propose a collaboration to study this new material (*62*, *63*). They went on to report the first reproducible preparation of analytically pure $(SN)_x$ via the solid-state polymerization of S_2N_2 (*66–68*) and characterization of its resulting properties. It was found that the lustrous golden material was highly conductive (1200-3700 Ω^{-1} cm^{-1}) (*69*) and exhibited a 10-fold increase in conductivity after treatment with bromine vapor (*52*, *70*).

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Figure 9. Alan G. MacDiarmid (1927-2007) and Alan J. Heeger (1936-). [Hall, N. Chem. Commun. ***2003****, 1; Reproduced by permission of the Royal Society of Chemistry.]*

Doped Polyacetylene

During the same year that MacDiarmid and Heeger started working on poly(sulfurnitride), MacDiarmid spent time at Kyoto University as a Visiting Professor (*54*). During his time in Japan, he visited the Tokyo Insititute of Technology and met Shirakawa over a cup of green tea after finishing his lecture. During this fateful meeting, Shirakawa showed MacDiarmid a sample of his silver-colored polyacetyelene film. The film captured MacDiarmid's interest and after inquiring how the material had been made, he asked if Shirakawa could come to the University of Pennsylvania for a year to work with him on the material (*47*, *48*, *54*). Shirakawa agreed to come to the U.S. and through supplemental funding from ONR Program Officer Kenneth Wynne (*62*, *63*), he began working with MacDiarmid and Heeger as a Visiting Scientist in September of 1976 (*47*).

Upon Shirakawa's arrival, he and MacDiarmid worked to improve the purity of the polyacetylene films in order to increase its conductivity. Instead, it was found that the purer the film, the lower its resulting conductivity (*54*). As Heeger and MacDiarmid had previously found that the addition of Br_2 to $(SN)_x$ resulted in significant increases in conductivity (*52*, *70*), it was thought that perhaps the impurities in the polyacetylene were acting as dopants and thus actually increased the conductivity of the polyacetylene (*54*). Shirakawa and Ikeda had previously treated polyacetylene with Br_2 or Cl_2 vapour and had found that within the first few minutes, a dramatic decrease in IR transmission occured without any visible change in the film's appearance. Continued treat-ment then resulted in the production of a white halogentated film with expected IR transmission (*48*, *71*). The change in transmission suggested that the inital halogen-treated material might have unusual electronic properties and thus it was decided to investigate the conductivity of the films upon bromine addition.

On November 23, 1976, Shirakawa and Dr. Chwan K. Chiang, a post-doctoral fellow of Heeger, measured the conductivity of *trans*-polyacetylene by four-point probe while adding bromine vapor (*47*, *48*). The moment the bromine was added, the conductivity rapidly increased, resulting in a change of approximately four orders of magnitude (from 10^{-5} to 0.5 S cm^{-1}) in only 10 min (*71*). Shortly thereafter, this was repeated using iodine to give similar results (*48*), although with a greater increase in conductivity to give silvery-black films with a maximum conductivity of 38 S cm^{-1} (*71*). That same year, they demonstrated that further optimization of the iodine treatment resulted in higher conductivities of 160 S cm^{-1} and even higher conductivities of 560 S cm^{-1} could be produced from the treatment of *cis*-polyacetylene with AsF_5 (*72–74*). It was then shown that the treatment of *cis*-polyacetylene with iodine also gave conductivity values above 500 S cm^{-1} (*74*).

The following year, it was demonstrated that polyacetylene could also be chemically doped with electron-donating species such as sodium to give conductivities of 8 S cm^{-1} (*73*). Maximum values of 200 S cm^{-1} for such electron-donor treated films were also reported (*75*). These collective studies demonstrated that the conductivity of chemically doped polyacetylene films was electronic and not consistent with conduction by an ionic mechanism (*73*). In addition, it showed that these films could be chemically doped with electron-acceptors (p-doping) or electron-donors (n-doping) in a manner analogous to simple classical semiconductors such as silicon (*73*, *75*). These collective results had shown that polyacetylene could be transformed from an insulator in its native form, to a semiconductor or even *quasi*-metal, depending on the extent of chemical doping. As such, polyacetylene now presented a new theoretical model for studying conduction mechanisms and metal–insulator transitions in organic materials. Heeger stated, however, that it took “some courage to propose the existence of a metal–insulator transition in an organic polymer” (*52*).

Epilogue

Following their initial work on polyacetylene, Shirakawa, MacDiarmid and Heeger all continued to work on conjugated polymers (*52*). Shirakawa returned to Japan to continue the study of polyacetylene, particularly the development of oriented polyacetylene films. In November of 1979, he moved from the Tokyo Institute of Technology to the Institute of Materials Science, University of Tsukuba, where he was appointed Associate Professor. In October of 1982, he was then promoted to full professor, the same year he was given the Award of the Society of Polymer Science, Japan. He formally retired from University of Tsukuba as professor emeritus at the end of March 2000 (*47*), just months after the announcement that the three of them had been awarded the 2000 Nobel Prize in Chemistry (*5*). Shirakawa reunited with Heeger and MacDiarmid at the 2004 International Conference on the Science and Technology of Synthetic Metals (ICSM) in Wollongong, Australia (Figure 10), the last time all three Nobel Laureates were present at the same event.

Figure 10. Heeger, MacDiarmid, and Shirakawa at the 2004 ICSM Conference in Wollongong, Australia.

MacDiarmid and Heeger also continued to study polyacetylene for the next several years at Penn, until Heeger moved to the University of California, Santa Barbara in 1982 (*64*). Following this, MacDiarmid increased his ongoing collaboration with physicist Arthur Epstein (The Ohio State University) and turned to the study of polyaniline (*52*), which remained his focus of study for the rest of his career. While MacDiarmid mantained his position at Penn, he also held positions at the University of Texas at Dallas, becoming the James Von Ehr Chair of Science and Technology and Professor of Chemistry and Physics there in 2002, and at Jilin University in China, becoming Professor of Chemistry there in 2004. MacDiarmid continued to work until his death at age 79, after falling down the stairs in his home on February 7, 2007, as he was rushing to catch a flight to New Zealand (*76*). Suffering from myelodysplastic syndrome, he was expected to have only a few weeks remaining and wanted to visit his family and friends in his native country.

