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Abstract

Differential scanning calorimetry (DSC) does not allow for easy location of the glass transition temperature of the polystyrene (PS) block in styrene-butadiene-styrene (SBS) block copolymers. Modulated DSC (MDSC), which deconvolutes the standard DSC signal into reversing and non-reversing signals, was used to locate the glass transition temperature (T_g) of both the polybutadiene (PB) and PS blocks in SBS. The T_g of the PB block was sharp at $-92°C$, but that for the PS blocks was extremely broad, from -60 to $125°C$ with a maximum at $68°C$ because of blending with PB. PS blocks were found only to exist in a mixed PS-PB phase, which concurred with the results from dynamic mechanical analysis. Annealing did not allow for a segregation of the PS blocks into a pure phase, but allowed for the segregation of the mixed phase into two mixed phases, one was PB-rich and the other PS-rich. It is concluded that three phases coexist in SBS: PB, PB-rich and PS-rich phases.

Keywords: styrene copolymer, SBS, calorimetry, modulated DSC

1. Introduction

Styrene-butadiene-styrene (SBS) is considered a two-phase thermoplastic block copolymer in which spherical polystyrene (PS) domains are dispersed in a polybutadiene

(PB) matrix [1,2]. The copolymer is commonly blended and it is often desirable to assess the degree of blending of the individual blocks with the blending material(s). In principle this may be assessed by a shift in the glass transition temperature (T_g) of the PS or PB blocks upon blending, but in practice a shift may be difficult to measure. The T_g of the PB block (T_g^{PB}) is sharp, around $-90°C$ as measured by DSC [3,4], but the T_g of the PS block (T_g^{PS}) is weak and subject to interpretation. For instance, Spaans et al.[3] measured T_g^{PS} at $60°C$, some $40°C$ lower than for homopolymeric PS (hPS), but Létoffé at al.[4] observed an endotherm at $50-80°C$ and could not locate T_g^{PS} precisely.

Here, we report on the use of modulated DSC (MDSC) and dynamic mechanical analysis (DMA) to measure T_gs in SBS. Glass transition temperatures were found for PB and for a mixed PB-PS phase, but not for a pure PS phase. From annealing experiments, it is shown that three phases coexist in SBS: PB, PB-rich and PS-rich phases.

2. Experimental

A linear untapered SBS elastomer with a 30:70 S:B wt ratio was supplied by Enichem (Europrene SOL T166, M_n=124000, M_w/M_n =1.04). Polymer pellets were pressed into a film at $150°C$ and cooled to room temperature before glass transition temperatures were measured by MDSC and dynamic mechanical analysis (DMA). The MDSC instrumentation and analysis methods are those described in detail earlier.[5,6] The SBS (5-10 mg) was heated under helium from $-120°C$ to $150°C$ at $3°C/min$, a modulation period of 60 s and an amplitude of $\pm0.47°C$. The reversing heat flow was converted to heat capacity by dividing by the underlying heating rate. The DMA was carried out using a Rheometric Scientific Solid Analyzer (RSA3). A strip of SBS of about 18 mm x 5 mm x

0.3 mm in length, width, and thickness was analyzed in tension from $-120\,°C$ to $100\,°C$ at a frequency of 3 Hz and a heating rate of $2°C/min$.

3. Results and Discussion

3.1 MDSC. The MDSC results for SBS are shown in Figure 1. The total heat flow, which is identical to that from standard non-modulated DSC, was deconvoluted into its reversing and non-reversing components as described by Reading and others[7-10]. The total heat flow curve showed three features: i) a large decrease in heat flow around $-90°C$, ii) a curved background between about -70 and $60°C$, iii) a change in baseline at $70°C$. As seen from the deconvolution, the change in the total heat flow around $-90°C$ arose from a decrease in reversing heat flow, due to T_g^{PB},[11] that overlapped with an endotherm. Consequently, the change in C_p at T_g^{PB} was not as intense as the total heat flow curve first indicated. It was 0.23 J/K/g rather than 0.34 J/K/g, some 30% lower.

The change in baseline in the total heat flow curve at $60-70°C$ was assigned to T_g^{PS} by Spaans et al.[3] and as the center of an endotherm by Létoffé et al.[4] The non-reversing heat flow in Figure 1 confirmed the existence of an endotherm, centered at $68°C$, the origin of which will be discussed later. The existence of a T_g in this region was not easily confirmed with the reversing heat flow curve, and it was from the dC_p/dT curve in Figure 2 that a maximum, a T_g, was also measured at $68°C$. This T_g coincided with an endothermic minimum also at $68°C$ in Figure 1.

