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Enhancement to the rate-dependent mechanical behavior of polycarbonate by incorporation of triptycenes

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ABSTRACT

The tensile and compressive properties of triptycene-polycarbonates were tested over 6 orders of magnitude in strain rate. Initially we studied a low molecular weight, low triptycene content PC blended with Iupilon® PC and then a series of higher molecular weight, higher triptycene content polymers. The PC blend with only 1.9 wt% triptycene displayed up to 20% increase in modulus and up to 17% increase in yield strength with elongations over 80% as compared to the Iupilon® PC. The higher molecular weight T-PCs (up to 26 wt% triptycene) exhibited improvements in modulus by over 20% and improvements in compressive strengths by nearly 50% at both low and high strain rates without any apparent sacrifice to ductility, as compared to Iupilon® PC. All samples containing triptycene units retained transparency and exhibited no signs of crystallinity or phase separation. Moreover, both the blends and triptycene-PC copolymers displayed significantly altered dynamic mechanical spectra, specifically, the emergence of a pronounced, new β' relaxation approximately 75 °C above the traditionally observed β relaxation in PC (approximately -100 °C). The enhancement of the mechanical properties observed provides valuable insights into the unique packing and interactions during plastic flow induced by the presence of triptycene units.

1. Introduction

Polycarbonate (PC) is a high-T_g ($\sim$150 °C) engineering thermoplastic with excellent ductility and optical clarity. It is non-corrosive, non-toxic, and chemically and thermally resistant. Furthermore, it has been found to have exceptional impact resistance via its ability to undergo large plastic deformations during most loading conditions. With such advantageous physical properties, the commercial applications of PC are widespread, including automobile parts, DVDs, sport bottles, windows, visors, anti-scratch coatings, and even bullet-proof glass. Any improvement in the mechanical behavior of this material would impact a wide range of industries.

Recently, the high-rate mechanical behavior of PC has become of interest due to its prominent role in transparent protection applications. The yield strength of PC increases with strain rate and has been found to exhibit a stronger rate sensitivity at very high rates of strain [1–3]. This variation in the rate sensitivity of the yield stress has been linked to the β-transition due to the restricted mobility of short chain segments at high rates (or, alternatively, at low temperatures) [2]. When the secondary motions are restricted due to either the time scale or the temperature of the deformation, an additional barrier to deformation must be overcome prior to yield. It is this enhanced deformation resistance under conditions of high strain rate, coupled with its ability to remain ductile and undergo large tensile deformations even when β motions are restricted [4], which makes PC such an attractive material for impact applications.

Modifications of a polymer system through chemistry and through blending can enhance the desirable rate-dependent mechanical behavior. Polymer nanocomposites and nanostructured

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polymers offer new opportunities in the design of lightweight material systems with exceptional impact-resistant capabilities [5–8]. In this study, we explore changes in the structural, thermal, and mechanical properties of PC induced by the presence of a unique chemical unit in the main chain.

The structural unit used in this study is an aromatic hydrocarbon known as triptycene. Triptycene has a rigid "paddlewheel" structure composed of three benzene rings and is a part of a larger family of molecules (iptycenes) that exhibit internal molecular free volume (IMFV). IMFV is defined as "the difference in volume between that which is generated by the geometry of a structure and that which is occupied by the structure itself" [12]. Long and Swager have extensively studied the effects of blending triptycene into liquid crystals and polymers [9,10]. In general, they found that in blends the minimization of total free volume was achieved by having molecular segments pack into the internal cavities (which comprise the IMFV) of the triptycene units.

When incorporated into a polymer chain, triptycene is attached through one of its benzene rings into the polymer backbone. Tsui and co-workers [11] have substituted triptycenes into polyesters and measured the associated changes in mechanical behavior. For 21 wt% triptycene content, the enhancement in mechanical properties was remarkable: a three-fold increase in both stiffness and strength, accompanied by a twenty-fold increase in strain to failure. These results were explained by the introduction of novel steric interactions (molecular threading and molecular interlocking) induced by the desire to minimize the IMFV inherent to the triptycene unit. It was shown later that these results were robust across three different types of iptycene units in varying concentrations [12].

In this study, the effect of triptycene on the mechanical performance of PC over a range in strain rates is investigated. Triptycene is incorporated into the molecular backbone of bisphenol-A polycarbonate, producing a material we refer to as triptycene-PC (T-PC). In some cases, T-PC was solvent blended with a bisphenol-A PC (trade name Iupilon®) producing materials of very low triptycene content. Herein, we investigate the mechanical and thermo-mechanical properties of both T-PC and T-PC blends, with triptycene contents ranging from 0 to 26 wt%. Triptycene-containing PCs displayed considerable improvements in modulus, compressive yield stress and tensile strength at both low and high strain rates.

2. Experimental

2.1. Materials

Table 1 lists the different types of polycarbonates that were used to prepare the materials characterized in this work. IUP is a high viscosity grade bisphenol-A polycarbonate supplied by Mitsubishi Engineering Plastics under the commercial name Iupilon® E2000. 0/100 and 7/93 T-PCs were both synthesized by Triton Systems, Inc. of Chelmsford, Massachusetts. 0/100 is a low molecular weight bisphenol-A polycarbonate that served as a baseline for 7/93, a triptycene-PC copolymer containing approximately 7.7 wt% triptycene hydroquinone. The high molecular weight 5/95, 15/85, and 25/75 T-PCs were synthesized by a process described in Section 2.3. The basic chemical structure of the monomers is given in Fig. 1.

Table 1
Homopolymer materials used in this study. Nomenclature is described in Fig. 1

Polymer	M_n[a] (g/mol)	M_w[a] (g/mol)	PDI[a]
IUP	29,900	67,000	2.2
0/100	13,100	30,100	2.3
7/93	5,900	22,000	3.7
5/95	28,200	55,700	1.98
15/85	29,600	60,700	2.05
25/75	29,900	67,500	2.26

[a] Average molecular weight values (M_n and M_w) and polydispersity index (PDI) determined via gel permeation chromatography (GPC) with THF eluent.

2.2. Preparation of blends

The low molecular weights of the 0/100 and 7/93 T-PC polymers (see Table 1) produced brittle samples; therefore, two blends with the commercial PC were prepared for mechanical characterization. PC blend was a 25 wt% blend of 0/100 ($M_n = 13{,}100$ g/mol) into IUP ($M_n = 29{,}900$ g/mol). T-PC blend was a 25 wt% blend of 7/93 T-PC ($M_n = 5900$ g/mol) into IUP, yielding an overall triptycene concentration of about 1.9 wt%. The blends were prepared by dilute solvent mixing with a spinner in dichloromethane at room temperature overnight. Solutions were allowed to evaporate in a fume hood for 2–3 days in Teflon® dishes, leaving behind partially crystallized white films. These films were ground into a fine powder and then stored in a vacuum oven, along with fine powder of IUP, at 120 °C overnight before melt processing. For all three polymers, transparent disks of about 50 mm in diameter and 3 mm in thickness were compression molded at 265 °C. Finally, the compression molded disks were machined into three specified sample geometries: cylinders, rectangular bars, and dogbones. All samples were dried at 55 °C under vacuum for a week before mechanical testing.

