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Chimeric Plastics: A New Class of Thermoplastics

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ABSTRACT: A new class of thermoplastics (dubbed "chimerics") is described that exhibits a high temperature glass transition followed by high performance elastomer properties, prior to melting. These transparent materials are comprised of cocontinuous phase-separated block copolymers. One block is an amorphous glass with a high glass transition temperature, and the second is a higher temperature phase transition block creating virtual thermoreversible cross-links. The material properties are highly influenced by phase separation on the order of 10−30 nm. At lower temperatures the polymer reflects the sum of the block copolymer properties. As the amorphous phase glass transition is exceeded, the virtual cross-links of the higher temperature second phase dominate the plastic properties, resulting in rubber-like elasticity. This article will particularly focus on plastics produced from phthalate-based polyester amorphous phases extended by urethane-derived second phases. Glass transitions from approximately 100−115 °C and subsequent elastomer phases to 150 °C are measured. The polymers exhibit high modulus ($G' = 1$ GPa), surprisingly high toughness (up to 2 times that of Bis-A polycarbonate) below the glass transition, and very high elongations and very low elastomer set subsequently. Materials are characterized by X-ray diffraction, DSC, AFM, dynamic mechanical spectroscopy, and tensile measurements. These materials may vastly simplify thermoplastic processes requiring high melt elasticity.

Introduction

Thermoplastic materials have been undergoing study and innovation for over 150 years. Materials exhibiting new properties are reported occasionally with some gaining economic significance. Achieving societal relevance requires that a new material have useful properties and those properties be accessible using economical processing methods.[1] This article will describe a new class of thermoplastics (dubbed "chimerics") having a block copolymer structure.[2] The materials exhibit a high temperature glass transition followed by elastomeric properties prior to melting. Below the glass transition temperature the materials are transparent and exhibit very high toughness. Above the glass transition temperature the materials exhibit very high elongation and low set properties, before melting to a traditional melt. Figure 1 graphically displays this behavior. The polymer blocks can vary but typically have a glassy block that phase separates from a second high temperature phase transition block. Upon exceeding the glass transition the melted glass is virtually cross-linked by the phase-separated higher temperature phase.[3] In the present article we will describe the structure resulting from glassy polyester blocks forming cocontinuous phases with polyurethane blocks. The phase separation and segregation are determined to be on the order of tens of nanometers, resulting in very tough glass properties below the glass transition (T_g) and very high elongation/low set elastomers below the melting point (T_m). These properties suggest that new levels of material performance can be attained using processing techniques requiring very high melt strength, which is typically difficult to achieve among thermoplastics. Because of the common nature of the polymer building blocks in these materials, their accessibility is very high and the potential for innovation is likewise very high.

Experimental Section

Materials. UNOXOL diol is a mixture of 1,3- and 1,4-cyclohexanedimethanol (CHDM).[4] It is a product of The Dow Chemical Company and was used after drying. The isomeric composition results from the hydroformylation and reduction of tetrahydrobenzaldehyde and is provided in Table 1. All other materials were purchased from Sigma-Aldrich and used as received.

Polyester Synthesis. Polyester polyols were synthesized by standard techniques[5] using a three-neck round-bottom flask, a Dean−Stark trap, and a thermocouple-controlled heating mantle. No antioxidant was added to the polymerization vessel, but oxidation was mitigated by running a steady N_2 stream over the reaction surface.

The relative amounts of diol and dimethyl ester were determined from the target molecular weight for the polyester polyol product. The average number of repeats n (as in A−(BA)$_n$) is extracted from the expression for the molecular weight of the polyester polyol:

$$M_w = M_w(\text{diol}) + n[M_w(\text{diol}) - 2 \times 1.008 + M_w(\text{ester}) - 2 \times (M_w(\text{ROH}) - 1.008)] \tag{1}$$

where ROH is the alcohol released by the transesterification (here methanol, $M_w = 32.04$ g/mol). In the polyester polyol there is one more monomer of diol A ($n + 1$) than B (n) such that

$$\text{mass(diol)}/\text{mass(ester)} = (n+1)M_w(\text{diol})/(nM_w(\text{ester})) \tag{2}$$

For example, in the reaction of UNOXOL with dimethyl isophthalate with a target molecular weight of 1000 g/mol the number of repeats can be extracted from

$$1000 = 144.21 + n[144.21 - 2 \times 1.008 + 194.18 - 2 \times (32.04 - 1.008)] \tag{3}$$

Thus, $n = 3.12$ and mass(diol)/mass(ester) = (4.12 × 144.21)/(3.12 × 194.18) = 0.981.