The dC_p/dT curve showed an extremely broad T_g in SBS, from about $-60°C$ to $125°C$ (Figure 2). Given that a shift in T_g signals interactions and mixing[12] and that the T_g of hPS is centered at $100°C$,[13] the T_g at $68°C$ in Figure 2 must arise from a mixed PS-PB phase, T_g^{PS-PB}. From the Fox equation[14] for copolymers: $1/T_g^{PS-PB}=W^{PS}/T_g^{PS}+W^{PB}/T_g^{PB}$,

W^i being the weight fraction and T_g^i the T_g of the homopolymers, it was calculated that the mixed phase contained 35% to 93% PS between $-50°C$ and $75°C$. PS and PB homopolymers are considered immiscible because two T_gs are found for many mixtures,[15] but complete immiscibility requires that the T_gs of the two phases be equal to the T_gs of the respective homopolymers,[16] which was not the case for SBS as seen in Figure 2. It is noteworthy that T_g^{PB} was well resolved from T_g^{PS-PB}, which indicated the existence of a separate and pure PB phase. This was consistent with the results for blends of hPS and hPB, which show that some PB dissolves in PS, but that PS is mostly insoluble in PB, the result being a depression in T_g^{PS} with an increase in PB content, but a constant T_g^{PB} with a variation in PS content.[17]

In SBS, the PS-rich phase may be frozen in a non-equilibrium state. In such a case, improved segregation of the PS and PB blocks would be expected after annealing above T_g^{PS-PB}. Figure 3 shows the results of annealing SBS for 1h at 110°C. The annealing allowed for greater segment mobility and more segregation, but this segregation remained quite incomplete as the original mixed phase segregated into a more discrete PB-rich phase, with a T_g at $-25°C$, and a PS-phase now richer in PS, with a higher T_g of 77°C. Annealing for 150h at 110°C did not lead to more segregation. Hence, it was concluded from Figure 3 that three phases coexisted in SBS; a PB, PB-rich and PS-rich phases. These phases were stable, likely because of the covalent bonds between the PS and PB segments. Very little pure PS, with a T_g at 100°C, was found, in contrast to what may be concluded based on tan δ from dynamic mechanical analysis, as seen below.

As indicated before, the non-reversing heat flow in Figure 1 showed two endotherms, centered at $-90°C$ and 68°C. As SBS is amorphous, the endotherms could not arise from

melting, and must be from enthalpy relaxation at T_g.[18]   The relaxation stems from cooperative chain motions in the T_g region[19] and increases upon the annealing of amorphous[19] and semi-crystalline polymers.[20]   Consequently, and as expected, the annealing of SBS lead to an increase in the size of the endotherms (not shown).

3.2 DMA. Unannealed SBS was analyzed by DMA and the results compared to those from MDSC. Figure 4 shows the correspondence between the storage modulus (E') and the reversing heat flow. Both signals overlapped at T_g^{PB}, where the rate of change coincided. Above 50°C, when T_g^{PS-PB} was exceeded, E' decreased rapidly. Figure 5 shows the correspondence between the loss modulus (E") and the non-reversing heat flow. The maxima in the loss modulus curve at −92°C and 68°C coincided with the enthalpy relaxation endotherms (minima). There was thus good correspondence between the T_gs and the endotherms obtained by MDSC and the DMA moduli. Both methods show the absence of a hPS phase in SBS.

The correspondance between the MDSC transitions and the peaks in the tan δ curve, i.e., the ratio E"/E', was not as good as with the moduli (Figure 6). A tan δ peak is often conveniently used to identify a T_g. For SBS, the T_gs on the tan δ curve were higher in temperature than those on the MDSC, E", and E' curves. For instance, the tan δ curve showed a peak at 90°C, some 20°C higher than in Figures 4 and 5. This is consistent with the 15°C difference observed for hPS.[19] As the peak on the tan δ curve is relatively close to the T_g of hPS at 100°C measured by DSC,[13] the tan δ peak is commonly assigned to a T_g from the pure PS block[21] rather than to a mixed PS-PB phase. This supports an earlier conclusion,[19] that tan δ peaks are only indirectly related to T_g.

4. Conclusion

The glass transitions (T_gs) and the associated amorphous phases in a linear SBS were analyzed by modulated differential scanning calorimetry (MDSC) and dynamic mechanical analysis (DMA). From the T_gs of annealed and unannealed samples obtained through the derivative of the reversing heat flow, it was found that polybutadiene (PB) segments existed both in a pure and a mixed PB phase, whereas polystyrene (PS) segments only existed in a mixed PB-PS phase with a significant PB content.