2.3. Synthesis and preparation of high molecular weight T-PCs

Glassware was oven-baked overnight and cooled down to room temperature under inert atmosphere. In a 500 mL three-neck reaction vessel, triptycene hydroquinone and bisphenol-A were added at the desired molar ratios (5:95, 15:85 or 25:75) to 1.08 equiv (to the total moles of triptycene hydroquinone and bisphenol-A) diphenyl carbonate (54.10 g, 0.25 mol). The reaction vessel was equipped with an overhead mechanical stirrer, a vacuum distillation head, and a gas outlet connected to a bubbler. While stirring, the vessel was evacuated and refilled with argon three times. The reaction mixture was then heated to 190 °C under a slow flow of argon (1–2 bubbles/s) and was kept at that temperature for 0.5 h. Tetramethylammonium hydroxide (50 μL, 10 wt% aqueous solution) and sodium hydroxide (9 μL, 0.1 wt% aqueous solution) were quickly injected into the vessel. After the mixture was stirred at 190 °C for another 0.5 h, the temperature was increased to 220 °C followed by slow decrease of pressure to 200 torr. After the mixture was stirred at 220 °C and 200 torr for 1 h, the temperature was increased to 250 °C and held for 0.5 h. At 250 °C, the pressure was stepwise lowered to 150 torr, 100 torr and 15 torr, and kept at each step for 0.5 h. Then, the temperature was increased to 280 °C, the pressure was decreased to 2 torr, and the mixture was stirred at this stage for 0.5 h. Finally, full vacuum (~0.8 torr) was applied to ensure maximum removal of phenol. When the content became unstirrable, it was removed from heating and stirring. The content was cooled to room temperature under full vacuum followed by the addition of 200–300 mL dichloromethane. The solution was

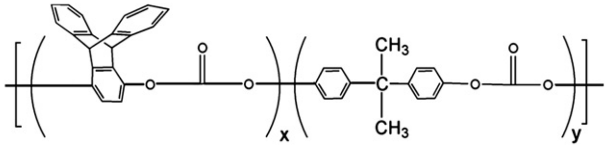

Fig. 1. Chemical structure of T-PC copolymers of composition x/y: 0/100, 7/93, 5/95, 15/85, and 25/75. The reference polycarbonate sample (IUP) had a composition of 0/100.

filtered through a 25 μm Teflon® filter followed by precipitation into 2 L methanol. The polymer was received as a pale white solid. Gel Permeation Chromatography (GPC) (Hewlett-Packard series 1100 GPC system) indicated that there was a single polymer component. The polymer was characterized by ^{1}H Nuclear Magnetic Resonance (NMR) (Inova-500 NMR Spectrometer) and the ratio calculated from ^{1}H NMR closely matched the feeding ratio. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.44–7.03 (m, ArH), 5.72 (s, CH), 1.70 (s, CH_3).

Disks of about 50 mm in diameter and 3 mm in thickness were compression molded using identical methods as described in the previous section, and the same cylinder and rectangular bar specimens' geometries were cut from these disks. Samples were again dried at 55 °C in vacuum for a minimum of one week prior to testing to ensure the removal of water.

2.4. Uniaxial compression tests

Uniaxial compression tests were conducted over a span of six orders of magnitude in strain rate, ranging from about $10^{-3}\ s^{-1}$ to $2000\ s^{-1}$. Specimens for all compression tests were of right circular cylinder geometry, with a diameter of approximately 5 mm and a height of 2.5 mm. Low to moderate rate testing ($10^{-3}\ s^{-1}$–$10^{-1}\ s^{-1}$) was conducted on a Zwick/Roell Z010 testing machine at constant engineering strain rates. Thin Teflon® sheets were placed between the Zwick platens and specimen surfaces, and WD-40 was used between the Teflon® sheets and platens to minimize friction and obtain homogeneous uniaxial compression conditions.

High-strain rate testing ($1000\ s^{-1}$–$2000\ s^{-1}$) was performed on a compressive split-Hopkinson pressure bar (SHPB) test apparatus designed in cooperation with and built by Physics Applications, Inc. of Dayton, Ohio. This apparatus employs solid aluminum pressure bars with a length of approximately 2.3 m and a diameter of 19.05 mm. The selected specimen geometry was chosen specifically for these high-rate compression tests, where it has been shown that an aspect ratio of 1:2 (height:diameter) is optimal in negating the effects of longitudinal and radial inertia in the specimen [13] while also minimizing wave attenuation in the strain gauge signals [14,15]. All high-rate specimens were lubricated with a thin layer of petroleum jelly on both faces immediately prior to testing, and little to no barreling was observed in the deformed specimens.

2.5. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) testing was performed on a TA Instruments Q800 Dynamic Mechanical Analyzer. Rectangular bar specimens (approximately 20 mm × 2 mm × 1.6 mm) were loaded in the DMTA with a tensile pre-load (0.01 N) and scanned at 2 °C/min; displacement control mode was used to oscillate about the pre-strain level such that total strain levels never exceeded 0.1% at temperatures below T_g. Materials were tested at frequencies of 1 Hz over the temperature range of −140 °C to 170 °C. IUP and the blends were then tested at 100 Hz over small ranges in temperature around identified material transitions.

2.6. Uniaxial tension tests

Uniaxial tension tests were performed on dogbone samples of 17 mm gauge length in the Zwick/Roell Z010 at a constant displacement rate of 5 mm/min. An extensometer applied to measure true strain within the gauge length was found to induce premature brittle failure in the specimens, and thus it was necessary to estimate engineering strain from cross-head displacement. This estimated strain is reported in the figures as "apparent engineering strain." Without an accurate strain measure, modulus values could not be calculated. Therefore, modulus is reported by using the storage modulus value obtained in the DMTA experiments, for a wide range of temperatures.

2.7. Additional characterization

A TA Instrument Q1000 Differential Scanning Calorimeter (DSC) was used to scan samples at 10 °C/min. Density measurements were taken using a Micromeretics AccuPyc 1330 He pycnometer by researchers at DuPont using an average of 10 data points. A TA Instrument Advanced Rheometer 2000 was used on circular disk specimens with the same geometry as used for compression testing. Frequency sweeps from 100 rad/s to 0.1 rad/s and temperature sweeps from 200 °C down to 160 °C at 0.1% strain were used to generate master curves through time-temperature superposition. Entanglement molecular weight (M_e) was calculated from the measured plateau modulus, which was identified by the minimum in the tan δ vs. frequency curve. The plateau modulus E is inversely proportional to the entanglement molecular weight M_e, $E = (4/5)\rho RT/M_e$. Three samples were tested per polymer for all characterization methods unless specifically noted otherwise.