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A 0.1 wt % loading of dibutyltin dilaurate was used in the reactions between UNOXOL and dimethyl isophthalate and dimethyl terephthalate (or mixtures thereof).

The reaction setup for the diol synthesis started with a 1000 or 2000 mL, three-neck reaction flask with a thermocouple port. A Dean−Stark trap (with thermometer and condenser attached) was placed on the first neck. A mechanical stir rod with a Teflon blade was placed in the middle neck. The third neck was capped with a removable glass stopper.

A split nitrogen bubbler line was fed into the top of the condenser via needle through a rubber septum. The apparatus was heated using a mantle with an external temperature control unit with feedback from a thermocouple inserted in the flask thermocouple port. The temperature did not exceed 200 °C.

The diol, dimethyl ester, and catalyst were bulk added to the flask. After a nitrogen atmosphere was established, the mixture was heated to melt and then constantly stirred at 30 rpm. The temperature was slowly increased to reflux, ensuring that the temperature of the vapor traveling up the primary chamber of the trap remained below 70 °C. Methanol is the expected byproduct, with a boiling point of 64.7 °C.

Reaction progress was monitored with regular sampling and ^{1}H NMR analysis. An NMR spectrum for polyUNOXOL isophthalate is shown in Figure 2 with assignments. A methyl peak (*E*) indicated unreacted methyl ester material, while the ratio of $-CH_2-OH$ (*F*) and $-CH_2-$ (*D*) ester peaks indicated the molecular weight of the product. Additional dimethyl ester was added to the reaction mixture if the molecular weight target could not be achieved (determined by the NMR). The reaction was considered complete when the quantity of unreacted methyl ester was below 1% and the ratio of the hydroxyl/ester content was on target.

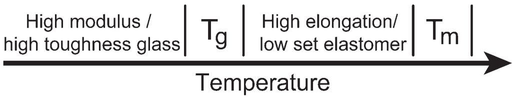

Figure 1. Schematic of the properties of new chimeric materials described herein.

Table 1. Isomeric Composition of UNOXOL Diol

isomers	composition (wt %)
trans-1,3-CHDM	24.0
cis-1,3-CHDM	32.8
trans-1,4-CHDM	30.2
cis-1,4-CHDM	13.0

Elastomers Synthesis. Methylene diphenyl diisocyanate (MDI) was kept in a freezer until use, when it was allowed to come to room temperature under dry conditions. All other materials were dried prior to use in a heated vacuum oven. The viscosity during the reaction was monitored using a calibrated torque sensor. Stoichiometry was strictly followed with a 2% equivalence excess of MDI. Elastomers were prepared in a Haake dispersive mixer using a prepolymer approach.[6] The synthesis technique involves adding polyester to premelted MDI in the Haake reactor at about 130 °C, allowing them to mix and react, followed by adding a 1,4-butanediol chain extender (BDO) to this mixture. The polymer components were then heated and rapidly mixed. The molecular weight of the reacting mixture increases rapidly as measured by machine torque until the temperature reaches about 200 °C, above which it falls as urethane reversion and polyurethane scrambling occur.[7] The Haake reactor was then allowed to cool down upon which machine torque rebuilds along with molecular weight. An idealized structure for these materials is provided in the Supporting Information.

Characterization. Hydroxyl numbers were obtained using a Mettler Toledo DL50 titrator using a phthalic anhydride-based derivatization and titration method (ASTM D4272-05). Proton NMR spectra were acquired on a Varian 500 MHz NMR using deuterated chloroform or DMSO as the solvent. Molecular weights were measured with a HP GPC using a THF mobile phase. Measurements were made on elastomers dissolved in hot 50/50 THF/DMF. The GPC was calibrated with PEG standards.

Dynamic mechanical spectroscopy (DMS) was obtained on an Ares II solids analyzer. Samples were obtained from 0.0625 in. thick compression-molded plaques. Sample test frequency

