Reactive Processing of Polymers: A) Reactive Processing of Engineering Thermoplastics; B) Reaction Injection Molding of Polyurethanes

H. G. Schmelzer[a]; R. J. Kumpf[a]

[a] Bayer Corporation, Pittsburgh, Pennsylvania

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REACTIVE PROCESSING OF POLYMERS: A) REACTIVE PROCESSING OF ENGINEERING THERMOPLASTICS; B) REACTION INJECTION MOLDING OF POLYURETHANES

H. G. Schmelzer and R. J. Kumpf
Bayer Corporation
100 Bayer Road
Pittsburgh, Pennsylvania 15205

ABSTRACT

As a class of materials, engineering thermoplastics have enjoyed phenomenal growth in sales. The capital investment required to develop and introduce a new engineering thermoplastic has, however, increased dramatically. In response to these competitive pressures, engineering resin producers have increasingly focused their R&D efforts towards improving the performance of existing resins. One approach is to move chemistry from reaction vessels into processing equipment. This strategy is often referred to as reactive processing. Successful development of new engineering polymer grades by reactive processing calls for a multidisciplinary approach, with expertise required in chemistry, polymer science, polymer engineering, computer modeling and statistical process control. The first part of this paper will give a survey of the research work at Bayer Corporation on the synthesis of block copolymers, compatibilized blends and impact modifiers.

Polyurethanes are inherently reactive processing polymers. They are usually processed as liquids, for example, for the manufacture of polyurethane foams and elastomers. The two-component polyurethane coatings fit also into this scheme. Polymerization takes place in the foam machine, in the molds, and on the painted substrate. The Reaction Injection Molding (RIM) technology

exemplifies in a unique way the reactive processing of polyure-
thanes. RIM combines the processing of liquids and the forming of
thermoset parts in a process which can match the cycle times of the
injection molding of thermoplastics. The second part of this paper
will give a survey of the RIM process, the chemistry of RIM
polyurethane/polyurea materials, and examples of their applications.

INTRODUCTION

Reactive Processing

The practical manufacture and application of synthetic polymers is usually
considered to consist of distinct steps: synthesis of the high polymer; processing of
the raw polymer into a useful semi-finished good (part, film, fiber); and final con-
struction of an item of commerce. The concept of "reactive processing" brings the
final two steps together.

The rationale for reactive processing is straightforward. Processing
equipment has long been used to expand product portfolios through addition of
additives, dyes, and pigments. This allows the chemical manufacturing plant to
concentrate on base polymers, thereby minimizing the average cost of goods.
Reactive processing simply takes the model a step further. The processing equip-
ment is seen not only as a mixing device but also as a true reaction vessel where
chemistry can be performed and controlled.

Reactive processing encompasses a rich collection of chemistries. The
objectives of reactive processing are equally diverse, ranging from viscosity
modification to the formation of micro-phase separated block copolymers. A
number of excellent review articles have been published that collect and categorize
the myriad chemical reactions that have been exploited in reactive processing.
Particularly noteworthy are articles by Lui and Baker [1], Brown [2], Tzoganakis
[3], and Dagli [4]. Xanthos has edited a highly recommended and comprehensive
book on reactive processing [5].

In general, six chemical strategies have been employed in reactive proces-
sing: bulk polymerization, graft reactions, inter-chain copolymer formation, coup-
ling reactions, and polymer functionalization. In the following section, we will
highlight literature examples that embody these strategies. We will then report spe-
cific examples of reactive processing from our laboratories.

Reactive Processing Chemistries
Bulk Polymerization

A classic example of bulk polymerization via reactive processing are poly-

urethanes. Polyurethane elastomers are segmented block copolymers prepared from low molecular weight polyesters or polyether polyols, monomeric diols or multi-functional alcohols, and isocyanates. This process will be described in some detail in a later section.

Graft Reactions

In graft reactions, a polymer is treated with a monomer, usually in the presence of an initiator. Often considerable technical challenges exist. Some are due to the large differences in viscosity between the polymer and the monomer that make efficient mixing and grafting difficult to achieve. Another problem is the control of side-reactions such as homopolymerization of the grafting component or crosslinking. The grafting site on the polymer can be a functional group or it can be formed *in situ* by, for example, hydrogen abstraction. The length of the grafts depends on the reactivity of the system and on the processing conditions.

