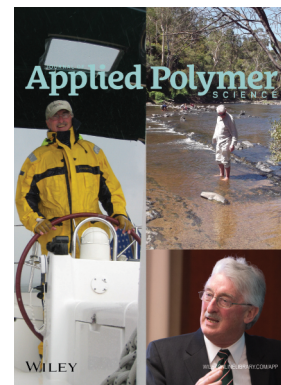


Special Issue: Sustainable Polymers and Polymer Science
Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)



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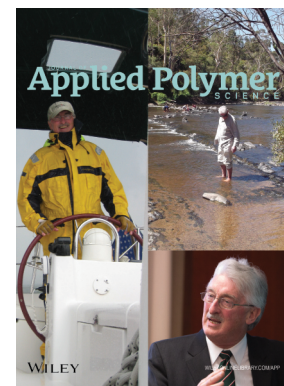
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Richard P. Wool's contributions to sustainable polymers from 2000 to 2015

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ABSTRACT: Professor Richard P. Wool led the resurgence of renewable and sustainable polymers. This began through the development of rigid structural composites from plant oils and renewable fibers. These developments required the use of chemical modification of triglycerides through acrylation, maleinization, and other methods while also using selected comonomers to affect the resulting polymer properties. In addition, high performing adhesives and foams were also prepared from modified plant oils. This work shows that lignin can be used as an additive in composites, and nontoxic and value added monomers and polymers from lignin can be prepared. These developments have found utility in composites, coatings, adhesives, electronics, and clothing. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43801.

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INTRODUCTION

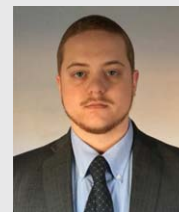
Renewable resources have been used to produce polymers since the beginning of the field of polymer science, including the development of nitrocellulose.¹ The development of natural polymers continued at a strong pace through the early 1940s, where Henry Ford was using soybean proteins to make structural parts for automobiles and the development of alkyd resins resulted in significant improvements in coatings. However, in the 1940s, the USA and other countries invested heavily in the petroleum industry to produce enough liquid fuel and chemicals to support the war effort. Concurrently, the rise in popularity of nylon derived from petroleum-derived chemicals resulted in a large focus on synthetic polymers and a loss of focus on renewable polymers. Through the mid-1990s, renewable polymer work continued as a minor portion of the polymers industry and focused on water-soluble and biodegradable polymers, and many established renewable polymers lost favor to synthetic polymers, like alkyd resins that were mostly displaced by epoxy resins and polyurethanes. Yet, there were researchers continuing to develop new renewable polymers for new applications through the late 1990s. Researchers were examining the use of cellulose fibers for replacement of glass fibers in composites.² Development of useful starch polymers continued as water-soluble adhesives, thickeners, binders, coatings, drug release agents, and flocculants,^{3,4} but no application to structural composites was identified as a result of its high water uptake and

brittle nature.⁵ Polylactic acid, derived from starch, was identified for use in biodegradable polymer applications, bone scaffolding, and low performance polymer applications. Protein-based polymers received little attention since the 1940s but some work continued on their use as adhesives and coatings.³

Probably among the most significant developments of new renewable polymers for high-performance applications outside of Wool at the time came from Gandini *et al.*⁶ They identified that furans derived from cellulose, hemicellulose, and carbohydrates could be used to prepare polymers including polyamides, epoxies, novolac resins, and others that showed promise for very high-performance applications.⁷ However, manufacturing of furan polymers at significant scales was not possible at the time because the chemical manufacturing of furans from biomass was not significant at the time. Furthermore, Gandini *et al.* did not demonstrate these technologies in composites.

Professor Richard P. Wool was a dynamic force within the polymers community and helped revolutionize the renewable polymers and composites industries.⁸ Wool, like others in the field, realized that the petroleum economy was finite, and development of a renewable economy for energy and chemicals was coming.⁹ He realized that plant oils are an abundant renewable resource and can be used to prepare polymers.¹⁰ Furthermore, he discovered that plant oils could be utilized to produce structural polymers for application to composites.^{11,12} In all, Wool identified that the only missing element between plant oil resins

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Dr. John La Scala received a B.S. in chemical engineering from the University of Virginia in 1997 and a Ph.D. in chemical engineering from the University of Delaware in 2002, where he was a member of the Wool research group. He is a senior scientist at the Army Research Laboratory (ARL) and was recently appointed as the Weapons and Materials Research Directorate Associate for Science and Technology. Throughout his career, he has continued his work in bio-based thermosetting resins, adhesives and coatings. His scientific advances are evidenced by over 50 open literature publications, patents, and numerous awards.



Joseph Stanzione, III received his M.S. at Drexel University and his Ph.D. at the University of Delaware, both in chemical engineering. He then joined the chemical engineering faculty at Rowan University in 2013. His teaching interests include thermodynamics; polymer science and engineering; green chemistry and engineering; and bio-based materials. His research program focuses on the utilization of woody biomass as an alternative chemicals feedstock, the development of next-generation lignocellulosic biorefineries, and bio-based polymers and composites.



displacing some of the petroleum composites resins market was chemical production of vegetable oils into monomers. On the other hand, other renewable chemicals and polymers emerging at the time, such as furans, required development of chemical processes and manufacturing facilities just to produce relevant chemicals in addition to chemical production of the monomers and/or polymers or were not conducive to the development of structural composites. Thus, Wool's vision helped begin a refocus on renewable polymers for functional and structural applications. Very large rises in oil costs in the 2000s helped produce a world-wide effort toward renewable chemicals and polymers that Wool played a significant role in influencing. The following sections of this article review Richard Wool's work on sustainable polymers since the inception of the ACRES laboratory in 1996, detailing his influence on this field.

UTILIZATION OF NATURAL FEEDSTOCKS

Due to concerns over the social, economic, and environmental sustainability of the production and consumption of polymers and composites, the development of polymers and composites from renewable resources has become an important area of research for both industry and academia.^{9,13,14} There are numerous classes of renewable resources, including cellulose, hemicellulose, lignin, plant oils, chitin, and proteins. Biodegradable and water-soluble polymers are currently manufactured from cellulose, the most abundant renewable resource.¹⁴⁻¹⁶ Recently, cellulosic materials have been used to produce small C-5 and C-6 sugars for chemical production,¹⁷ but this industry

did not exist at a significant capacity until the late 2000s. Lignin production is approximately 20 billion tons annually,^{9,13} but most is burned for energy. Lignin is used as functional additives or filler in formulated products,¹⁷⁻²⁰ and numerous researchers have investigated the use of lignin to make value added chemicals and materials.^{17,20,21} Some chemicals, such as vanillin, are produced from lignin, but generally, few chemicals are produced and even fewer are cost competitive with petroleum-derived chemicals. Worldwide plant oil production is over 500 million tons per year for food and chemicals for beauty products, adhesives, coatings, and other applications.¹⁰ Although plant oils are produced at a lower rate and are more expensive than lignocellulosics, plant oils are the most abundant renewable resource that is also a liquid at room temperature, enabling far simpler manufacturing processes to produce plant oil-based polymers relative to lignocellulosic polymers directly from the raw renewable resources. Thus, plant oils were a logical starting point for the development of high-performance polymers and composites.

