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Glass transitions and amorphous phases in SBS–bitumen blends

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Abstract

Blends of bitumen with 3–10% of a styrene–butadiene–styrene (SBS) block copolymer were investigated by means of modulated differential scanning calorimetry (MDSC) in an effort to better understand the miscibility and structure of the blends, along with the composition of the mixed phase(s). This relied on the measurements of the glass transition temperatures (T_g) in bitumen and SBS in their blended and unblended states. In the unblended state, bitumen showed four T_g's, and SBS showed two. In the blends, a new T_g arose from a phase of mixed composition, which contained polybutadiene (PB) segments and about 30% of the maltenes. The blends also showed anti-plasticization as a shift of the T_g's from the paraffins in bitumen and the PB block in SBS moved away from each other. The results indicate that the PB block has good interactions with bitumen, but that the polystyrene (PS) block does not.

Keywords: Bitumen; Asphalt; Block copolymer; Styrene copolymer; SBS; Blends; Binders; Calorimetry; Modulated DSC; Glass transition temperatures, T_g

1. Introduction

Polymer–polymer and polymer–diluent systems have been of interest for several decades and the thermodynamics that govern their stability is well established [1–5]. The same thermodynamic framework can be applied to blends of polymers and bitumen, but with added complexity in that the temperature–composition phase diagram is three-dimensional because bitumen is not a single component diluent [6].

Bitumen is a complex viscoelastic mixture of oligomeric hydrocarbons, the average degree of polymerization being about 10 [7]. The chemical complexity of bitumen precludes any precise molecular identification. As a result, bitumen is often conveniently characterized by its chromatographic fractions, the maltenes and the asphaltenes (As), which are, respectively, soluble and insoluble in *n*-heptane. The maltenes can be fractionated further in classes of compounds called saturates (S), aromatics (A) and resins (R) [8,9]. The SARAs fractions increase in molecular weight, aromaticity, and heteroatomic content in the order S < A < R < As [10]. The SARAs terminology can be confusing, however, because the aromatics fraction (A) most often contains little conjugated ring structures [10]. Table 1 provides the composition of the fractions in more classical terms.

SBS and bitumen are regarded as compatible in that their mixtures show enhanced physical properties over the lone constituents [11]. However, this says little about the compatibility and interactions of the components or the phases in the blends. Brion and Brûlé [12] showed that SBS is swollen with saturates and aromatics, which implies an interaction of the copolymer with these bitumen fractions. More recently, Masson et al. [6] demonstrated that pi-electrons in the polybutadiene (PB) unit of SBS were responsible for much of the interactions between SBS and bitumen. In spite of these findings, the understanding of the phase structure of SBS–bitumen blends remains incomplete. This paper addresses the issue of mixing and the composition of the amorphous domains in homogeneous SBS–bitumen blends rich in bitumen. This may help to understand the phase behavior and the stability of these blends [6], and may provide a fresh perspective on blend characteristics, the low temperature behavior being an important one.

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Table 1
Typical composition of SARAs fractions

Fraction	Composition
Saturates	*n*- and *iso*-alkanes
Aromatics	Alkylated cyclopentanes and cyclohexanes
Resins	Alkylated and cycloalkylated aromatic rings
Asphaltenes	Alkylated condensed aromatic rings

In general, mixing can be assessed from the glass transition temperature (T_g) of the materials in their blended and unblended states. A shift in T_g between the pure and the blended state signals mixing, and this is conveniently measured by differential scanning calorimetry (DSC) [2]. With SBS–bitumen blends, however, DSC lacks the capability of resolving overlapping T_g's and only the T_g of the predominant bitumen-rich phase is reported [13,14]. In contrast, T_g's for bitumen-rich, polybutadiene-rich and polystyrene-rich phases were reported with dynamic mechanical analysis [15–17].

In recent work on bitumen and its fractions [7,18], it was shown that modulated DSC (MDSC) allows for the deconvolution of signals [19,20] from amorphous and ordered phases. The method thus has a much greater resolution than standard DSC. Typically, the amorphous phase gives rise to a reversing heat flow, which is readily converted to the apparent specific heat capacity (c_p) and its derivative ($\mathrm{d}c_p/\mathrm{d}T$), which highlights the T_g's.