3. Low molecular weight blends' results

3.1. Homogeneous, amorphous blends

0/100 and 7/93 T-PCs exhibited depressed T_g values compared to IUP, as might be expected from their lower molecular weights. Blending resulted in one visible T_g that was equivalent for both PC and T-PC blends (Fig. 2). DSC indicated no signs of crystallinity in the blends, and all three polymer samples were optically transparent (Fig. 3). Although there appears to be a first-order like transition for 0/100 T-PC around 270 °C, this is likely related to the solvent filtration used to purify the polymer post-synthesis. The peak is not present after thermal cycling. The room temperature densities of IUP, PC blend, and the T-PC blend were comparable at 1.19 g/cc, 1.20 g/cc and 1.20 g/cc, respectively. Entanglement molecular weights were 1920 ± 90 g/mol, 2100 ± 150 g/mol, and 2190 ± 210 g/mol for IUP, PC blend, and T-PC blend, respectively.

3.2. Compression testing

Stress–strain curves from uniaxial compression tests comparing IUP, PC blend and T-PC blend are shown in Fig. 4. It should be noted that the end points of the stress–strain curves correspond to the termination of the particular compression test and not with sample failure. In particular, the maximum strain achieved in the high-rate tests (using the SHPB) is linked to the strain rate (due to the nature of applying the load through a pressure bar) where higher maximum strains are obtained for higher rate tests. The compression true stress–strain curves of each material exhibit the classic glassy amorphous polymer behavior of a rate-dependent yield stress followed by immediate post-yield strain softening followed by subsequent strain hardening. Interestingly, the PC blend and the T-PC blend each exhibits a greater amount of post-yield strain softening as compared to the IUP material. After softening, all three materials exhibit similar stress–strain behavior.

Compressive yield stress results are summarized in Table 2 and in Fig. 5. All three materials displayed two distinct regimes of rate-dependent yield behavior, with a significant transition in rate sensitivity occurring over the range of strain rates ($10^0\ s^{-1}$–$10^2\ s^{-1}$)

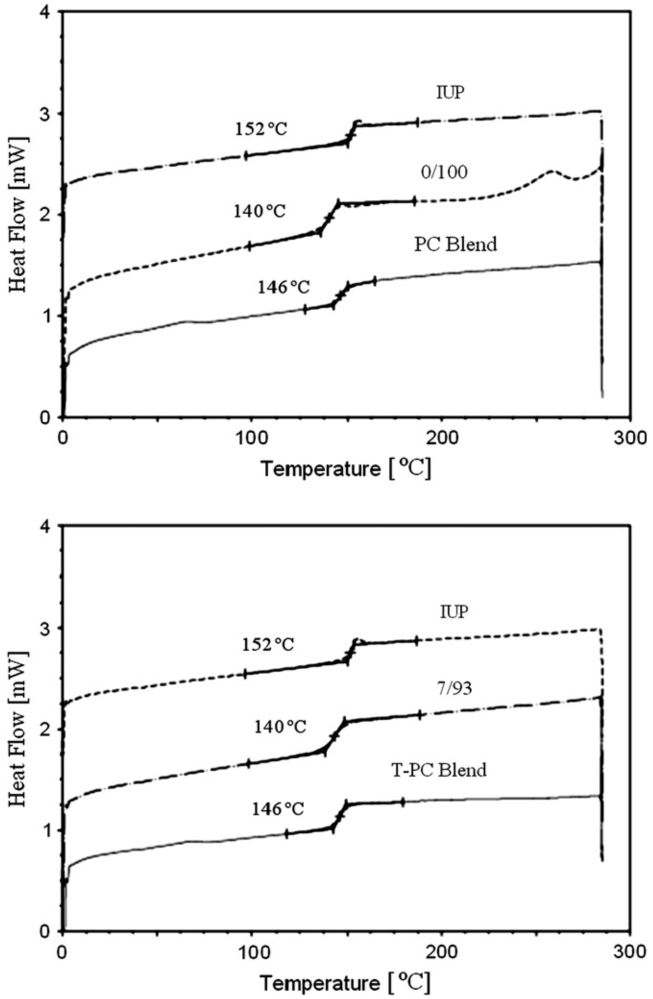

Fig. 2. 2nd cycle DSC scans of IUP, 0/100 and 7/93 polymers along with the 1st cycle scans of the blends after compression molding. 1st cycle scan of IUP disk was identical to the 2nd cycle scan of the IUP powder. T_gs are labeled next to the curves.

not accessed by either testing instrument. In the high-rate regime ($>10^3$ s^{-1}), yield stress was observed to be much more sensitive to changes in strain rate than in the low and moderate rate regimes (10^{-3} s^{-1}–10^{-1} s^{-1}). This finding was consistent with literature data [1–3] for Lexan® PC. The trend was the same in the polymer blends studied here. At every strain rate measured, the PC blend exhibited a yield strength superior to that of IUP by 6–10%. The yield stress of the T-PC blend was found to be greater than that of the PC blend by 5–7% and 12–17% greater than the IUP. It should be noted that a Lexan® PC (tested in a previous study [2] under all of the same conditions) exhibited higher yield stress values than the IUP. As can be seen in Table 2, this particular Lexan® has values on par with that of the PC blend, but less than the T-PC blend (and significantly less than the high molecular weight and higher triptycene content T-PCs described in Section 4.2).

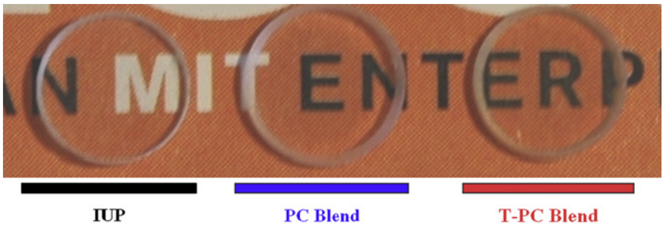

Fig. 3. Both blends display the same level of optical transparency as IUP, the commercial Iupilon® PC. Specimens shown are approximately 6 mm in diameter and 2 mm in height.

3.3. Thermally activated mechanical relaxations

Dynamic mechanical testing in tensile mode was used to probe the temperature and frequency dependencies of each material's response to small scale deformation. Comparative results for all three polymers are summarized in Fig. 6. In general, the character of the storage modulus curve was the same for all three polymers. PC and T-PC blends showed a lower glass transition temperature (both ≈ 162 °C from tan δ) compared to IUP (≈ 167 °C from tan δ) consistent with the DSC results. But despite the lower T_g, both blends displayed enhanced stiffnesses relative to IUP across most temperatures in the glassy regime. At all temperatures above -75 °C and below T_g, the PC blend had a storage modulus (G') 5–10% higher than IUP while the modulus of T-PC blend was 14–20% higher. The modulus values at room temperature (25 °C) for IUP, PC blend and T-PC blend were 1.89 GPa, 2.03 GPa, and 2.15 GPa, respectively.

