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Miscibility studies on blends of Kraton block copolymer and asphalt

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Abstract

Miscibility phase behavior in blends of SBS copolymers (Kraton 1101) and asphalt has been investigated through establishment of thermodynamic phase diagrams. The observed phase diagram of the SBS/asphalt blend is an upper critical solution temperature (UCST) type with a maximum at about 20% copolymer and around 200 °C. The study on kinetics of phase decomposition has been carried out by means of time resolved light scattering at the 6/94 Kraton 1101/asphalt composition. Time-evolution of structure factor has been analyzed in the context of temporal scaling laws. The growth regime is seemingly dominated by the late stage of phase decomposition where the hydrodynamic effect is dominant. As typical for a deep off-critical quench, the cessation of domain growth occurs presumably through physical pinning. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: SBS block copolymer; Asphalt; Phase diagram

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1. Introduction

In recent years, there is a growing interest on asphalt modifications [1–6] for use in high performance specialty pavements such as open graded pavements (OGP) in which large gravels have been selectively utilized for creating open interconnected channels in the pavements. One of such high performance specialty asphalts, commercially known as 'Cenaphalt' [6], has received special attention because of its unique characteristics. For instance, the Cenaphalt-modified OGP can drain out rainwater readily, preventing undesirable events such as hydroplaning of vehicles, water splashing and fogging from the wheels, among other [6]. In addition, tire traction and visibility on highways have been shown to improve greatly. Of particular importance is that the noise level on the open graded paved road can be suppressed considerably [6].

This kind of specialty road pavement does not come by easily as lesser amount of asphalt would be required for paving open graded porous surfaces. The strength, stiffness and adhesion of asphalt to gravel must be greatly improved in order to sustain the pavement performance. It is not surprising to witness various attempts to modify asphalt properties via chemical modification and/or physical blending. The major efforts have been thus far directed to viscoelastic characterization of asphalt and rubbery materials [2–5]. The addition of rubbery homopolymers to asphalt has been shown to improve low temperature embrittlement, but there was little or no improvement in stiffness and strength of asphalt.

The miscibility studies on modified asphalt have been perceived to be impractical because asphalt contains natural or manufactured aliphatic and aromatic hydrocarbon derivatives (generally known as Bitumen) with dark appearance. Although the significance of miscibility between asphalt and polymer modifiers has been recognized, such an issue has not been addressed in open literature until recently. Yamamoto and Kyu [7] were probably the first to establish a phase diagram of telechelic epoxy terminated polybutadiene and a major, but lighter ingredient of asphalt called 'maltene' containing naphthalenic and paraffinic derivatives. The study on kinetics of phase separation showed no identifiable period corresponding to the early stage of spinodal decomposition (SD). The apparent diffusivity during phase separation and dissolution was measured to estimate the spinodal point. In the growth regime, the scaling exponents showed strong dependence on quenched temperature, but it invariably resulted in the failure of the temporal universality scaling.

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In this paper, we continue our effort for the elucidation of miscibility in blends of asphalt and polymer modifiers or copolymers containing soft and glassy segments such as styrene–butadiene (SB) diblock and styrene–butadiene–styrene (SBS) triblock copolymers [8]. Our preference of block copolymers over rubbery homopolymers is due to the fact that the soft segments would, in principle, improve toughness and low temperature cracking/embrittlement of asphalt pavement, while the hard segments would improve modulus and strength of the modified asphalt. Another advantage is the possibility of controlling block length, composition, topology, and functionalization of the copolymers via careful synthetic routes to optimize the asphalt properties.

In this paper, the miscibility in blends of asphalt and well-characterized commercial SBS copolymer (Kraton 1101) has been investigated through establishment of cloud point phase diagrams and kinetics of phase decomposition so as to determine the optimum processing window and to control phase morphology for improved pavement performance.

2. Experimental section

The copolymer used in this study was Kraton 1101 from Shell Co. [8]. This Kraton grade is basically a mixture of SBS triblock with SB diblock in the ratio of 86:14 formed through coupling of the SB diblock copolymers during in situ polymerization. The number-average molecular and weight-average weights of the copolymers were 136,000 for the triblock and 159,000 for the diblock with 33% styrene in the copolymers and the molecular weight distribution was 1.15. These copolymers were blended with asphalt (Showa-Shell) in various proportions by co-dissolving in tetrahydrofuran. The compositions of the Showa-Shell asphalt were approximately 30% asphaltene, 50% naphthalinic, and 20% paraffinic derivatives by weight. The blend solutions were solvent cast at ambient temperature by spreading onto an optical microscope glass and covered with a cover glass to prevent oxidation. These blend samples were then kept in vacuum oven for 24 h at 65 °C. Later, all specimens were heated once to 180 °C for 10 min and cooled down to room temperature at natural cooling rate prior to experiment.