Triglycerides

Upon moving to the University of Delaware to be the director for the Center for Composite Materials, Wool began thinking of how biomass could be used to make useful structural composites. He realized that plant oils had many similarities to petroleum, and could be cracked or chemically modified to produce useful monomers and polymers. Triglycerides are composed of three fatty acid chains joined together at a glycerol center

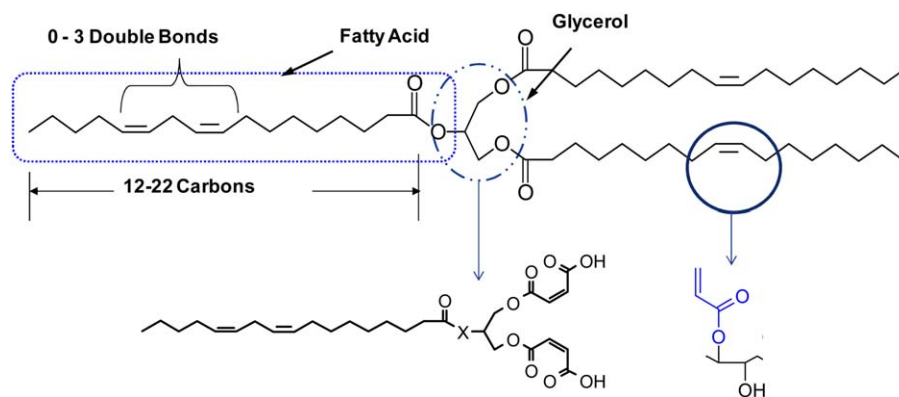


Figure 1. Schematic of common plant oil triglycerides showing the general methodology to functionalize unsaturation sites and the glycerol center. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Figure 1) and are the main component of animal oils and plant oils, such as soybean oil, linseed oil, etc.¹⁰ Triglycerides are used in animals and plants for energy storage and cellular components.²² Common plant oils contain fatty acids that vary in length from 12 to 22 carbons with 0–3 double bonds per fatty acid.²³

Wool's collaboration with S. Kusefolgu, Bogazaci University, Turkey, enabled them to identify various synthetic routes to prepare monomers that can polymerize via free radical, addition/condensation, and ring opening methods.¹² There were three main methodologies to produce these monomers (Figure 1): chemical modification at the unsaturation sites, chemical modification at the ester/glycerol linkage, and a combination of both methods. There was a fourth method of functionalization at sites allylic to the unsaturation sites, but this was explored to a lesser degree. The first major synthetic preparation methodology was through the utilization of the triglyceride unsaturation sites. Many common plant oils, like soybean and corn oil, have three or more unsaturation sites per molecule.¹⁰ This allows the functionalization of a high percentage of fatty acid arms to prevent the development of significant amounts of fatty acid segments pendant to a polymer network that would plasticize the network.^{11,24} Although epoxidized triglycerides had already been used, these generally resulted in poor performance because the epoxies were secondary and reacted to low extents and at slow rates with diamines.²⁵ Wool and Kusefoglul realized that acrylation/methacrylation of the epoxy with acrylic/methacrylic acid would produce a primary vinyl species capable of free-radical polymerization. Furthermore, the resulting hydroxyl groups vicinal to the acrylate could be reacted with maleic anhydride to attach maleate half esters also capable of free-radical polymerization. The second method involved reacting the triglycerides with poly-hydroxyl alcohols, such as glycerol, to produce mono-glycerides and then reacting the remaining hydroxyl groups on the alcohol core with maleic anhydride (Figure 1). The third methodology involved preparing monoglycerides where both the glycerol hydroxyl groups and unsaturation sites were functionalized (Figure 1).

Through his collaboration with G. Palmese, they realized that many of the polymers were similar to unsaturated polyester resins,^{26,27} and, thus, should be processed similarly using styrene

or other reactive diluents to reduce the viscosity and aid polymerization. The resins were found suitable for polymer and composite manufacturing by resin transfer molding, reaction injection molding, and vacuum assisted resin transfer molding, among many other techniques. These chemistries, and use of reactive diluents, were the basis of Wool's seminal patent, *High Modulus Polymers and Composites from Plant Oils*, that established the chemical methodologies to produce processable resins and structural composites from plant oils.¹²

AESO. Wool established a partnership with John Deere and produced a composite hay bailer door using a resin blend of acrylated epoxidized soybean oil and styrene to infuse the glass skins sandwiching a foam core. This achievement was awarded the 1998 Innovation in Real Materials Award from The International Union of Materials Research Societies and demonstrated to the world that the concept of structural composites from plant oils was feasible.

Khot, Wool, and others examined the properties of triglyceride-based polymers and composites.¹¹ The primary focus of the paper was on the properties of acrylated epoxidized soybean oil (AESO) blended with styrene to make neat resins and composites. Depending on the particular monomer and resin composition, tensile moduli of 1–2 GPa, and glass transition temperatures (T_g s) of 70–120 °C were obtained for the AESO resins. At glass fiber contents of 35 wt %, the composite exhibited a tensile modulus of 5.2 GPa, a flexural modulus of 9 GPa, a tensile strength of 120 MPa, and a flexural strength of 206 MPa. Hemp composites of 20 wt % fiber content exhibited a tensile strength of 35 MPa and a tensile modulus of 4.4 GPa. The flax composite materials exhibited tensile strengths of 20–30 MPa,¹¹ which was lower than that of hemp fiber composites likely because of the shorter fiber length for the flex used. Composites comprising of an AESO-based polymer and both natural and synthetic fibers were shown to have properties between that of all-glass and all-natural composites with lower costs. This paper has the most citations of all of the renewable polymer papers from Wool and has effectively provided a roadmap for many other researchers, including the development of fatty acid monomers as styrene replacements.²⁸ Although the properties of the renewable resins and composites were good, the work showed that the properties were similar to that of lower end

unsaturated polyester resins and composites and composites using renewable fibers did not demonstrate desired performance. Thus, improvements in resin and composite properties were necessary. Additionally, chemical engineering of the desired monomers was necessary to enable manufacturing.

Williams and Wool investigated the use of a soybean oil-based resin for composite applications using natural fiber reinforcement to produce highly bio-derived composites with outstanding performance.²⁹ Resins were produced containing at least 50 wt % AESO. The resins were combined with natural fibers. To increase adhesion to the resin and obtain high-performance, the natural fibers were treated with basic solutions. The resulting low-cost composites had tensile strengths of 4.7 GPa with 40 wt % flax, which was very similar to that of composites made using commercial vinyl ester, unsaturated polyesters, and epoxy resins.

O'Donnell, Wool, and others studied the synthesis of composite materials from plant oil-based resins and plant fibers to demonstrate the utility of these composites toward construction/civil engineering.³⁰ Composite panels were created using vacuum-assisted resin transfer molding from AESO and natural fiber mats consisting of flax, cellulose pulp, and hemp. The low-cost natural composites possessed flexural moduli of 1.5–6 GPa. The AESO resin reinforced with E-glass fiber exhibited a flexural modulus of 17 GPa. The composites were proposed to be suitable for applications such as housing construction materials and automotive parts, and even I-beam demonstration articles were produced. Dweib, Wool, and others further investigated the use of all natural composite sandwich beams manufactured from soybean oil and natural fibers for structural applications in 2004–2006.³¹ The AESO resin exhibited a flexural modulus of 1 GPa. Incorporating natural fiber reinforcement of 20–55 wt % increased the flexural modulus to 2–6 GPa. The AESO-based composite offered many advantages such as high strength and stiffness to weight, survivability in severe weather conditions, desired ductility, fatigue resistance, and design flexibility. Due to the advantages of the soybean oil-based composite, a similar composite was tested for suitability in roof structures and yielded adequate mechanical performance.³² A modified vacuum-assisted resin transfer molding technique was utilized to manufacture the composite structures. The final composite structures were coated with either a polyester gel coating or Minwax[®] Helmsman[®] Spar Urethane to reduce moisture absorption.

To simultaneously maximize the use of bio-based materials and the composites properties, Morye and Wool examined the mechanical properties of glass/flax hybrid composites based on a modified soybean oil matrix.³³ A resin mixture of AESO and styrene was prepared and utilized in the formation of the composite materials. The mechanical properties of the glass/flax hybrid composites were found to be dependent on both the glass/flax ratio and the arrangement of fibers. Asymmetric composites exhibited lower tensile strengths than symmetric composites at the same glass/flax ratio. Failure mechanisms were also found to be dependent on the arrangement of fibers. Proper selection of the arrangement of fibers in the composite resulted in improved flexural and impact performance.

