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High Strength Polyolefin Block Copolymers

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The phase behavior, dynamic mechanical response, processing characteristics, and physical properties of hydrocarbon block copolymers prepared by complete hydrogenation poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) SBS triblock and SBSBS pentablock copolymers have been explored by several research groups in the past years.[1−9] Control of the precursor poly(butadiene) regiochemistry allows the physical state of the hydrogenated "soft" blocks to be adjusted between rubbery poly(ethylethylene) and semicrystalline poly(ethylene) (PE or E). Hydrogenation of poly(styrene), creating poly(cyclohexylethylene) (PCHE or C), leads to several property improvements, including an elevated glass transition temperature, $T_g \approx 145$ °C, enhanced UV stability, and a very small stress-optic coefficient.[1−4,6−8,10] Perhaps the only drawback with PCHE is extreme brittleness due to its large entanglement molecular weight, $M_{e,C} \approx 40$ kg mol^{-1}.[10] However, creation of CEC and CECEC block architectures can impart significant improvements in toughness, making these "polyolefin" copolymers attractive candidates for commercial applications.[1]

Recent experiments with shear aligned CECEC and CEC specimens, strained in tension along the lamellae normal, revealed a distinctive toughening mechanism in the former, while the latter failed in a brittle manner.[8] These results suggest that bridging of center C blocks in CECEC suppresses brittle failure of the glassy layers. This communication describes a processing procedure applied to the same lamellar-forming pentablock and triblock materials and a CE diblock copolymer. Extrusion and cold-drawing resulted in specimens with tensile strength (σ_{TS}) as much as 5 times that derived from conventionally compression-molded tensile bars. Experiments with mixtures of pentablock and dioctyl phthalate (DOP) have provided insight into the origins of mechanical strength in microphase-separated thermoplastics.

CECEC pentablock, CEC triblock, and CE diblock copolymers were prepared by a combination of anionic polymerization and catalytic hydrogenation;[4] the CECEC and CEC materials were provided by the Dow Chemical Co., while CE was prepared at the University of Minnesota. All three compounds contain nearly symmetric compositions, E blocks with approximately 25 ethyl branches per 1000 backbone carbons (stemming from approximately 10% 1,2-addition in the poly(butadiene) precursor), and molecular weights that placed the order−disorder transition temperatures (T_{ODT} as established by dynamic mechanical spectroscopy (DMS) measurements) between 230 and 245 °C. Characterization results for these three polymers are listed in Table 1. E block crystallinity was determined by differential scanning calorimetry (DSC) while the T_g of the C block was estimated from DMS measurements. DMS measurements were performed using 25 mm diameter parallel plate with an approximately 1 mm gap (Rheometrics ARES); we restrict our attention to isochronal ($\omega = 1$ rad/s) dynamic storage modulus (G') measurements while heating or cooling at 2 °C/min.

Table 1. Characterization Data for CE, CEC, and CECEC Block Copolymers

sample	M_n (kg mol^{-1})	M_w/M_n[a]	wt % C	PE crystallinity (%)[d]	T_{ODT} (°C)[e]
CE	18	1.04[b]	50	37	232
CEC	34	<1.05	61	15−20	243
CECEC	55	1.03[c]	55	20	231

[a] Determined by size exclusion chromatography (SEC) with PS calibration standards. [b] Determined for SB precursor in THF at 25 °C. [c] Measured in trichlorobenzene at 135 °C. [d] Percent of E block in crystalline form as determined by DSC. [e] Determined by DMS.

Table 2. Characterization Data for the CECEC/DOP Blends

wt % polymer	T_{ODT} (°C)[a]	T_g PCHE (° C)[a]	T_m PE (°C)[b]	PE crystallinity (%)[b]	*D* spacing (nm)[c]
100	232	125	83	18.3	17.0
97	219	119	83	20.8	17.6
95	207	108	83	20.7	17.1
93	201	105	84	21.9	17.6
90	180	95	88	22.6	17.6
85	162	88	91	25.3	17.7
80	141	83	93	28.3	17.7
75	120	65	92	31.3	18.1

[a] Determined by DMS. [b] Determined by DSC. [c] Determined by SAXS at 25 °C after heating and cooling above the T_m of the E blocks.

