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A High-Performance Recycling Solution for Polystyrene Achieved by the Synthesis of Renewable Poly(thioether) Networks Derived from *D*-Limonene

Keith Hearon,

Department of Biomedical Engineering, Texas A&M University, 3120 TAMU, 5045 Emerging Technologies, College Station, Texas 77843-3120, USA

Landon D. Nash,

Department of Biomedical Engineering, Texas A&M University, 3120 TAMU, 5045 Emerging Technologies, College Station, Texas 77843-3120, USA

Jennifer N. Rodriguez,

Department of Biomedical Engineering, Texas A&M University, 3120 TAMU, 5045 Emerging Technologies, College Station, Texas 77843-3120, USA

Alexander T. Lonnecker,

Department of Chemistry, Texas A&M University, PO Box 30012, College Station, TX 77842-3012, USA

Dr. Jeffery E. Raymond,

Department of Chemistry, Texas A&M University, PO Box 30012, College Station, TX 77842-3012, USA

Dr. Thomas S. Wilson,

Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550-9234, USA

Prof. Karen L. Wooley, and

Department of Chemistry, Texas A&M University, PO Box 30012, College Station, TX 77842-3012, USA

Prof. Duncan J. Maitland

Department of Biomedical Engineering, Texas A&M University, 3120 TAMU, 5045 Emerging Technologies, College Station, Texas 77843-3120, USA

Keith Hearon: keith.hearon@poly6.com

Abstract

Nanocomposite polymers have been prepared using a new sustainable materials synthesis process in which *D*-Limonene functions simultaneously both as a solvent for recycling polystyrene (PS)

waste and as a monomer that undergoes UV-catalyzed thiol-ene polymerization reactions with polythiol co-monomers to afford polymeric products comprised of precipitated PS phases dispersed throughout elastomeric poly(thioether) networks. These blended networks exhibit mechanical properties that greatly exceed those of either polystyrene or the poly(thioether) network homopolymers alone.

Keywords

renewable polymers; recycling; nanocomposites; thiol-ene click chemistry

As consumer demands drive increased global production of plastic products and waste, the need for innovative strategies for improving environmental sustainability continues to grow. As long as non-environmentally degradable plastics are produced, the development of improved recycling techniques must continue in order to decrease additional material consumption and to reduce non-degradable plastic waste content in landfills.^[1] There is hope that progress in polymer science will eventually give rise to alternative plastic materials that may eliminate the need for the production of petroleum-based and other non-degradable plastics altogether, and recent studies have investigated the development of naturally based polymers, such as polycarbonates derived from coffee extracts,^[2] terpene-^[3] and fatty acid-derived^[4] heteropolymers and cellulose-based polymer composites,^[5] among others. One drawback that often surrounds sustainable materials development is the seemingly pervasive notion that improving the environmental suitability of materials comes with a sacrifice in material functionality.^[6] Studies reporting material selection strategies often weigh material capabilities against environmental sustainability,^[7] and recycling processes in general are assumed to bring about some degree of material deterioration.^[8] This work is built upon an alternative premise, that the development of new sustainable materials with increased inherent value (i.e., well-engineered, value-driving material properties) is possible through innovative design at the materials engineering level. We report a novel approach to sustainable materials development that is based upon a new strategy for thermoplastic polymer recycling with a notable advancement in renewable polymer synthesis. By combining petroleum-derived polymers with bio-based monomer feedstocks, biphasic, blended polymer products are produced and are shown to exhibit facile tunability of physical and material properties. This one-pot, solvent-based recycling approach yields neat recycled products without the use of solvent evaporation or solute precipitation, and the functional utility of the resulting polymer blends greatly exceeds that of either homopolymer alone.

Reported herein is a new method for recycling polystyrene (PS), in which special consideration is given to expanded polystyrene (EPS) waste used in food and beverage packaging applications. The difficulties associated with EPS recycling have been widely publicized. It is estimated that over 3 million tons of EPS are produced each year globally, with roughly 70% of EPS products being single-use food and beverage packaging.^[9] Because both transporting low-density EPS waste and cleaning it to remove contaminant residue greatly increase cost and time required for EPS recycling, an overwhelming majority of food-contaminated EPS waste is not recycled.^[10] EPS recycling is often sub-categorized