One important example of this type of chemistry is the grafting of maleic anhydride (MAH) to polypropylene (PP) [6, 7, 8]. A radical initiator, such as dicumyl or benzoyl peroxide, is utilized in the formation of the grafting side by hydrogen abstraction. The so-formed reactive species then reacts with the MAH to form pendant succinic or maleic anhydride groups. The MAH is either dry-blended onto the PP and fed to the throat of the extruder or metered together with the initiator into the molten PP downstream. The melt temperatures in the reaction zones vary between about 230 and 280°C and the resulting MAH grafted PP typically contains 0.5-2% of bound MAH. Side-reactions such as crosslinking, degradation, and MAH homopolymerization, can under proper conditions, be controlled [9].

The MAH graft gives PP a reactive site that can be used for further modification of the polymer. The anhydride pendant can, for example, be reacted with nucleophiles, and using this concept, PP-grafted-nylon (PP-g-PA) copolymers have been synthesized by reacting the PP-g-MAH with PA. The nucleophilic PA amine and endgroups react with the anhydride and form imides. The PP-g-PA copolymer finds use as a compatibilizer for PP/PA blends and can, in this case, be formed *in situ* during the processing of the blend [10, 11].

Inter-Chain Copolymer Formation

A number of condensation polymers are "living" in that at higher temper-atures they undergo inter-chain cross reactions. For example, polyesters and poly-carbonates easily transesterify, polyamides can undergo catalyzed transamidation and polyurethanes are subject to transurethanization reactions. These interchain reactions have been exploited to form copolymers via reactive processing.

For example, polycarbonates are tough, transparent engineering polymers prepared from the reaction of bisphenols and phosgene or bisphenols and diphenylcarbonate. Because of their high temperature stability, polycarbonates are particularly amenable to reactive processing. Polycarbonates are known to readily react with polyesters via acidolysis, alcoholysis, and main chain transesterification. Researchers at Bayer Corporation have reported reactive processing routes to polycarbonate/polyetherketone and polycarbonate/polyethersulfone block copolymers in extruders and kneaders [12, 13, 14]. Polyetherketones and polyethersulfones were prepared that contain ester groups at specific intervals along the polymer backbone. These polymers were then extruded or kneaded with polycarbonates. This approach to polycarbonate modification will be discussed in more detail later.

Coupling Reactions

Condensation polymers are inherently end-functionalized. These endgroups can be used in reactive processing. For example, the amino and/or carboxylic acid functionality of nylons offer a "handle" for reactive processing. Triacca *et al.* have reported the reactive compatibilization of PA6/poly(styrene-co-acrylonitrile) (SAN) blends [15]. The most efficient compatibilizers, as measured by particle size reduction, were imidized acrylic polymers. These polymers are miscible with the SAN phase and can react with polyamide. Another interesting example is poly(styrene-co-acrylonitrile) containing 1% oxazoline. These functionalized polymers were added to SAN/PA6 blends in a single-screw extruder. The amino and carboxylic acid endgroups of the PA6 open the oxazoline ring and couple the two polymers. Addition of the oxazoline-containing SAN dramatically improved the physical properties of the blends. Whereas the simple blends failed at 2.8% elongation, the elongation-to-break improved to 170% in the reactive blends. Furthermore PA/SAN laminates showed a fourfold increase in adhesion when the oxazoline-containing SAN was used.

Controlled Degradation

One potential side-reaction during graft reactions is degradation of the base polymer, initiated by free radicals originating from either oxygen or a radical initiator. If mastered, this reduction of molecular mass can however be used productively, as in the case of controlled degradation of PP. The high-melt viscosity and high elasticity level resulting from both high molecular mass and molecular mass distribution in virgin PP makes it difficult to process and limits its use in

several applications. If PP is treated with free radicals at high temperatures during extrusion, the molecular mass can be lowered and the molecular mass distribution can be narrowed by chain scission. The method yields a material with improved flow properties that can be used in high speed fiber and film extrusion as well as injection molding. Researchers at Exxon developed a process for the production of "Controlled Rheology" grade PP having a considerably improved processability [16, 17]. The first commercial process utilized oxygen in the air as the free radical source and the extrusion was carried out at temperatures as high as 400°C. Air was introduced together with the polymer into the throat of the extruder, where the temperatures were also the highest, which maximized the generation of free radicals. Currently, radical initiators such as dicumyl peroxide and di-t-butyl peroxide are used rather than oxygen as the free radical source, which has allowed the reactions to be carried out at considerably lower temperatures.