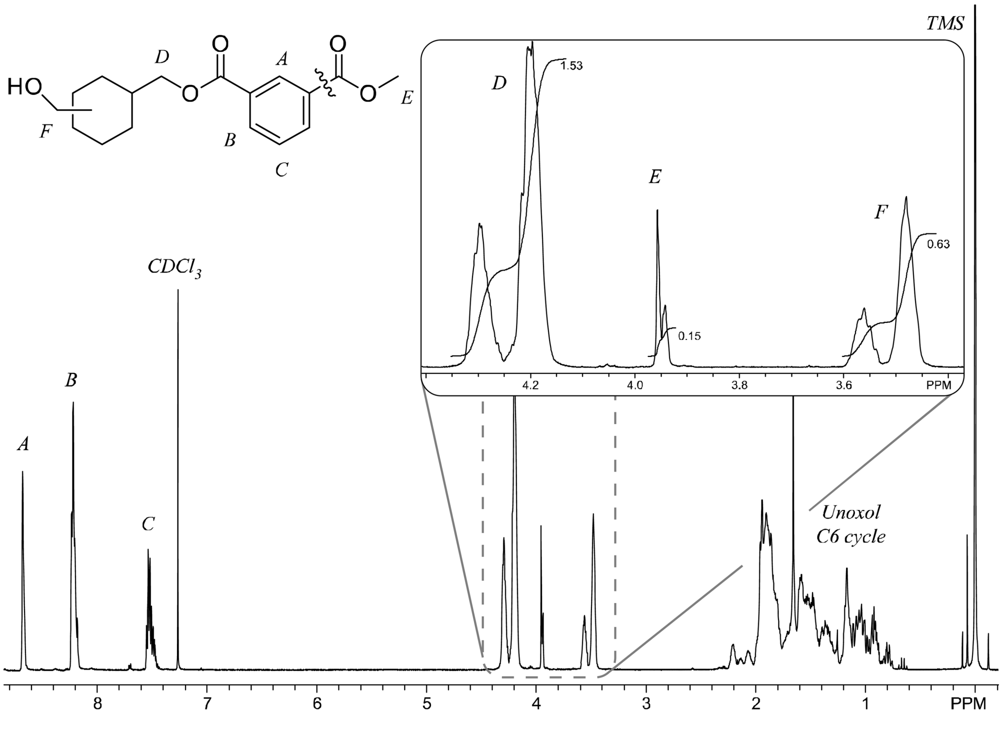

Figure 2. Representative ^{1}H NMR spectrum from a polyester made from UNOXOL diol and dimethyl isophthalate.

Table 2. Thermal Transitions of Polyester Blocks Used in These Experiments

diacid	M_n	T_g (°C)	T_m (°C)
isophthalic	510	−6.2	
isophthalic	1096	23.5	
50% isophthalic, 50% terephthalic	1037	26.9	
20% isophthalic, 80% terephthalic	1035	28.8	
terephthalic	514	39.8	
terephthalic	1055	26.6	71 (melt)

was 1 Hz and strain was 0.2−0.5%, ensuring measurement within the linear viscoelastic range for each of these materials as determined by a strain sweep. Tensile and hysteresis testing was performed on an Instron 4202 frame using Blue Hill software. Strain rates were 2 in./min. High temperature hysteresis measurements were made at 2 in./min with two cycles extended to 300% strain based on original sample gauge length, separated by a 5 min hold time at 0% extension.

Small-angle X-ray scattering (SAXS) analyses were performed using the following procedure. Specimens were cut to a width of 5 mm and a thickness of 3 mm. Conditioning of the X-ray beam was achieved using a multilayer optic and triple pinhole collimation. All samples were analyzed under vacuum in normal beam transmission mode. Cu Kα radiation (λ = 1.541 84 Å) was employed. An area detector was used to collect the scattering intensities. SAXS exposure time was set for 30 min. The 1-d SAXS data were analyzed using the commercial software platform JADE.

Samples were prepared for AFM imaging by cryomicrotomy at −50 °C from compression-molded specimens. Tapping Mode AFM (TMAFM) images were acquired on a Veeco Instruments Multimode using a Nanoscope IV controller (software v 6.13r3). Silicon cantilevers and tips were used. Typical tapping conditions were $A_0 \sim 2.0$ V, $A_{sp} \sim 1.7$ V, and $r_{sp} = 0.85$ with the tip interaction repulsive in nature. Images were acquired at a resolution of 1024 scans/image. Images were postprocessed using a third-order polynomial fit followed by a zero-order LMS fit and a 7 × 7 median filter to remove directional noise using a SPIP image processor (v5.1.3 Image Metrology).

Results and Discussion

The phase characteristics of the synthesized polyesters are detailed in Table 2. In all cases the dimethyl ester of the indicated acid was reacted with UNOXOL diol. This provided an amorphous and rigid polymer backbone, which also minimized the potential for polyester crystallization.[8] Such crystallization could have led to a high melting polyester phase, complicating the polymer rheology.

PolyUNOXOL isophthalates and the UNOXOL polyester with a 50/50 blend of isophthalate and terephthalate were amorphous and transparent solids. The UNOXOL polyesters with higher levels of terephthate were all semicrystalline by inspection, but only the higher molecular weight polyol made with 100% terephthalate presented a measurable melting endotherm.