Following his move to the University of California, Santa Barbara (UCSB), Heeger collaborated there with chemist Fred Wudl to probe the ability to tune the electronic properties of conjugated materials via molecular structure (*52*). In addition to his faculty position as Professor of Physics, Heeger also served as the Director of UCSB's Institute for Polymers and Organic Solids (*64*). In 1990, the discovery of polymer LEDs by Richard Friend, Andrew Holmes, and colleagues at Cambridge provided the field the promise of an important technological application and Heeger turned his attention to poly(phenylene vinylene)s (PPVs) and their applications to LEDs. That same year, he started UNIAX, one of the first companies to focus on the commericalization of conducting polymers (*62*, *63*). In 1992, a postdoctoral researcher (Serdar Saricifici) in Heeger's group discovered photoinduced electron transfer from semiconducting polymers to acceptors such as C_{60}, resulting in the development of organic photodetectors and photovoltaic cells (*62*), an area of research to which Heeger still very actively contributes.

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Comparisons and Conclusions

In hindsight, it is quite clear that the work of Heeger, MacDiarmid, and Shirakawa on doped polyacetylene sparked the significant growth in the study of such materials, thus resulting in the current widespread multidisciplinary field of conjugated and conducting polymers. However, considering that some of the previous results were also quite impressive for the time, it might be asked what factors of the polyacetylene work contributed to such widespread interest, in comparison to the previous work in polypyrrole and polyaniline. Obviously, doped polyacetylene gave more conductive materials, but the previous work on polyaniline actually gave conductivities on par with the intially reported polyacetylene values (30 vs. 38 S cm^{-1}) (*41*, *71*). Yet, it has been stated that the discovery of polyaniline's electronic conductivity did not give rise to great excitement at the time (*6*).

One important factor may have been differences in the dissemination of the published results. The work of Weiss and coworkers on polypyrrole was published only in Australian journals, which Weiss believed he had a strong duty to support. However, Weiss himself believed that this contributed to the fact that the work received little attention (*27*). Likewise, with the exception of a couple reports, the majority of the work of Buvet and Jozefowicz was limited to the French literature. In comparison, the work on polyacetylene was broadly published in a number of international journals and thus more widely read by the scientific community.

Another equally important factor was the physical form of the materials investigated. Both of the previous studies were the investigation of dark powders that had to be pressed into pellets to investigate the resulting conductive properties. In comparison, polyacetylene was the first example of a conductive organic material in the form of a plastic film. In fact, not just a plastic film, but a *silvery, metallic-looking film,* which easily captivated those that looked at it, just as it initially captivated MacDiarmid when first shown the new film by Shirakawa (*47*, *48*, *54*).

In the end, the field of conjugated materials owes much to the work of Heeger, MacDiarmid, and Shirakawa, which initiated the rapid growth of a niche area of scientific interest into the wide community of organic electronics today. As such, it was with great joy that the field received the news in the fall of 2000, that they were being justly recognized by the Nobel committee for their contributions. However, it is also important for all of us to understand how far back this field stretches and all of the important early contributions that helped shape its beginnings. As MacDiarmid concluded in his Nobel lecture: We all owe so much to those who have gone before us - "we stand on the shoulders of giants." (*54*).

Acknowledgments

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Chapter 11

Polymeric Biomaterials: A History of Use in Musculoskeletal Regenerative and Reconstructive Medicine

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This chapter provides an overview of the application of synthetic polymeric biomaterials in musculoskeletal regenerative and reconstructive medicine with selected examples. Hydrogels capable of cell and growth factor delivery were assessed for injectable cartilage tissue engineering. Injectable composite scaffolds incorporating bone morphogenetic protein-2 (BMP-2) were developed to regenerate critical-sized defects in a rat femoral defect model. Advanced scaffold design was achieved by computer aided stereolithography. Nerve tubes with multiple parallel channels were investigated as guidance scaffolds for peripheral nerve and spinal cord regeneration. All of these demonstrated the versatility of synthetic polymers as multifunctional, interactive, and biodegradable bioscaffolds with virtually unlimited possibility for performance optimization through polymer and surface chemistry modification and physical manipulation.

Introduction

Musculoskeletal tissue repair, which is almost involved in every aspect of surgical specialty such as wound healing, tissure disease, and congenital deficiencies treatment, has been a major concern for practicing physicans and surgeons throughout the history (*1*). While there have been enormous

In 100+ Years of Plastics. Leo Baekeland and Beyond; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

accompolishments, severe limitations exist in many situations, due to either the tissue's poor ability to self-repair (such as cartilages and intervertebral disc), or the complications associated with recovery (such as spinal cord and bone), or the scarce availability of donors (such as liver) (*1*, *2*). With the development and integration of materials science and molecular and cellular biology, the emerging tissue engineering and regenerative medicine seem to provide the only promising solution to those compelling problems so far. In general, tissue engineering aims to assist the body in regenerating functional tissues by providing a temporary 3D structural support and interactive environment with proper bio-signals released in a temporally and spatially-controlled fashion to guide and control the adhesion, proliferation, and differentiation of the (seeded) cells into part of, or a whole tissue (Figure 1). This is achieved either by direct *in vivo* implantation, or *in vitro* culture followed by implantation. To make body movement possible and at will, the fully functional musculoskeletal system must includes bone, muscle, and associated elements such as cartilage, connective tissue, vascular elements, and nervous components. Therefore, in orthopedics, the full restoration of function would require a systemic recovery with all of these components. Current targets of challenge include bone, cartilage, and nerve (*3*).

The underlying principle of tissue engineering can be understood through the cell-biomaterial-host interactions. Three key componenets of tissue engineering can be identified as cells, biomaterial scaffolds, and bio-active factors such as growth factors, among which the choice of biomaterials is often critical for successful tissue regeneration. Basically, a scaffold should be biocompatible, allowing and directing cell adhesion, proliferation, and differentiation, containing internal interconnecting channels for nutrient diffusion and tissue growth, exhibiting biodegradation kinetics matching the new tissue formation, and possessing biomechanical properties sufficient for temporary structural support (*4*). Both natural and synthetic materials have been used successfully as scaffolds. Notably, synthetic polymers have played a pivotal role in the development of this field (*5*). Nowadays, synthetic polymers perhaps represent the largest and most diverse class of biomaterials. It is thus the focus of this chapter to provide an overview of the application of synthetic polymers in musculoskeletal regenerative and reconstructive medicine with selected examples. The relevant issues in biology and surgery will also be discussed.