All three materials exhibited a low temperature secondary (β) transition as apparent in the loss modulus as well as noticeable in the rate of increase in the storage modulus below 0 °C. For the case of PC blend, the β-peak was nearly identical to that of IUP, occurring at -103 °C and -108 °C for IUP and PC blend, respectively (from loss modulus). For the T-PC blend, this peak shifted to a lower temperature, -118 °C. The most noticeable difference in the loss modulus curves was the emergence of an additional transition at about -20 °C. This peak, labeled as β' in Fig. 6, was seen in both the PC blend and the T-PC blend where its intensity in the T-PC blend is equivalent to that of the β-peak. Close examination of the data for IUP revealed that Iupilon® PC indeed had a shoulder (barely discernible) in the β' region.

In Lexan® PC, the β-peak has been reported to shift linearly by 15 °C with each order-of-magnitude (OoM) in strain rate from 1 Hz to 100 Hz [2]. An approximate shift in the peak positions per OoM was therefore calculated and labeled on the curves in Fig. 6. Movements of the shoulder in IUP were not tracked due to the inability to accurately determine an actual peak position. The β-peak was seen to shift about 16 °C/OoM in IUP, which is consistent with reported values [2]. In PC blend, the β-peak shifted at a slower rate of 12 °C/OoM while the β-peak in T-PC blend shifted at a slightly higher rate of 18 °C/OoM. The β'-peaks in both blends shifted at comparable rates of 13–14 °C/OoM.

3.4. Tensile stress–strain data

Uniaxial tension tests (shown in Fig. 7) were conducted on dogbone samples to examine the tensile ductility of these polymers. All three polymers displayed characteristic ductile cold drawing behavior (including necking, neck stabilization and subsequent neck propagation) with nominal failure strains over 80%. The IUP and PC blend exhibited nearly identical behavior, with the PC blend demonstrating a slightly higher tensile yield stress and slightly lower tensile stress at failure. On the contrary, the T-PC blend exhibited a higher tensile yield stress as well as a higher tensile stress during cold drawing. Yield strength values were consistent with trends observed in uniaxial compression tests, with T-PC blend having the highest yield stress and IUP having the lowest. Post-yield, the stress–strain curve of PC blend overlapped with that of IUP, exhibiting flat engineering stress levels for about 40% apparent engineering strain (associated with sample drawing) before the samples began to strain harden. During this transition, some irregularities in the stress–strain profile were noticeable as "dips" or "bumps." This corresponded to the neck propagating to

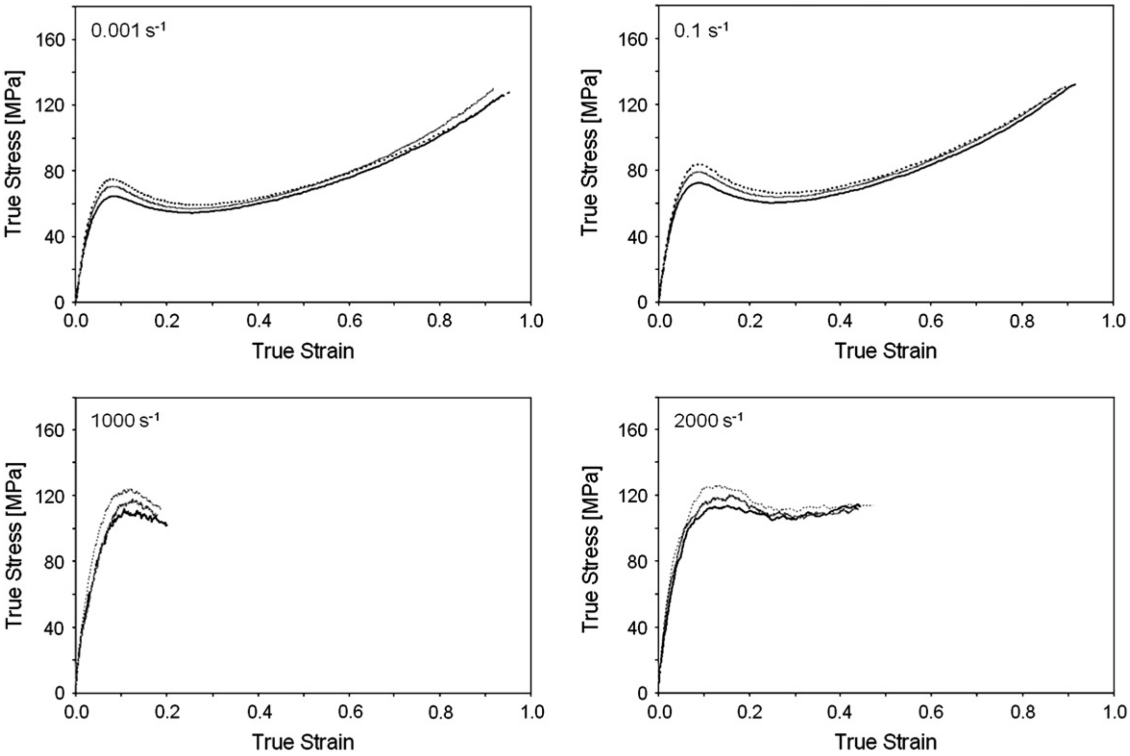

Fig. 4. Uniaxial compression tests at varying strain rates of IUP (solid line), PC blend (hashed line) and T-PC blend (dotted line).

Table 2
Compressive yield strengths at various engineering strain rates[a]

Material	Strain rate				
	0.001 s^{-1}	0.01 s^{-1}	0.1 s^{-1}	1000 s^{-1}	2000 s^{-1}
Lexan[b]	70 MPa	74 MPa	78 MPa	112 MPa	117 MPa
IUP	64 MPa	68 MPa	72 MPa	109 MPa	112 MPa
PC blend	70 MPa	74 MPa	79 MPa	116 MPa	119 MPa
T-PC blend	75 MPa	79 MPa	84 MPa	123 MPa	125 MPa

[a] Standard deviations for low strain rates were less than 1 MPa. Standard deviations for high strain rates were about 1 MPa.

[b] Data from Lexan® 9034 PC [2].

the edge of the gauge length and impinging upon the tapered section just before the grip areas of the dogbone samples. This effect was also present in the T-PC blend but at higher strains and was followed by a failure shortly thereafter.

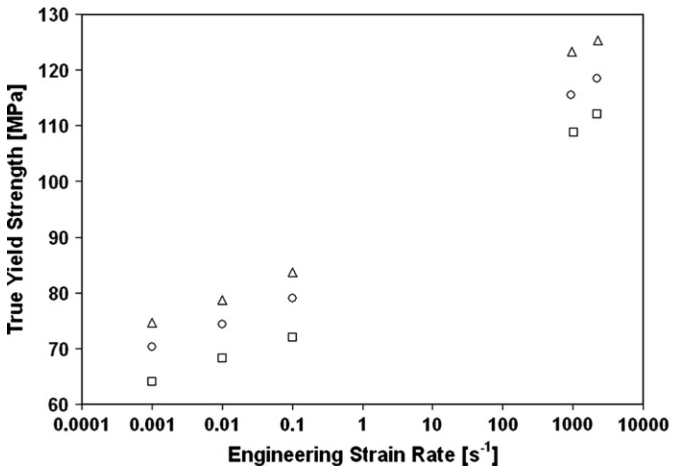

Fig. 5. Engineering strain rate dependence of the yield strengths of IUP (square), PC blend (circle) and T-PC blend (triangle).