The chimerics (polyesters reacted with polyurethane components) made with these polyols were uniformly transparent, suggesting that polyester crystallization is inhibited in the presence of polyurethane, as has been observed before.[9] DSC and DMS data both show transitions related to polyester T_g and polyurethane melting but no apparent contribution from polyester crystallization.

The novel performance of chimerics is shown in Figure 3, which typifies the materials as a class. Additional data can be found in the Supporting Information. The room temperature tensile behavior is similar to that of other glassy thermoplastics such as Bis-A polycarbonate (see Figure 3b). A significant difference is in the overall room temperature toughness which is calculated from the integral under the stress strain curve.[10,11b] The toughness of Chimerics is up to 2 times that of the Bis-A polycarbonate—traditionally considered a very tough thermoplastic.[11a] Because of

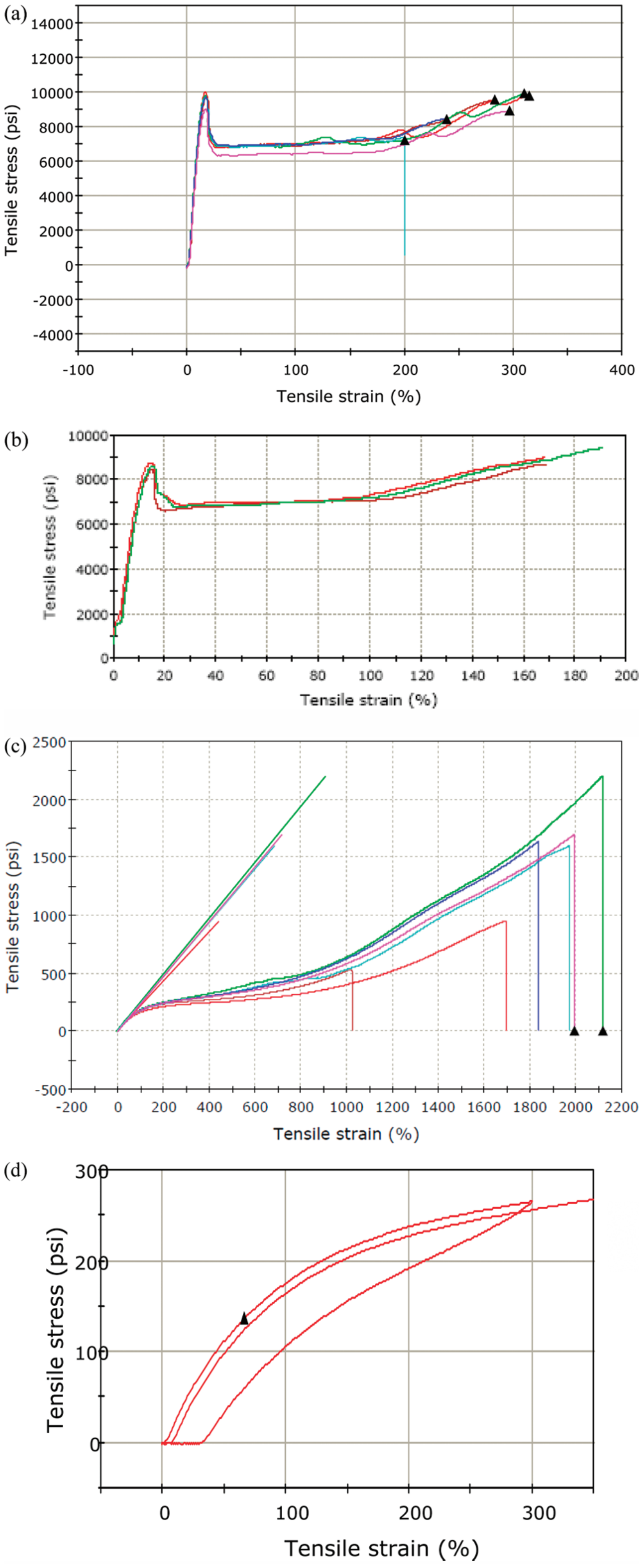

Figure 3. Tensile measurements for a chimeric composed of 40 wt % of a MDI-BDO phase and a polyUNOXOL 80/20 terephthalate/isophthalate of M_n 1035 g/mol phase. Stress−strain curves for (a) the above chimeric at room temperature, (b) Bis-A polycarbonate (comparative) at room temperature, and (c) the above chimeric at 134 °C. (d) Hysteresis loop for the above chimeric measured at 134 °C.