CECEC/DOP blends were prepared by dissolution of both components in benzene followed by freezing in liquid nitrogen and then drying under vacuum (0.1 Torr) overnight at 25 °C. Table 2 lists the physical property characteristics of the blends. Subsequently, these mixtures were extruded using a capillary rheometer fitted with a 30 mm long and 1.0 mm diameter cylindrical die at an extrusion rate of 10 s^{-1} and a temperature at the order−disorder transition temperature of the CECEC/DOP mixture (see Table 2) followed by immediate cooling in an ice water bath.

Portions of the extruded samples were further processed at room temperature by drawing to the completion of necking, resulting in extensions of approximately 300% (100 wt % CECEC) to 650% (75 wt % CECEC) (Figure 1a). A small fraction of this additional strain was recovered when the specimens were released, e.g., a CECEC sample drawn to 300% had a permanent set of 270% strain, while the final length of a 650% drawn 75 wt % CECEC material reflected roughly 500% strain. This overall process led to stiff and clear fibers of approximately 0.5 mm in diameter.

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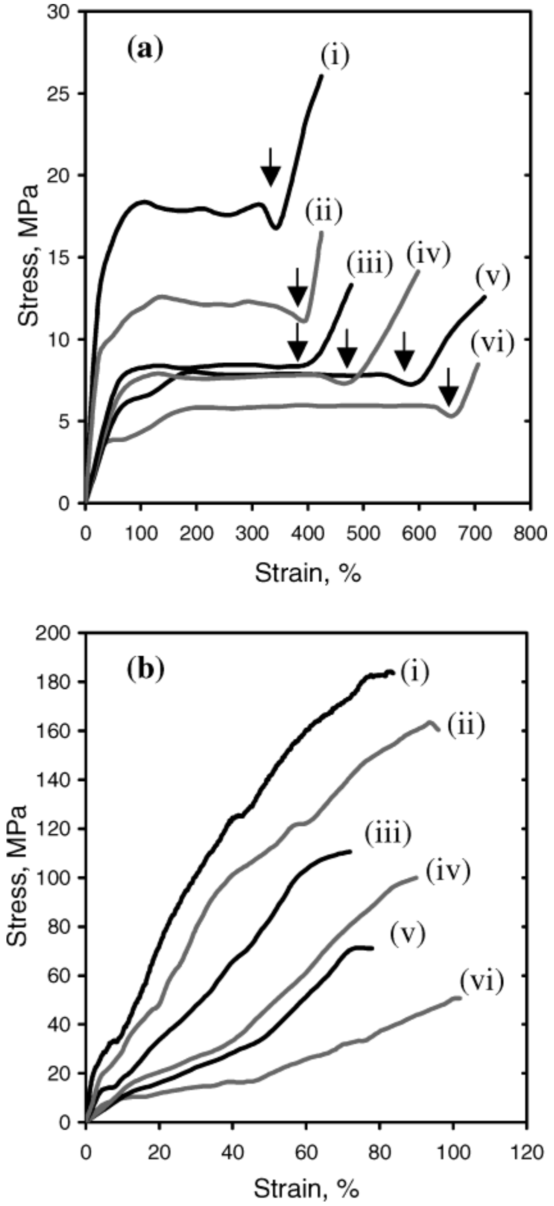

Figure 1. Representative engineering stress−strain curves for CECECE/DOP mixtures: (i) 100 wt %, (ii) 95 wt %, (iii) 90 wt %, (iv) 85 wt %, (v) 80 wt %, (vi) 75 wt % CECEC; (a) before drawing, (b) after drawing to complete necking as identified by the arrows in (a).

Tensile testing of the extruded materials was performed at room temperature using a MINIMAT tensile tester (Rheometrics Scientific) operated at a cross-head speed of 5 mm min^{-1} (strain rate of 0.017 s^{-1}). At least 10 specimens were tested in each case reported to establish a reproducible result. Figure 1a illustrates representative stress−strain curves for extruded CECEC/DOP blends, i.e., prior to drawing. Each sample displayed an elastic region followed by yielding and a constant stress plateau region that is accompanied by neck propagation. Complete necking is signaled by strain hardening with failure following shortly after this point. Here we note that failure always occurred in close proximity to the grips, leading us to conclude that the measured tensile strengths represent lower estimates. In general, the addition of DOP depresses the yield stress, resulting in a more ductile material with a lower tensile strength. The neat CECEC extrudate yields at about 18 MPa, followed by necking, and fails at an average stress of 23 ± 3 MPa and 430% strain. This response is typical for unoriented CECEC and consistent with the results from previous work.[11]