For the determination of phase diagrams, various blend compositions ranging from 2 to 90 vol% of the copolymer were prepared. However, the temporal evolution of pattern (structure) and phase separation dynamics was pursued primarily on the 6/94 copolymer/asphalt unless otherwise stated. The kinetics of phase growth in blends was studied using a one-dimensional CCD camera (Reticon detector, EG&G) that permits simultaneous measurement of scattered intensity versus scattering angle. The sample was preheated to 200 °C for 2 min (this temperature may vary with individual experiments) to ensure complete homogenization of the blend. It was then immediately transferred to the heating block that was controlled at predetermined experimental temperatures to allow simultaneous measurement of the scattered intensity versus scattering angle. The temporal evolution of the scattering peak maximum was used to calculate the growth of domain size in the blends. A Nikon Optical microscope (Optiphot-12) was used for mimicking the structural changes during phase transition. A Mettler hot stage (FP-82HT) and a central processor (FP-90) were used for temperature control.

Thermal transitions of the Kraton modified asphalts were characterized by means of differential scanning calorimetry (DSC) (Du Pont 9900 thermal analyzer) attached with a 910 DSC heating module and a microprocessor for data acquisition and analysis. The DSC instrument was calibrated using an indium standard. The vacuum dried samples were packed into the DSC aluminum pans and encapsulated with the lids. A blank aluminum pan was used as a reference in the DSC cell. Nitrogen gas was purged to provide an inert gas atmosphere in the DSC cell during the experiment. The heating rate was 10 °C/min unless indicated otherwise.

3. Results and discussion

3.1. Miscibility and phase diagram

The miscibility behavior of the Kraton/asphalt blends was investigated by means of DSC. Fig. 1 shows the variation of glass transitions with Kraton/asphalt blends. The T_g of the styrene segment in the copolymer, being a minority component, was not clearly discernible in the DSC thermograms. The T_g of the butadiene segment in the copolymer appeared around -85 °C, but it shifted with

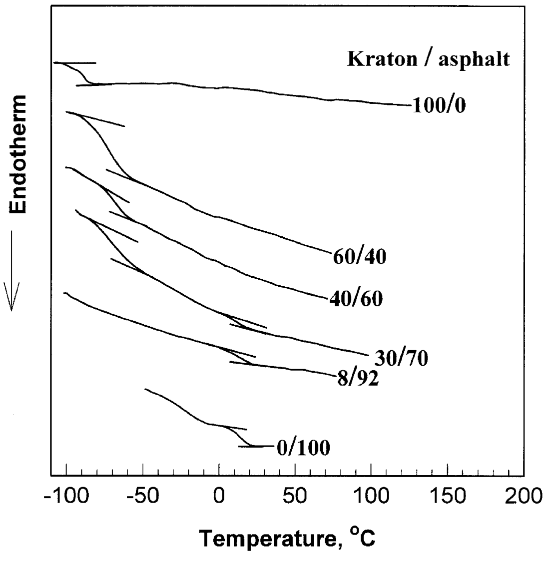

Fig. 1. DSC thermograms of Kraton/asphalt blends, showing the movement of the T_g of the butadiene segment in the copolymer at low asphalt compositions and the dual transitions in the higher asphalt compositions.

increasing asphalt and saturated at about −65 °C in the 60% asphalt concentration. The movement of T_g of the butadiene segment in the copolymer may be attributed to partial miscibility of butadiene and asphalt at low asphalt concentrations. When the asphalt content exceeds critical concentration, there appear two distinct T_gs. The T_g of the asphalt remains unchanged upon further increase of asphalt content, suggestive of immiscibility character of the Kraton/asphalt blends. The observed miscibility behavior of the Kraton/asphalt appears complex, but it may be explicable through establishment of phase diagram. It should be pointed out that asphalt contains mixed monomers and oligomers from petroleum residue. However, optical microscopic investigation shows no identifiable phase-separated structure in neat asphalt, thus it is fair to regard the mixture of Kraton/asphalt as a pseudo-binary system.