Chemical engineering of the triglyceride monomers was necessary to enable manufacturing. La Scala and Wool explored the effects of fatty acid composition on the acrylation kinetics of epoxidized triacylglycerols.³⁴ It was shown that multiple epoxies per fatty acid caused a decrease in the reactivity of the epoxies due to steric hindrances and the rate constant of acrylation increased as the number of epoxies per fatty acid decreased. An acrylation kinetic model was derived to predict rate constants from fatty acid distributions and the model closely matched that of the experimentally obtained rate constants. La Scala and Wool further investigated the effect of fatty acid composition on the epoxidation kinetics of triacylglycerols.³⁵ Fatty acid composition was shown to have a significant effect on the rate constant. The steric and electronic effects caused fatty acids with different levels of unsaturation to exhibit different reactivities. A model was derived to predict the epoxidation kinetics of oils based on the fatty acid composition.

To identify and expand the processing window of acrylated epoxidized plant oils for composites applications, La Scala and Wool investigated the properties of fully and partially acrylated olive oil, soybean oil, corn oil, linseed oil and others.²⁴ Epoxidized and acrylated triglycerides were synthesized from various plant oils and model triglycerides to determine the effect of the molecular structure on viscosity. The viscosity of the unmodified oils was found to decrease as the level of the oil unsaturation increased. The chemical modifications of the triglycerides increased intermolecular interactions, which resulted in increased viscosity. The slight polarity of the epoxidized triglycerides caused higher viscosities than that of the unmodified triglycerides. The acrylated epoxidized triglycerides were significantly more polar, resulting in appreciably higher viscosities. The viscosities of the acrylated epoxidized triglycerides were also found to increase as the average distance of the acrylate group from the fatty acid chain ends decreased and as the distance of the acrylate group from the glycerol center increased. Although oils with low degrees of acrylation had the lowest viscosities, that viscosity was still high enough (~2000 cP) to require use of reactive diluents for liquid molding applications. Furthermore, that level of acrylation results in weak and flexible polymers³⁶ that are not appropriate for composite applications. Resins with appropriate polymer properties for composites had viscosities ranging from 10,000 to 100,000 cP.

To identify the property range of acrylated plant oils and expand their utility for composites and other applications, La Scala and Wool investigated the properties of fully and partially acrylated olive oil, soybean oil, corn oil, linseed oil, and others.³⁶ Acrylated triglycerides were synthesized and both homopolymerized and copolymerized with styrene. In both homopolymerization and copolymerization of the acrylated triglycerides, the crosslink densities of the resulting cured thermosets were found to gradually increase at low levels of acrylation and linearly increase at higher levels of acrylation. The T_g of the cured thermosets increased linearly with crosslink density and ranged from -50 to 92 °C. By using simple empirical relationships, the T_g of acrylated triglycerides was found to be a clear function of the level of acrylation of triglyceride-based polymers.³⁷ Using this and the concept of the twinkling fractal

theory where polymer components twinkle between the glassy and rubbery state, the dynamic mechanical storage modulus, loss modulus, and $\tan \delta$ were able to be predicted as functions of temperature. Effectively, the percent drop in the elastic modulus was found to be equal to the percentage of acrylated triglycerides in the triglyceride-based polymers with T_g values less than that of ambient temperature. The $\tan \delta$ was also able to be accurately predicted based on the percentage change of functional triglycerides relaxing from glassy to rubbery as a function of temperature. Furthermore, thermal and mechanical properties increased with the linseed oil resins with the highest degree of unsaturation, which had the highest thermal and mechanical properties while oils, like olive oil, with low degrees of unsaturation had the lowest thermal and mechanical properties. In all, properties could be tailored from soft and flexible to hard and rigid through use of different plant oils or levels of acrylation.

Nanocomposite enhancements to the properties of AESO resins were explored to increase thermal and mechanical properties. Thielemans, Wool, and others explored the utilization of impure carbon nanotubes as reinforcements in AESO composites.³⁸ Impure multiwall carbon nanotubes were dispersed in an AESO-based resin using mechanical stirring. Upon curing, the polymerized thermosets had improved moduli of up to 30% with dispersed multiwall carbon nanotubes. The polymer matrix was shown to have good adhesion to the carbon nanotubes; however the use of impure multiwall carbon nanotubes was found to only be viable at small volume fractions. Lu, Wool, and others investigated the synthesis of clay nanocomposites based on plant oils in 2004.³⁹ Modified clay was introduced into AESO and styrene before crosslinking reactions and the formation of a nanostructure was confirmed. 3 wt % clay loading was fully exfoliated, but 5 wt % clay was not. As a result, the mechanical properties were maximized for samples with 3 wt % clay loading with a modulus increase from 0.9 to 1.12 GPa and a strength increase from 34.8 to 38.9 MPa with nearly no effect on T_g ($\sim 70^\circ\text{C}$).

Maleic Anhydride Modified Triglycerides. Ultimately, the AESO resin system had significant limitations in the glass transition that can be reached, as T_g s above 100°C were not attainable. As a result, Wool pushed his group to develop triglycerides with higher degrees of functionalization to pin down the aliphatic triglyceride arms into the polymer network. Methods to develop more highly functionalized plant oils, including maleinized acrylated epoxidized soybean oil (MAESO), were found to increase polymer properties as a result of increased crosslink density.¹¹ T_g increased linearly from 107 to 116°C as the number of maleates increased from 2.0 to 2.3 per triglyceride and modulus at room temperature increased to 1.55 GPa.¹¹ Furthermore, glass fiber composites using MAESO as the resin had only slightly reduced properties relative to Derakane 411-C50/glass fiber composites, and having flexural modulus of 34.5 GPa and strength of 669 MPa.

Campanella, Wool, and others investigated the synthesis of composite materials from a plant oil-based resin and northern red oak (*Quercus robur*) leaves.⁴⁰ Plant oil-based resins, MAESO and MAELO, were synthesized and were found to be suited for

high temperature resin transfer molding and vacuum-assisted resin transfer molding processing. Due to the waxy epidermal layer of the leaves, the leaves were dewaxed prior to composite synthesis. The compatibility of the leaves with the resin was able to be improved with silane treatment, which resulted in composites with an increase in storage modulus at 30°C of about 14%. Based on the composite modulus, the leaf storage modulus at 30°C was calculated to be approximately 5.3 GPa. The plant oil-based composites were found to have potential uses in high volume applications with low costs, such as construction, housing, toys, and furniture.

Lu, Wool, and others explored the synthesis of soybean oil-based resins for sheet molding compound applications,⁴¹ to move the application of plant oil resins into household furniture and other midperformance applications. MAESO was synthesized and copolymerized with styrene to form rigid polymers. The resulting polymers exhibited storage moduli ranging from 1.9 to 2.2 GPa at 25°C and T_g s ranging from 100 to 130°C based on the $\tan \delta$ thermograms. Optimized reaction conditions and a stoichiometric ratio of three maleates per triglyceride enabled significant improvement in the modulus and T_g . Lu and Wool further investigated the thickening behavior and mechanical properties of MAESO-based polymers for sheet molding compound applications.⁴² When divalent cations from MgO were introduced to the resin, a rise in viscosity of three orders of magnitude occurred due to the complexation of MgO with the terminal acid groups on maleic anhydride as typical for sheet molding resins. With increased heating, the viscosity of the sheet rapidly decreased two orders of magnitude prior to cure, enabling flow to conform to the part mold. The degree of thickening was found to have no effect on the mechanical properties of the resulting cured resins. The flexural strengths of the cured resins were 61–87 MPa and the flexural moduli were 1.6–2.4 GPa. The cured resins also exhibited tensile strengths of 27–44 MPa and tensile moduli of 1.6–2.5 GPa.