Polymer Functionalization-Halogenation

Related to the grafting of chains to a polymer backbone discussed in an earlier section is the functionalization or the alteration of an existing functionality of a polymer. Both grafting and polymer functionalization in reactive processing must battle the same shortcomings as most other polymer analogous reactions. The problems associated with lower conversions and reaction rates, compared to reactions involving low molecular mass analogs, sometimes become more pronounced in reactive processing owing to the significantly shorter reaction times. That this and other significant chemical and engineering problems can be overcome is grandly exemplified by the extruder halogenation process of butyl rubber developed by Exxon [18].

In this process, butyl rubber, a copolymer of isobutylene and small amounts of isoprene, is functionalized in an extruder with either chlorine or bromine. the first problem encountered is the enormous difference in viscosity between polymer and halogen gas, which makes good mixing very difficult. An inherent property of butyl (and halobutyl) rubber is its low gas permeability. This complicates the mixing of the two phases, as does the fact that the halogenation reaction must be carried out at temperatures below normal rubber-processing temperatures. The chemistry must in addition be carried out in a specific manner because it is only the isoprene part (about 2% of the copolymer) that is to be halogenated. A further requirement is that the halogenation level has to be at least 90% in order to produce an acceptable product. Finally, the problems associated with handling halogens and the hydrogen halides in an extruder should not be underestimated.
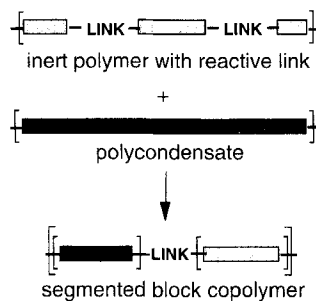
Figure 1.   General approach to reactive processing of polycarbonate.

The problems were overcome by the development of an extruder screw configuration that maximized the generation of surface area by moving two co-continuous phases along the whole reaction zone. The use of slotted double or triple flighted screw sections and control of polymer feed rate provided good mixing without generating too much heat by shear.

We have recently published a more detailed review on the reactive processing of engineering thermoplastics [19]. This report will present recent specific examples of the application of reactive processing to thermoplastics (modified polycarbonates) and thermosets (polyurethanes).

Reactive Processing of Polycarbonate

At Bayer Corporation we have focused on the reactive processing of engineering thermoplastics, specifically polycarbonate. Polycarbonate has diversified into quite a few markets. This has occurred despite the fact that the basic polymer structure - with notable exceptions - has remained unchanged for the past 30 years. Clearly, reactive processing offers a cost effective route to modified polycarbonates.

We have investigated the synthesis of various block copolymers, compatibilized blends, and impact modified resins using reactive processing. This article will focus on the synthesis of impact modified resins.

Our general approach to the reactive processing of polycarbonate is shown in Figure 1. The proposal focus lies not only on chain ends but also on the polymer backbone. A polymer containing reactive groups along the backbone is reacted with polycarbonate. A key example is the polycarbonate/polyethersulfone block copolymer reported earlier. The target of this current work is a low-temperature impact modified polycarbonate. Polycarbonate exhibits a well known ductile to
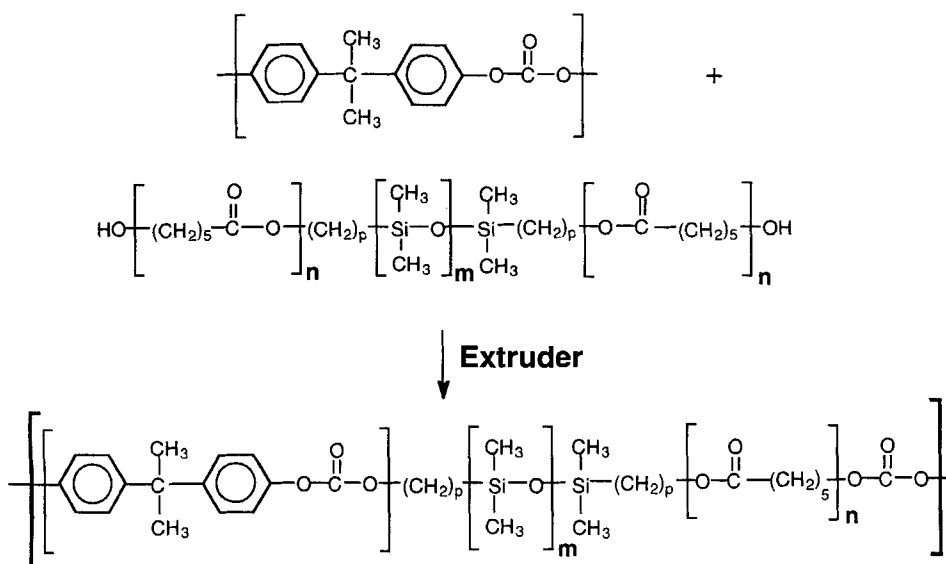
Figure 2.   Synthetic scheme for producing siloxane-modified polycarbonate.

brittle transition at -20°C. The goal of this research was to shift this transition to -40°C.