Fig. 2 shows the variation of scattered intensity of the 6/94 Kraton/asphalt blend obtained in the cloud point measurement at an arbitrary scattering angle of 10°. The heating rate was 1 °C/min. The scattered intensity decreases with increasing temperature and levels off at about 175 °C. In the cooling runs, a reverse trend was observed, except that hytheresis exists in the cloud points between the heating and cooling cycles that may be attributed to the kinetic effect. To avoid possible degradation due to prolong exposure at elevated temperatures, the cloud points were obtained from the heating runs. These cloud points were crosschecked in the optical microscopic investigation.

Fig. 3(a) shows a change of phase-separated domains during the course of heating from 110 to 190 °C. The initial two-phase structure appears interconnected and the domains grow in size through coalescence (see 110 °C). This growth process is expedited as the blend gains mobility in the vicinity of 130 °C. The length scale of the domains diverges when the system approaches the coexistence point and the structure seemingly disappears around 180 °C. In the cooling run from 200 °C, tiny droplet structure develops around 173 °C, but it is clearly discernible only when the temperature reached 166 °C (Fig. 3(b)). The domains coarsen further with continued cooling while the droplet structure becomes more distinct. In some area of the microscopic view, these droplets appear slightly interconnected due to their proximity that makes the two-dimensional images look somewhat interconnected when projected on the basal plane. In the slow cooling, the off-critical composition passes through the metastable region before entering to the unstable region. Hence, phase separation must be triggered in the metastable region through nucleation and growth (NG). With continued cooling, the system is thrust deeply into the unstable region where SD is dominant; hence there may be a crossover of the mechanism from NG to SD. These emerging textures are presumably determined by the competition between the NG and SD subjected to the cooling rates. Although the observed structure evolution based on the microscopic investigation qualitatively confirms the phase reversibility, the texture evolves in different morphological routes during phase separation and phase dissolution. It is extremely

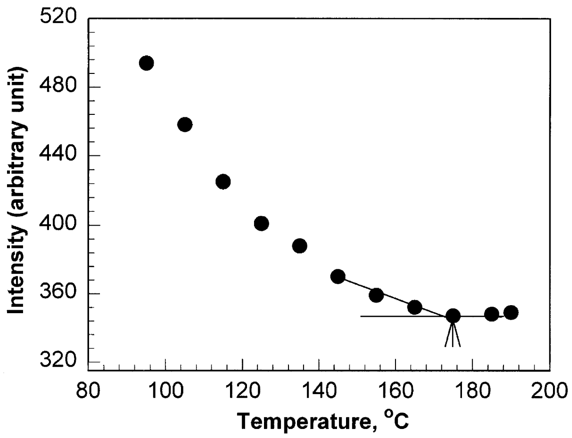

Fig. 2. Variation of scattered intensity during the course of heating the Kraton/asphalt blend at a heating rate of 1 °C/min.

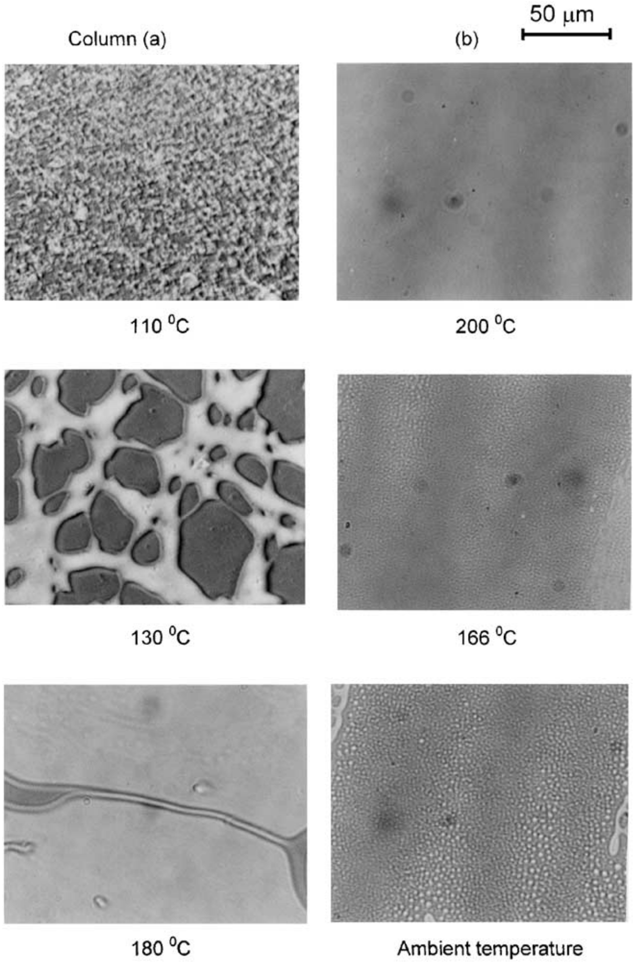

Fig. 3. Evolution of phase-separated domains during the course of: (a) heating from 110 to 190 °C, (b) cooling from 200 °C to ambient temperature. The heating and cooling rates were 1 °C/min.