To improve the properties of the sheet molding compound, Lu and Wool also synthesized sheet molding compound resins from linseed oil, which has a very high degree of unsaturation, higher than that of most plant oils including soybean oil.⁴³ Maleinated acrylated epoxidized linseed oil (MAELO) was copolymerized with styrene and the cured resins exhibited storage moduli of approximately 2.5 GPa at 30°C and T_g s above 100°C based on the $\tan \delta$ thermograms. The resins were capable of reaching a molding viscosity quickly and remaining stable. The flexural strengths of the cured resins were found to be roughly 100 MPa and the flexural moduli were found to be 2.8 GPa. These properties were higher than that of the soybean oil-based resins as a result of the higher degree of functionalization and crosslinking for the MAELO as was also observed in the AESO systems.³⁶ The linseed oil-based resin exhibited properties comparable to that of commercial unsaturated polyesters and applicable for sheet molding compound applications. Clay nanocomposites based on MAESO were prepared and complete exfoliation of the clay was possible up to 3 wt % clay loading and intercalation at 5 wt %.³⁹ With addition of 3 wt % clay, the storage modulus at 30°C increased by 13%, while T_g decreased from 136 to 130°C . Thermal stability was minimally improved

with maximum decomposition temperature rising from 420 to $\sim 425^\circ\text{C}$ with addition of 3–10 wt % nanoclay.

Wool, Lu, and others hold a patent for the preparation of sheet molding compound resins from plant oils.⁴⁴ The polymer resin was synthesized from functionalized natural triglyceride oil to contain ethylenic unsaturation, hydroxyl groups, and carboxylic acid functionality. The hydroxyl and carboxylic acid groups provide thickening with divalent metal ions, and the unsaturated polyester oligomers have the ability to be crosslinked by copolymerization. The oligomers were mixed with copolymerizable monomers, initiators, and other additives to form the sheet molding compound paste, which can then be combined with fibers to form a sheet. The materials are then molded and cured to create the composite material.

Other maleate chemistries were explored in place of AESO to improve polymer properties. Eren, Wool, and others explored the polymerization of maleic anhydride-modified plant oils with polyols.⁴⁵ Unsaturation of soybean oil triglycerides were reacted with maleic anhydride in an ene reaction to produce succinic acid residues allylic to unsaturation sites that move one carbon atom down the fatty acid chains. The succinic anhydride groups were capable of reacting with hydroxyl groups to produce succinate half esters and could connect the fatty acid to the alcohol through addition. The reaction of the anhydride functionalized soybean oil and alcohols produced a polymeric half-ester without the formation of byproducts. All the alcohols used had multiple hydroxyl groups and, thus, crosslinking of triglycerides would occur over the course of the reaction. Glycerol and short chain polyethylene glycols were highly effective in crosslinking the material producing a semirigid solid due to their primary alcohol groups with little steric hindrance. Castor oil, on the other hand, only oligomerized due to the secondary and sterically hindered alcohols. Additionally, Esen, Wool, and others reacted monomethyl maleate with epoxidized soybean oil (MESO) to form methyl maleates that could not oligomerize the triglycerides through a condensation reaction, but could crosslink through free-radical polymerization.⁴⁶ MESO was photopolymerized using ultraviolet light and free-radically homopolymerized and copolymerized with styrene, methyl methacrylate, and vinyl acetate. As expected, the homopolymers did not polymerize enough to be crosslinked due to the fact that maleates react poorly with each other. The dynamic modulus of MESO copolymerized with styrene was found to be 105 MPa, and thus preparing a relatively rubbery material at room temperature. Maleinized MESO was also synthesized by reacting maleic anhydride with the hydroxyl groups that formed from the reaction of ESO with monomethyl maleate. The maleinized MESO was copolymerized with styrene, resulting in a dynamic modulus of 140 MPa. Although not stated in the paper, the maleinized MESO had a far higher viscosity relative to MESO because the carboxylic acid half esters in maleinized MESO oligomerized triglycerides and produced significant hydrogen bonding, but would make this resin highly useful for sheet molding compound applications. On the other hand, MESO could not be used for sheet molding compound applications because of the lack of carboxylic acid groups necessary to form physical entanglements upon addition of divalent cation salts.

Although the toughness of plant oil polymers were not poor relative to unsaturated polyesters, the toughness of free-radically polymerized crosslinked resins is generally far lower than that of epoxy-amine or polyurethane systems. As a result, Lu and Wool explored toughening agents for triglyceride-based thermosetting resins in 2008.⁴⁷ Liquid rubber (carboxyl terminated poly(butadiene-*co*-acrylonitrile)) and vinyl terminated poly(butadiene-*co*-acrylonitrile), epoxidized soybean oil (ESO), and nanofiller (organo-treated clay) were utilized to increase the toughness of MAESO thermosetting resins cured with 33 wt % styrene. Liquid rubber was found to form a secondary elastomeric phase dispersed in the polymer matrix; however, the liquid rubber only provided a small increase in overall toughness, decreased the storage moduli at 30°C by a maximum of 0.79 GPa, and decreased the T_g by a maximum of 6°C . The use of ESO increased overall polymer toughness whereas it led to increased plastic deformation resulting in a critical strain energy release rate (G_{IC}) increase from roughly 200 J/m^2 for MAESO to 800 J/m^2 for MAESO with 15 wt % ESO, but at the expense of a decrease in T_g of approximately 30°C . Inorganic nanofiller was found to increase the fracture toughness of the cured resins to nearly 400 J/m^2 at 5 wt % nanoclay without decreasing the modulus or T_g of the cured resin; therefore, making the inorganic nanofiller the best option to add toughness to the triglyceride-based thermosets.

Monoglycerides. Soybean oil monoglycerides (SOMGs) represented another important route to producing bio-based polymers. Rather than having on average 1.5 functional groups per fatty acid chain for soybean oil, SOMG enables an average of 3.5 functional groups per molecule, which could enable further increases in the T_g and mechanical properties and could enable reductions in viscosity and thereby improve processing capability for composites. Can, Wool, and others explored the synthesis of rigid thermosetting polymers from the radical copolymerization of soybean oil monoglyceride maleates with styrene in 2001–2002.^{48,49} Soybean oil monoglycerides (SOMGs) were synthesized through the reaction of soybean oil with glycerol, in a reaction analogous to that for the production of biodiesel. The SOMG was then reacted with maleic anhydride to produce SOMG maleate half esters. The SOMG maleates were copolymerized with styrene to produce a rigid thermoset with similar mechanical properties to commercially available polyesters and vinyl esters. The cured resin had a T_g of approximately 133°C according to the $\tan \delta$, storage modulus (E') of 0.94 GPa at 35°C , tensile strength of 29.36 MPa, and a tensile modulus of 0.84 GPa. The high measured T_g with relatively low modulus and strength indicates that the T_g measured by $\tan \delta$ is a significant overestimation from the real T_g of this resin system. Analysis of the reaction content of the resin showed that there is a large fraction of diglycerides and significant fraction of triglycerides that likely cause significant relaxation prior to the temperature at the $\tan \delta$ maximum.

In 2006, Can, Wool, and others examined the synthesis and mechanical properties of soybean oil and castor oil-based monoglyceride resins.^{50,51} The maleinization of the alcoholysis products of soybean oil and castor oil with various polyols provided triglyceride-based monomers. The cured resins possessed

a wide range of properties that were dependent on the triglyceride chemical structure. The triglyceride-based polymers exhibited flexural moduli of 0.8–2.5 GPa, flexural strengths of 32–112 MPa, and T_g s of 72–152 °C based on the $\tan \delta$ thermograms. The castor oil-based polymers exhibited significantly higher moduli, strengths, and T_g s compared to the soybean oil-based polymers. In general, both castor oil- and soybean oil-based polymers showed comparable properties to that of high-performance unsaturated polyester resins. Clay nanocomposites based on soybean oil pentaerythritol maleates (SOPERMA) blended with styrene were prepared and exfoliation was possible up to 3 wt % clay loading and intercalation at 5 wt %.³⁹ With addition of 3 wt % clay, the storage modulus increased by nearly 20%, while T_g decreased only slightly from 130 to 126 °C.