Young's modulus was not obtained from these tensile tests, since cross-head displacement was used to monitor the strain and hence does not give a good measure at small strains. The strain is reported in Fig. 7 as an "apparent engineering strain" defined as the cross-head displacement divided by the gauge length. Results from the tensile tests are summarized in Table 3 along with the tensile modulus measured from DMTA.

3.5. *Discussion*

Both DSC and DMTA confirmed that the blending process resulted in homogeneous, amorphous polymer samples. Each of the blends exhibited a single glass transition, that was an average between the higher T_g from the Iupilon® PC and the lower T_g from the lower molecular weight PCs. The density was seen to increase slightly for the blends but within one standard deviation of the pure Iupilon® PC. Despite these relatively minor differences, the mechanical properties seemed to be very sensitive to composition. Both blends exhibited enhanced values for stiffness and yield strength in both compressive and tensile tests. While the increase in stiffness and yield strength from IUP to PC blend can be attributed to blending effects, the additional improvements from PC blend to T-PC blend are more likely related to the presence of triptycene units. Thus, enhancements bought about by the presence of triptycene units occurred with only a 1.9 wt% triptycene content.

When incorporated into a polyester, triptycenes have been shown to induce novel steric inter-chain interactions, such as molecular threading and molecular interlocking through the minimization of IMFV, while inhibiting crystallinity [1,2]. These enhanced lateral interactions resulted in higher stiffnesses and strengths while also improving ductility through an extended sample drawing region believed to be associated with molecular threading. However, in the present study, due to the larger diameter of the bisphenol-A component with pendant methyl

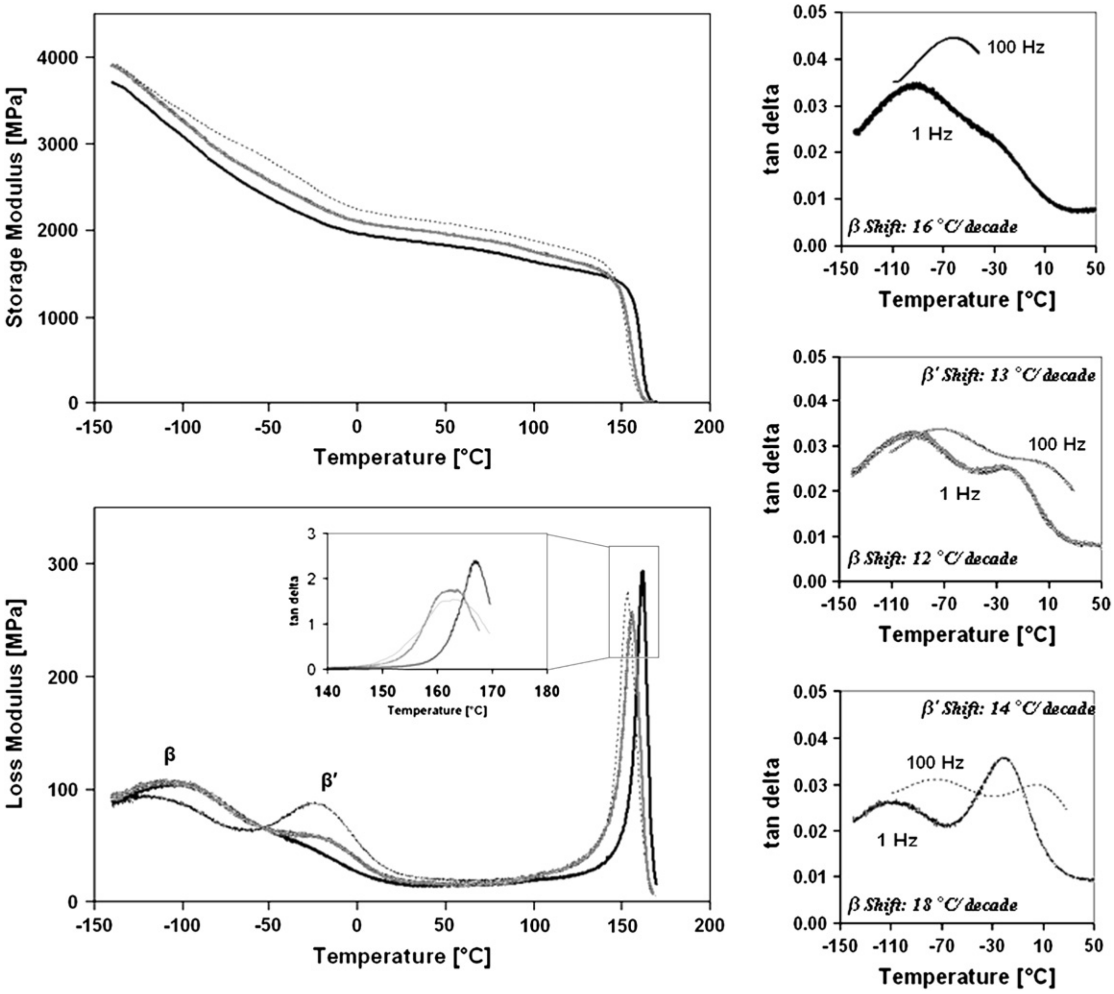

Fig. 6. DMTA of IUP (solid line), PC blend (hashed line) and T-PC blend (dotted line). Curves are at 1 Hz unless labeled otherwise.

side-groups, the PC chain may not thread through triptycene cavities as efficiently as the polymers containing linear aliphatic components used in previous studies. Unlike the polyester-based systems [11], there was no triptycene–triptycene interlocking region observed in the high strain data. Before discussing the specific compressive and tensile properties, we analyze the DMTA data to build a framework to understand how these chain packing interactions directed the mechanical properties observed.

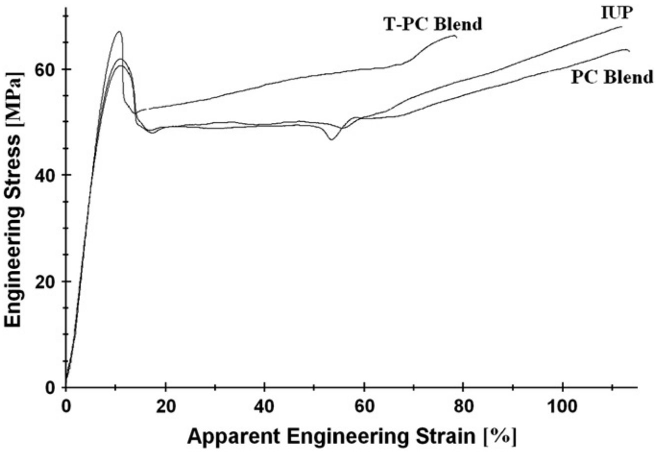

Fig. 7. Uniaxial tensile tests of dogbone samples for IUP, PC blend and T-PC blend.