Given the measured sharpness of the T_g from the PB phase (T_g^{PB}) and the extraordinary breadth of the T_g from the PS-rich phase (T_g^{PS-PB}), it should be relatively easy to determine a shift in T_g^{PB} and assess the degree of blending of the PB phase with a diluent or another polymer, but this may be more difficult to do with the already mixed phase. We will report shortly the case for which bitumen is the diluent.

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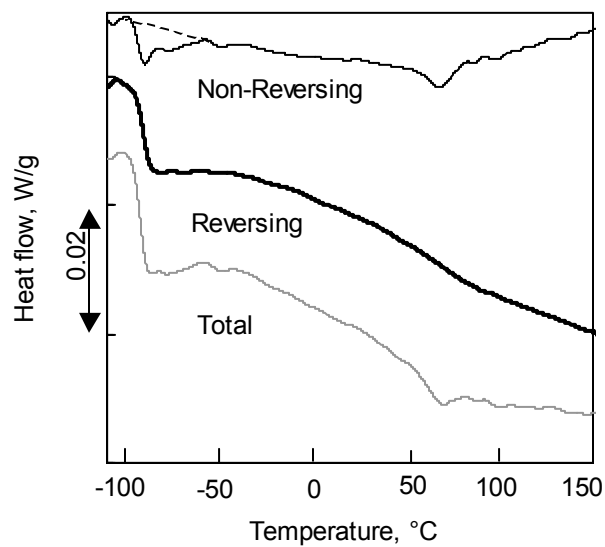
Figure captions

Figure 1. MDSC for SBS with a 30:70 S/B ratio
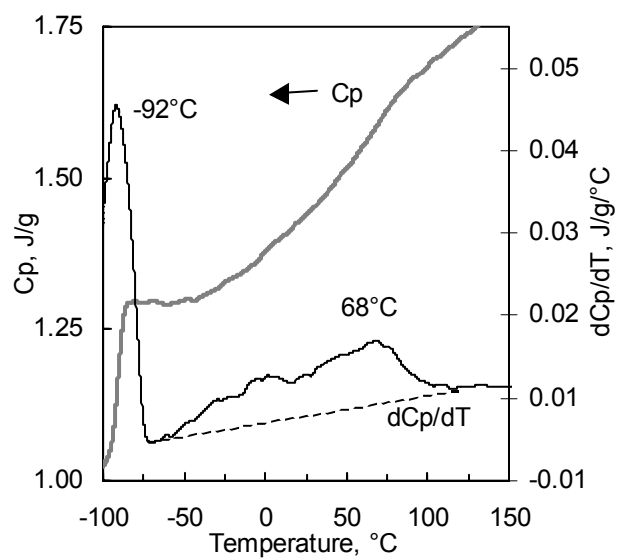
Figure 2. Heat capacity curve and its derivative for SBS.

Figure 3. dCp/dT curve for annealed SBS.

Figure 4. Storage modulus (E') and the reversing heat flow (RHF) curves for SBS.

Figure 5. Loss modulus (E") and the non-reversing heat flow (NRHF) curves for SBS.

Figure 6. DMA results for SBS.

Figure 1. MDSC for SBS with a 30:70 S/B ratio.