Combinations of Functionalized Plant Oils with Bio-Based Monomers. Most prior work developed triglyceride polymers with use of styrene as a reactive diluent to aid in processing and increase the thermal and mechanical properties. Reduction of styrene in the resin reduces exposure to this toxic chemical and if replaced with a bio-based monomer, would increase the bio-based atomic efficiency of these resins. Beach, Wool, and others examined the properties of thermosets derived from modified triglycerides and bio-based comonomers to increase the renewable content in these resins and composites and to reduce the content of styrene.⁵² AESO was cured with either dibutyl itaconate or ethyl cinnamate to synthesize thermosets with a high (>90%) concentration of bio-based carbon. The comonomers, dibutyl itaconate and ethyl cinnamate, are cellulose-derived and potentially lignin-derived, respectively. Both AESO cured with dibutyl itaconate and AESO cured with ethyl cinnamate exhibited substantial degradation at 390–400 °C, which is similar to that of pure AESO. Also, T_g s were found to decrease as the amount of comonomer content in the resin decreased. AESO cured with ethyl cinnamate typically exhibited storage modulus values 5.0–26.8 MPa higher at 30 °C, depending on blend amounts, than AESO cured with dibutyl itaconate. Alternative approaches such as fiber reinforcement were suggested to improve the overall polymer performance to obtain properties comparable to that of petroleum-derived comonomer systems.

In 2009, Campanella, Wool, and others investigated the utilization of acrylated fatty acid methyl esters as styrene replacements in triglyceride-based thermosets in 2009 to prepare nearly 100% bio-based resins.⁵³ AESO and maleinated castor oil monoglyceride were used as bio-based crosslinkers and diluted with either styrene or an acrylated fatty acid methyl ester-based monomer. The utilization of acrylated fatty acid methyl ester monomer as a reactive diluent resulted in polymers with significantly lower T_g s than polymers with styrene as the reactive diluent. Ternary blends of acrylated fatty acid methyl esters, styrene, and maleinated castor oil monoglyceride provided acceptable properties comparable to petroleum-based resins and reduced overall HAP and VOC emissions. The ternary blends exhibited storage moduli of 1.2 GPa at 30 °C and T_g s of 100 °C based on the $\tan \delta$ thermograms.

In 2011, Campanella, Wool, and others further explored methacrylated lauric acid, a fatty acid-based monomer, as a styrene replacement in soybean and castor oil-based thermosets.⁵⁴ Resins containing methacrylated lauric acid exhibited higher viscosities and T_g s on the order of 60 °C, which is substantially lower than resins containing styrene. In order to create polymers with acceptable properties, styrene was still required in the amount of 25 wt %. The incorporation of both styrene and methacrylated lauric acid together as the reactive diluent resulted in resin viscosities of roughly 600 cP at 25 °C and cured polymers with T_g s of approximately 100 °C.

Campanella, Wool, and others investigated triglyceride-based thermosetting resins with various reactive diluents in 2015.⁵⁵ In addition to traditional reactive diluents such as styrene, vinyl toluene, divinylbenzene, and methyl methacrylate, methacrylated lauric acid was utilized as a reactive diluent in MAESO resins. The traditional reactive diluents blended with MAESO exhibited comparable resin viscosities to commercial resins. A ternary blend of MAESO, MFA, and styrene resulted in resins that exhibited acceptable viscosities at 25 °C of approximately 1890 cP while maintaining overall polymer properties. The cured resins exhibited storage moduli of 1.4 GPa at 30 °C and T_g s of 85 °C based on the $\tan \delta$ thermograms. Bulk molding compounds using approximately 12% resin with 44% calcium carbonate, 28% chopped glass fibers, and minor amounts of other components had flexural strengths of 115 MPa, flexural moduli of 8.2 GPa, tensile strengths of 32 MPa, and tensile moduli of 10.6 GPa. Increasing the amount of MFA in the resin resulted in increased toughness and bio-based content while reducing HAP emissions.

Foams. Wool identified that foams are found in many commercial and household products, and plant oil-based polymers may be used to develop relevant structural foams. Bonnaillie and Wool explored the synthesis of thermosetting foams with high bio-based contents in 2007.⁵⁶ A pressurized CO₂ foaming process was implemented to produce AESO-based foams with a bio-based content of 96 wt %. The density of the cured foams was controlled by the utilization of a partial vacuum before gelation. The AESO-based foams exhibited compressive strengths on the order of 1 MPa and compressive moduli on the order of 20 MPa, comparable to that of semirigid industrial foams.

Campanella, Wool, and others further studied the synthesis of polyurethane foams from soybean oil in 2009.⁵³ Polyols from soybean oil were synthesized to produce soybean oil monoglyceride (SOMG), hydroxylated soybean oil (HSO), and soybean oil methanol polyol (SOMP). SOMG was found to have the highest reactivity due to the fact that it was the only polyol containing primary hydroxyl groups in addition to a secondary hydroxyl group. The polyurethane foams synthesized from SOMG with a synthetic polyol, glycerol propoxylate, contained small and uniform cells; however, foams synthesized from the other soybean-oil-based polyols had cells that were larger and less uniform. Water content, type of isocyanate, and catalyst amount were found to affect the morphology of the foams. The

polyurethane foams exhibited tensile strengths of 1.7–2.5 MPa and T_g s of -10 to 12 °C via differential scanning calorimetry.

Other Plant Oil-Based Polymers. Considering the difficulty in making highly rigid polymers and the relative ease in making soft and flexible polymers, Wool and others applied triglyceride chemistry, engineering, and materials science towards developing pressure sensitive adhesives and elastomers. Richard Wool was an adhesion expert and had a fascination with pressure sensitive adhesives like Scotch Tape™ and Post It Notes™ and noted that noncrosslinked or lightly crosslinked polymers were the target for these applications. Bunker and Wool used methyl oleate, which can be derived from triglycerides, as a starting material. They chemically modified it to produce acrylated methyl oleate (AMO), a monomer that possesses a similar structure to that of petroleum-based acrylate monomers that are used in pressure sensitive adhesives (PSAs), such as hexyl acrylate.⁵⁷ AMO was emulsion polymerized with small amounts of methyl methacrylate to form high molecular weight polymers with high latex solids content; however, long reaction times were required. Bunker, Wool, and others further investigated paths to improve the aqueous emulsion polymerization of AMO.⁵⁸ Miniemulsion polymerization was utilized and showed significant improvement to the polymerization of AMO. The overall reaction time was significantly decreased while also decreasing the amount of surfactant necessary. The AMO polymers exhibited peel energies of 200 J/m² and hold times of 10 min, which was significantly lower than that of Scotch Tape™ (250 J/m² peel energy and roughly 1500 min hold time). However, modification with maleic acid enabled properties equivalent to that of Scotch Tape™. Purified methyl oleate was substituted with methyl esters from E. I. du Pont de Nemours and Company's high oleic soybean oil and olive oil to reduce cost. The resulting polymers had PSA properties, but were inferior due to higher extents of crosslinking as a result of a significant percentage of polyunsaturated fatty acids.

Wool and Bunker hold a patent for the synthesis of a PSA from plant oils that have a low content of volatile compounds and low odor.⁵⁹ Fatty acid methyl esters, derived from plant oil triglycerides, were functionalized to create polymerizable groups. A polymer was obtained through the polymerization of an internally plasticizing and crosslinking long chain methyl ester and one or more copolymerizable unsaturated monomers. The PSA was created containing an aqueous dispersion of a mixture of the synthesized polymer and a surface-active agent.

Zhu and Wool explored the synthesis of nanoclay reinforced soybean oil-based elastomers.⁶⁰ Acrylated oleic methyl ester was synthesized from triglycerides and was filled with nanoclay to synthesize a soybean oil-based elastomer. The nanoclay was able to be intercalated up to 15 wt % clay, but not exfoliated. Tensile strengths of the resulting elastomers increased linearly from 0.08 to 0.58 MPa as nanoclay content increased from 0 to 10 wt %, while the elongation at break increased from 85% to 190% , and the initial degradation temperature increased from 133 to 150 °C. Furthermore, the results indicated that the resulting polymers biodegrade and degradation rate is slightly increased with addition of nanoclay.