From a polymer chemist's point of view, there is an obvious solution to this problem: synthesize a copolymer containing a low T_g segment. The chemistry of polycarbonate is amenable to this strategy. One can substitute some of the bisphenol A with a low T_g telechelic oligomer. An obvious choice is polydimethyl siloxane. Although this is possible on a laboratory scale, this is not practical on an industrial scale. Our research focused on a reactive processing route to a similar polymer. The reactive processing chemistry is shown in Figure 2. The reactants are polycarbonate and a polycaprolactone-polysiloxane-polycaprolactone triblock copolymer.

The experimental set-up is shown in Figure 3. The liquid polydimethyl siloxane/polycaprolactone triblock copolymer is pumped directly into the extruder. By carefully varying stoichiometry process parameters and screw parameters, we were able to control the extent of reaction.

There are quite a few possible products from this reaction. The various possible structures are shown in Figure 4. As would be expected, we were able to use NMR to directly observe the mixed carbonates (Figure 5).

The goal of this research was low temperature toughness. Incorporation of the siloxane copolymer dramatically improved the notched izod impact strength at

Extruder set-up
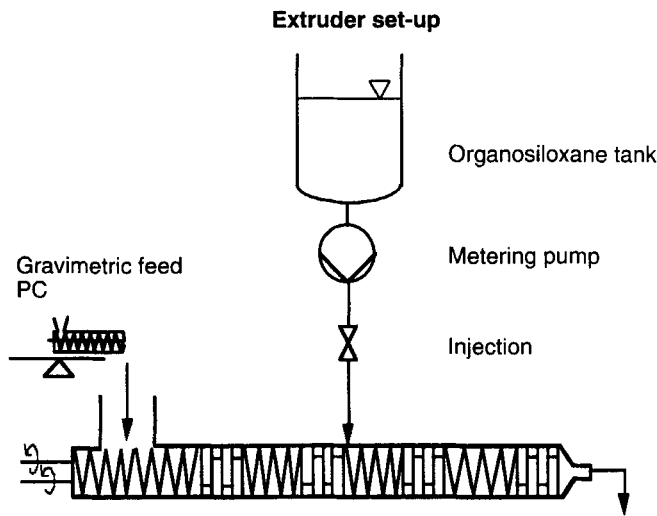
Figure 3.   Experimental set-up for producing siloxane-modified polycarbonate.
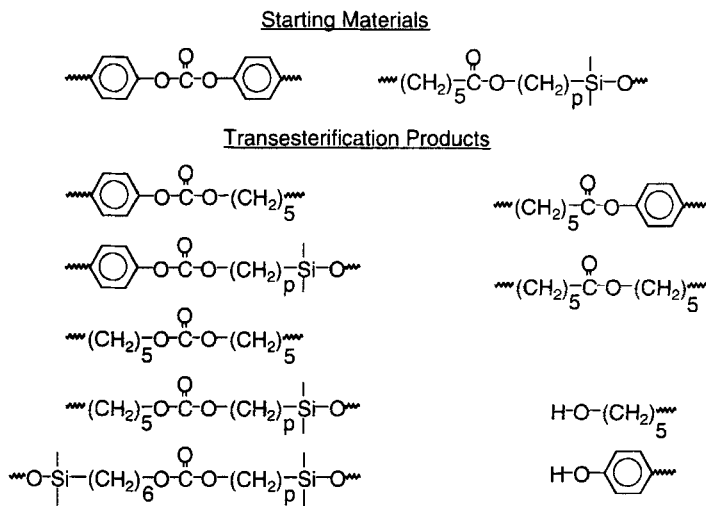
Figure 4.   Possible alcoholysis and transesterification products from reaction to produce siloxane-modified polycarbonate.

-40°C. Figure 6 compares the -40°C impact strength of typical polycarbonate with the reactive processing product.

The next section will address the reactive processing of thermosets, specifically polyurethanes.

