



Thermoplastic elastomers of alloocimene and isobutylene triblock copolymers

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ABSTRACT

A novel triblock copolymer, having a center block of high molecular weight polyisobutylene (PIB) and alloocimene (allo) end-blocks, was synthesized and the mechanical properties characterized. The phase-separated morphology consists of tethered PIB, with the glassy allo domains functioning as reinforcing filler. Thus, at ambient temperature the dynamic modulus is larger than that of PIB homopolymer by about 40%, and there is pronounced reinforcement from the glassy domains. The triblock polymer exhibits thermoplastic elastomer behavior, consistent with the structure. For temperatures above the allo glass transition (71 °C), the material undergoes an order–disorder transition, which causes substantial softening; however, this lability of the mechanical response is largely reversible. Since the repeat units of polyisobutylene cannot be crosslinked, this new material offers a route to processible, PIB based networks.

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1. Introduction

PIB is an unusual polymer, having distinctive characteristics such as (i) very low permeability [1] due to slow diffusion of dissolved gases; (ii) a propensity for strain-induced crystallization [2,3] despite slow thermal crystallization; (iii) high mechanical damping and energy dissipation [4,5]; and (iv) anomalous segmental relaxation dynamics [6,7] that includes a spectacular breakdown of time-temperature superpositioning [8]. These properties have led to many applications [9]. PIB is also resistant to crosslinking, either free radical initiated or by sulfur vulcanization, and consequently commercial PIB (“butyl rubber”) is usually a copolymer with isoprene to provide reactive sites. However, only 2–5 mol% isoprene can be incorporated; thus, butyl rubber cures very slowly and only to a limited degree. Various isobutylene block copolymers [10–16] have been synthesized, and thermoplastic PIB elastomers are particularly intriguing for their commercial potential [17–21].

Recently the controlled/living emulsion copolymerization of isobutylene with 2,6-dimethyl-2,4,6-octatriene (alloocimene or

“allo”) was reported, yielding block copolymers with allo-rich sequences coupled to polyisobutylene (PIB) [22,23]. A detailed description of the triblock synthesis will be published [24]. The diblock polymers exhibit thermoplastic elastomer properties, with allo-rich domains serving as physical crosslinks. Preliminary characterization of the triblock PIB-allo copolymers indicated significant tensile strength (~12 MPa) and elongation (600%) [22]. The conjugated diene side chains of the allo units also provide the possibility for chemical modification. Due to the high allo content, these thermoplastic elastomers cure very efficiently and much faster than butyl rubber. In this work we characterize the mechanical properties and their relation to structure in a poly(allo)-*b*-PIB-*b*-poly(allo) triblock copolymer.

2. Experimental

Isobutylene and alloocimene were sequentially reacted to form the triblock, with details of the synthesis found elsewhere [24]. The polymer studied herein had a number average molecular weight of 260 kg/mol (polydispersity = 1.6). The respective block molecular weights were in the ratio 0.21:1:0.13, with the allo content from ¹H NMR equal to 25.5% by weight. Dynamic mechanical experiments were carried out on an Anton Paar MCR 502 using a parallel plate geometry at low strains, and with a cone and plate geometry to quantify the strain dependence. The surface of a spin-coated

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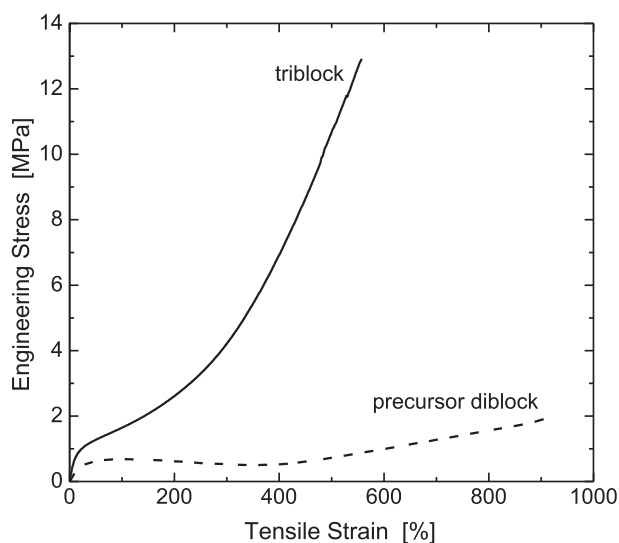


Fig. 1. Stress – strain response measured in extension of the precursor diblock (dashed line: $M_n = 254$ kg/mol; $M_w/M_n = 1.47$; 15.9 wt. % allo), and of the triblock obtained after addition of the second allo block (solid line: $M_n = 244$ kg/mol; $M_w/M_n = 1.63$; 25.5 wt. % allo).