General Aspects

The invention of "Bakelite", or polyoxybenzylmethylenglycolanhydride, by Leo Baekeland (*6*) in the early 1900s' probably marked the beginning of the "Plastic Age" of our time. By definition, polymers are long chain molecules that consist of a large number of subunits (monomers) covalently bonded together with a variety of architectures such as linear, branched, cyclic, and cross-linked

(Figure 2). Synthetic polymers are usually prepared by polymerization of monomers via either a chain growth or condensation mechanism. The major parameters affecting the polymer properties include the types of monomers to be incorporated, the chemistry and sequence by which the monomers are joined together, total molecular weight and polydispersity, and molecular architecture. In addition, their properties could be further tuned by physical processing into different forms, such as porous foams (*7*), swellable hydrogels (*8*), and blends (*9*). One unique feature about polymers is that the monomers along the chain could interact strongly and behave collectively to exhibit a wide range of properties, including "smart" responsive behavior, not found in monomers (*10*). For example, the slight hydrophobicity of the monomer, *N*-isopropyl acrylamide, imparts the thermo-sensitivity of the corresponding poly(*N*-isopropyl acrylamide) in water (*11*). In addition, the mechanic properties of polymers depend critically on molecular weight (or the number of monomers). This is also how Nature uses polymers. From a simple set of 20 canonical amino acids, proteins of disparate structures and properties can be created to serve various, specific, but distinct functions. In comparison, synthetic polymer chemistry and polymer engineering are still in their infancy, in view of our limited control so far over the chemistry and other major parameters affecting the physical properties of polymers. Nevertheless, the possibility for optimizing synthetic polymers' properties through chemical modification and physical manipulation is virtually unlimited. Therefore, many opportunities still exist for improvement in the performance characteristics of synthetic polymeric materials.

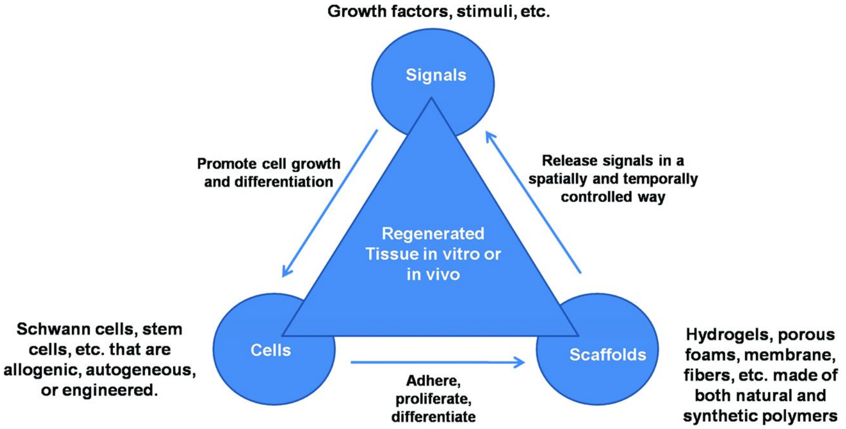


Figure 1. Strategy for tissue engineering.

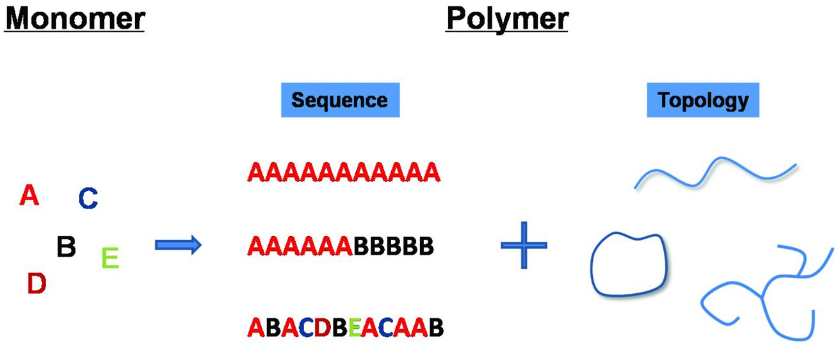


Figure 2. The polymer concept: long chain molecules of different topology consisting of various monomers covalently linked together in specific sequence.

Although the synthesis and characterization of polymers have already made significant progress since the early 1900s, it wasn't until two decades later that people gradually accepted Staudinger's macromolecular hypothesis. The rational design and synthesis of polymers, first by Carothers in the 1920s, unambiguously proved the long chain nature of polymers and later led to a burgeoning polymer industry with diverse materials available such as nylon, polyethylene, Dacron (polyethyleneterepthalate), Teflon (polytetrafluoroethylene), and silicones (e.g. polydimethylsiloxanes), which have been found to be increasingly useful in health care over the years. Their first applications were in dental and medical devices invented by pioneering surgeons, engineers, and chemists between the 1930s and 1960s with little government regulation. Despite many dramatic failures, these attempts set the foundation for the current multidiscinplinary endeavors in biomaterials research. The limits of the available polymeric materials of those times in terms of poor biocompatibility, degradation profiles, and mechanical properties led to the *de novo* design of novel synthetic polymeric biomaterials in the 1970s. Biodegradable polymers, such as poly(lactic-co-glycolic acid) (PLGA), were successfully developed for orthopedic applications at that time. The idea of combining cells with these synthetic materials to create new tissues and organs was only a more recent event. It was shown by Langer et al. in the 1980s that a 3D porous scaffold made of synthetic polymers could allow vascularziation after implantation and create functional liver tissue. Since then, many different tissues have been successfully regenerated using various polymer scaffolds, leading to the rigorous field of regenerative medicine. The continuous development of molecular and cell biology, in combination with the more specific design and engineering of novel synthetic polymers, holds great promise for the successful clinical application of regenerative medicine strategies in the future.