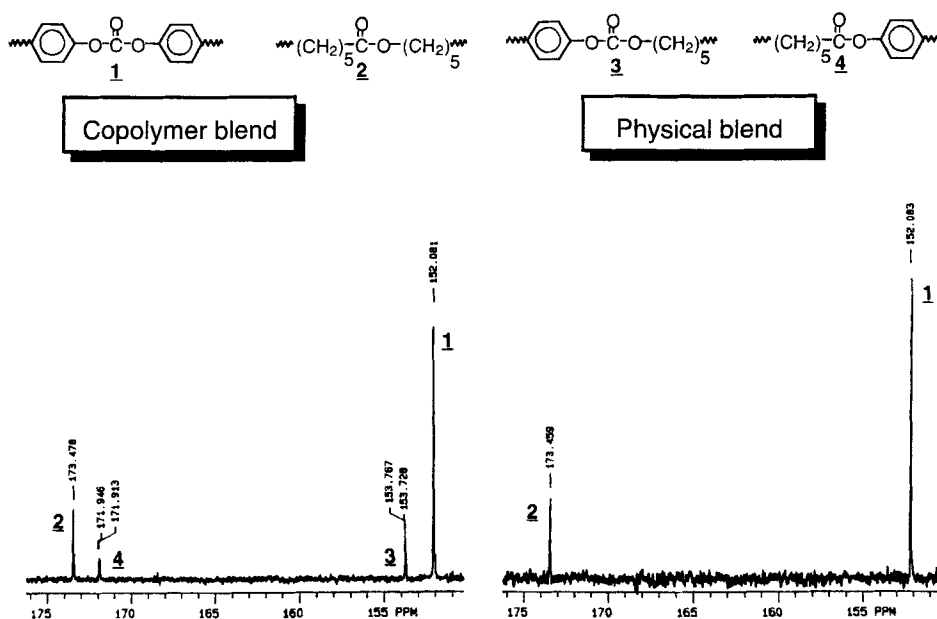**Figure 5.** ^{13}C NMR spectrum of siloxane-modified polycarbonate.

Reactive Processing of Polyurethanes

Polyurethanes are inherently reactive processing polymers. The so-called one-component systems and even thermoplastic polyurethanes can be included in this statement. According to the definition of reactive processing, polyurethanes belong to the category in which reactive monomers and oligomers are processed, neat or in solution. In a typical operation, the reactive components are processed as liquids, for example, for the manufacture of polyurethane foams and elastomers. The so-called two-component polyurethane coatings fit also into this scheme. Polymerization takes place in the foam machine, in the molds, and on the painted substrates. The Reaction Injection Molding (RIM) technology exemplifies the reactive processing of the liquid polyurethane components, i.e., the monomers and oligomers or, in terms of the polyurethane chemist, the di- or polyisocyanates, the soft-segment-forming polyester and polyether polyols, and the chain extenders.

The RIM technology takes advantage of polyurethane chemistry in several ways regarding:

- Energy and cost savings
- The capability to produce thermoset materials

Notched Izod impact @ -40°C
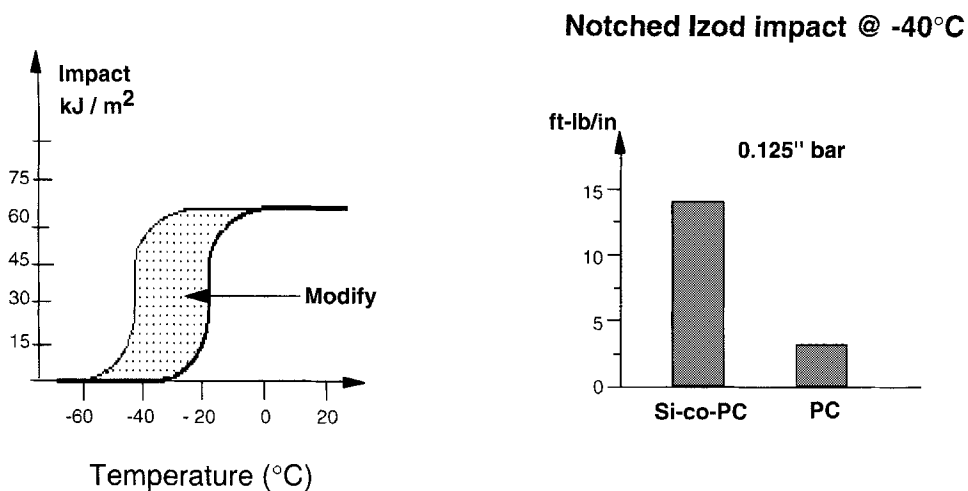
Figure 6.   Notched izod impact at 0.125" test bars a) polycarbonate; b) siloxane
modified polycarbonate.