In this paper, the derivative of the apparent heat capacity, obtained from the reversing heat flow, is used to better define the composition of the phases in SBS–bitumen blends. The results from the ordered and partially ordered phases (mesophases), as obtained from the non-reversing heat flow, will be reported later.

2. Experimental

2.1. Materials and blends

A bitumen labelled ABA was obtained from the Strategic Highway Research Program in the USA. A linear SBS was obtained from Enichem (SOL T166). The bitumen and copolymer characteristics are shown in Table 2. The bitumen composition was obtained by thin-layer chromatography-flame ionization detection [8] and the molecular weight of SBS by gel permeation chromatography as described before [6].

Table 2
Material characteristics

	Bitumen	SBS
Saturates	11[a]	–
Aromatics	16[a]	–
Resins	57[a]	–
Asphaltenes	16[a]	–
Styrene	–	30[a]
M_w	3500	124000
M_w/M_n	2.46	1.04

[a] wt.%.

Blends of bitumen with 3, 6 and 10% by weight SBS were prepared. The lower concentration is typical of that in paving applications, whereas the higher concentrations are more typical of waterproofing and sealing applications. The blends were prepared at 165 °C by stirring for 1 h, after which time a homogeneous mixture was obtained as observed by epi-fluorescence microscopy [6]. The stability of these blends and the related thermodynamics, including the effect of composition and molecular weight was treated in detail before [6]: the blend with 3% SBS is stable during hot storage, but the blends with 6 and 10% SBS segregate at 140 and 120 °C, respectively. Here the blends were studied in their homogeneous state, prior to segregation. For this purpose, the blends were cooled to 22 °C after their preparation, and maintained there for at least 1 week before analysis.

The MDSC instrumentation and data analyses were described in detail earlier [7,18]. Blends were heated from −120 to 100 °C at 3 °C/min, a modulation period of 60 s and an amplitude of ±0.47 °C. The total heat flow obtained from MDSC was deconvoluted into the reversing and non-reversing heat flows. The apparent c_p and its derivative, $\mathrm{d}c_p/\mathrm{d}T$, were calculated from the reversing heat flow [7,18].

3. Results and discussion

3.1. Unblended materials

The reversing heat flow and $\mathrm{d}c_p/\mathrm{d}T$ curves for bitumen are shown in Fig. 1. The derivative allows for improved analysis of the T_g's over the reversing heat flow or c_p curves alone. The $\mathrm{d}c_p/\mathrm{d}T$ curve highlights four T_g's, T_g^A to T_g^D, that arise from different amorphous phases in bitumen. In general, the T_g increases with the stiffness, polarity, aromaticity, and molecular weight of the repeat molecular structure within the amorphous phase [21]. Three T_g's were observed in bitumen before [7], in agreement with those shown in Fig. 1: T_g^A arises from the maltene phase and it is the most intense transition; T_g^B arises from a maltene–asphaltene interfacial region of mixed composition likely rich in resins and which

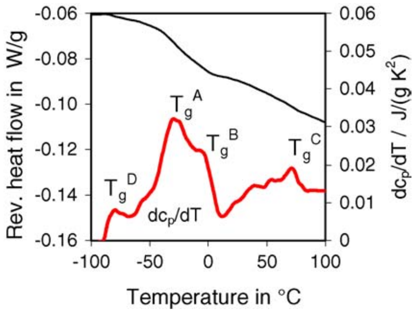

Fig. 1. Reversing heat flow curves for bitumen ABA. Exo is up.

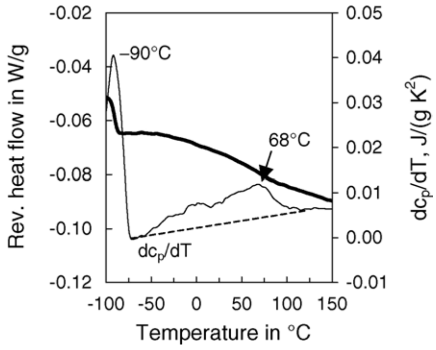

Fig. 2. Reversing heat flow and dc_p/dT curves for SBS. Exo is up.

for convenience can be called an interphase, although it may not be a strictly separate phase; T_g^C is from the asphaltenes. T_g^D was not observed before, but given the T_g of the saturates extracted from bitumen [18], and the relationship between T_g and molecular structure [21] T_g^D must arise from a phase rich in flexible paraffinic segments.