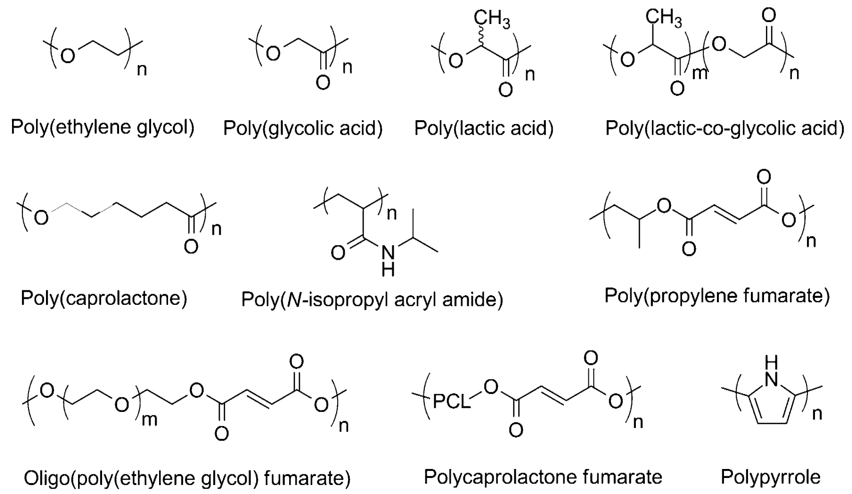


Chart 1. Chemical structures of typical synthetic polymers in regenerative medicine

Chart 1 shows the chemical structures of typical synthetic polymers currently used in regenerative medicine. One important criterion for polymeric biomaterials is their biocompatibility. Following the implantation of a polymeric biomaterial, a series of events occur at the polymer-tissue interface, that include hematoma formation and inflammation. If the material has low biocompatibility, it will be rejected by the body or lead to the formation of a scar-like fibrous capsule around it. If the material can elicit an appropriate, desired response in a specific application, such as neovascularization and osteoblastic secretion of osteoid matrix in the case of bone tissue engineering, it can be viewed as biocompatible for bone regeneration. Another important criterion is biodegradability, which refers to the breakdown of polymer chains into monomers or oligomers that can be cleared from the body. Two advantages are apparent in this approach: (1) it eliminates the need to take out the implant after the tissue is regenerated and thus also eliminates the morbidity and pain associated with the surgical procedure; (2) it allows concomitant kinetically controlled drug release. It is very desirable if the degraded products are common metabolic species and if the degradation can proceed in a controlled fashion spatially (in bulk or from the implant surface) and temporally.

In practice, there are strict regulatory issues associated with the evaluation of biomaterials in terms of biocompatibility, biodegradability, and performance. Preclinical testing includes both *in vitro* and *in vivo* experiments, where *in vitro* testing (such as scaffold degradation, cell-scaffold interactions, and scaffold toxicity) serves as a useful tool in determining if the material needs to be further evaluated *in vivo*. The next step is that animals are used to model the *in vivo* environment in humans, and serve as a bridge between *in vitro* studies and human clinical trials. The choice of animal model often depends on several factors including (1) biological and structural goal of the study, i.e. the anatomical and biochemical similarity between the animal model and human; (2) the cost and technical feasibility of chosen model, i.e. the number of animals needed should be as small as is practical to achieve the scientific goals of the study; (3) historical experience with the model. It should be mentioned that although animal models are an essential and indispensable component of the preclinical evaluation for new medical products, they are still not sufficient to draw a conclusion on the product's performance in humans. Clinical studies are always necessary to do that, beginning with a first human use safety study. A reasonable interpretation of the testing results will need to take into account the complexity of living biologic systems and the large difference and variability between individuals. To this end, statistics are routinely employed to assist the design of experiments and the extraction of meaningful information from the results. Overall, the development of a viable scaffold material is typically a complex, multidisciplinary, iterative process that begins with polymer design, synthesis, and characterization, moves to scaffold fabrication and *in vitro* mechanical property and degradation profile testing, then to toxicity and biocompatibility evaluation via cell culture *in vitro*, and finally to *in vivo* testing in appropriate animal models and human clinical trials.

Regenerating connective tissue with progression to full restoration of function is a complex, composite material process involving bones, muscles, cartilage, tendons, ligaments, vessels, and nerves. The role of synthetic polymers in this process is to function as the scaffold for cell attachment and the vehicle for controlled release of bioactive molecules at the site of tissue regeneration. Based on an understanding of their biology for specific applications, the development of polymeric biomaterials is focused primarily on the following subjects: (1) polymer synthesis and physical structure-property relationships; (2) scaffold formulation and administration; (3) scaffold microstructure and chemistry; and (4) scaffold as delivery vehicle for bioactive molecules. The synergistic effect between different factors should also be recognized (*12*). Selected examples in bone, cartilage, and nerve regeneration will be briefly discussed in the following sections.

Injectable Polymers for Cartilage Tissue Engineering

The articular cartilage, being an avascular tissue, has been known for its poor ability to heal after injury. The long term consequence of cartilage injuy is usually degenerative arthritis. This cartilage disorder, arthritis, is a painful condition without satisfactory regenerative treatment options so far. The most effective treatment continues to be replacement of the affected joint with a prosthesis that has articulating metal and polymeric (polyethylene) bearing surfaces. Under certain circumstances such as autologous transplantation of periosteum to the site of injury, articular cartilage shows enhanced regeneration capability (*13*). Thus, tissue engineering involving biodegrable polymer scaffolds with appropriately seeded cells and nutrients seems to be a promising approach (*14*). The scaffold can be either preformed *in vitro* or crosslinked *in vivo*. While preformed scaffolds are advantageous in covering large irreparable lesions, it is very desirable to develop injectable formulations of the scaffold to deliver *in situ* photo-crosslinkable hydrogels via minimally invasive procedures for the treatment of small-sized defects with arbitrary shapes (Figure 3) (*15*).

Hydrogels for biomedical use are crosslinked hydrophilic polymer networks swollen by biological fluids (*3*). The crosslinking can be achieved either by chemical means (such as photo-, thermo-, or redox-initiated covalent bonding), or physical methods (such as entanglements, crystallization, or ionic bond formation). Photo-initiated crosslinking allows spatial and temporal control over gel formation. The presence of a comonomer and a porogen can accelerate the photo-crosslinking and create a porous structure, respectively. The ability to control both the polymer's chemical composition and crosslinking density permits variation of the hydrogel's physical form from that of a viscous fluid to a rigid solid, with the common feature being that it is wet and soft. Interestingly, if the polymer network can undergo a phase transition upon the trigger of an external stimulus (e. g. temperature or pH), the hydrogel could be considered "smart" because it is responsive. When combined with biodegradability, this is a feature very desirable for applications like drug delivery (*16*). Last but not least, the structural similarity between hydrogels and living tissue decreases protein adhesion on the implant surface and lessens the likelihood of a possible foreign body reaction. Due to their versatility, hydrogels have found many applications in regenerative medicine, including drug and growth factor delivery (*16*), cartilage tissue engineering (*17*), bone tissue engineering (*18*, *19*), and nerve regeneration (*20*, *21*), either as a scaffold or as a second phase within the pores of another biomaterial scaffold.