Table 3. Room Temperature Properties of Chimeric Materials from Polyesters and Polyurethanes

polyester diacid	M_n polyester	PU (MDI-BDO) (wt %)	elastomer polyester T_g (°C)	E' (MPa)	yield strain (%)	elong at break (%)	toughness (MPa)
isophthalic	510	40	114	1044	14	70	33
isophthalic	1096	40	103	812	10	320	164
50% isophthalic, 50% terephthalic	1037	40	109	962	17	336	177
80% terephthalic, 20% isophthalic	1035	40	111	891	17	314	164
terephthalic	1055	40	107	669	17	310	149
isophthalic	510	50	111	1076	16	167	82
isophthalic	1096	50	106	938	16	340	178
50% isophthalic, 50% terephthalic	1037	50	112	920	16	318	180
80% terephthalic, 20% isophthalic	1035	50	113	891	18	279	150
terephthalic	1055	50	111	752	16	247	115
Bis-A polycarbonate			150	800	15	190	98

limitations of molding methods employed here, we were unable to get useful impact measurements from chimerics or polycarbonate. High rate tests are helpful for judging usefulness for certain high rate/high toughness applications. The use and applicability of toughness measured by tensile measurements such as presented here have been covered elsewhere.[11]

When chimerics exceed the polyester glass transition, the MDI-BDO polyurethane block maintains its structural integrity due to its higher melting point and its cocontinuous morphology within these materials (vide infra). From the polyester glass transition temperature to the PU melting point (typically around 150 °C for a 40−50 wt % MDI-BDO phase[12]) the materials exhibit elastomeric properties.[13] Figure 3c shows a representative stress−strain curve for a chimeric elastomer with unusually long elongation at break up to 20 times the initial gauge length. The elastomeric recovery is demonstrated in Figure 3d where the cyclic elongation and recovery at 134 °C is demonstrated, with an unrecoverable set of about 8% following 300% elongation. This shows the chimeric high temperature elastomer recovery to be quite good, even relative to room temperature elastomers, and extraordinary under such elevated temperature conditions. Additional hysteresis loops for other chimerics, as well a graphical explanation of the extractable physical parameters from hysteresis loops, are provided in the Supporting Information.

Table 3 also shows that the properties of these materials are a strong function of the polyester molecular weight. While exhibiting a higher polyester T_g, materials employing low molecular weight polyesters show much less ductility and no high temperature elastomer phase, instead transitioning directly to a polymer melt. The implications of this structural data on the polymer properties and morphology will be discussed later.

The origin of chimeric properties is a feature of the underlying molecular and phase structure of the materials. Their optical transparency suggests that the phases are either amorphous (with identical refractive index) or dispersed below dimensions capable of scattering light. Thermoplastic polyurethanes, of which the present materials are a subset, can be optically transparent[6]—transmitting over 90% of incident light—and yet still show discrete scattering peaks by X-ray diffraction techniques. Figure 4a is the small-angle X-ray scattering pattern collected for the indicated materials. Organized phase structure will often appear as broad maxima in the scattering at angles above the prominent direct beam intensity.[14] None of the scattering patterns indicate a prominent scattering peak which, in this case, would have allowed us to suggest an organized periodic phase-separated structure common for polyurethane elastomers.

The material made with 40 wt % PU and polyUNOXOL terephthalate (M_n = 1055 g/mol) shows increased intensity at 2Θ between 0.5° and 1°. Scattering as seen in Figure 4a is often descriptive of uncorrelated phase-segregated structures, but elastomeric properties in the absence of covalent cross-links are certainly not.[15] Particle size distribution determined from the