- The utilization of the isocyanate-amine reaction leading to the preferred
  polyurea structure.

Thermoplastic polymers are processed as completely polymerized products,
for example, in the form of pellets that are remelted and injection-molded. The
finished part normally remains thermoplastic. Depending on the functionality of the
total system, polyurethanes can be produced with any desired crosslink density to
form thermoset materials that have some advantages over thermoplastics.

The RIM process combines the reactive processing of liquids and the
forming of thermoset parts in a more economical process than injection molding.
The polyisocyanate component (A-side) and the resin mixture (B-side), consisting
of the polyether polyol, chain extender and any catalyst used, are metered and
pumped through a mixing device directly into a mold. The energy-consuming
remelting and extrusion operation of the normal injection molding process is
eliminated. A prerequisite for the RIM process was that the reaction be fast enough
to match the cycle times of the injection molding of thermoplastics.

This prerequisite could be fulfilled in the first phase of the technical intro-
duction of the RIM technology with the great variety of homogeneous catalysts
which are available to polyurethane chemistry, and eventually through the capability
to master the fast reaction of di- and polyisocyanates with di- or polyamines leading
to polyurethanes with partial or even only polyurea structures (which are, according
to this widely accepted classification, also referred to as polyurethanes).

Cl   Cl

H_2N—〈 〉—CH_2—〈 〉—NH_2
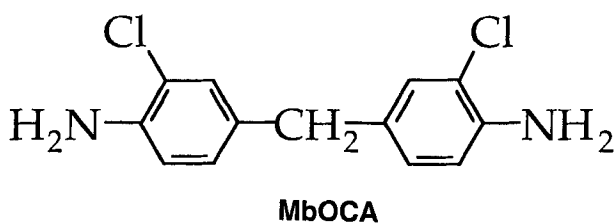
MbOCA

Figure 7. Chemical structure of 3,3'-Dichloro-4,4'-diaminodiphenyl methane (MbOCA).

The manual casting process for polyurethane elastomers from diisocyanates, polyether diols and ordinary glycols as chain extenders led to a paradigm shift in the generation of rubber-elastic materials. Ordinary aliphatic and aromatic diamines react much too fast with diisocyanates to be useful as chain extenders for the hand casting process. The introduction of diamines with reduced nucleophilicity, for example, through electron-withdrawing substituents, led to a breakthrough here. 3,3'-Dichloro-4,4'-diaminodiiphenylmethane, MbOCA (Figure 7), became the compound of choice as the diamine chain extender for cast elastomers, specifically for the chain extension of prepolymers based on toluene diisocyanate (TDI) and polybutylene glycol.

Physical properties of the elastomers derived from this combination equal the properties of the elastomers based on 4,4'-diisocyanatodiphenylmethane (MDI), polyester diols and glycol chain extenders, like butanediol-(1,4). Glycol chain extenders do not provide comparable elastomer properties with TDI-based systems. The fact that chain extension of TDI systems with diamines leads to elastomers with excellent physical properties shows, in very practical terms, the advantage of the polyurea structure. The polyurea structure obviously compensates for the lack of "symmetry" in the TDI molecule.