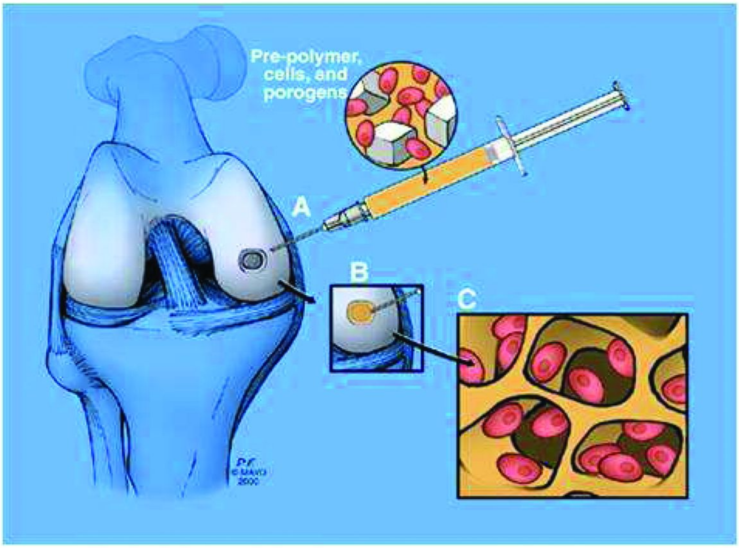


Figure 3. Hydrogel for injectable articular cartilage tissue engineering.

Typical synthetic-polymer-based hydrogel systems in musculoskeletal regenerative medicine include oligo (poly(ethylene glycol)fumarate) (OPF) (*17*), poly(ethylene glycol diacrylate), poly(vinyl alcohol), poly(acrylic acid), and poly(hydroxyl ethyl methacrylate) (*3*). The importance of control over the physical and chemical properties of the hydrogel is that these properties influence the behavior of embedded cells. The effect of composition, surface chemistry, crosslinking density, and three-dimensional architecture of OPF hydrogel in cartilage tissue engineering applications has been studied in detail (*17*). The backbone of OPF is composed of biocompatible poly(ethylene glycol) (PEG) and fumaric acid. PEG is widely used in biomedical applications due to its biocompatibility, hydrophilicity, and resistance to protein and cell adhesion. It increases the water solubility of the polymer formed from it and its co-monomers. The OPF crosslinking occurs via the UV initiated polymerization of the double bonds on the OPF macromer's fumarate moieties and the crosslinking comonomer, *N*-vinylpyrrolidinone (NVP). The crosslinking density was controlled by varying the OPF macromer concentration and NVP/OPF ratio, resulting in control of the swelling ratio and mechanical properties (such as the compressive modulus). Figure 3 shows the direct injection of the precursor solution (OPF macromer, NVP, and Irgacure 2959 photoinitiator in deionized water) into a mold, and subsequent photocrosslinking of the macromer by the NVP under UV irradiation. The crosslinked hydrogel takes the shape of the mold and can be swollen to different equilibrium swelling ratios depending on the crosslinking density. Higher crosslinking densities resulted in lower swelling ratios, but led to higher moduli. The crosslinking density also affected the cell behavior, as the chondrocytes adopted a flattened, spread morphology in highly crosslinked hydrogels but remained rounded in those with lower crosslinking densities. The cells were also photo-encapsulated within the hydrogel, and maintained high viability throughout a 3-week culture period, after which they expressed the mRNA of type II collagen and produced cartilaginous matrix. These findings suggest that OPF hydrogels are promising for potential clinical cartilage tissue engineering applications, because the prepolymers with viable cells can be injected as a fluid into the cartilage defect site and subsequently polymerized in situ using UV irradiation in a spatially and temporally controlled fashion. The porogen dissolution, cellular secretion of cartilage matrix into the newly formed pore structure, and subsequent gradual scaffold degradation is the process by which the porous hydrogel promotes both chondrocyte cell growth and expression of phenotypic function, and guides tissue regeneration.

Advanced Scaffolds for Bone Regeneration

Bone is a dynamic organ capable of self-repair after injury. However, bones with defects of a critical size, which depends on the particular bone in question, will not heal to their original condition, and fibrous nonunion results. The skeletal deficiencies that occur as a result of trauma, diseases, and congenital abnormalities call for additional strategies to complement the current autograft and allograft treatment options (*4*). There have been significant advances in using porous scaffolds to support the migration, proliferation, and differentiation of osteoprogenitor cells for guided 3D bone formation. This section discusses various aspects of the development of synthetic polymer scaffolds for bone tissue engineering.

Typical synthetic polymers that have been used as bone engineering scaffolds include poly(α-hydroxy acids), polydioxanone, polyanhydrides, poly(caprolactones) (PCL), and poly(propylene fumarates) (PPF) (*22*). They have appropriate chemical and physical properties for fabrication into 3D structures that have sufficient mechanical strength to provide temporary structural support to the skeletal reconstruction region, and sufficient biological properties to support osteoblast attachment, proliferation, and osteoid deposition. After that, they degrade and are excreted from the body. Poly(α-hydroxy acids), such as poly(lactic acid) (PLA), poly(lactic-co-glycolic acid) (PLGA), and poly(glycolic acid) were among the first group of biodegradable polymers to be fabricated into 3D foams for bone engineering (*23*). However, they are relatively difficult to further modify. PPF possesses several advantages in this regard. The fumaric acid double bond allows secondary crosslinking during composite polymer processing into 3D structures. An example is its use as an injectable, moldable material, which is a favorable feature for those surgical applications amenable to a minimally invasive solution. Synthetic modification of PPF can also be performed, such as in its main chain copolymerization with PCL and/or PEG (*24*). The molecular weight dependence of various physical properties of PPF have been systematically studied (*25*). Changes can be made to the polymer recipe for different purposes, and include varying the crosslinker, the photoinitiator, and the co-monomer. Porogens such as inorganic salts or paraffins are used to create a porous scaffold, and fillers such as hydroxyapatite fibers or nanoparticles are used to enhance the mechanical properties. These are all factors that permit the generation of a wide range of scaffold properties for different specific clinical needs.