For SBS, two T_g's are identified on the dc_p/dT curve (Fig. 2). The PB block gives rise to the sharp T_g at −90 °C (T_g^{PB}). A mixed PS–PB phase gives rise to the broad T_g with a maximum at 68 °C (T_g^{PS-PB}). This maximum arises from a PS-rich phase that contains about 20% PB [22].

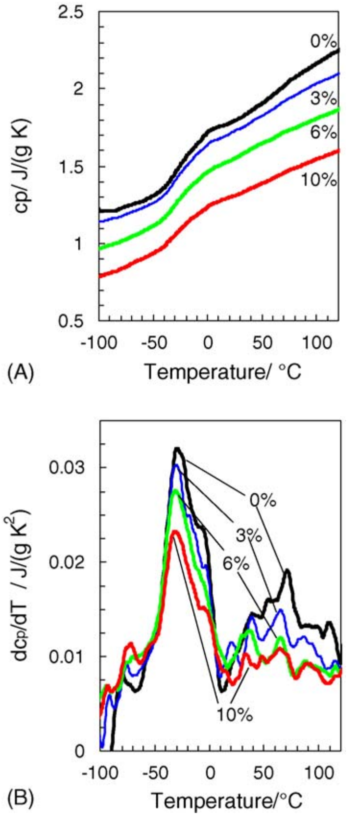

Fig. 3. c_p (A) and dc_p/dT (B) curves for bitumen–SBS blends with 0–10% SBS.

3.2. Bitumen–SBS blends

The c_p curves for the blends with 0, 3, 6, and 10% SBS are shown in Fig. 3A. The increase in apparent c_p between −100 and 120 °C is 1.1 J/(g K) for bitumen, but it is lower for the blends, the decrease being proportional to the SBS content. The c_p curves show a most noticeable increase between about −50 and 10 °C, along with much less noticeable increases at −70 and 70 °C. From Fig. 3A, it is difficult to draw conclusions about phases less important than the main phase; dc_p/dT curves are essential to highlight secondary phases (Fig. 3B). The general profile of the dc_p/dT curves for bitumen–SBS blends is much like that for bitumen. There are important changes that provide information on the miscibility of bitumen and SBS, however. Between −50 and 120 °C, three T_g's in bitumen ($T_g^{A,B,C}$) lose intensity in slightly greater proportion than expected based on the SBS content, and as will be discussed later, this indicates a loss of amorphous material in the phases responsible for $T_g^{A,B,C}$.

With each increment in SBS, there is a decrease in the ratio dc_p^B/dc_p^A measured from the height of the derivative peaks at T_g^A and T_g^B (Fig. 3B). It is 0.7 for bitumen and it gradually decreases to 0.5 for the blend with 10% SBS. Given that T_g^A and T_g^B arise from the maltenes and the maltene–asphaltenes interphase, respectively, the decrease in dc_p^B/dc_p^A indicates that SBS hinders interactions between maltenes and asphaltenes and prevents to some extent the formation of a maltene–asphaltene interface. In other words, SBS hinders the dissolution of asphaltenes into maltenes. This can occur either because of steric exclusion of asphaltenes from the interphase, or because of preferential interactions of SBS and asphaltenes. However, SBS was shown to mix preferentially with saturates and aromatics, and not with the asphaltenes [6,12]. The change in c_p^B/c_p^A thus indicates that asphaltenes become increasingly excluded from a mixed phase when the SBS concentration increases. As a result, the bitumen phase becomes enriched in asphaltenes, which is consistent with previous findings [6,12].