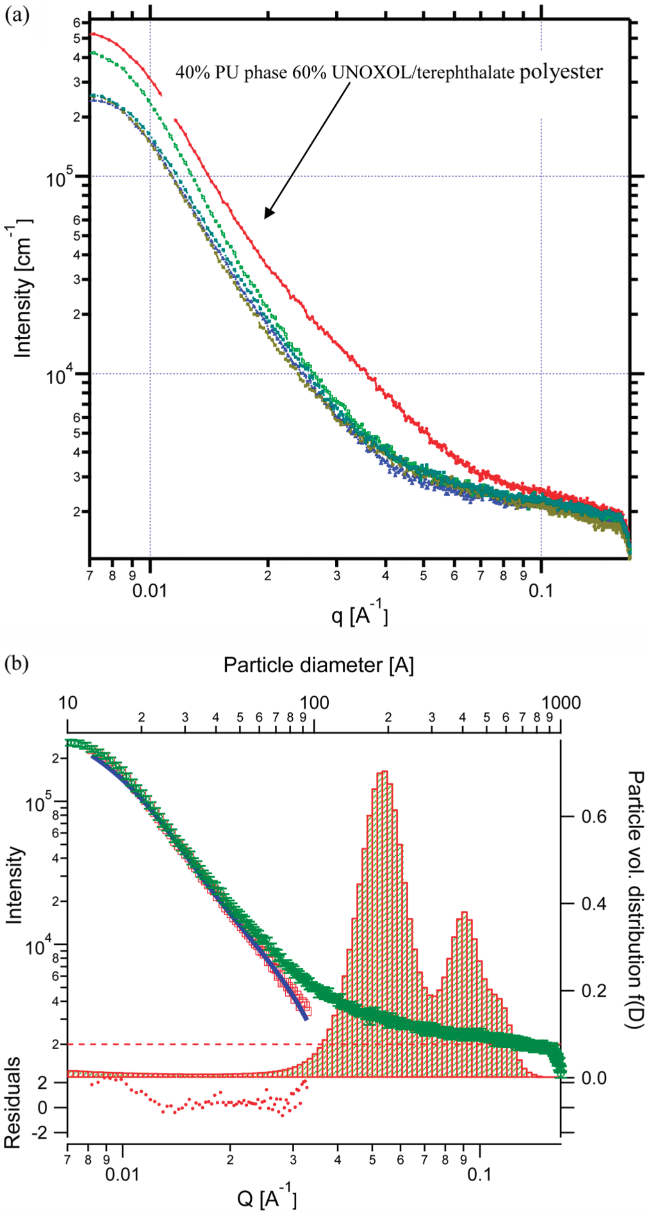

Figure 4. (a) Small-angle X-ray scattering pattern of several chimeric materials from this study. Unmarked lines include 40% polyurethane 60% UNOXOL isophthalate, 40% polyurethane 60% UNOXOL terephthalate/isophthalate (80/20), 50% polyurethane 50%UNOXOL isophthalate, and 50% polyurethane 50% UNOXOL terephthalate/isophthate (50/50). (b) Deconvolution of scattering size populations assuming spherical scattering centers from a 40% PU phase 60% UNOXOL/terephthalate chimeric.

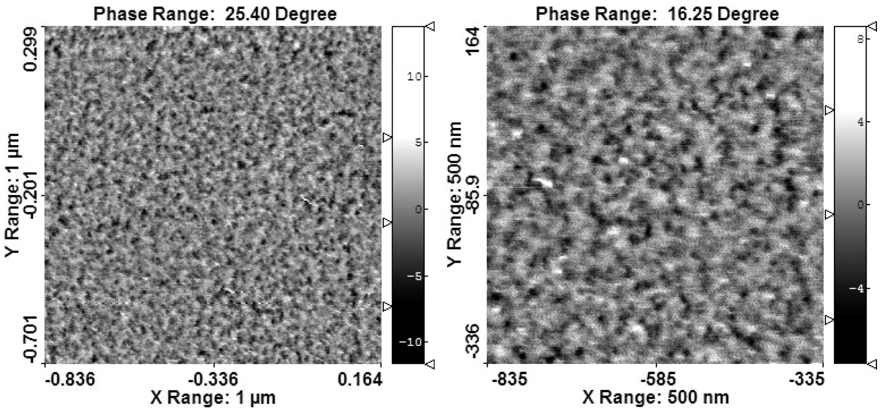

Figure 5. TMAFM of a material composed of 40 wt % of a MDI-BDO phase and a polyester phase of UNOXOL diol reacted with a 80/20 mixture of terephthalic and isophthalic acids.

background-corrected SAXS pattern (assuming spherical scattering geometry) is shown in Figure 4b for a material made with 40 wt % PU and polyUNOXOL terephthalate (M_n = 1055 g/mol). The model fit suggests the existence of phase-separated structures at very low size scales. The very small scales are consistent with the transparent optics of these materials.

Tapping mode AFM phase images (Figure 5) confirm two highly dispersed and cocontinuous phases consistent with polyurethane systems observed previously by us and others.[3d,15] It is an open question as to which phase (dark or light) is the MDI-BDO polyurethane phase and which is the polyUNOXOL phthalate polyester phase. However, given the similarity in structure of the light phase in these images to those of polyurethane and polyurea phases in other AFM images, it seems likely that the light color phase is the quasi-lamellar polyurethane phase structure[16] and the dark color phase is the amorphous polyester phase.