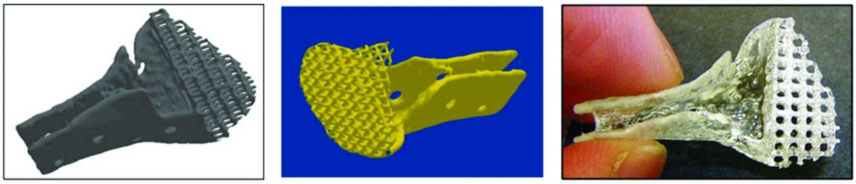
The performance of scaffolds is directly related to the fabrication process that determines scaffold properties. These properties include its mechanical performance, its overall size and shape, and its porosity. The pores themselves possess several properties that are pertinent to scaffold function. These include pore size, shape, interconnectivity, surface area, surface roughness, and surface chemistry. The scaffold usually requires a high degree of interconnected macroporosity to facilitate cell migration and nutrient diffusion. When used in an injectable form, the scaffold can crosslink in situ and take arbitrary shapes. When precise control over micro- and macrostructure is necessary, solid free form fabrication methods can be used. For example, to construct a complex temporomandibular joint (TMJ) scaffold, computed tomography (CT) scans were first used to generate a 3D image of that portion of the opposite TMJ that matches the anatomical defect site which requires reconstruction. This image was converted into an STL computer file to enable computer-aided design (Figure 4). The design file was transferred as input to the stereolithography instrument, which fabricated a biomimetic 3D scaffold in a controlled fashion. The effects of resin formulations and laser parameters on this process have been studied in detail (*26*). Other fabrication processes, such as the solvent casting/particulate leaching method (*23*, *27*), and the phase inversion/particulate leaching method (*28*), offer less control, but are also less costly and more commonly used.

Bone metabolism is a synergistic process controlled by endocrine, immune, and neurovascular systems, as well as by internal and external stimulation factors. The use of osteoinductive growth factors, such as the bone morphogenetic proteins (BMP), is often beneficial for bone regeneration in specific clinical circumstances (e.g. smokers, diabetics, osteoporosis). Due to the short biological half-lives and rapid local clearance of these proteins, the local application of high doses of BMP is sometimes necessary. The use of polymeric scaffolds to serve as a delivery vehicles for the protein, in addition to their roles in structural support and cell attachment, is a promising strategy currently under intense research. The release profile of BMP-2 and its effects on bone formation were studied in three scaffolds: (1) a BMP-2 loaded gelatin hydrogel scaffold, (2) BMP-2 loaded PLGA microparticles (MPs) embedded in a PPF scaffold, and (3) MPs embedded in a PPF scaffold surrounded by a gelatin hydrogel (*29*). The microparticles are synthetic polymers that have been fabricated into three dimensional spheres, and loaded with the molecule to be delivered. The polymer PLGA has been used here because it is an already FDA approved material that has a degradation profile (and BMP release profile) which can be controlled by varying the lactic acid to glycolic acid ratio in the copolymerization recipe. When combined with a non-invasive monitoring method, it provided detailed and reproducible BMP-2 release profiles both *in vitro* and *in vivo* (Figure 5) (*30*). The gelatin hydrogel (which simulates current clinical use) showed a burst release profile while the rest showed sustained release consistent with scaffold degradation. The bone formation was analyzed by μCT at 6 and 12 weeks after implantation, and the reconstructed μCT images are shown in Figure 5. There was significantly more bone in the MPs/PPF implants than those in gelatin and MPs/PPF/gelatin implant. In addition, the MPs/PPF scaffolds were the only ones to show significant increase in bone formation over time. Therefore, the non-porous structure of the gelatin hydrogel seemed to be a less favorable substrate for bone formation, and the sustained release of BMP-2 from the composite (microparticle containing) scaffolds appears to have enhanced bone formation.

Designer Conduits for Nerve Repair

Similar to bone, peripheral nerve tissue has a capability to regenerate. However, this is not the case for spinal cord tissue, where the natural healing response after spinal cord injury usually results in a glial scar and a generally non-permissive regeneration environment that prevents axonal regeneration.for restoration of spinal cord function. Patients with spinal cord injury often suffer from paralysis and respiratory complications. The past two decades have witnessed the evolution of peripheral nerve guidance tubes in tissue engineering from a concept, to a research tool, and further to a clinical device as an alternative for autologous nerve injury repair. Currently, commercially available nerve tubes are mostly single lumen conduits to assist the repair of relatively small defects (≤ 2cm) in the peripheral nervous system. There is simply no similar treatment available for spinal cord injury so far. Recent research efforts are mainly focused on improving the peripheral nerve guidance tubes to bridge large nerve gaps and possibly to repair spinal cord injuries. However, preliminary results from experiments using polymer scaffold tubes for guided axon regeneration following spinal cord injury in animal models has produced hope that the clinical strategies used in treating peripheral nerve injuries might be translatable to the central nervous system (*31*). However, this is a complex process, far from mature, and still requires close, synergistic collaboration between experts in chemistry, physics, biology, neuroscience, and clinical medicine. This section briefly summarizes the state-of-the-art of nerve regeneration.