The decrease in c_p at $T_g^{A,B,C}$ related to the increase in SBS in the blend arises partly due to a loss of amorphous material in the phases responsible for $T_g^{A,B,C}$. This material ends up in a new phase with a transition around −70 °C (Figs. 3 and 4). As expected from a mixed maltenes–PB phase, the T_g of the new phase is between T_g^{PB} and T_g^A, and increases in intensity with an increase in SBS, as highlighted by the dotted line for T_g^{NEW} in Fig. 4. However, given a T_g^{PB} of −90 °C, a T_g^A of −30 °C, and the rule of mixtures ($T_g^{NEW} = W^A T_g^A + W^{PB} T_g^{PB}$, W being the weight fraction), T_g^{NEW} was expected to be −31 to −34 °C for blends with 3–10% SBS (PB content of 2–7%). A T_g^{NEW} around −70 °C indicates that PB blends only with a small weight fraction of the maltenes. With the rule of mixtures, it is calculated that only about 30 wt.% of the maltenes blend with PB. Given that SBS is swollen by the saturates and aromatic fractions from bitumen [12] it is likely that the maltenes portion

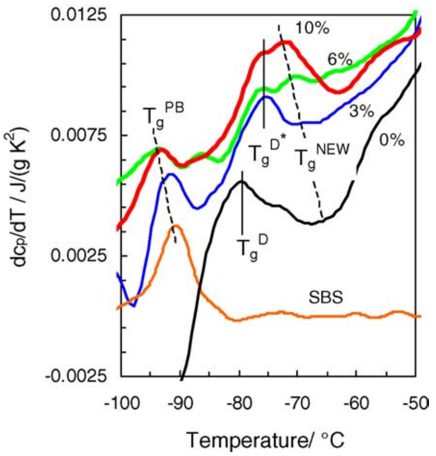

Fig. 4. Low temperature region for SBS and its blends with bitumen. The curve for SBS is 3% of its true intensity to allow for its comparison with the blends.

that blends with PB is rich in alkanes and cyclo-alkanes (Table 1).

Fig. 4 also shows that T_g^{PB} and T_g^{D} move away from each other, rather than towards each other. In general, the partial mixing of two phases with independent T_g's leads to a shift in T_g's, with the T_g's moving towards each other due to mixing [2]. Plasticization occurs when the T_g of a polymer is depressed by the action of a small molecule with a lower T_g [23]. In contrast, anti-plasticization occurs in SBS–bitumen mixtures as T_g's more away from each other: when PB is swollen by saturates, T_g^{PB} is shifted down from −90 to −93 °C, whereas T_g^{D} is shifted up from −81 to −76 °C, this shift being indicated by T_g^{D*} in Fig. 4. This anti-plasticization can be explained by a loss of the lightest oils from the saturate fraction towards the PB domain. The result is a stiffer saturate fraction and hence a T_g^{D} higher by 5 °C (T_g^{D*}), and a softer PB fraction with a T_g lower by 3 °C. Table 3 lists the various T_g's in SBS-modified bitumen.

Fig. 5 shows the temperature range where T_g^{PS-PB} from PS-rich domains overlaps with the T_g^{C} region from the bitumen asphaltenes. At an SBS concentration of 10% or less, T_g^{PS-PB} does not contribute to the dc_p/dT response from the blends, which show a decrease and a shift in the bitumen maxima. An important decrease in the maximum at 55 °C concurs with a shift of the maxima at 40 and 70 °C towards lower temperatures as shown by the arrows in Fig. 5. This temperature shift indicates that the asphaltenes are affected by SBS and it suggests that mixing occurs mainly with flexible PB segments. The mixing of the asphaltenes with pure PS segments (T_g at 100 °C), or with the plasticized PS of the mixed PS–PB phase (T_g at 68 °C), would cause an upshift in the temperature of the maxima in the T_g^{C} region, which would be especially visible below 68 °C, e.g., with the transition at 40 °C.

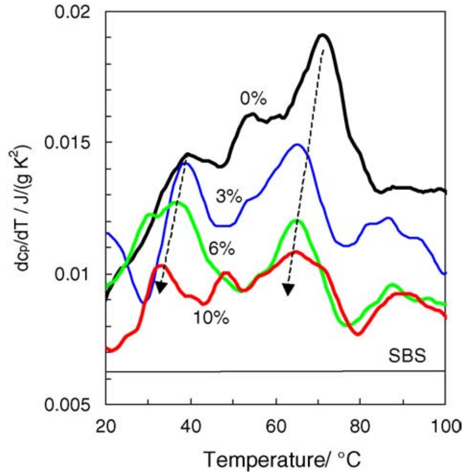

Fig. 5. High temperature region for SBS and its blends with bitumen. The curve for SBS is 3% of its true intensity and shifted up 0.005 units to allow for its comparison with the blends.