using three groups: (1) material recycling, the reduction of EPS volume using compression or dissolution in solvent; (2) chemical recycling, the breaking of covalent bonds to regenerate monomers or other small molecules; and (3) thermal recycling, the combustion of EPS waste to generate energy.^[11] The simplest and most common method of recycling EPS is material recycling by mechanical compaction, and mechanical EPS densifiers are commercially available from multiple sources.^[12] Since mechanical densifiers require that EPS be contaminant free before compaction, mechanical densification is not ideal for recycling food or drink contaminated waste items. Solvent-based material recycling has been shown to be tolerant of some contaminated EPS substrates because many contaminants are insoluble in solvents that dissolve EPS and can be removed using coarse filtration after EPS dissolution.^[13] The solubility and behavior of EPS in multiple solvents has been previously reported.^[14] Polystyrene has been shown to be soluble in aromatic solvents such as toluene, and studies have also reported the solubility of PS in the naturally occurring citrus fruit extract *D*-limonene,^[15] which has a similar dielectric constant to that of toluene.^[15, 16] In the late 1990's and early 2000's Sony Corporation instituted a solvent-based recycling effort in Japan, in which *D*-limonene was used to recycle EPS waste, which was reclaimed from solution by evaporation of *D*-limonene. Sony's report of this recycling process is extremely in-depth, but this recycling effort appears to have been abandoned sometime between 2004 and 2006.^[17] Considering the low inherent value of recycled polystyrene, Sony's apparent decision to cease this recycling effort may have been financially motivated. Other studies have reported limonene-based recycling processes in which PS is reclaimed from solution in limonene using electrospinning^[18] or by precipitation by mixing with supercritical carbon dioxide.^[19]

The primary novelty in the present study stems from the idea that *D*-limonene can both dissolve polystyrene and can also function as a diene monomer in thiol-ene reactions to enable a new method of PS reclamation from solution. Thiol-ene "click" chemistry is a powerful synthetic tool that is being implemented in increasingly diverse areas of polymer science.^[20] The reaction between C=C and SH functional groups, which is often UV catalyzed but can also proceed under elevated temperature conditions, is highly efficient, tolerant of many functional groups, and capable of proceeding under mild conditions.^[21] A number of network polymers have been prepared from polyfunctional alkene and polythiol monomers and utilized in applications ranging from medical to commodity devices.^[22] *D*-Limonene, shown in Figure 1, consists of two C=C groups and is, theoretically, capable of functioning as a monomer in thiol-ene polymerization reactions with a co-monomer such as trimethylolpropane tris(3-mercaptopropionate) (TMPTMP). A poly(thioether) network synthesized from *D*-limonene would thus be, by definition, derived from a naturally-occurring precursor. We observed that at temperatures near 25 °C, *D*-limonene and TMPTMP mixtures are immiscible, although brief 365 nm UV irradiation and/or heating eventually results in the formation of a homogeneous solution that can be transferred to a mold without further network formation occurring until subsequent exposure to UV irradiation. Previous studies have reported the synthesis of polymers through multi-step processes in which *D*-limonene is first functionalized and then subjected to various methods of polymerization,^[23, 24] and in a recent study, the reactivities of the double bonds in limonene with various thiol groups are reported.^[25] However, to our best knowledge, none

of these studies has reported the bulk thiol-ene polymerization and thermomechanical characterization of a network polymer consisting solely of *D*-limonene and a polythiol co-monomer. The ester linkages in TMPTMP also afford the synthesis of a poly(thioether) network that is biodegradable, and Claudino, *et al.* have noted this concept and proposed the use of limonene-*co*-poly(mercaptopropionate) networks as synthetic materials for degradable tissue scaffolds.^[25]

Because of the flexible nature of the thioether linkage, many poly(thioether) networks are elastomeric and possess poor mechanical integrity at and above 25 °C.^[26] Such elastomeric behavior was predicted for the *D*-limonene-based network homopolymer whose synthesis is shown in Figure 1 and was observed upon neat polymer synthesis and handling. The addition of PS additives to this poly(thioether) network was predicted to increase modulus and improve toughness and mechanical strength, and the synthesis of biphasic polymer blends comprised of PS additives dispersed in limonene-*co*-polythiol networks was therefore attempted both to improve network mechanical integrity and to demonstrate a new method of PS recycling. It is well-known that the functional utility of PS can be increased by the synthesis of PS/rubber blends or co-polymers, and high impact polystyrene (HIPS) can be prepared by dissolving a thermoplastic such as polybutadiene in styrene and curing the solution to produce biphasic materials. These polymers possess improved mechanical strength and toughness in comparison with that of PS.^[27] Other studies have reported the synthesis, microstructural imaging, and thermomechanical characterization of other thermoset/thermoplastic heteropolymer blends, including PMMA, PS and polyurethane additives in polyester network matrices^[28] and polyetherimide additives in epoxy network matrices.^[29] To our best knowledge, a polymer blend comprised of a thermoplastic additive dispersed in poly(thioether) matrix has yet to be reported.