Table 3
Tensile mechanical properties

Material	ρ^{a} [g/cc]	E^{b} [GPa]	$\sigma_{y}{}^{c}$ [MPa]	$\varepsilon_{b}{}^{d}$ [%]
IUP	1.19	1.89	61	110
PC blend	1.20	2.03	63	110
T-PC blend	1.20	2.15	67	80

[a] ρ: density, standard deviations ≈ 0.01 g/cc.
[b] E: Young's modulus from DMTA (1 Hz at 25 °C), standard deviations ≈ 0.02 GPa.
[c] σ_y: tensile yield strength, standard deviations ≈ 1 MPa.
[d] ε_b: strain to break, highest value observed.

The compressive yield behavior of many polymers including PC is often correlated with sub-T_g thermally activated mechanical (β) relaxations [16] that are indicative of accessible deformation modes related to the molecular motions of specific segments of the polymer chain. It has been shown that the variation of the compressive yield strength of PC with strain rate is directly related to its β relaxation [1,2]. While it is debated as to whether the phenyl motions or carbonate motions dominate this relaxation, modifications to the main chain that affect the mobilities of either the phenyl or the carbonate groups have been shown to alter the shape and position of the β-peak [17–19]. However, it has also been shown that the β relaxation involves intra-chain *and* inter-chain cooperative motions [19,20]; and therefore, any local molecular restrictions would have to influence multiple repeat units in order to affect the β relaxation. The blending process did not result in any changes to the β relaxation as the loss modulus curves for IUP and

PC blend were identical around that transition. Therefore, the shift in peak position of the β relaxation for T-PC blend can be attributed solely to triptycene interactions. It is possible that the triptycene units function as local inhomogeneities in the chain backbone, which disturb the cooperative motions of the bisphenol-A PC. However, copolymerizations with aromatic groups in as high as 25 mol% that do not chemically alter the phenyl or carbonate groups in the main chain of PC have been shown to leave the β relaxation unaffected [21,22]. Therefore, we suggest two plausible explanations for changes to the β relaxation. First, it is possible that the triptycene units do not engage in the types of molecular threading seen in polyester studies. Instead, the IMFV associated with each triptycene unit is left unoccupied increasing the total free volume in the system. This increase in free volume affords greater molecular mobility to the PC chain resulting in a lower T_β and T_α. This would imply that there should be a lower density in the triptycene-containing PC (which however was not observed). M_e data imply a lesser degree of entanglements, but the effects of molecular weight distribution on the data are not accounted for. The literature does not mention that either an increase in free volume nor samples with low molecular weight (unless below 6–9 units of PC monomer) dampen the intensity of the β-peak.

The second possibility is that the triptycenes *do* engage in molecular threading with constituents of the PC main chain. Since molecular threading would create localized restrictions, it might be expected that the β relaxation would therefore occur at a higher temperature. However, the β peak was seen to appear at a lower temperature. This may occur for two reasons. First, it has been suggested that the β relaxation consists of two overlapping contributions: a lower temperature peak from carbonate rotation and a higher temperature peak from phenyl rotation [17]. The suppression of one of these mechanisms while leaving the other intact would serve to narrow the peak. Second, the facility of a particular motion will also lower the temperature at which that peak occurs. The data in Fig. 6 imply that the phenyl motions were dampened and carbonate motions were facile. This is unlikely to occur from localized free volume enhancements. Furthermore, increasing free volume has been shown to *decrease* yield strengths in PCs [21,23–27] which is in contrast to what was observed here. Therefore, we propose that the presence of increased inter-chain interactions introduced by molecular threading accounts for the enhancement of mechanical properties. The data suggest that the triptycene units interact with the phenyl units and enhance cooperative motions of the carbonate units. Increased inter-chain interactions would also explain the enhanced yield strengths observed, given the opposite effect expected from the lower T_gs.

DMTA revealed that PC and T-PC blends had an additional peak (β′) appearing as a minor shoulder in IUP. This peak, which occurred at about −20 °C, showed that blending the lower molecular weight PC with the Iupilon® PC enhanced a minor relaxation. While the exact mechanism is unclear, it could be possible that the lower molecular weight PC had a shifted β-peak which appeared as a separate peak in the blends. It is also possible that the presence of low molecular weight PC induces additional molecular motions in the high molecular weight PC similar to what is seen in polyester–PC copolymers [21]. In either case, the enhancements to Young's modulus and yield strengths of PC blend over IUP are accompanied by the emergence of this additional peak. In the T-PC blend, the β′-peak was even more intense, and the Young's modulus and yield strengths are again increased.

The difference in the stress–strain behavior between tension and compression at large strains is a result of the differences in the evolution of molecular orientation during uniaxial tension vs. that during uniaxial compression. Uniaxial compression results in a preferential biaxial chain orientation in a plane perpendicular to the loading axis; whereas, uniaxial tension aligns the polymer chains along the loading direction. Most significantly, the tensile data show that embrittlement, normally associated with the enhancements to modulus and yield strength, did not occur.

4. High molecular weight T-PC results

4.1. High molecular weight, higher triptycene content T-PC samples

The positive mechanical properties trends observed for the blends spurred us to develop T-PCs with higher triptycene content and with molecular weights comparable to that of commercial PC (Table 1). Three polymers with increasing triptycene content (5/95, 15/85, and 25/75 T-PCs) were prepared for characterization using the identical procedures as for the blends in the previous section (the corresponding weight percentages of triptycene are listed in Table 4). All three T-PC materials were optically transparent. DSC was used to confirm that the samples were amorphous through the absence of any sharp crystalline melting peaks and the display of a strong glass transition (T_g). Values displayed in Table 4 show that the T_g initially decreased with the addition of approximately 6 wt% triptycene but then increased with additional triptycene content. Density measurements showed a slight increase with triptycene content, and the entanglement molecular weight (M_e) as measured by the plateau modulus in melt rheometry also increased by more than a factor of two with triptycene content from 0 wt% to 26 wt%.