(2000 rpm) film was imaged by atomic force microscopy (Cypher ES AFM, Asylum Research, CA) under nitrogen at various temperatures from RT to 90 °C; that is, through the allo softening point. The substrate temperature was controlled by the heating stage of instrument, with a thermocouple integrated with the sample stage, and the AFM probe cell sealed from the environment to minimize heat loss. Temperature was increased at 0.1C/s, with ~15 min equilibration at each measurement temperature. Transmission electron microscopy (TEM) was performed on 50 nm thick, cryo-microtomed films, with OsO₄ staining used to enhance the contrast.

3. Results and discussion

Fig. 1 compares the stress–strain response of the triblock and the precursor diblock, measured in tension at a nominal strain rate of 0.1 s^{−1}. The tethering the PIB chains at both ends increases the stress at failure by about a factor of 6. The tensile strength of the triblock, 13 MPa, is substantial for a rubbery polymer lacking covalent crosslinks. The failure strain is ~600%, consistent with thermoplastic elastomer behavior.

The triblock has a phase-separated morphology, as evidenced indirectly by its thermoplastic elastomeric behavior (**Fig. 1**), and directly with AFM and TEM images shown in **Fig. 2**. The dark regions in the TEM micrograph represent the stained allo phases, and the continuous light phase represents the PIB. The phase

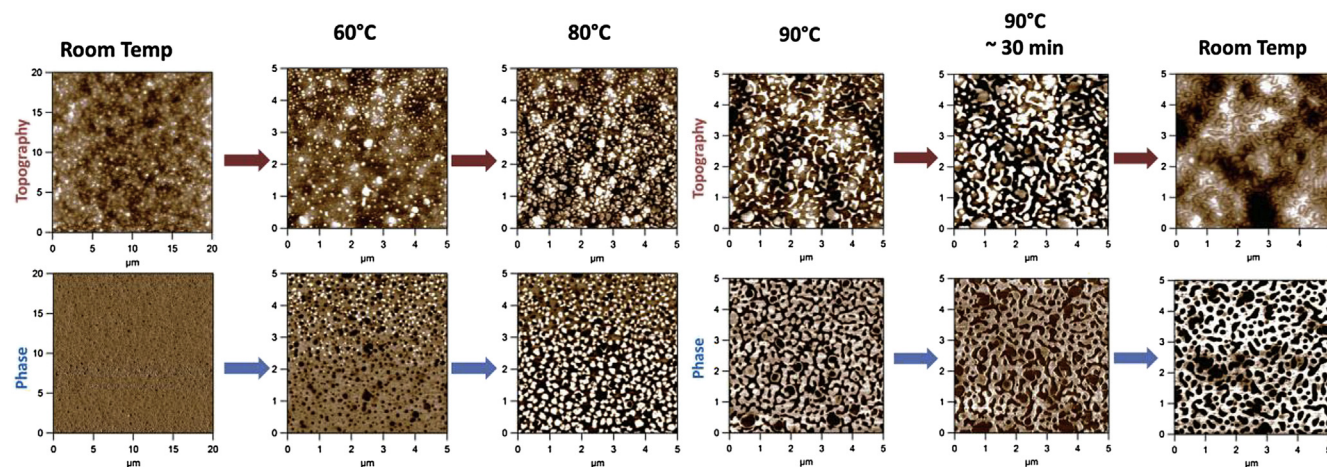
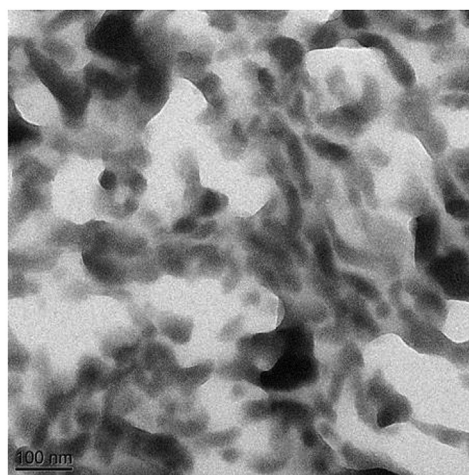


Fig. 2. (upper) TEM of the triblock at RT. (lower) AFM images of the topography and phase images of the spun-cast triblock copolymer at various temperatures through the softening point of the allo domains. The AFM image was obtained with hard tapping; brighter spots in phase image indicate a softer surface relative to the darker areas.

morphology is irregular, the allo phases ranging from 50 to 250 nm in size. In the AFM images probing the surface of the polymer film, the lighter regions correspond to the hard allo phases, while the continuous darker area represents the soft PIB phase. Heating through the glass transition temperature of the allo domains coarsens the phase structure, suggesting the order–disorder transition is below this T_g .