Lignin

Lignin is a highly crosslinked biopolymer that is found in the cell walls of vascular plants and is produced in excess of 50 million tons annually.⁶¹ The molecular structure of lignin is determined by the ratio of three primary precursors, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, and can vary significantly between different species of plants.^{62,63} The majority of industrial lignin is produced as a waste product from the Kraft process in the pulp and paper industry and burned for low-value energy recovery.⁶¹ Due to the aromatic nature of lignin (Figure 2), there is potential for lignin to be utilized as a feedstock for benzene-based aromatic polymers and fine chemicals when strategically depolymerized that cannot be readily generated from other common renewable sources. Additionally, macromolecular lignin could be chemically modified to enable utilization and bonding into a polymer network to stiffen the material and perhaps improve thermal properties.

In 2004, Thielemans and Wool examined the use of butyrate kraft lignin as a compatibilizing agent for natural fiber reinforced thermoset composites.⁶⁴ Butyrate kraft lignin (BKL) was added to an unsaturated thermosetting resin mixture of AESO and styrene. The BKL was found to improve the interfacial adhesion between the resin and reinforcing flax fibers. Solubilizing the BKL into the AESO resin resulted in viscosity increases from 165 to 400 cP for 10 wt % BKL. Composites made with short wheat straw, which allow for better resin penetration and fiber wetting, exhibited a flexural strength of 29 MPa for an addition of 5 wt % BKL. Thielemans and Wool also investigated the sedimentation of lignin onto flax fibers for use in natural fiber composites in 2005.⁶⁵ By treating flax fibers with lignin, fiber wettability was improved and the contact angle between the fiber and resin decreased. This resulted in improved mechanical properties of the fiber composites when compared to lignin-free composites. Lignin was also used to investigate the solubility of modified lignin into nonpolar solvents such as styrene for use in unsaturated polyester and vinyl ester resins.⁶⁶ Both pine kraft lignin and hardwood kraft lignin were modified to create butyrate lignins and butyrate/methacrylate lignins. The solubility behavior of the modified lignin was able to be described by the Flory-Huggins solubility theory. The modified lignin was fully soluble in styrene, allowing the modified lignin to be incorporated into the composites.

In 2012, Stanzione, Wool, and others investigated the use of lignin-based monomers for composite applications to replace styrene.⁶⁷ Lignin model compounds, guaiacol, eugenol, and vanillin, were investigated as bio-based starting materials to synthesize reactive diluents for liquid molding resins. Guaiacol, eugenol, and vanillin were methacrylated via esterification with methacrylic anhydride and a catalytic amount of DMAP. Methacrylated guaiacol (MG) and methacrylated eugenol (ME) were shown to be potential bio-based reactive diluent replacements for styrene in liquid molding resins. Both MG and ME were low viscosity, nonvolatile liquids at 25 °C. MG and ME exhibited viscosities of 17.1 and 27.9 cP, respectively. Both MG and ME were blended with a commercial vinyl ester resin (bismethacryl glycidyl ether of bisphenol A, VE828) and the cured resins possessed T_g s of 127 and 153 °C, respectively, via differential

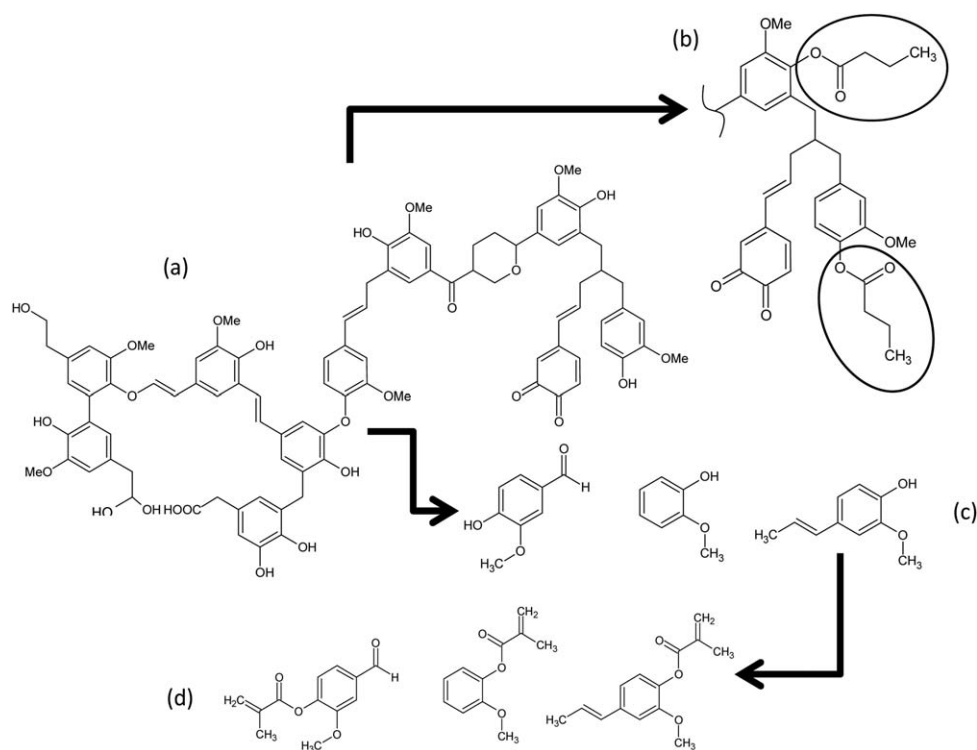


Figure 2. (a) Lignin structure. (b) Butyrated lignin structure. (c) Lignin model compounds. (d) Methacrylated lignin model compounds.

scanning calorimetry, which is comparable to that of commercial VE828-styrene based cured resins. Methacrylated vanillin (MV) was a solid at 25 °C; thus, significantly limiting its viability as an effective reactive diluent. However, vanillin was later investigated as a potential basis to create a bio-based resin. Vanillin was methacrylated using a two-step, one pot synthesis to create a vinyl ester resin with a 1:1 mole ratio of MV (mono-functional monomer) to glycerol dimethacrylate (cross-linking agent).⁶⁸ The synthesis pathway utilized was solventless, required minimal amounts of catalysts, and moderate reaction temperatures while no by-products were generated. The resin exhibited a viscosity of 87 cP at 25 °C, and the cured resin produced a thermoset with a broad T_g of 155 °C, based on the $\tan \delta$ thermogram, and a temperature of maximum decomposition rate of 426 °C in a nitrogen atmosphere. The potentially 100% bio-based cured resin produced comparable thermomechanical and thermogravimetric properties to that of commercial vinyl ester cured resins while eliminating VOC and HAP components and emissions.

Lignin has the potential to yield valuable bio-oils consisting of aromatic molecules when strategically depolymerized. These lignin-based bio-oils were investigated to determine if a bio-oil can be utilized in the development of bio-based vinyl ester resins without requiring extensive separations.⁶⁹ A methacrylated lignin-based bio-oil mimic was synthesized and used as a low viscosity reactive diluent in a standard commercial vinyl ester resin (VE828). The methacrylated bio oil was comprised of phenol, guaiacols, and catechols that were methacrylated via esterification with methacrylic anhydride. Curing of the VE828-methacrylated bio-oil resin resulted in hard transparent thermo-

sets with temperatures of maximum decomposition rate greater than 400 °C and initial decomposition temperatures greater than 300 °C in a nitrogen atmosphere. The cured resins also exhibited T_g s greater than 115 °C, based on the loss modulus thermograms and storage moduli greater than 2.5 GPa at 25 °C. The thermogravimetric and thermomechanical properties of the cured resins were comparable to that of commercial petroleum-based and vinyl ester-based high-performance cured resins.

Expanding on this work of lignin-based monomers, Holmberg, Wool, and others investigated functionalized lignin model compounds for use in generating designer block polymers for elastomers and other applications.^{70,71} Renewable homopolymers and block polymers were synthesized from vanillin via functionalization and reversible addition-fragmentation chain transfer (RAFT) polymerization. The T_g of the vanillin-based homopolymer was found to be 120 °C via differential scanning calorimetry with degradation temperatures above 300 °C in a nitrogen atmosphere, which are comparable to polystyrene. Block polymers were synthesized by chain extending the vanillin-based homopolymer with lauryl methacrylate, which is a model fatty-acid derived monomer. The copolymers were shown to be able to self-assemble into a body-centered cubic sphere morphology with the hard, vanillin-based blocks surrounded by the soft lauryl methacrylate block. The controlled polymerization of lignin model compounds and the subsequent chain extension with a different comonomer enables the design and synthesis of bio-based homopolymers and block polymers with adjustable properties.