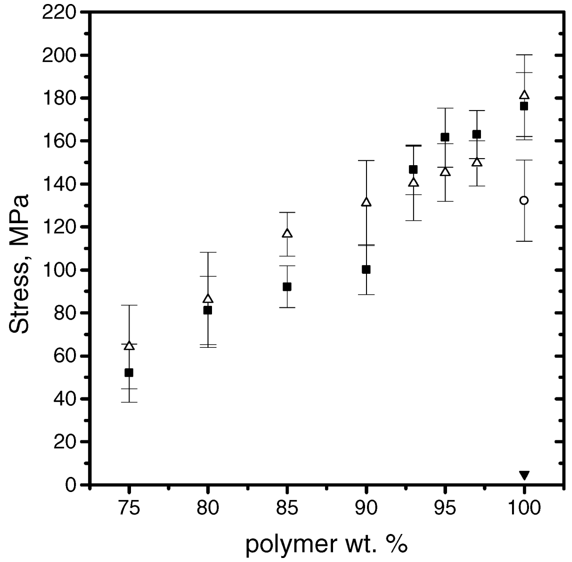

Figure 2. Engineering failure stress for drawn CEC (○), and CECEC/DOP blends, as a function of polymer concentration (in wt %): Δ, aged 3 days; ■, aged 30 days after extrusion. CE (▼) measurement refers to undrawn specimens, which were too brittle to strain.

Figure 1b documents representative stress−strain data for the drawn (i.e., prestrained) CECEC/DOP blends. The average tensile strength of these samples was significantly larger than the undrawn counterparts. For example, the undrawn 75 wt % polymer sample failed at an average stress of 8 MPa while the drawn 75 wt % polymer sample failed at an average stress of 52 MPa. This type of strain hardening has been observed in semicrystalline homopolymers such as poly(propylene) and gel-spun poly(ethylene)[12,13] and even in glassy polymers such as poly(styrene).[14] Figure 2 depicts the ultimate (engineering) tensile strength for each of the CECEC/DOP blends tested. Failure stress increases linearly with polymer concentration, and all the CECEC/DOP blends failed at a similar failure strain (80−120%, Figure 1b), independent of aging time up to 30 days. The measured tensile strengths for drawn neat CEC and (undrawn) neat CE are also shown in Figure 2.

Addition of DOP influences these block copolymers in at least three ways. First, addition of DOP reduces the order−disorder transition temperature (T_{ODT}) as indicated by DMS and small-angle X-ray scattering (SAXS) measurements (Table 1). According to previous work,[15,16] a solvent is considered to be neutral when $\chi_{\text{ODT}} \sim \phi^{-(1.3-1.6)}$, where ϕ is the volume fraction of block copolymer. In preliminary experiments, we found that χ_{ODT} for the CECEC/DOP blends scales with $\phi^{-1.36}$. Also, the periodic spacing, D, of a lamellar block copolymer decreases upon dilution with a neutral solvent.[16−18] In a separate experiment, the CE diblock was blended with DOP (from 55 to 100 wt % polymer), and D (measured using SAXS at 135 °C) decreased with increasing DOP concentration, scaling as $D \sim \phi^{0.22}$, which is within the range calculated by Whitmore and Noolandi[18] for block copolymers in a neutral solvent where $D \sim \phi^{p}$ with $0.22 \leq p \leq 0.4$, depending on the segregation strength between blocks. Second, the glass transition temperature of the C blocks is significantly depressed in the DOP impregnated samples. T_g was associated with the