The softening of the allo-rich domains is seen directly in the dynamic modulus measured at low strain amplitude over a range of temperatures (Fig. 3). There are peaks in the loss modulus associated with the local segmental dynamics of each phase; these occur at temperatures corresponding to the calorimetric glass transitions at -67 and 71 °C for the PIB and allo phases, respectively. Between these temperatures there is a region over which the dynamic modulus is relatively flat, varying from ca. 400–600 kPa over a 40° temperature range. This corresponds to the rubbery plateau of the PIB block, augmented by the effect of the tethered end-blocks. Note that time-temperature superpositioning cannot be applied to obtain isothermal master curves in the frequency regime, because of the morphology changes at higher temperatures (Fig. 2), which alters the mechanical response. This is in addition to the usual thermorheological complexity due to the different temperature sensitivity of the local segmental and the global chain modes, observed generally for polymers [25] including PIB [8]. This breakdown to time-temperature superpositioning is apparent in the loss modulus curves shown in the inset to Fig. 3.

The plateau modulus of PIB homopolymer has been measured by different groups [26–28], with a value of $G_N^0 = 290 \pm 35$ kPa (indicated by the horizontal dashed line in Fig. 3). This is about 40% less than the plateau in the storage modulus measured for the triblock. G_N^0 for the latter is larger due to the contribution from the tethered allo domains. For neat PIB, the entanglement molecular weight $M_e = 10.5$ kg/mol [29]. Since this entanglement spacing is inversely proportional to the plateau modulus, if the higher G_N^0 for the triblock were solely due to a larger concentration of crosslinks (diblock tethering in addition to the entanglements), the chain length between the domains would be ca. 40% smaller (~ 4 kg/mol). This is almost an order of magnitude smaller than the actual PIB block length of 25–41 kg/mol. The inferences is that the dominant

mechanism for the high plateau modulus cannot be the network structure of the triblock elastomer; rather the allo domains act as reinforcing filler.

A reinforcing filler increases the modulus of the polymer, primarily because the inextensibility of the particles (or glassy end-block domains) amplifies the strain of the PIB chains; this hydrodynamic effect is strain independent. A mechanism specific to the materials is detachment or disruption of the particles or dispersed phase from the matrix, which introduces nonlinearity into the mechanical response. The latter very generally is known as the Payne effect [28,30]. The contribution to the modulus from the hard domains can be estimated using various empirical models, having the generic form [31],

$$G = (\phi_1 G_1^n + [1 - \phi_1] G_2^n)^{1/n} \quad (1)$$

The subscripts refer to the two phases having moduli G_i and volume fraction ϕ_i . The parameter n ranges from 0 (series coupling), yielding a lower bound on the modulus, to 1 (parallel coupling), which gives an upper bound. A common value is $n = 1/5$, corresponding to the model of Davies [32], which assumes macroscopic homogeneity, isotropy, and co-continuous phases. From the measured plateau modulus and using 3 GPa for the glassy modulus of the hard domains, we obtain $n = 0.7 \pm 0.1$. This is substantially larger than the value of 0.2 associated with co-continuity of the phases, and is consistent with the dispersed domain structure seen in Fig. 2.

The mechanical spectra in Fig. 3 were measured at low strain amplitude ($\sim 0.1\%$). To assess the thermal and mechanical lability of the allo domains, we measured the strain dependence of the dynamic modulus at various temperatures (Fig. 4). At low temperatures, well below the glass transition temperature of the allo domains, there is a marked effect of strain, the storage modulus decreasing for strains exceeding ca. 1%. This result indicates that deformation disrupts the hard domain structure. This phenomenon, the Payne effect, is well known for rubbery polymers reinforced with hard particles. For particulate fillers the strain associated with a modulus decrement falls in the range from ca. 1–100%, increasing for lower concentrations of particles [29,33]. The energy loss associated with breakup of the structure gives rise to a peak in the loss modulus (not shown). The block copolymer

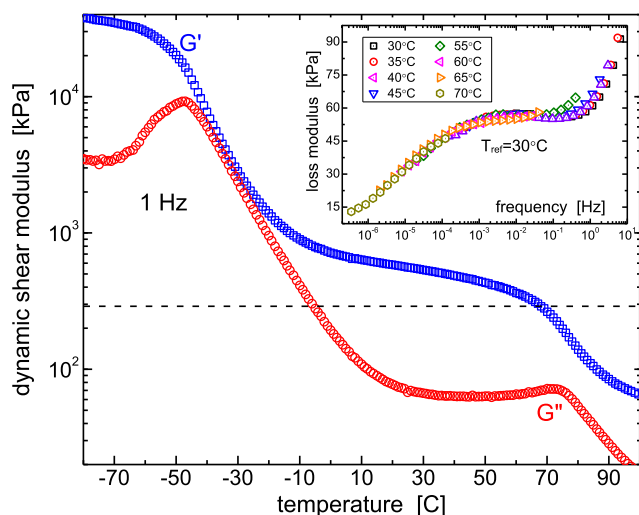


Fig. 3. Dynamic modulus measured at 1 Hz and 0.1% strain. The glass transitions of the two phases are evident as peaks in the loss modulus. The horizontal dashed line represents the rubbery plateau modulus of PIB homopolymer, which is significantly smaller than the plateau modulus of the triblock. The inset shows the loss modulus as a function of frequency for various temperatures, illustrating the breakdown of time-temperature superpositioning.