4.2. Compression testing

Uniaxial compression testing was conducted on specimens of circular disk geometries. Stress–strain curves are shown in Fig. 8. As before, the end points of the stress–strain curves correspond with the termination of the particular compression test and not with sample failure. At all strain rates, the stress–strain curves of all T-PC polymers displayed the same characteristic behavior as IUP, and the

Table 4
Structural, thermal, and mechanical properties of a family of IUP and high molecular weight T-PCs. Standard deviations provided in parentheses where appropriate. Standard deviations for all yield strain values were ±1%

Sample	IUP	5/95	15/85	25/75
Triptycene content [wt%]	0	6	16	26
ρ [g/cc]	1.19 (±0.01)	1.20 (±0.01)	1.21 (±0.01)	1.21 (±0.01)
T_g[a] [°C]	153/162	147/157	164/170	176/183
M_e [g/mol]	1920 (±90)	2390 (±30)	3320 (±200)	4160 (±450)
Modulus[b] [GPa]	1.89 (±0.01)	2.06 (±0.02)	2.23 (±0.01)	2.33 (±0.01)
σ_y/ε_y (at 0.001 s^{-1}) [MPa]/[%]	63 (±1)/10	75 (±1)/11	86 (±1)/11	90 (±1)/13
σ_y/ε_y (at 0.01 s^{-1}) [MPa]/[%]	66 (±1)/11	78 (±1)/11	90 (±2)/12	97 (±1)/13
σ_y/ε_y (at 0.05 s^{-1}) [MPa]/[%]	69 (±1)/10	80 (±1)/12	94 (±1)/12	99 (±1)/14
σ_y/ε_y (at 1000 s^{-1}) [MPa]/[%]	107 (±1)/12	124 (±1)/11	141 (±2)/11	152 (±1)/12
σ_y/ε_y (at 2100 s^{-1}) [MPa]/[%]	113 (±1)/12	133 (±1)/11	148 (±2)/12	160 (±1)/12

[a] T_g values measured from both differential scanning calorimetry and dynamic mechanical analysis loss modulus curves presented as DSC/DMTA in the table.
[b] Tensile modulus measured from DMTA storage modulus curves at 25 °C.

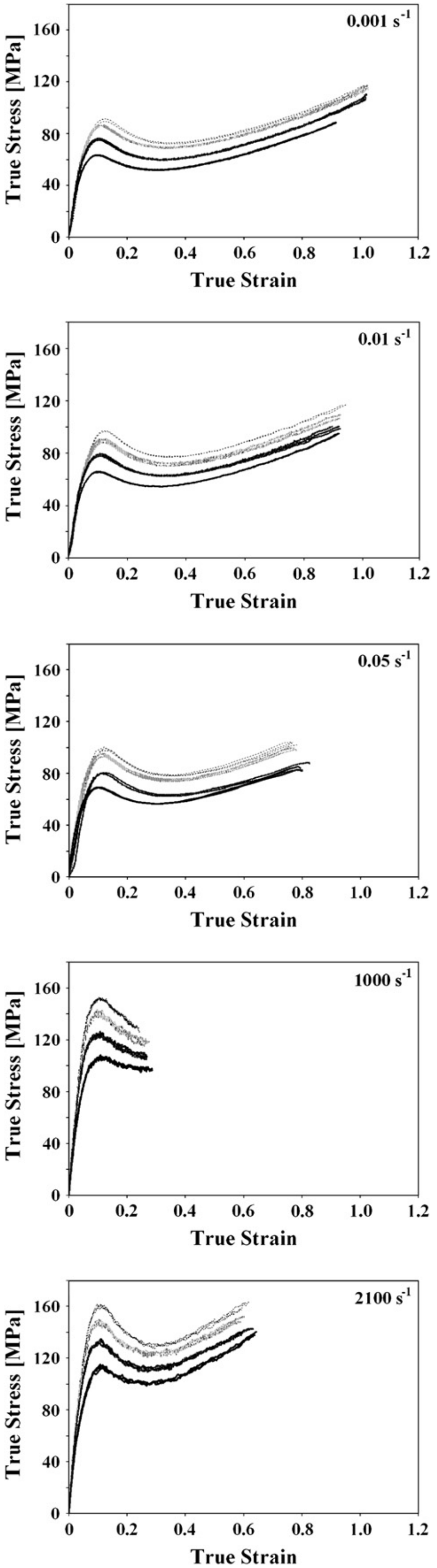

Fig. 8. Uniaxial compression tests at varying strain rates (top-slowest, bottom-fastest) for IUP (solid line), 5/95 (dark hashed line), 15/85 (light hashed line), and 25/75 (dotted line) PC and T-PC polymers.

mechanical properties of the T-PC copolymers were consistently superior to that of IUP, with enhancements increasing with triptycene content. Yield strengths, compiled in Table 4, are shown graphically in Fig. 9. The rate dependence of the yield strength shifts significantly upon transitioning from low strain rates ($0.001\ \mathrm{s}^{-1}$–$0.05\ \mathrm{s}^{-1}$) to high strain rates ($\geq 1000\ \mathrm{s}^{-1}$). Enhancements to the yield strength with increasing triptycene content were also of greater magnitude at high strain rates, making the *percentage* improvements approximately constant across all rates of deformation. Yield strengths of 5/95 T-PC, 15/85 T-PC, and 25/75 T-PC were consistently 16–19%, 31–37%, and 42–47% greater than that of IUP, respectively. Yield strains were also seen to increase with triptycene content.

4.3. Thermally activated mechanical relaxations

DMTA was conducted to obtain storage modulus and loss modulus data as a function of temperature at 1 Hz. These curves, exhibited in Fig. 10, show that the room temperature modulus increased systematically with triptycene content (values in Table 4). DMTA confirmed the T_g (labeled the α-transition) behavior observed in DSC. The low temperature storage modulus data were tied directly to the low temperature thermal–mechanical transitions visible in the loss modulus data. In the IUP, the prominent β-transition peak occurred at about −103 °C. This peak shifted to −109 °C for the 5/95 T-PC. The β-transition did not shift consistently with increasing triptycene content as the peaks for 15/85 and 25/75 T-PCs were located at −95 °C and −101 °C, respectively. In the 5/95 T-PC, an additional peak arose between the well-documented α- and β-transitions. This transition is labeled β′ in Fig. 10 and occurred around −24 °C. This β′-peak was not readily visible in either the IUP or 15/85 T-PC. However, it reemerged in the 25/75 T-PC at about −21 °C, although with less intensity than in the 5/95 T-PC sample.

4.4. Discussion

All three higher molecular weight, higher triptycene content T-PC materials were amorphous and transparent. The *decrease* in the glass transition temperature for the 5/95 T-PC was not consistent with our previous work showing the trend of T_g with triptycene-content in copolyesters or for the trend of T_g for the higher triptycene content T-PCs. The M_e measurements showed that the entanglement molecular weight increased strongly with triptycene content (by a factor of 2 over PC for the 25/75 T-PC). This strong

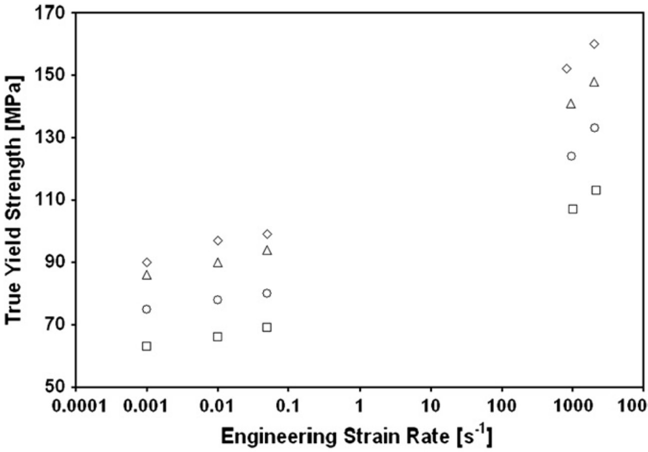

Fig. 9. Plot of yield strengths vs. strain rates for IUP (square), 5/95 (circle), 15/85 (triangle), and 25/75 (diamond) PC and T-PC polymers.

composition dependence of the entanglement density suggests different backbone conformations and chain packing with increased triptycene content.