Most recently, Wool and others submitted a patent application on the development of Bisphenol alternatives derived from

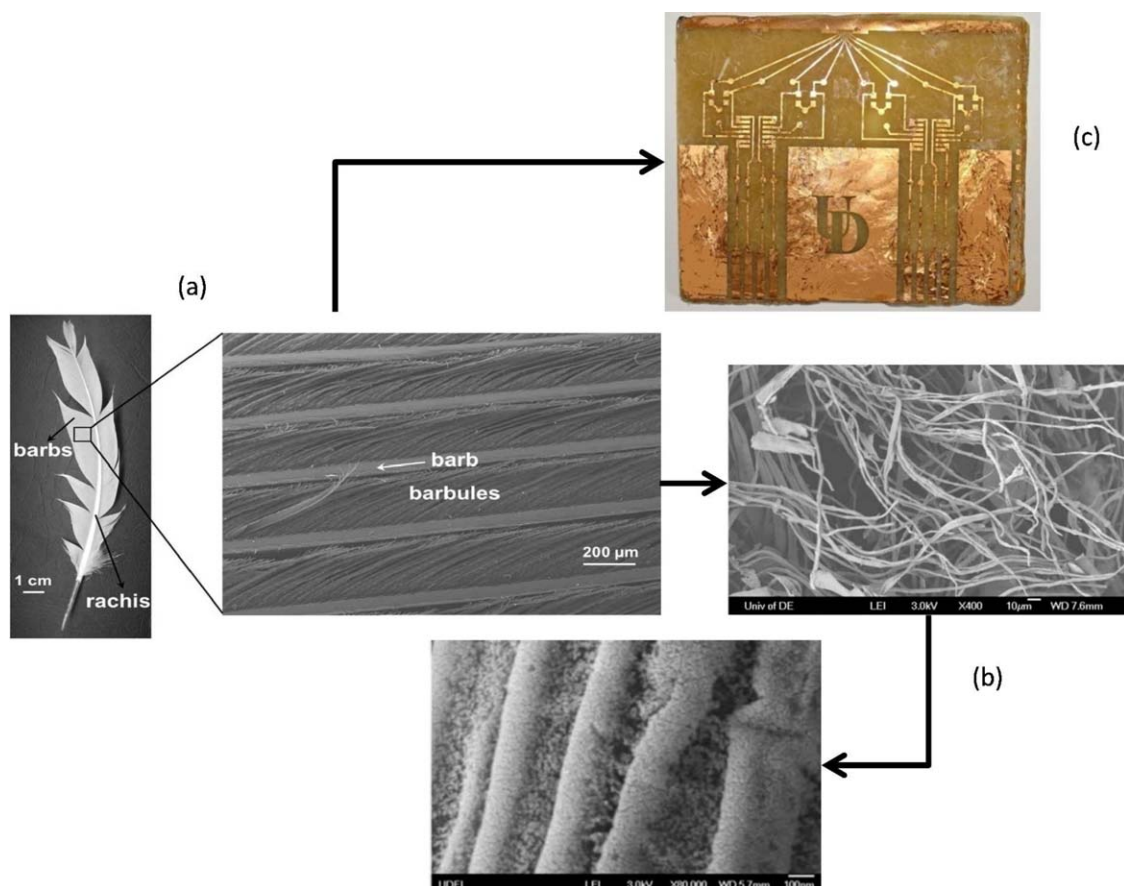


Figure 3. (a) The branch structure of a chicken feather. (Reproduced from [82], with permission from Society of Plastics Engineers.) (b) Adsorbent material from chicken feathers. (Reproduced from [78] with permission from John Wiley & Sons.) (c) Printed circuit board composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

renewable substituted phenolics.⁷² In particular, they showed that vanillyl alcohol and guaiacol, which can be derived from lignin, can be combined to produce a bisphenol alternative, bisguaiacol F. The resulting compound is anticipated to have significantly reduced toxicity relative to bisphenol A, a known endocrine disruptor.⁷³ Epoxy-amine, vinyl ester, methacrylates, and polycarbonates were prepared from bisguaiacol F. The resulting polymers had slightly lower thermal (15–20 °C) properties relative to bisphenol A polymers, likely due to the loss of the rigidizing methyl groups on the methyl bridge connecting the phenyl units.

Chicken Feathers

Natural fibers are considered to be a renewable and independent resource that has the potential to replace synthetic petroleum-based fibers. Four billion pounds of chicken feathers are generated in the United States and can be utilized as a natural feedstock for the production of bio-based fibers.⁷⁴ Chicken feathers are keratin-based materials composed of two dissimilar segments, barbs, and barbules, as shown in Figure 3. Barbs are thicker with diameters in the range of 30–100 μm where barbules originate from the barb fibers and have diameters of approximately 6 μm.^{75,76} Chicken feathers are considered to be waste, which require costly disposal; however, utilizing chicken feather fibers for the production of composites provides profits

for the poultry industry as well as introduces a solution for chicken feather disposal.

In 2005, Hong and Wool investigated the use of chicken feather fibers (CFFs) for the application of bio-based composites.⁷⁷ CFFs were utilized in a volume fraction of 30% with AESO. The hollow CFFs were not filled by resin infusion, resulting in a significant amount of air retained within the hollow structure of the CFFs. Due to the retention of air within the fibers, the dielectric constant for the composite was in the range of 1.7–2.7, which is significantly lower than that of conventional silicon dioxide, epoxy, or polymer dielectric insulators which possess dielectric constants in the range of 3.8–4.2; however, the composite has a low enough coefficient of thermal expansion (similar to that of silicon materials or polyimides used in printed circuit boards) for electronic applications. Incorporating CFFs into the AESO resin enhanced the storage modulus at 40 °C from 1.3 to 2.1 GPa, enhanced the fracture toughness from 1.5 to 1.8 MPa, and enhanced the flexural strength from 34.8 to 45.2 MPa and the flexural modulus from 0.9 to 1.6 GPa.

Senoz and Wool examined the conversion of CFFs into high temperature resistant and adsorbent fibers through a two-step pyrolysis method in 2010.⁷⁸ The first step to the pyrolysis method occurred at 215 °C for 24 h and provided a fibrous structure with no subsequent melting, while the second step,

occurring at 400–450 °C for 1 h, resulted in a microporous material that exhibited narrower pore size distributions relative to commercially available activated carbons. The pores of the pyrolyzed CFFs had diameters less than 1 nm, meaning the pyrolyzed CFFs could be used in applications such as hydrogen storage, adsorption, and small gas molecule separation. Senoz, Wool, and others further investigated the physical and chemical changes of CFFs during pyrolysis in 2012.⁷⁹ The experimental data showed that disulfide bond cleavage and peptide crosslinking occurred simultaneously and suggested that crystalline melting is dependent on disulfide bond cleavage. By carefully tuning the torrefaction profile, conditions were able to be achieved such that useful fibrous material could be obtained. The pyrolyzed CFFs were further tested for the application of hydrogen storage.⁸⁰ The pyrolyzed CFFs were able to adsorb 0.4 wt % excess hydrogen at room temperature and 1.5 wt % excess hydrogen at 77 K (−196.15 °C) due to their microporous nature. Due to the large availability of chicken feathers and the ability to store significant amounts of hydrogen, pyrolyzed CFFs have the potential to provide a solution to the issue of hydrogen storage in an environmentally friendly and bio-renewable fashion. In 2013, Senoz, Wool, and others later investigated the use of pyrolyzed CFFs within composite materials.⁸¹ Pyrolyzed CFFs were incorporated into AESO and methacrylated lauric acid resins to add reinforcement for low density and rubbery polymer applications. Storage moduli, tensile moduli, tensile strengths, and fracture toughnesses of the composites were all found to be directly proportional to fiber content. By varying fiber content, a wide variety of mechanical properties were able to be achieved such as storage moduli in the range of 20–300 MPa and tensile moduli in the range of 10–150 MPa. These properties are generally too low for structural composites applications due to the low T_g of the resulting material, but could make these useful for adhesives or elastomeric materials.