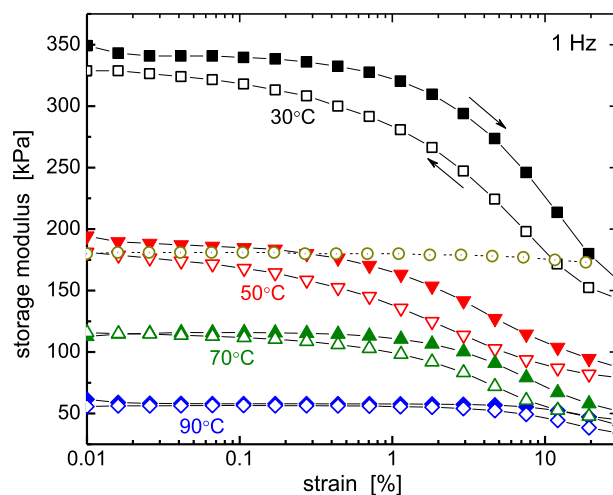


Fig. 4. Dynamic modulus as a function of strain measured at various temperatures. There is a significant Payne effect and hysteresis below the glass transition of the allo domains. The circles are data at 30 °C for the triblock copolymer mixed with 25% PIB homopolymer; its behavior is linear.

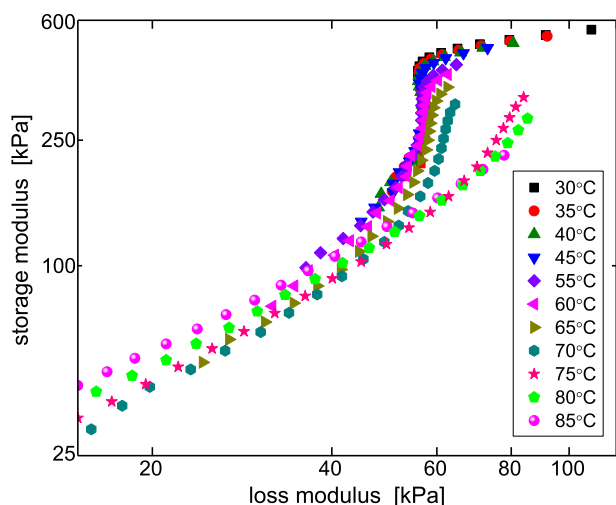


Fig. 5. Double logarithmic plots of the dynamic moduli for various temperatures. The marked change in behavior at the highest temperatures, corresponding to the softening of the allo domains, is consistent with an order–disorder transition.

recovers its structure over time, as seen in the decreased hysteresis for a strain cycle executed after a rest period. The initial behavior is reproduced for sufficiently long times between measurements.

Also included in Fig. 4 are measurements on the triblock blended with 25% PIB homopolymer ($M_w = 46$ kg/mol). From the molecular weights the expectation is that the homopolymer is miscible with the PIB block [34,35]; thus, it functions to dilute the tethering from the allo domains, with consequent decrease in the storage modulus and disappearance of the Payne effect (Fig. 4). Similar behavior was observed in the neat PIB homopolymer – the dynamic modulus is invariant to strain amplitude over the measured range.

The effect of temperature on the strain non-linearity of the triblock was also measured. As T_g of the allo blocks is approached, their softening reduces the reinforcement of the rubbery PIB. In combination with dissolution of the domains as the block become miscible, the Payne effect disappears (Fig. 4). This phase mixing is indicated in the AFM results (Fig. 2), and supported by data in Fig. 5, showing the storage modulus versus the loss modulus for all temperatures. As shown by Han and coworkers [36], in such plots an order–disorder transition is manifested by an abrupt change in behavior, as seen herein for the triblock.

4. Conclusions

The mechanical properties of a novel triblock copolymer of polyisobutylene with alloocimene end blocks were investigated. The material has a phase-separated morphology that gives rise to thermoplastic elastomer behavior. The network structure deriving from the morphology is labile to both temperature and strain, although these changes are physical and thus reversible. At temperatures around the glass transition of the allo domains, which is

above the order–disorder transition, phase mixing transpires. Although the behavior is reversible, it could limit the upper use temperature for applications of the material. However, in addition to the significant increase in the modulus derived from the triblock structure, advantage can be taken of the unsaturation of the end blocks for chemical modification that alters the physical or chemical properties.

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