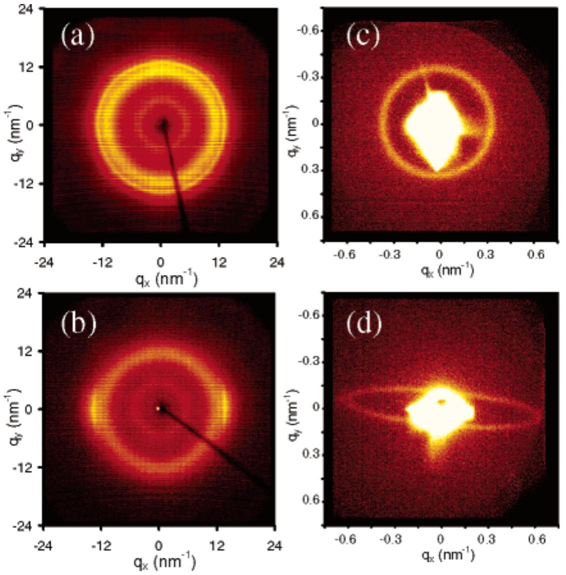

Figure 3. X-ray scattering patterns obtained from CECEC pentablock copolymer in the undrawn state (a and c) and after drawing to a state of complete necking (b and d), where the specimens were drawn in the vertical direction. Panels (a) and (b) were obtained using a WAXS instrument while (c) and (d) were recorded with a SAXS instrument.

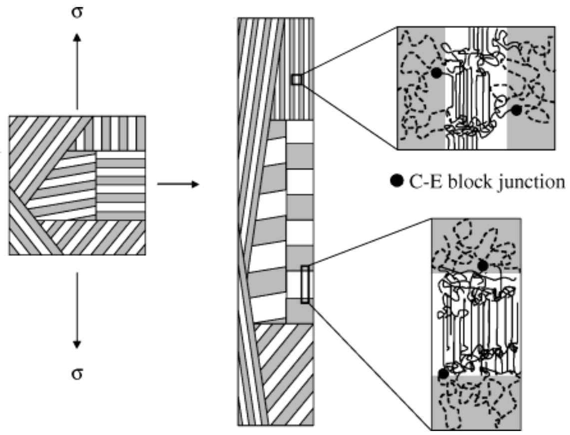

Figure 4. Illustration of proposed microstructure for undrawn and drawn CECEC pentablock copolymer. Enhanced tensile strength in the drawn material is attributed to E block entanglement and chain alignment and immobilization of C−E block junctions at the glassy C domain boundary.

peak in tan δ as measured by DMS. The T_g for neat CECEC was determined to be 125 °C while for the 75 wt % CECEC $T_g \approx 65$ °C.[19] In a separate set of experiments, we determined that addition of 25 wt % DOP to a PCHE homopolymer ($M_n = 8$ kg mol^{-1}) lowered T_g from 121 to 44 °C by DSC. We assume that the C blocks in the CECEC/DOP blends are similarly plasticized.[20] Third, the percent crystallinity and the melting temperature of the E blocks increased significantly with the addition of DOP. For example, DSC measurements reveal a sharp endotherm at about 92 °C for the 75 wt % CECEC, nearly 10 deg higher than in the neat CECEC (Table 2). Furthermore, the integrated heat of melting indicates roughly 50% greater E block crystallinity in CECEC after addition of 25 wt % DOP. We attribute the enhanced crystallinity to dilution of the E domains with the neutral DOP, which facilitates packing of E blocks into folded and fringed crystallites.

E domain crystallinity is evident in room temperature wide-angle X-ray scattering (WAXS) patterns, as illustrated in Figure 3. A narrow ring of wide-angle diffraction indicates a random distribution of E crystallites in the undrawn extruded CECEC specimen (Figure 3a). Drawing and necking sweeps all the diffraction into two narrow, high intensity arcs on either side of the symmetric rings of uniform intensity associated with amorphous polymer (Figure 3b). From this we can conclude that the drawing process induces crystal alignment, with the molecular axis of the E chains oriented along the direction of strain. DSC traces obtained after drawing are nearly indistinguishable from those acquired before this processing step, indicating no significant change in the degree of crystallinity or melting point.

Two-dimensional SAXS patterns obtained from undrawn CECEC extrudates reveal an isotropic arrangement of lamellae (Figure 3c). However, drawing transforms the circular ring of first-order diffraction into an elliptical pattern (Figure 3d) with an aspect ratio of about 5.4, close to what is anticipated (5.2) for the affine deformation of randomly distributed grains of lamellae at 300% strain and constant density. Similar SAXS patterns were reported by Hsiao and co-workers[21] after cold drawing poly(ether ester) block copolymers. WAXS and SAXS results from all the CECEC/DOP mixtures resemble the data shown in Figure 3. A schematic illustrating these structural changes is presented in Figure 4.