The novel process reported herein enables the simultaneous densification, purification, and reclamation of food or beverage-contaminated EPS waste. As shown in Figure 2(a), food or drink-contaminated EPS waste can first be immersed in a reservoir containing *D*-limonene. After mixing and EPS dissolution in *D*-limonene, a liquid bilayer forms. In the last image in Figure 2(a), the bottom layer consists of Coca-Cola™ and the top layer consists of an EPS cup provided by Chick-fil-A, Inc. dissolved in *D*-limonene ($M_w \sim 396$ kDa). Through basic extraction, the bottom layer contaminants can be drained, and upon coarse filtration, a purified solution of polystyrene in *D*-limonene remains. As shown in Figure 2(b), reclamation of polystyrene is achieved by addition of polythiol co-monomer and photoinitiator and subsequent heating to 140 °C, which results in a homogeneous dissolution of all species. Pouring of this hot solution into a pre-heated mold and subsequent UV irradiation causes the formation of an elastomeric poly(thioether) network, after which phase separation of polystyrene proceeds, producing dispersed polystyrene microphases and/or nanophases throughout the network. Demonstrating the change in optical behavior from transparency to opacity that occurs upon PS heterophase addition to *D*-limonene-*co*-polythiol networks, macroscale images of *D*-limonene-*co*-TMPTMP films containing 0% and 30% PS additives are provided in Figure 2(c). The iPhone 4™ protective case prototype pictured in Figure 2(b) was fabricated to demonstrate the processability of these new materials into a geometry representative of that of a potential industrial application.

We synthesized blended polymers containing recycled PS additives dispersed in α -limonene-co-polythiol network matrices to create a series of polymer blends with greater toughness than either homopolymer exhibits individually. α -Limonene functions simultaneously as a solvent for dissolving polystyrene (PS) waste and as a monomer that undergoes UV-catalyzed thiol-ene polymerization reactions with polythiol co-monomers to afford polymeric products comprised of precipitated PS phases dispersed throughout elastomeric poly(thioether) networks. By varying PS additive composition, we sought to achieve tailorability of microstructural morphology, modulus, toughness, tensile strength and strain capacity in order to demonstrate a broad application range for the new material system. We believe that this work marks the first instance in which the successful bulk synthesis and mechanical characterization of network polymers comprised solely of α -limonene and polythiol co-monomers are reported in the literature, and the demonstrated synthetic utility of this naturally-derived polymer system as a new PS recycling strategy provides a unique materials-based avenue to achieving environmental sustainability, while combining non-renewable and renewable materials to produce blended networks that exhibit remarkable mechanical properties.

In order to understand the effects of increasing PS additive composition on microstructural morphology, SEM images of samples containing 0, 10, 20, and 30% overall weight fraction PS were taken and are provided at 3000 $\times$ magnification in Figure 3. For the SEM images in Figure 3, the samples were prepared by immersion in liquid nitrogen, cold fracturing, attempted thermoplastic PS phase extraction using dichloromethane, sample drying, and gold sputtering prior to imaging. Consequently, the more lightly-colored phases in Figure 3 correspond to poly(thioether) networks, and any cavities shown represent empty space that corresponds to extracted thermoplastic PS phases. In general, poly(thioether) network phases appear to decrease in average size with increasing PS composition, although the specific morphologies corresponding to the varying PS phases are notably different in nature. In Figure 3(a), 0% PS shows only a single poly(thioether) phase, and in Figure 3(b), 10% PS shows what appear to be ~ 3 -5 μm sized cavities corresponding to PS phases that were dispersed throughout a network matrix similar to that shown in 3(a). In Figure 3(c), 20% PS appears to have generated a bimodal microstructural morphology with spherical $\sim 3\mu\text{m}$ network phases and cavities that could correspond to PS microphases of similar size and geometry. In Figure 3(d), the network obtained following extraction of the 30% PS composition appears to exhibit a bimodal microstructure with spherical network and PS phases that are sub-micron in size and of similar homogeneity and distribution to the 20% PS sample in 3(c). Our interpretation of the SEM images is limited to a qualitative assessment to confirm that phase segregation had occurred uniformly throughout the matrix material, as quantitative interpretation is complicated by potential perturbations to the initial blended networks during the processing steps.