Born and Hespe [20] elucidated the phenomenon of the polyurea structure through their X-ray studies. They found that the urea group, which is more polar than the urethane group, forms strong bifurcated hydrogen bonds. Consequently, the intermolecular (interchain) interaction of the polyurea structure is stronger, the segregation of hard and soft segments of the polyurea is more marked, and the melting range of the hard segment domains of the polymer is higher than in the polyurethane structure. This explains the superior mechanical properties, the higher modulus (at comparable hard segment contents), the higher heat distortion temperature, and the low thermoplasticity in the non-crosslinked state of the polyurea materials. Even a single urea group shows hard segment character.
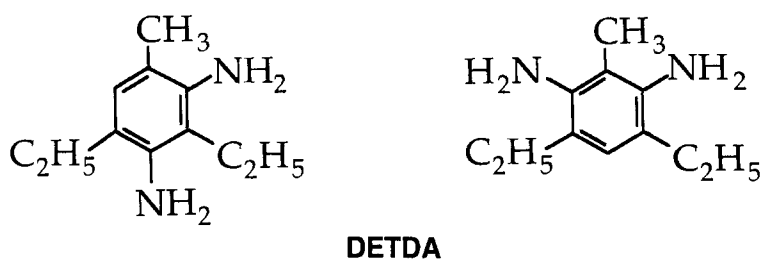
Figure 8. Chemical structure of DETDA, di-ethylated product of the 30:20 isomer mixture of 2,4-and 2,6 toluene diamine.
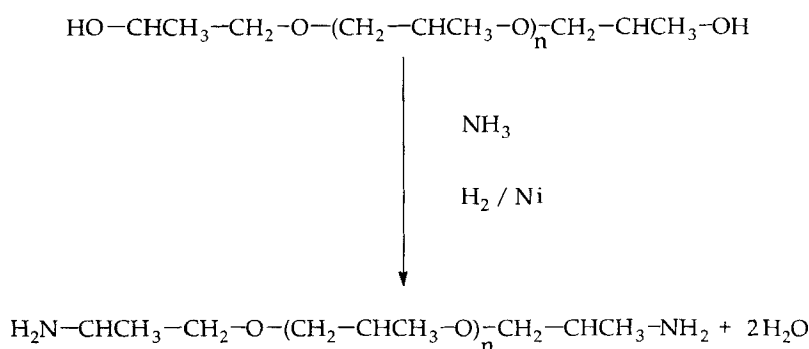
The fast reaction of di- or polyisocyanates with di- and polyamines leading to polyureas has additional advantages. These include: short curing times, i.e., short process cycles; no need for heating of the (liquid) components; no need for post-curing; and no need for the use of catalysts which can detrimentally influence the properties of the elastomers especially upon aging. These advantages and, of course, the fast isocyanate-amine reaction provided exactly what the RIM process needed to compete successfully with injection molding of thermoplastics.

The flywheel for RIM started to turn when the automotive industry introduced the technology for the manufacture of car fascias. These are the elastomeric bumper covers which became an important part of the total concept to make a car that could withstand a five-mile-per-hour impact without damage.

The first RIM polymers were polyurethanes, based on a B-side mixture of polyether polyols and diol chain extenders. The polyurethane reaction had to be highly catalyzed. Physical properties were sufficient for automotive fascia applications, but cycle times were still slower than those of injection molding. A real breakthrough for RIM in the automotive area occurred when DETDA was introduced as chain extender (Figure 8) [21].

DETDA consists of the di-ethylated product of the 80:20 isomer mixture of 2,4- and 2,6-toluene diamine (TDA), the technical raw material for TDI. The reactivity of the amino group is lowered through the steric hindrance of the ethyl groups, but DETDA reacts much faster with isocyanates than MbOCA and is too fast for the manual casting process for the manufacture of polyurethane elastomers.

For the new RIM generation using DETDA, long chain polyether polyols were used as soft-segment-forming components, i.e., these materials have a polyurethane-polyurea structure. Cycle times of these systems are reduced to one

$$HO-CHCH_3-CH_2-O-(CH_2-CHCH_3-O)_n CH_2-CHCH_3-OH$$

$$NH_3$$

$$H_2 / Ni$$

$$H_2N-CHCH_3-CH_2-O-(CH_2-CHCH_3-O)_n CH_2-CHCH_3-NH_2 + 2H_2O$$

Figure 9. Amine terminated polyethers are produced through reductive amination of polyether polyols.

