

Glass transitions and amorphous phases in SBS–bitumen blends

J-F. Masson*, Gary Polomark, Peter Collins

Institute for Research in Construction, National Research Council of Canada, 1500 Montreal Road, Ottawa, Canada K1A 0R6

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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.

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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.

* Corresponding author. Tel.: +1 613 993 2144; fax: +1 613 952 8102.
E-mail address: jean-francois.masson@nrc.gc.ca (J-F. Masson).

Table 1
Typical composition of SARAs fractions

Fraction	Composition
Saturates	<i>n</i> - and <i>iso</i> -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 (dc_p/dT), 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

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.%.

SBS by gel permeation chromatography as described before [6].

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, dc_p/dT , were calculated from the reversing heat flow [7,18].

3. Results and discussion

3.1. Unblended materials

The reversing heat flow and dc_p/dT 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 dc_p/dT 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

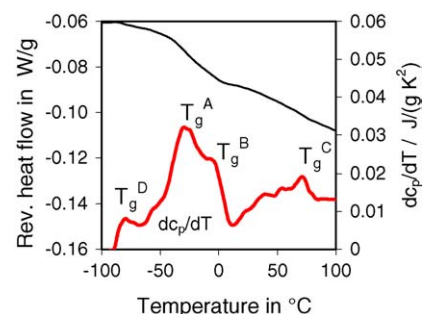


Fig. 1. Reversing heat flow curves for bitumen ABA. Exo is up.

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