While SEM provides some insights into the microstructure of the bulk phase, direct evaluation of the surface morphology of the composite system was also performed. Given the importance of exposed-face character to mold release properties, bioactivity and tribological response, it is critical to assess the intrinsic phase behavior and topography at the surface. To provide such characterization, atomic force microscopy (AFM) of the

composite systems at 0, 10, 20 and 30% PS weight fraction were obtained. Topographic maps of the micrographs of the assessed systems are provided at two separate scales, $20\ \mu\text{m} \times 20\ \mu\text{m}$ and $3\ \mu\text{m} \times 3\ \mu\text{m}$ and are provided in Figure 3(e). The $3\ \mu\text{m} \times 3\ \mu\text{m}$ rendering also has phase contrast overlaid to elucidate phase boundaries where present. While generally following the trends observed in SEM, the findings for this series can be summarized as follows: (1) 0% PS displayed a small amount of residual processing residues, exhibited exceptional flatness with shallow pitting (*ca.* 10 nm deep) and had no indication of intrinsic phase boundaries, (2) 10% PS displayed some PS sheeting at the microscale, similar to the gaps observed by SEM and possessed *ca.* 500 nm PS phase domains at smaller scale, (3) 20% PS displayed the largest microscale heterogeneity, exhibited the roughest surface morphology of the samples observed, had pitting and protrusions consistent with the scale of the features observed in the solvent etched PS SEM figures, and displayed microscale phase separation wherein the PS domain expressed smaller sub-domains on scales similar to that observed in the 10% PS system, and (4) the 30% PS sample presented an overall more homogeneous surface on the microscale with periodic large protrusions which appeared to be surface buckling; in the homogeneous regions, fully isolated PS nanodomains (<200 nm) saturated the landscape.

To determine the effects of increasing polystyrene composition on the thermomechanical behavior of the *D*-limonene-*co*-TMPTMP networks imaged in Figure 3, dynamic mechanical analysis (DMA) experiments were run in tension on 0, 10, 20, and 30 wt% PS samples. Figure 4(a) shows plots of storage modulus *versus* temperature for *D*-limonene-*co*-TMPTMP, -PETMP, and -DPEHMP networks. The increase in rubbery modulus from TMPTMP to PETMP-based networks as polythiol functionality increases from 3 to 4 is expected and indicates an increase in crosslink density with increased monomer functionality. The lack of an increase in rubbery modulus from PETMP to DPEHMP as functionality increases from 4 to 6 is most likely the result of poor monomer miscibility and high DPEHMP viscosity, which could prevent the reaction of functional groups and prevent network formation. Figures 4(b), 4(c) and 4(d) show DMA characterization data for *D*-limonene-*co*-TMPTMP networks containing varying PS additive compositions. Plots of (b) storage modulus, E' , (c) loss modulus, E'' , and (d) tangent delta *versus* temperature for each PS composition are shown, and each PS-containing rubber whose DMA is shown in Figures 4(b-d) exhibits a thermal transition below $-10\ ^\circ\text{C}$ that is consistent with the glass transition of the *D*-limonene-*co*-TMPTMP poly(thioether) network and also exhibits a thermal transition near $100\ ^\circ\text{C}$ that is consistent with the glass transition of polystyrene. As polystyrene composition increases, the storage and loss modulus of each sample increase with a clear trend at temperatures between the glass transition of the rubber network and the glass transition of polystyrene. Figure 4(e) shows that both E' and E'' increase roughly two orders of magnitude at $25\ ^\circ\text{C}$ as PS composition is increased from 0 to 30%. The toughening effect that arises from creating a material with combined glassy and rubbery phases is demonstrated in Figure 4(f), which shows average strain-to-failure data for 0%, 30% and 100% PS *D*-limonene-*co*-TMPTMP samples at $25\ ^\circ\text{C}$. While the 100% PS material exhibits brittle behavior at $25\ ^\circ\text{C}$ and fails at 1.8% strain and the 0% PS material exhibits weak elastomeric failure and fails at a stress of 1.2 MPa, the 30% PS material exhibits a more ductile behavior and fails at 55% strain while also exhibiting a failure stress greater than 12

MPa. While the average toughness of the 100% PS sample at 25 °C was $0.34 \pm 0.06 \text{ MJ/m}^3$ and that of the 0% PS sample was $0.13 \pm 0.02 \text{ MJ/m}^3$, that of the 30% PS sample was $5.03 \pm 0.82 \text{ MJ/m}^3$. This increase in toughness at 25°C of more than an order of magnitude in comparison with that of either homopolymer is promising, and a toughness of $\sim 5 \text{ MJ/m}^3$, while lower than that of poly(acrylonitrile-*co*-butadiene-*co*-styrene (ABS) and some other high-performance HIPS resins reported in the literature, actually exceeds reported toughness values for a number of HIPS materials.^[30] The thermomechanical behavior as a function of PS fraction, taken in conjunction with the micro- and nano-domain features observed for the PS phase in this series by SEM and AFM, indicate that the observed toughening for the 30% PS material can be explained by the existence of a high number of nanodomains, which allow expression of a large surface to volume ratio for the PS fraction.