The principal finding of this report is a process for producing uncharacteristically strong ($\sigma_{TS} \geq 175$ MPa) thermoplastic polyolefin materials. Comparison of the neat CECEC pentablock performance with the plasticized results, and the behavior of undiluted CEC and CE, offers insights into the molecular mechanisms responsible for strengthening plastics and elastomers.

One of the strongest known polymeric materials is ultrahigh molecular weight gel-spun poly(ethylene), marketed under the trade names Spectra and Dyneema, which displays a tensile strength as high as 4 GPa. Assuming the aligned E crystals bear the entire tensile load, and based on 55% E (Table 1) and 18% crystallinity (Table 2), we would anticipate up to 10% of this strength in CECEC. This is just twice the measured tensile strength, a remarkable result given the molecular weight of CECEC is a small fraction (<5%) of that characteristic of gel-spun poly(ethylene). However, the DOP mixture data argue against this model.

Mixing DOP with CECEC reduces σ_{TS} dramatically; addition of 25% DOP results in a quarter of the neat tensile strength. Yet the crystallinity increases with added diluent (Table 2), arguing against a strengthening mechanism based solely on oriented poly(ethylene) blocks. We believe strength is derived from a combination of two factors: load bearing E blocks and pinning of both ends of the E blocks at glassy C domains (see Figure 4). Adding DOP to the pentablock weakens the glassy domains, and we speculate this leads to chain pullout at lower stress levels. The data from neat CEC and CE support this hypothesis. CEC is about 25% weaker than CECEC, which can be attributed to the absence of bridging and looping central C blocks.[8,9] And CE is extremely brittle, clear evidence that pinning of the E blocks plays a central role. Thus, we propose a mechanism whereby a network of entangled, semicrystalline, E blocks function like molecular pulleys, constrained from unraveling by localization at the C/E interface. An oriented lamellar morphology adds an additional, beneficial, constraint that inhibits lateral failure of the entangled E network.

This model is related to one recently suggested by Tong and Jerome,[22] who proposed that the strength of ABA-type thermoplastic elastomers can be accounted for by a simple linear relationship

$$\sigma_{\mathrm{TS}} = \alpha + \beta / M_{\mathrm{e}} \tag{1}$$

where α and β are constants that account for the strength of the hard (glassy) and rubbery domains, respectively, and M_{e} is the molecular weight between rubbery entanglements. On the basis of tensile strength data obtained from a variety of thermoplastic elastomers, Jerome and Tong find $\alpha = 9.5$ and $\beta = 1.45 \times 10^5$. Taking $M_{\mathrm{e,E}} \approx 800$ g mol^{-1} [23] yields $\sigma_{\mathrm{TS}} = 190$ MPa, nearly equal to what we report for CECEC. However, we believe this agreement is coincidental. Tong and Jerome note that the reported tensile strength for SBS is about 30 MPa, far below the value calculated, 100 MPa, based on eq 1 (with $M_{\mathrm{e,B}} = 1600$ g mol^{-1}),[23] which they attribute to weak segregation between the S and B microdomains. Patel et al.[2] describe similar behavior for a $\mathrm{CE_EC}$ elastomer, where $\mathrm{E_E}$ refers to a poly(ethylene-*r*-ethylethylene) random copolymer. (These authors also report higher strength for spun fibers although different measurement conditions preclude comparison with our data.) Our findings for the CECEC/DOP mixtures also are correlated with a decreasing T_{ODT} and hence melt state segregation strength (see Table 2). However, E crystallization likely neutralizes this effect at room temperature, implicating glass strength (i.e., the constant α) as the critical factor that controls failure in block copolymer thermoplastics and elastomers. Ruokolainen et al.[6] also demonstrated the importance of glass strength in a cyclindrical CEC triblock where physically aged and freshly cooled specimens exhibited brittle and ductile failure, respectively.

The role of crystallinity in establishing σ_{TS} remains an unanswered question. The suggested "pulley" mechanism should be operative regardless of the state of E aggregation. We are designing polymers with noncrystalline soft blocks (e.g., CPC and CPCPC where P denotes poly(ethylene-*alt*-propylene)) to evaluate this issue.

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