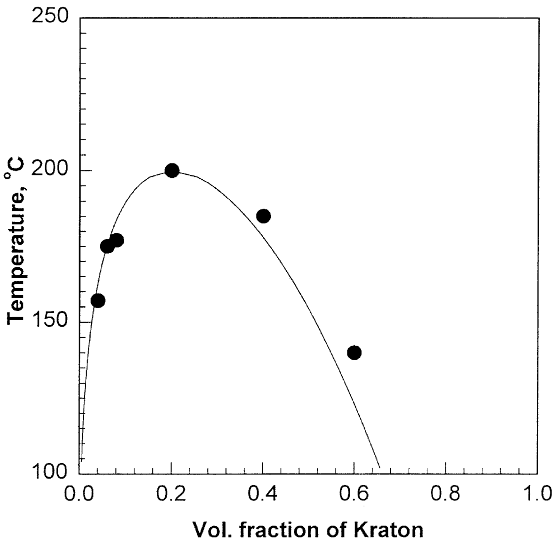

Fig. 4. A ‘cloud point versus volume fraction’ phase diagram of Kraton/asphalt blends.

difficult to pinpoint the exact cloud point from the visual inspection. In view of such uncertainty, the cloud point obtained by light scattering, which is intermediate between the heating and cooling runs under the optical microscope, was utilized in the phase diagram. A similar light scattering experiment was undertaken for other compositions to determine the loci of the cloud point curve.

Fig. 4 shows the cloud point phase diagram obtained by light scattering. The phase diagram is an upper critical solution temperature (UCST) in character with a maximum around 20 vol% of the block copolymer and around 200 °C. In principle, the phase diagram should include the order–disorder transition (ODT) of the SBS block copolymer [9]. The ODT transition of the SBS Kraton copolymer is estimated to be around 260 °C, which is evidently beyond the temperature range where the PB segments as well as asphalt would degrade [10,11]. For the practical purposes, we shall focus on the macroscopic phase separation between the block copolymer and asphalt; and hence only the UCST is shown in Fig. 4. Since the phase diagram is skewed to the asphalt-rich side, the effect of the ODT temperature of the block may be prevalent only in the copolymer-rich side, but its effect would be inconsequential to the studies on blend miscibility in the asphalt-rich side and also to the dynamics of phase separation at the 6 vol% that is of interest to the following kinetic study.

In the US, the SBS content is typically about 3–4% in polymer modified asphalt (PMA) formulations. In regards to OGP applications, a larger SBS amount is needed to sustain the strength of PMA binders. Typically, the SBS concentration in the Japanese high viscosity binder is 6 vol% as this formulation gives the best performance-to-cost ratio for the OGP applications [6]. Hence, we shall focus on the spatio-temporal growth of domain morphology at the 6/94 Kraton/asphalt composition that ultimately controls the properties of the SBS modified asphalt.

3.2. Phase separation dynamics

A temperature quench experiment was undertaken by transferring rapidly the 6/94 SBS/asphalt blend from 200 °C to ambient temperature. Fig. 5 shows the temporal evolution of the scattering curves. The scattering peak first appears at a large wavenumber, $q \sim 4.3\ \mu\mathrm{m}^{-1}$, suggesting the occurrence of phase separation presumably through SD. The peak shifts rapidly to a smaller scattering angle suggestive of domain growth. There is no time period where the peak remains stationary with time suggesting the lack of the early stage of spinodal decomposition [12,13]. It is possible that the early stage of SD is probably too fast that it may be missed during the experiment. Although the observed scattering peak is suggestive of spinodal, it is by no means a proof. A similar thermal quench induced phase separation experiment was undertaken at 50 and 70 °C. The late stage of domain growth may be analyzed in the context of power law scaling [14–18], viz.

$$q_m \propto t^{-\alpha} \quad (1)$$

$$I_m \propto t^{\beta} \quad (2)$$

where q_m and I_m are the maximum wavenumber and the corresponding scattered intensity maximum. The length scale may be estimated as $\xi = 2\pi/q_m$.