In this work, we report a multicomponent process for sustainable materials development that combines an innovative polystyrene recycling technique with a breakthrough achievement in renewable polymers synthesis to afford a new polymer system with tunable physical and material properties. Through a well-engineered material design strategy, blended polymeric materials comprised partly of recycled thermoplastic PS components and partly of *D*-limonene-derived poly(thioether) network components exhibit mechanical integrity that greatly exceeds that exhibited by either component alone. By varying PS composition between 0 and 30 wt %, storage modulus at 25°C can be tuned over the range of 1 to 370 MPa, and these materials consequently may be suitable for use in a diverse array of polymeric applications. One set of applications that appears promising is that of impact resistant polymers, and the fabrication of a cellular phone protective case prototype was demonstrated in this work to provide an example of one potentially well-suited industrial application. Future studies will investigate the effects of various synthetic conditions on the microstructures of the biphasic materials to provide a basis for determining structure-property relationships, and further characterization of thermomechanical properties, tensile behavior, and impact strength will then be used to identify trends relating material structures to mechanical properties.

Concerning the significance of this work with respect to the broader scope of renewable materials development, this work demonstrates that environmental suitability in new polymers can be achieved without sacrificing functional utility. If innovative material design were to become a staple component of sustainable materials development, the scientific community could produce new classes of materials that excel from both environmental stewardship and material functionality standpoints. Concerning the significance of the specific process for preparing naturally-derived polymers from *D*-limonene that is reported, a number of studies have stated the potential significance of such naturally inspired network polymers for use in soft polymer applications^[24] (and in implantable tissue applications in the case of *D*-limonene-*co*-poly(mercaptopropionate) networks).^[25] While previous studies have provided excellent groundwork for limonene-based poly(thioether) synthesis using a “ground-up chemistry-based approach,” we have chosen to address terpene-derived polymer synthesis instead from a “top-down materials synthesis approach,” in which bulk materials are first synthesized, mechanically characterized and evaluated on material grounds for potential industrial relevance. This work should complement previous chemistry-focused

works very well and should provide a unique perspective on terpene-derived polymer synthesis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Synthetic approach for the preparation of poly(thioether) networks derived from D-limonene and the polythiol TMPTMP

Figure 2.

(a) Simultaneous densification and purification of beverage-contaminated EPS waste cup containing 300 mL of Coca-Cola™. The cup completely dissolves in *D*-limonene, and separation of the Coca-Cola waste contaminant layer from the polystyrene/limonene solution occurs immediately after stirring is stopped; (b) Successful fabrication of iPhone 4™ protective case prototype made from *D*-limonene-*co*-TMPTMP + 30% PS additive demonstrates processability of *D*-limonene-based poly(thioether) networks with recycled PS additives into a geometry representative of that of one potential industrial application; (c) Macroscale images of 0% PS (*top*) and 30% PS (*bottom*) *D*-limonene-*co*-TMPTMP network polymer films

Figure 3.

(a-d) SEM images taken at 3000 $\times$ magnification showing microstructures of *D*-limonene-co-TMPTMP networks containing PS weight fractions of (a) 0%; (b) 10%; (c) 20%; (d) 30%. All scale bars are 30 μm . Prior to SEM imaging, samples were immersed in liquid nitrogen and fractured, immersed in dichloromethane to extract the PS phases, dried, and gold sputtered; (e) AFM Micrographs of 0-30% PS wt/wt *D*-limonene-co-TMPTMP networks. Top: 3D topography for a $20\ \mu\text{m} \times 20\ \mu\text{m}$ area. Bottom: $3\ \mu\text{m} \times 3\ \mu\text{m}$ area with topography

(3D) overlaid with a grey scale rendering of the phase contrast image (range $\pm 5^\circ$ in all images).

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Figure 4.

(a) DMA data showing plots of storage modulus versus temperature for d-limonene-co-TMPTMP, PETMP, and DPEHMP network polymers indicate network thermomechanical behavior for all three samples; DMA data showing (b) storage modulus, E' , (c) loss modulus, E'' , and (d) tangent delta for samples containing 0, 10, 20, and 30%; (e) strain-to-failure data showing an order of magnitude higher toughness for 30% PS blends in comparison with that of 0% and 100% neat polystyrene; (f) table showing effect of increased PS composition on storage modulus, E' , and loss modulus, E'' , at 25°C