The selection of polymeric biomaterials is the first step in the design process. Unlike bones, that serve the structural support of the body, nerve is a soft tissue. Thus the mechanical characteristics of nerve conduits should have a modulus and flexibility to match the natural tissue that they replace, and which will hopefully grow through them as it regenerates. The swelling, permeability, and degradation profile are all important parameters for a nerve tube. Synthetic biodegradable polymers that have been used as conduit materials include PLA, PLGA, PGA, PCL, polycaprolactone fumarate (PCLF), and PEG hydrogels (*31*). For example, Wang et al. have investigated the physical characteristics (such as glass transition temperature, surface morphology, and rheologic properties) of photo-cross-linked hybrid polymer networks of PPF and PCLF, and related those physical properties to the *in vitro* responses of SPL201 cells (a conditionally immortalized Schwann cell precursor line for myelinating axons) grown on scaffolds made from those polymer blends (*32*, *33*). Various stimuli can promote the growth of neural tissue, such as electrical, chemical, biochemical, and topological cues. The incorporation of such signals in the scaffold can be useful for the purpose of eliciting the desired cellular responses. For example, an OPF hydrogel was modified with a positively charged monomer, [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (Figure 6a). The resulting hydrogels were found to support the attachment of dorsal root ganglion (DRG) explants and to stimulate neurite outgrowth from the DRGs (Figure 6b,c). The DRG cells will mainly aggregate on the unmodified hydrogels (*20*). Conductive polymers, such as polypyrrole, have been used to fabricate semi-interpenetrating polymer networks (IPNs) with OPF and PCLF (*21*, *34*). The electrical conductivity of the IPN increases with polypyrrole fraction in the IPN up to a maximum value of 6 mS/cm. The choice of different anions used in this system allows further fine tuning of the properties. *In vitro* studies of neural cells cultured on these IPNs showed a higher attachment and proliferation rate of PC12 cells (a neuronal cell line) as well as longer and more numerous neurite extensions from DRGs. Poly(3,4-ethylenedioxythiophene) has also been used for various neural engineering applications because of its physical, electrical, and biocompatibility characteristics (*35*).



(a) 3-D reconstruction from CT scans (b) Converted to STL file (c) Fabricated TMJ scaffold

Figure 4. Advanced scaffold design by CAD stereolithography.

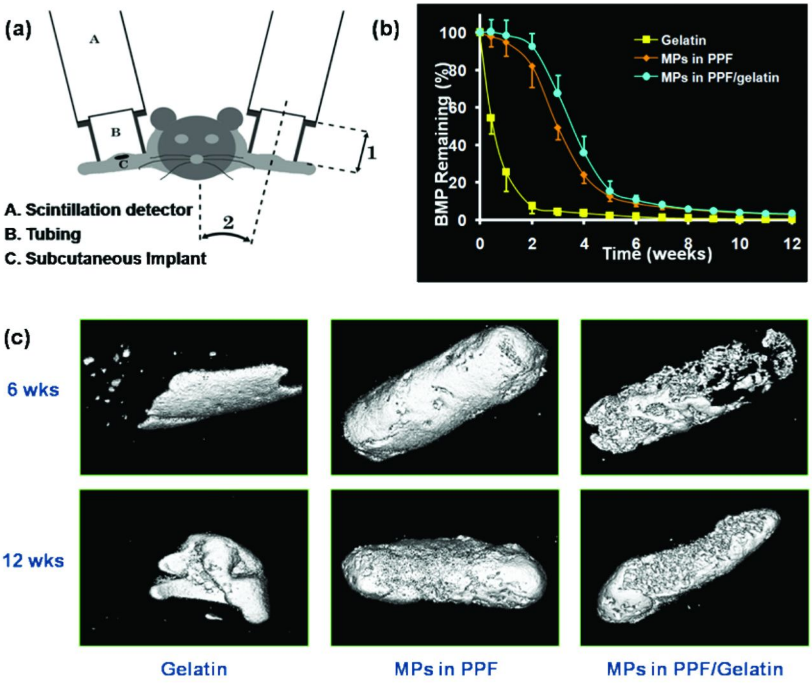


Figure 5. (a) Non-invasive detection method for remaining BMP-2 during controlled release process, and (b) the measured in vivo retention profile of BMP-2 in three different scaffolds. Adapted with permission from reference (29, 30). Copyright 2008 Elsevier.

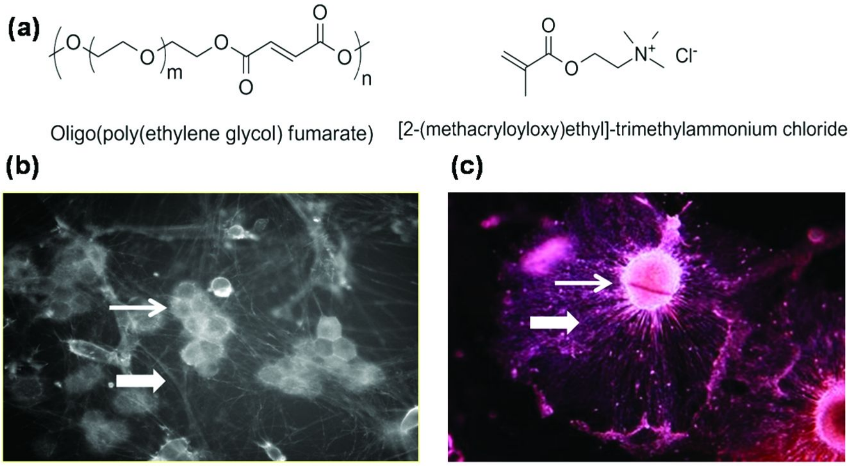


Figure 6. Charged hydrogels have been synthesized from the monomers shown in (a). The DRGs cultured on these charged monomers (b, c) show robust neurite outgrowth that does not occur on non-charged surfaces fabricated from the same monomers. The thicker arrows point to the neurites in b and c. The thinner arrows (b) and (c) point to the DRGs. Adapted with permission from reference (20). Copyright 2009 Elsevier.

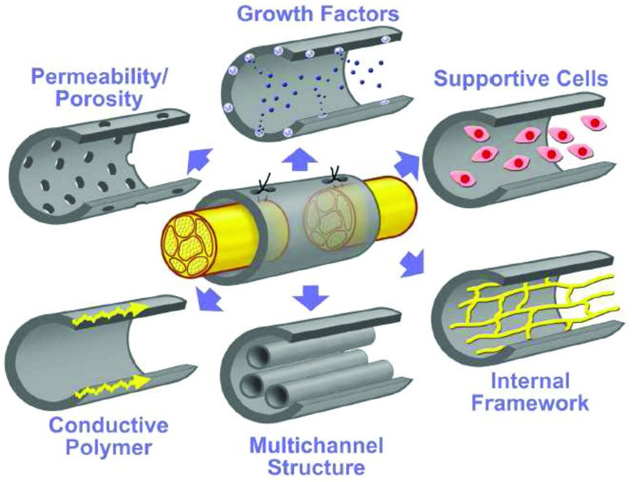


Figure 7. Advanced nerve conduit design. Adapted and reprinted from references (36, 37). Copyright 1999, 2009.