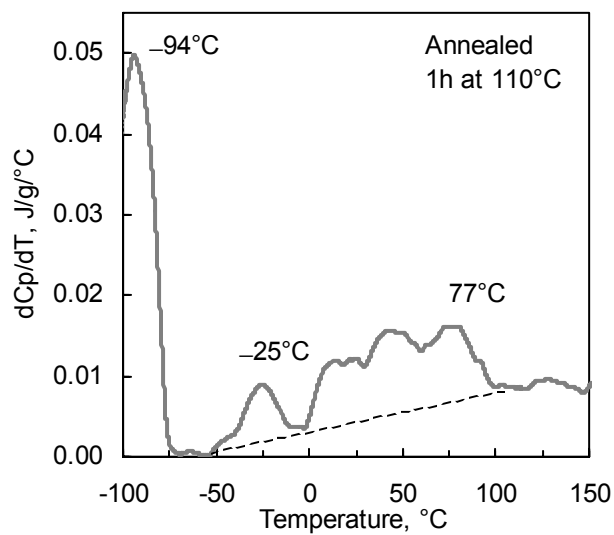Figure 2. Heat capacity curve and its derivative for SBS.
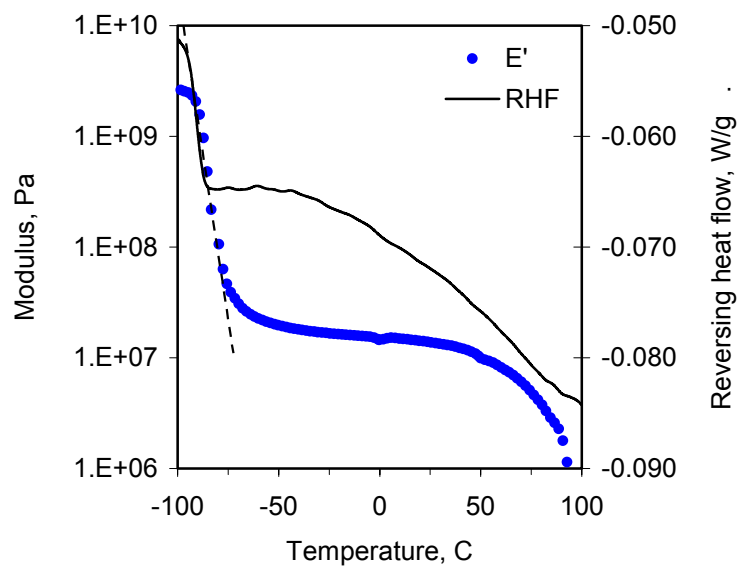
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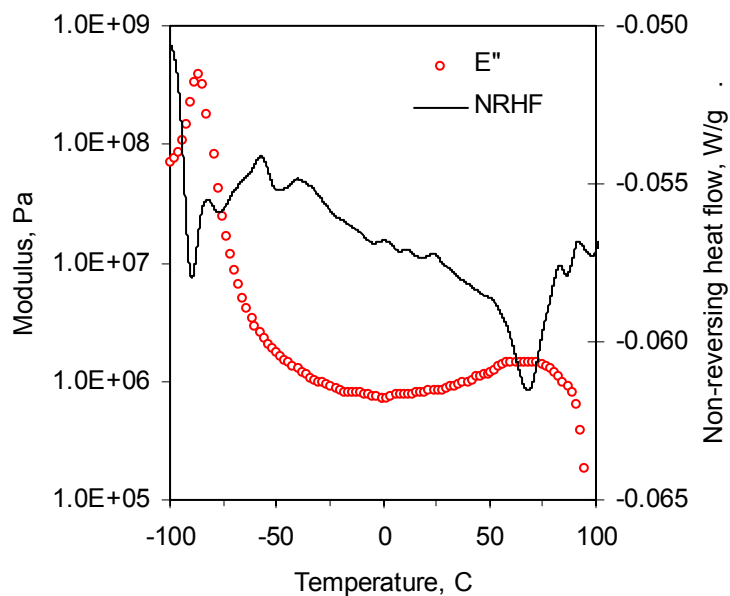Figure 4. Storage modulus (E') and the reversing heat flow (RHF) curves for SBS.
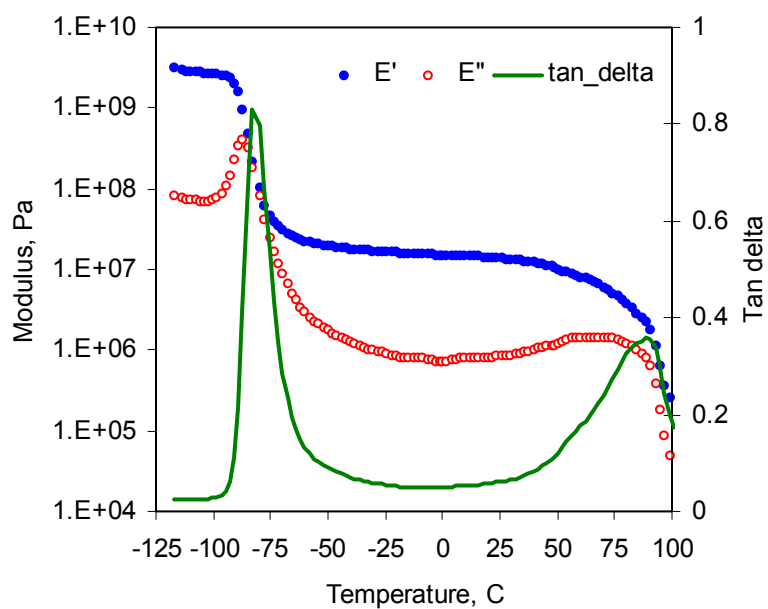
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