In 2011, Zhan and Wool studied the mechanical properties of CFFs for use in composites.⁸² The mechanical properties of the feather barbs were investigated from a statistical standpoint. The tensile modulus and tensile strength of the CFFs were found to be approximately 3.6 and 203 MPa, respectively. It was found that the variances of tensile modulus and tensile strength for different feathers were significant, most likely due to the vast heterogeneity of the CFFs. Zhan, Wool, and others further investigated the use of CFF reinforced epoxy composites for electrical applications.^{83,84} Composites with epoxy, CFFs, and E-glass fibers were fabricated and investigated for the potential application of printed circuit boards (PCBs). The CFF composites had electrical resistivities that were two to four orders of magnitude higher than that of E-glass fiber composites. The composites with hybrid fibers possessed a similar dielectric constant and loss tangent to commercial PCBs, showing that the CFFs could potentially be used for PCB applications. Zhan and Wool further explored the development of greener materials for PCBs in 2013.⁸⁵ Bio-based composites were synthesized from phthalated AESO, CFFs, and E-glass fibers and investigated as potential replacements for traditional E-glass fiber reinforced epoxy composites in PCBs. The bio-based composites exhibited flexural strengths in the range of 84–100 MPa and flexural mod-

uli in the range of 8.7–10.5 GPa, dielectric constants of approximately 0.02, coefficients of thermal expansion in the range of 19.4–29.2 ppm °C^{−1}, and flammability characteristics that were comparable to that of traditional composites for PCB applications. Zhan and Wool investigated the thermal expansivity of CFFs reinforced epoxy composites.⁸⁶ CFFs were found to have negative coefficient of thermal expansion values that were temperature dependent in the axial direction due to their semi-crystalline structure and positive coefficient of thermal expansion values in the radial direction. The utilization of CFFs in composite materials was found to reduce the overall coefficient of thermal expansion and minimize the coefficient of thermal expansion mismatch between composites and other components.

TWINKLING FRACTAL THEORY

A fundamental understanding of the nature and structure of the glass transition in amorphous materials is currently seen as a major unsolved problem in solid-state physics, including that of polymers. Wool proposed the Twinkling Fractal Theory (TFT), of which the main element is the development of dynamic percolating fractal structures near the glass transition.^{87,88} The key concept of the TFT is derived from the Boltzmann population of excited states in the anharmonic intermolecular potential between atoms, coupled with percolating solid fractal clusters near T_g . As the glass transition is approached from above, dynamic solid fractal clusters begin to form and will percolate rigidity. The percolation cluster is a solid fractal which, to the observer, appears to “twinkle” as glassy/solid and rubbery/liquid clusters interchange in dynamic equilibrium. The TFT describes the molecular weight dependence and role of crosslinks on the T_g for polymers, as well as the Flory-Fox rule of mixtures. Wool and Campanella investigated the rate dependence and time-temperature superposition of the TFT.⁸⁹ The rate dependence of T_g for both differential scanning calorimetry thermal heating and cooling rates as well as dynamic mechanical analysis frequencies were described by the TFT. The TFT was also found to describe the rate and temperature dependence of the yield stress in polymers and the strong and fragile nature of the viscosity behavior of liquids. Stanzione, Strawhecker, and Wool observed the twinkling fractal nature of the glass transition, supporting the TFT.⁹⁰ The twinkling fractal characteristics of amorphous atactic polystyrene were captured using atomic force microscopy. Two-dimensional height atomic force microscopy images showed that the percolated solid fractal clusters have lifetimes that are cluster size dependent and exist for longer time scales at lower temperatures. Both the fractal dimensions and cluster lifetimes were found to be in agreement with the TFT, exhibiting experimental evidence for the twinkling fractal nature of the glass transition.

OTHER SUSTAINABLE POLYMERS RESEARCH

The production of textiles, apparel, and footwear causes resource depletion and environmental pollution, among other problems. Water-resistant, breathable, composites as leather substitutes (eco-leather), a thermosetting resin, and a hard composite from bio-based sources such as plant oils, natural fiber cloth,

and chicken feather fibers were developed.^{91,92} These materials, combined with commercially available and environmentally friendly natural textiles, were utilized to make coats and shoes. Wear tests and questionnaire surveys conducted proved that the environmentally friendly materials used in the coats and shoes were comfortable for the wearer. The renewable bio-based materials developed from plant oils and natural fibers were described as wearable, versatile, and practical. Wearers expressed that they would be interested in buying apparel and footwear products made from these environmentally friendly materials as long as the design and style met their requirements.

Wool, Schiltz, and others hold a patent for the formation of an injection moldable biodegradable starch polymer composite.⁹³ The invention provides an injection moldable, biodegradable plastic containing corn starch, low-density polyethylene, ethylene acrylic acid copolymer, and glycerol and details an improvement to form an injection moldable plastic by neutralizing the acidic portion of the ethylene acrylic acid copolymer by the addition of sodium hydroxide. Also, the invention details a method for forming an injection moldable biodegradable plastic by either premixing a quantity of ethylene acrylic acid copolymer with a quantity of polyethylene then subsequently adding corn starch and sodium hydroxide or premixing a quantity of corn starch and sodium hydroxide then subsequently adding ethylene acrylic acid and maintaining the overall temperature between approximately 71 and 93 °C during mixing.

CONCLUSIONS

Richard P. Wool led the development of bio-based polymers from various renewable resources. His realization that plant oils can be chemically modified to produce crosslinkers analogous to unsaturated polyesters was novel through modification of the fatty acid unsaturation, the triglyceride glycerol center, or both. This enabled development of structural polymers and composites from plant oils and was a major development in the field. Acrylated epoxidized soybean oil, maleinized acrylated epoxidized soybean oil, and maleinized soy oil monoglyceride are a number of the key resins that he helped develop. For structural resins and composites, having higher degrees of functionalization resulted in higher T_g , strength, and modulus, but also generally resulted in higher resin viscosities, but less than that of the family of UPE monomers. Furthermore, some approaches were shown, such as use of monomethyl maleate that can be used to keep resin viscosity relatively low. This work further demonstrated that renewable reinforcements, such as flax and chicken feathers, can be used to produce good structural composites using plant oil resins while having very high renewable contents. These composites are able to be produced using liquid molding and sheet molding compound manufacturing processes. Modifications to lignin allowed the incorporation of lignin into plant oil resins to further increase the renewable content while improving certain key properties. Wool's research also demonstrated the ability to produce pressure sensitive adhesives and polyurethane foams from plant oil. To enable improved properties, he began investing the use of chemicals derived from lignin to make high-performance polymers. His work demonstrated the ability to produce high-performance styrene replacements to obtain sustainable vinyl esters and unsatu-

rated polyester resins. Through his teachings, the use of lignin-derived chemicals to synthesize bisphenol A replacements for numerous polymer applications have been developed. During all of this chemistry work, he continued to develop a physical and understanding of polymeric materials including gaining a more fundamental understanding of adhesion,⁹⁴ reputation dynamics,⁹⁵ and of the glass transition and its impact on polymer properties.^{87–90} All of his work has helped to enable a paradigm shift in renewable polymer development. Richard Wool has left behind a legacy that has been taken up by other research groups including Palmese, La Scala, Stanzione, Bonnaille, Larock, Kessler, Webster, Thielemans, Epps, Sun, Kusefoglu, and others.^{28,70,96–103} In addition, he has commercialized the AESO, MAESO, other modified plant oils, and eco-leather based on maleinized oils and chicken feathers to directly increase the sustainability of polymeric materials for commercial applications.

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