Fig. 6 shows the power law plot of the length scale versus elapsed time in a double logarithmic form. Phase separation takes place rapidly for a few ten seconds and quickly levels off. It can also be noticed that there is a systematic trend for leveling off the length scale, i.e. the asymptotic average domain size increases with increasing temperature of quenching or reducing quench depth. This observed phenomenon is consistent with the general perception that the smaller the quench depth (smaller supercooling), the

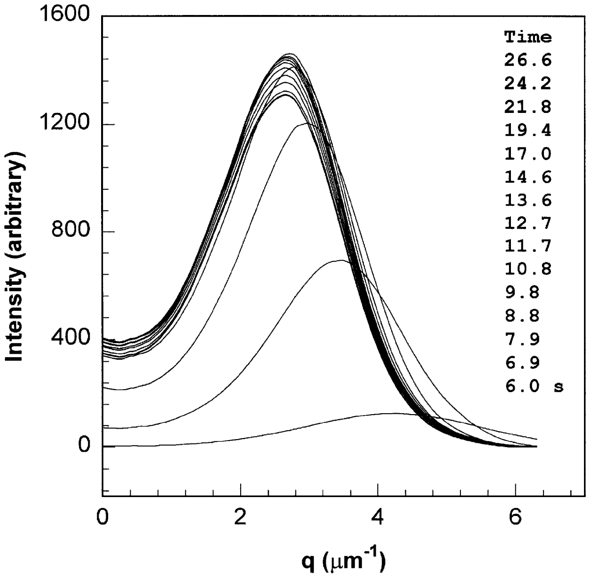

Fig. 5. Time-evolution of scattering profiles of the 6/94 Kraton/asphalt blend following a temperature quench from 200 °C to ambient temperature.

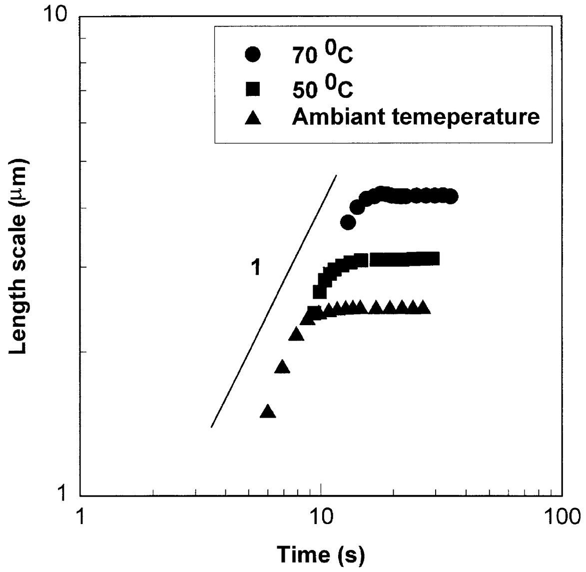

Fig. 6. Dynamical scaling of domain growths in the 6/94 Kraton/asphalt blend subjected to various indicated T quenches from 200 °C.

larger the average domain size (or the length scale). In all quenches, the slope of the temporal growth is unity, which corresponds to the late stage of domain growth where hydrodynamic effect plays a dominant role [16]. The cessation of the growth dynamics of the 6/94 Kraton/asphalt blend at a longer time may be attributed to the physical pinning effect that has been commonly observed in the off-critical quenching.

4. Conclusions

The present study is probably the first to establish a phase diagram of the Kraton/asphalt blend. The observed phase diagram was found to be of the UCST type with a maximum at 20% copolymer and at about 200 °C. The T_g of the butadiene segment of the copolymer showed the systematic movement with increasing asphalt up to 60 vol%, suggesting the partial miscibility of the pair. However, there is no miscibility between the PS segment and asphalt. With further increase of asphalt, the asphalt T_g remained stationary, suggesting the immiscibility character at high asphalt contents, which is in agreement with the UCST phase diagram. In the kinetic studies at the 6/94 Kraton/asphalt blend, it was found that the smaller the quench depth (smaller supercooling), the larger the average domain size (or length scale). In all quenches, the slope of the temporal growth is 1, which corresponds to the late stage of domain growth in which the hydrodynamic effect dominates. The physical pinning of the 6/94 Kraton/asphalt blend leading to the cessation of the domain growth is important for the pavement applications.

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