Table 3
Sub-zero T_g's in SBS–bitumen blends

T_g (°C)	Composition
−93	PB-rich phase plasticized by the light oils
−90	Unblended PB block
−81	Light oils in bitumen (T_g^{D})
−76	Light oils anti-plasticized by the loss of the lightest fraction (T_g^{D*})
−73 to −71	PB-rich phase swollen with maltenes (T_g^{NEW})
−30	Maltenes (T_g^{A})
−5	Maltene–asphaltene interphase (T_g^{B})

4. Conclusion

The reversing heat-flow signals from MDSC were used to investigate the extent of mixing in SBS–bitumen blends with 3, 6 and 10% SBS by weight. Bitumen and SBS, respectively, show four and two T_g's. Based on the shifting of the T_g's in the blends, there was no evidence of blending of bitumen with the PS block, but there was evidence that bitumen blended with the PB block at all the SBS concentrations investigated. The blends contained a new phase of mixed composition with a T_g close to −70 °C. This phase contained some PB and an estimated 30% of the lighter maltenes, namely, the alkanes and cyclo-alkanes. Not all the PB was in the mixed phase, however, as the remainder was found in a PB-rich phase swollen with the lighter alkanes. Hence, the miscibility of SBS–bitumen blends is controlled in great part by the PB block in SBS, and by the lighter maltenes in bitumen.

References

[1] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, 1953.
[2] O. Olabisi, L.M. Robeson, M.T. Shaw, Polymer–Polymer Miscibility, Academic Press, New York, 1979.
[3] L.A. Utracki, Polymer Alloys and Blends: Thermodynamics and Rheology, Hanser Publisher, New York, 1989.

[4] D.R. Paul, C.B. Bucknall (Eds.), Polymer Blends, Wiley-Interscience, New York, 2000.

[5] M.M. Coleman, J.F. Graf, P.C. Painter, Specific Interactions and Miscibility of Polymer Blends, Technomic Pub. Co., Lancaster, 1991.

[6] J-F. Masson, P. Collins, G. Robertson, J.R. Woods, J. Margeson, Energy Fuels 17 (2003) 714.

[7] J-F. Masson, G. Polomark, Thermochim. Acta 374 (2001) 105.

[8] J-F. Masson, T. Price, P. Collins, Energy Fuels 15 (2001) 955.

[9] L. Raki, J-F. Masson, Energy Fuels 14 (2000) 160.

[10] J.G. Speight, The Chemistry and Technology of Petroleum, 3rd ed., Marcel Dekker, New York, 1999.

[11] C.P. Valkering, D.J.L. Lancon, E. deHilster, D.A. Stoker, Asphalt Pav. Technol. 59 (1990) 590.

[12] Y. Brion, B. Brûlé, Étude des mélanges bitumes-polymères: composition, structure, propriétés, Report PC-6, French Central Laboratory for Roads and Bridges [LCPC], Paris, France, 1986 (in French).

[13] D. Lesueur, J.-F. Gérard, P. Claudy, J.-M. Létoffé, D. Martin, J.-P. Planche, J. Rheol. 42 (1998) 1059.

[14] J.-M. Létoffé, L. Champion-Lapalu, D. Martin, J.-P. Planche, J.-F. Gérard, P. Claudy, Bull. Labo. Ponts Chaussées 229 (2000) 13.

[15] U. Isacsson, X. Lu, Mater. Struct. 28 (1995) 139.

[16] K.G. Woodly, J. Inst. Asph. Technol. 38 (1986) 44.

[17] J.H. Collins, Asph. Pav. Technol. 60 (1991) 43.

[18] J-F. Masson, G. Polomark, P. Collins, Energy Fuels 16 (2002) 470.

[19] M. Reading, Trends Polym. Sci. 1 (1993) 248.

[20] P.S. Gill, S.R. Sauerbrunn, M.J. Reading, Therm. Anal. 40 (1993) 931.

[21] M.C. Shen, A. Eisenberg, Rubber Chem. Technol. 43 (1970) 95.

[22] J-F. Masson, S. Bundalo-Perc, A. Delgado, J. Polym. Sci. B 43 (2005) 276.

[23] F.W. Billmeyer, Textbook of Polymer Science, 3rd ed., Wiley-Interscience, New York, 1984.