It might be tempting to describe chimerics as standard polyurethanes with a high T_g "soft segment". This is not the case for many reasons including the following: (1) Polyurethane block copolymers typically have a well-defined *d*-spacing[13d] (highly probable distance between scattering centers) which these materials do not have (2) While the soft segment T_g of polyurethanes normally increases when incorporated into the polyurethane phase, an increase of 80 °C as routinely observed in Chimerics is unprecedented.[7] (3) Thermoplastic polyurethanes do not elongate 200−300% 80 °C below their soft segment glass transition. (4) Polyurethane thermoplastics show significant changes in properties as a function of phase volume.[16] Chimerics show very weak dependence on phase volume in the range studied here.

The two-phase composite chimeric structure described by the TMAFM images should allow us to gain understanding of the relationship between the block copolymer phases. It is difficult to tell if the interphase region is sharp or highly phase-mixed by inspection of the images. Given the very high and uniform dispersion of the phases, it would be natural to assume that the interfacial region is highly mixed and that the properties of the phase mixing influence the low and high temperature properties greatly. This is necessarily the case given the large increase in polyester glass transition temperature upon reacting with the MDI-BDO blocks. The T_g increase of the polyester phase is likely a combined result of the presence of a high T_g modifier in the phase and polyester chain confinement by the nearly lamellar urethane phase.[16] The TMAFM images illustrate the intimacy of the cocontinuous phase structure.

Using simple two-phase composite calculations[18] and dynamic mechanical analysis, we can estimate the extent of phase mixing in these systems. Figure 6 is a representative dynamic mechanical analysis of a 40 wt % polyurethane content chimeric. The shear modulus is seen to fall from about 1 GPa below the polyester T_g to about 3 MPa above T_g. While the modulus falls to a typical elastomer value, the tan(delta) stays at a low and reasonably steady value of about 0.2. Materials with 50 wt % polyurethane content have a very similar shape but fall from 1 GPa to about 3.3 MPa above T_g.

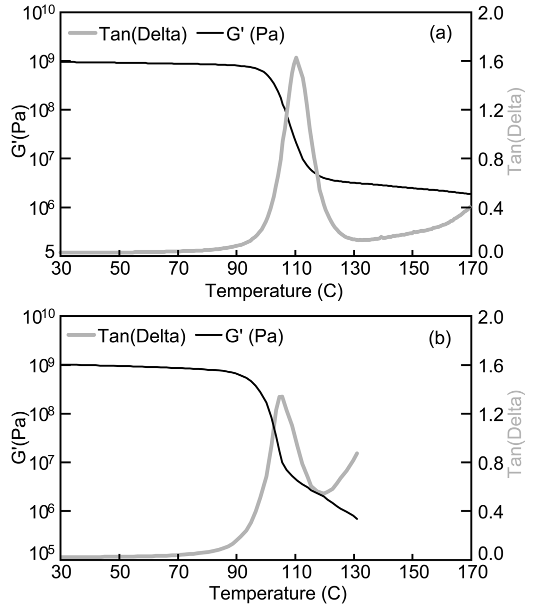

Figure 6. Dynamic mechanical spectra of chimeric materials made from polyesters of molecular weight (a) ∼1000 g/mol and (b) ∼500 g/mol.

We can estimate the modulus for a macroscopic cocontinuous composite material from the moduli of its phases when (1) assuming noninteractivity; (2) mass fraction is equivalent to volume fraction (the effect of deviation will be discussed below); (3) above its glass transition the polyester does not contribute to the overall modulus G' and the polyurethane phase is invariant; (4) below the polyester T_g, the phases have equivalent moduli $G'_{\text{hard}} = G'_{\text{soft}}$ = 1 GPa. Then the Davies equation[19] for shear modulus of this composite material above the polyester T_g would be approximated by

$$G' = G'_{\text{hard}}(\rho)^5 \qquad (4)$$

where ρ is the volume fraction of the polyurethane phase. Using this simple equation, shear moduli of 10 MPa for a 40% polyurethane content material and 32 MPa for a 50% analogue are predicted and can be compared to the measured values of 3.0 and 3.3 MPa, respectively. Thus, the Davies equation predicts a modulus higher than that measured by between a factor of 3 and a factor of 10. Conversely, using eq 4, the calculated PU volume fractions required to obtain the measured shear moduli would be about 31% and 32% instead of 40% and 50% PU actual content, respectively. Because the expected density of a PU phase (1.05−1.1) is lower than that of an amorphous aromatic polyester phase (1.2−1.3), the volume fraction of PU in such composites are higher than their mass fractions. In this case the congruence of weight and volume only accentuates the difference between the shear moduli predicted by the Davies equation and those measured experimentally.

Another possibility would be to use the standard open cell foam correlation.[20] This is generally written for tensile deformation rather than shear; however, the scaling is the relevant feature of this hypothesis, scaling as the second power of the hard phase rather than the fifth. This analysis would predict an even higher post-T_g modulus than the Davies model.