Several scaffold fabrication parameters have been investigated to assess their effect on scaffold performance. These include the conduit architecture, the tube diameter, the number of lumina, the lumen wall thickness, and the tube stiffness. Figure 7 shows some of the modifications of the single lumen nerve tube that have been assessed to date (*36*, *37*). Orientation is very important in guiding the growth of axons. Multi-channeled scaffolds have been developed to guide axons to regenerate in a pattern that maintains their proper orientation so that they reinnervate the appropriate target muscles (*38*). Figure 8a shows such a highly porous, multichannled conduit structure. Methods have been developed for in vitro characterization of these multichannel conduits in terms of their bending, deformation, swelling, and degradation behavior, as well as the scaffold interconnectivity (*39*) and permeability (*40*). The effects of tube diameter and number of channels on these properties and cell responses have shown (*41*) that smaller diameter channels promote greater regeneration than larger diameter channels due to less fibrous rim formation within the channel. The performance of single channel and 4-channel conduits was superior to that of conduits with other numbers of channels with respect to the magnitude of axonal regeneration within them (*42*). Other scaffold design parameters currently under investigation include channel surface texture and scaffold hydrophilicity. These two parameters affect the extent of cell attachment in the channels.

Support cells and growth factors are often loaded into scaffolds to enhance the regeneration process. Schwann cells, harvested from the peripheral nervous system and cultured before use, are effective as support cells. Schwann cells constitute the myelin sheath that envelopes peripheral nerves, and which serves as the "insulation" that enhances their ability to conduct electrical impulses. The Schwann cells, when implanted in a nerve tube channel, form into a cable that traverses the channel. The regenerating axons attach to this cable and migrate along it. The Schwann cells also produce molecules that enhance the axonal regeneration. The disadvantage in this approach is the necessity for harvest and culture of the cells before *in vivo* use. Neural stem cells and olfactory ensheathing cells have also been loaded into PLGA scaffolds and found to effectively facilitate the cross-channel regeneration of axons (*43*). Neurotrophins are protein growth factors that promote nerve growth by blocking natural cell death. These and other chemical factors (e.g. enzymes that inhibit scar formation) have been incorporated into scaffold channels. Scaffolds that have been appropriately designed with respect to their chemical composition, architecture, signalling molecules, and seeded cells can support axonal regeneration along the entire length of the channel of channels in the scaffold. Figure 8c shows the microscopic images of longitudinal sections along a single channel in a multi-channel scaffold made of PLGA, loaded with neural stem cells, and implanted into a spinal cord resection gap one month prior to harvest and specimen processing. Axonal tracing techniques were used to determine the origins of these axons (*44*). The labeling of neuronal cells with fast blue clearly indicated that the axons grew all the way through the channels and exited into the distal spinal cord for distances up to 14 mm (Figure 8b) (*45*). Although functional restoration in the animals has not been demonstrated, these results are very encouraging.

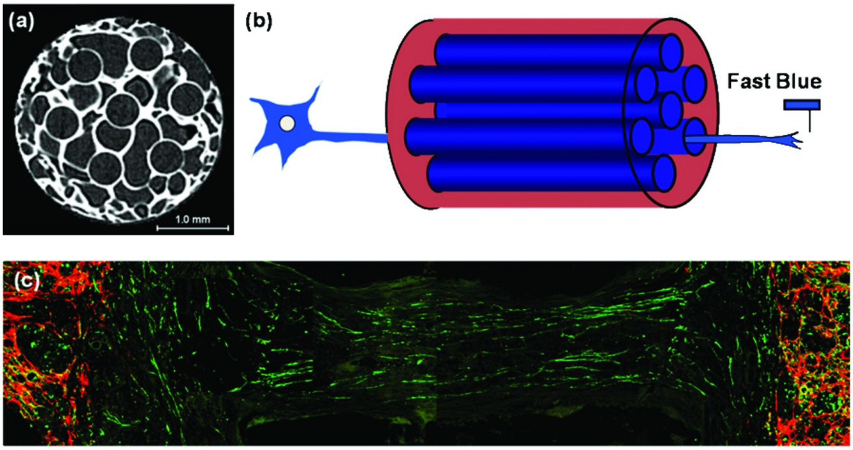


Figure 8. (a) Cross-sectional view of a multichannel porous conduit for spinal cord regeneration; (b) technique of fast blue dye neuronal labeling as a method to trace the origin of axons regenerated through the tube; (c) a longitudinal view of regenerating spinal motor axons (green) that entered a single tube channel from the proximal spinal cord (orange on left), exited the scaffold, and re-entered the distal spinal cord (orange on right). Adapted with permission from reference (38). Copyright 2006 Elsevier.

Concluding Remarks

In summary, we have provided an overview of the applications of synthetic polymeric biomaterials in musculoskeletal regenerative and reconstructive medicine, and discussed selected examples to illustrate the basic principles in their application. These examples include the use of hydrogels capable of cell and growth factor delivery as injectable scaffolds for cartilage tissue engineering. Additionally, composite scaffolds that have precise external geometry and internal pore microarchitecture, and that incorporate bone morphogenetic protein-2 have been developed to regenerate bone defects. Finally, conduits with multiple parallel channels have been investigated as guidance scaffolds for peripheral nerve and spinal cord regeneration. While the versatility of synthetic polymers to fabricate multifunctional, interactive, and biodegradable scaffolds is apparent from the examples presented here, the currently available choices of polymeric biomaterials for these applications is not extensive, and there is plenty of room for novel synthetic schemes and further optimization of existing polymers. The design of polymeric biomaterials for biomedical applications needs to begin with an understanding of the specific clinical need under consideration and its associated biological, mechanical, and functional requirements. For example, the monomer can be selected from metabolic intermediates to enhance biocompatibility during subsequent polymer degradation *in vivo*, and the incorporated bioactive signaling molecules can be selected according the desired cellular activity. Looking back at the 100+ years of synthetic polymers since the invention of the first synthetic polymer, Bakelite, we hold the belief in the virtually unlimited possibilities for optimization of polymer properties through chemical modification and physical processing. We are optimistic that the future of polymeric biomaterials for use in clinical applications promises to improve the health of our population.

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