The unexpected decrease in T_g for the 6 wt% triptycene may be due to the alteration of the chain packing by the triptycene units not being compensated by the loss of chain mobility (from molecular threading) resulting in an overall net lowering of the glass transition. However, at higher triptycene content, the lateral interactions and restricted chain mobilities from the triptycene groups overwhelmed the increase in M_e; so the T_g increased significantly (by 24–176 °C for the 25/75 T-PC).

The β-transition peak initially shifted towards lower temperatures with increasing triptycene content but then shifted to the opposite direction, appearing to be progressively approaching the original position of β in the PC homopolymer. It has been suggested that bisphenol-A PC requires approximately 6–9 connected repeat units to express its β-transition [18,19], which is believed to involve both inter-chain and intra-chain cooperative motions [19,20]. Based on the assumption of random copolymerization, the average number of PC repeats between T-PC units for the 5/95, 15/85, and 25/75 samples is 19, 5–6, and 3, respectively. Since the 25/75 T-PC is well below the required 6–9 units of uninterrupted bisphenol-A PC repeats, the β-transition should have been mostly eliminated. Two possible explanations for why it remained significant are i) single triptycene-containing blocks still exhibit a β-transition or, ii) through the inter-chain interactions brought on by the minimization of IMFV about the triptycene units, the cooperative motions of the bisphenol-A PC blocks are enhanced. While these two explanations are not mutually exclusive, the non-monotonic movements of the β-transition with increasing triptycene content favor the latter, where the effects of IMFV have also been observed to be non-monotonic.

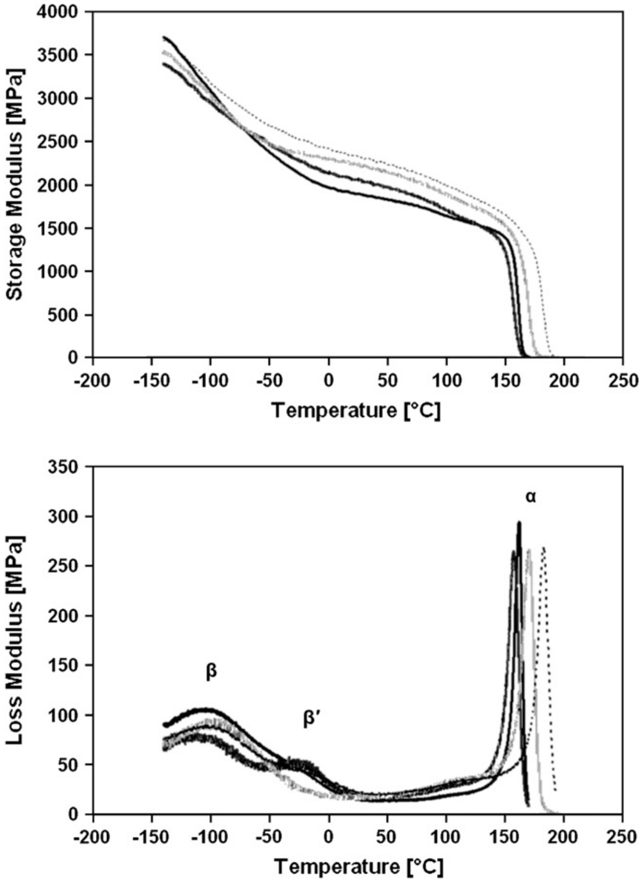

Fig. 10. DMTA of IUP (solid line), 5/95 (dark hashed line), 15/85 (light hashed line), and 25/75 (dotted line) PC and T-PC polymers.

Additionally, the emergence of the salient new transition (β′, as also seen in the blends) appeared in the 5/95 T-PC, hallmarking the possibility of unique behavior in these samples. However, the disappearance of this peak in the 15/85 T-PC and then its *reappearance* in the 25/75 T-PC are perplexing. At least three samples per polymer were tested and not a single one contradicted this finding. There was no readily apparent explanation for this, as it did not correlate with any of the other structural, thermal or mechanical observations seen here. It could represent some sort of "optimization" of the molecular motions responsible for the relaxation spectra, but the molecular origin of the new low temperature β′ transition is unclear.

Most importantly, the higher triptycene content in high molecular weight T-PCs resulted in enhanced mechanical properties. The modulus, compressive yield strength, and compressive yield strain are all increased. The modulus increased approximately on par with triptycene content, but the yield strengths displayed outsized percentage enhancements relative to the triptycene weight percent (in some cases, as high as two to three times). The benefits were nonlinear and seemed to saturate with increasing triptycene content. The increase in compressive yield strain indicated possible enhancements to ductility.

5. Conclusions

This study focused on the influence on mechanical behavior brought about by the incorporation of triptycene units into the well-known and commercially important thermoplastic, polycarbonate. Two types of material systems were investigated and compared to commercial PC: a low molecular weight, low triptycene content polymer that could only be studied in blends with the commercial PC and a series of higher triptycene content, higher molecular weight polymers. The 25 wt% blends of a 7.7 wt% triptycene-containing PC was found to enhance the stiffness of a commercial Iupilon® PC at all temperatures. Blends of the triptycene-containing PC enhanced the compressive yield strength of the Iupilon® PC by as much as 17%. Loss modulus data revealed that the PC β-transition was significantly altered by blending in the 7/93 T-PC polymer, creating two distinct low-temperature loss peaks (β and β′) where there had only been one in the Iupilon® PC homopolymer. The triptycene-containing PC blend was optically transparent, amorphous, and showed no evidence of phase separation. There were notable differences in the stress–strain responses in compression vs. tension. Tensile data indicated that the molecular threading in the triptycene-containing PC blend was less efficient than in the triptycene-containing polyesters studied previously. This, combined with the relatively low molecular weight and low concentration of triptycene units (1.9 wt% overall), resulted in no detectable region of molecular interlocking in the tensile stress–strain measurements. The three high molecular weight, well entangled, higher triptycene content copolymers (from 8 wt% to 26 wt%) exhibited improved mechanical properties. The new β′ peak was 75 °C above that of the β peak, the glass transition increased by up to 24 °C while the entanglement molecular weight increased by about a factor of 2×. Importantly, there was a nearly 50% increase in the compressive yield strength over Lexan PC for the 26 wt% sample at high strain rate (2000 s^{-1}). This work shows the ability for the insertion of a chemical unit with internal molecular free volume to create new types of chain packing and interactions during plastic deformation. The improvement of the compressive yield strengths of T-PCs over homopolymer PC by as much as 40% at both low strain rates and high strain rates indicates that these novel triptycene-enhanced

PCs could offer a competitive commercial material for use in lightweight, high impact resistance applications.

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