These results suggest that (1) a significant amount of the polyurethane phase transits T_g along with the polyester phase at the first transition and (2) the high melting polyurethane phase-separated volume is somewhat insensitive to the amount added. This is qualitatively consistent with the thermal data presented previously: (1) the very high T_g of the phthalate polyester (~110 °C in the composite vs ~25 °C for the pure polyester and ~80 °C for semicrystalline PET), indicating the possible presence of a higher T_g modifier and (2) only a 5 °C polyester phase T_g increase when the polyurethane fraction of the chimeric is increased from 40% to 50%, suggesting that polyester phase behavior does not change much in response to changes in overall composition.

The phase composition values obtained applying the Davies equation to the experimentally measured mechanical property data can then be inserted into the Fox equation[21] to deduce if the expected glass transition values are poorly predicted from the components in the polymerization. According to the Fox equation, raising T_g from the pure polyester value of ca. ~25 °C to the observed 110 °C in the composite would require a very large amount (~70 vol %) of a high T_g modifier. Deviations from the Fox equation are not unknown however, sometimes underpredicting T_g significantly.[22] In this case, the positive deviation could be due to the previously mentioned chain confinement.

An alternative proposition, consistent with much of the data, is that the hydroxy-terminated polyester phase is capable of substituting for the BDO in the polyurethane phase, creating a new phase that is quite unrelated to the polyester phase initially intended. This would result in a smaller amount of phase-separated polyurethane phase than predicted based on volume additions since a part of the polyurethane phase would now be a constituent of a new polyester−polyurethane amorphous phase. Such a composite phase could influence T_g by additional hydrogen bonding between the dissolved urethane and polyester carbonyls. This is also consistent with the insensitivity of the polyurethane melting point (T_m) to increasing hard segment volume, of which T_m is known to be a very sensitive function in standard polyurethane polymers. This also leads to a situation where phase morphology is a function of the conditions (time and temperature) of processing as typically occurs in thermoplastic polyurethanes.[23]

Lastly, the relevance of the lower molecular weight polyester phase on resulting polymer properties is revealing. Table 3 shows that reducing the M_n of the polyester from ~1000 to ~500 g/mol increases chimeric T_g substantially, while reducing low temperature ductility. Furthermore, the high temperature elastomer properties are no longer present when using the 500 g/mol polyester. Instead, the material transits directly to a melt state (Figure 6b). The effect of reducing the molecular weight of the polyester phase has several structural and rheological consequences. The rheological consequences are illustrated by comparison of Figures 6a and 6b. First, it reduces the ability of the polyester phase to respond independently of the polyurethane and interfacial phases, thus reducing the polymer ductility. Second, it reduces the block size of the higher temperature polyurethane phase, reducing its ability to phase separate into a load-bearing cocontinuous structure. Last, it has a substantial effect on the volume of interfacially mixed material. The equation for the interfacial volume of a two-phase system capable of forming a third, interfacial, phase is given by[24]

$$V_i = \frac{(r+l)^3 - r^3}{r^3} V_2 = ((1+l/r)^3 - 1)V_2 \qquad (5)$$

where V_i is the interfacial volume, V_2 is the volume fraction of a dispersed phase, r is the radius of a dispersed phase domain, and l is the interfacial thickness. This equation shows that, regardless of chemical details and only fixing the interfacial thickness, the volume fraction of the interphase will increase dramatically as the dispersed volume dimension (r) decreases. Thus, we can infer that there is a minimum acceptable molecular weight of the phases to obtain desired properties and that the interfacial properties do not contribute constructively to the high temperature elastomer behavior. However, it is possible that in the presence of well-defined two-phase materials the interfacial material may contribute to the low temperature ductility, providing a relatively compliant matrix to absorb energy.

Conclusion

A new class of thermoplastics (named "chimerics") is described that exhibits typical thermoplastic properties below a high glass transition temperature, except for having exceptionally high toughness (about 1.5−2 times that of Bis-A polycarbonate). Above the glass transition chimerics exhibit high performance elastomer properties: very high elongation at break, low permanent set, and low hysteresis. The properties are a reflection of the block copolymer phase structure and the rheology of each respective block. The phase separation of the blocks is on the order of tens of nanometers and the concomitant interfacial mixing affects the phase and mechanical properties of the composite material. These materials offer a significant opportunity for further study of alternative polymer blocks, further definition of the polymer kinetics by which interfacial properties become dominant, and further definition of the nature of the phase transitions.

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Supporting Information Available: Hysteresis data for various chimerics. This material is available free of charge via the Internet at http://pubs.acs.org.

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