minute and are thus competitive with cycle times of injection molding. These polyurethane-polyureas, compared to materials with only the polyurethane structure, have higher flexural modulus, better heat resistance (i.e., lower heat sag), and improved impact resistance at low temperatures. They were suited for the manufacture of car body panels. The Pontiac Fiero of General Motors became the symbol of the new technology.
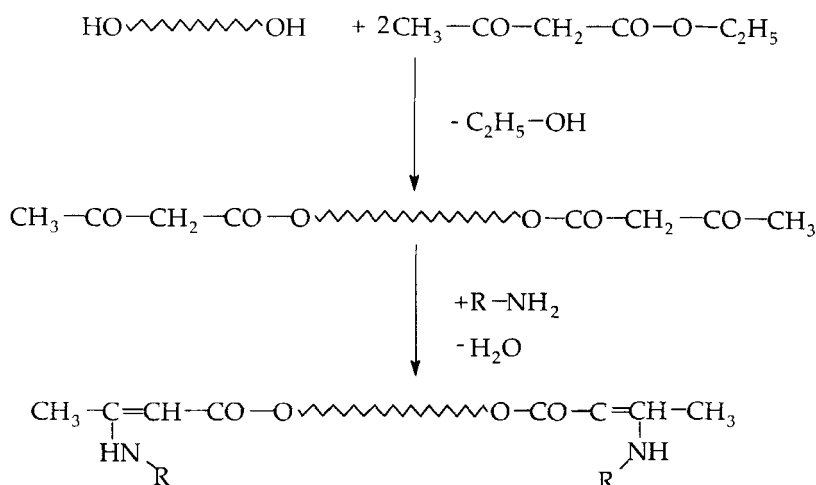
However, automotive requirements became even more stringent. In particular, the industry required RIM fascias and body panels that could withstand the temperatures of the normal on-line paint bake cycles without distortion (all fascias and body panels are painted off-line). This requirement can be met through a RIM elastomer which contains exclusively urea groups, using as the B-side mixtures of DETDA and amine-terminated polyethers (ATPE).

Significant research efforts have been made over the six decades of polyurethane chemistry to synthesize ATPEs [22]. For many years, the commonly known Jeffamines had been commercially available. They are produced through the reductive amination of typical polyether polyols (Figure 9) [23].

These aliphatic ATPEs are suited for the RIM process although they are considered somewhat fast even for this process.

In our laboratories, we have developed the so-called aminocrotonates. They are synthesized by capping of poleyther polyols with acetoacetate groups and subsequent reaction with diamines (Figure 10) [24].

Through the choice of the diamine, it is possible to tailor the reactivity of these ATPEs in a very desirable way for the RIM process.

$$HO \backslash \!\!\!\backslash \!\!\!\backslash \!\!\!\backslash \!\!\!\backslash OH \quad + 2CH_3-CO-CH_2-CO-O-C_2H_5$$

$$- C_2H_5-OH$$

$$CH_3-CO-CH_2-CO-O \backslash \!\!\!\backslash \!\!\!\backslash \!\!\!\backslash \!\!\!\backslash O-CO-CH_2-CO-CH_3$$

$$+R-NH_2$$
$$- H_2O$$

$$CH_3-\underset{\underset{R}{HN}}{C}=CH-CO-O \backslash \!\!\!\backslash \!\!\!\backslash \!\!\!\backslash \!\!\!\backslash O-CO-\underset{\underset{R}{NH}}{C}=CH-CH_3$$

Figure 10.   Synthesis of aminocrotonates.

TABLE 1. Physical Properties of a Polyurea Rim Elastomer

Density, kg/m^3	1132
Flexural Modulus, MPa	631
Tear Strength, Die C, kN/m	97
Tensile Strength, MPa	35
Elongation, %	130
Heat Sag, mm	
(100 mm overhang at 163°C)	5.0
(150 mm overhang at 121°C)	7.5
Izod Impact Strength, Notched, J/m	360

It must be added to the preceding information that the high moduli or stiffnesses, which are required for automotive parts, can only be achieved through the addition of milled glass fibers to these polyurethane formulations. Again, the machines, which were developed for the RIM process, could also master this requirement. The following table (Table 1) summarizes some of the physical data for a polyurea RIM elastomer designed for automotive body panels.

This was not the end of the development of the RIM technology. Systems with ever increasing moduli have been developed, and a further breakthrough

became possible through the use of preforms. These are non-woven glass fiber mats which are preformed to the shape of the final part. They are positioned into the mold before the RIM formulation is injected. With this technology, parts can be obtained which provide a structural strength so that they can compete with steel, for example, in the continued efforts to lower the weight of the car.

CONCLUSION

There are a number of incentives to consider reactive processing as a route to new materials: the cost of developing entirely new engineering resins using traditional polymerization chemistry, familiarity with the properties and processing attributes of the base resin, shortened product development cycles, and tailored physical properties.

The technical problems involved in reactive processing are not, however, trivial. Mixing materials with widely different viscosities is problematic. The final properties of the material are sensitive to myriad variables: processing temperature, residence times, shear rates, screw design, polymer molecular weight and polymer miscibility.

Successful development of new polyurethanes and new engineering polymer grades by reactive processing will call for a multi-disciplined approach with expertise required in chemistry, polymer science, polymer engineering, computer modeling, and statistical process control. With such an approach it may be possible to economically develop and produce specialty engineered materials for niche and emerging markets.

ACKNOWLEDGMENTS

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