Dynamic Mechanical Properties of Polystyrene-Block-Poly[ethylene-*co*-(ethylene-propylene)]-Block-Polystyrene Triblock Copolymer/Hydrocarbon Oil Blends

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ABSTRACT: Blend systems of polystyrene-*block*-poly(ethylene-co-(ethylene-propylene))-*block*-polystyrene (SEEPS) triblock copolymer with three types of hydrocarbon oil of different molecular weight were prepared. The E'' curves as a function of temperature exhibited two peaks; one peak at low temperature ($\cong -50°C$), arising from the glass transition of the poly[ethylene-*co*-(ethylene-propylene)] (PEEP) phase and a high temperature peak ($\cong 100°C$), arising from the glass transition of the polystyrene (PS) phase. The glass transition temperature (T_g) of the PEEP phase shifted to lower temperature with increasing oil content. The shifted T_g depended on the types of oil and was lower for the low molecular weight oil. The T_g of PS phase of the present blend system, were found to be constant and independent of the oil content, when molecular weight of the oil is high. However, for the lower molecular weight oil, the T_g of the PS phase also shifted to lower temperatures. This fact indicates that the oil of high molecular weight is merely dissolved in the PS phase. The E' at (75°C, at which temperature both of PEEP and PS phases are in glassy state, was found to be independent of oil content. In contrast, at 25°C, at which temperature the PEEP phase is in rubbery state, the E' decreased sharply with increasing oil content. This result indicates that the hydrocarbon oil was a selective solvent in the PEEP phase. It mainly dissolved in the PEEP phase, although slightly dissolved into the PS phase as well, when molecular weight of oil is low. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3001–3006, 2011

Key words: polystyrene-*block*-poly(ethylene-*co*-(ethylene-propylene))-*block*-polystyrene triblock copolymer (SEEPS); hydrocarbon oil; viscoelastic property; glass transition; modulus

INTRODUCTION

A-B-A type of triblock copolymers, such as polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) and polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS), possesses unique physical properties distinct from those of the corresponding homopolymers.[1–6] It is well known that at low temperatures such block copolymers have an ordered micro-domain structure in the form of spheres, cylinders, and lamellae.[7–11] In this respect, the block copolymers display behavior analogous to particulate-filled polymers or vulcanized rubbers. This unique feature makes SBS and SIS interesting for commercial applications. However, these triblock copolymers including unsaturated rubber component have limited resistance to degradation from exposure to high temperatures and ultraviolet radiation.[12] This poor resistance to degradation is a clear limitation of the unsaturated block copolymers. Hydrogenation of these block copolymers improves the resistance to degradation to the level found in saturated polymers, and in this way, the elastomer of block copolymers can be hydrogenated to give more resistance. These types of block copolymers include polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene (SEBS), polystyrene-*block*-poly(ethylene-*co*-propylene)-*block*-polystyrene (SEPS) and polystyrene-*block*-poly(ethylene-*co*-ethylene-propylene)-*block*-polystyrene(SEEPS). These triblock polymers have many applications, for instance, as thermoplastic elastomers,[1,2] pressure sensitive hot-melt adhesives,[3] and viscosity stabilizers for oils.[4]

Formulating certain styrenic triblock copolymers with a midblock-selective solvent results in a soft, highly elastic gel with thermoplastic properties. Examples of useful selective solvents are highly refined, aromatic-free, "paraffinic oils," which are a mixture of saturated aliphatic and alicyclic hydrocarbons. It has been mentioned that these oils have a solubility parameter close to that of the elastomeric midblock and quasi-incompatible with the polystyrene (PS) end

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blocks of the triblock copolymers.[13] However, the effects of oils on the physical properties of these triblock copolymers have not been fully elucidated, especially for the effect of molecular weight of oils.

Dynamic mechanical measurements of polymers can be correlated with their structure and morphology and are very sensitive to the physical properties of the glass transition temperature (T_g) region. The dynamic mechanical properties of triblock copolymers have previously been investigated,[14–19] although emphasis has been devoted to investigation of their morphology. In triblock copolymers, e.g., SBS and SIS, it is difficult to detect T_g of the PS phase, particularly when the PS content is low (<30% by weight), in which case the glass transition is smeared out. Moreover, in triblock copolymers with low PS content, the maximum peak is expected to be lower, thereby making the glass transition of the PS phase less evident.

Recently, Sugimoto et al.[20] have measured the dynamic mechanical properties of SEBS/hydrocarbon oil blends as a function of temperature. They found that the oil is a selective solvent for the olefinic PEB but a nonsolvent for PS, and that the oil is present in the PEB phase and plasticizes the phase. Additionally, they found the oil does not affect the peak position of the loss modulus E'' at lower temperatures, owing to the similar T_g of the oil and PEB phases. The oil used in their case had a relatively high molecular weight of 750 (g/mol).

Different molecular weight oils possess different degrees of solubility and so the T_g should also be affected. In this study, we prepared SEEPS-1 blended with three types of oil by melt blending and carried out dynamic mechanical measurements of the blends. On the basis of the experimental findings, we discuss the effect of the content and molecular weight of oil on the T_g of the PS and PEEP phases.

EXPERIMENTAL

Materials

SEEPS triblock copolymer (designated SEEPS-1) of commercial grade (SEPTON-4033, Kuraray Co. Ltd., Japan) was used in this study. The molecular weight of SEEPS used in this study was determined by gel permeation chromatography (GPC) using PS elution standards. The total weight-average molecular weight M_w of SEEPS-1 was 84×10^3 and the weight fraction of the PS block was 0.30. Three types of Diana Process Oil (Idemitsu Kosan Co. Ltd., Japan) were used: PW380 (Oil-1), PW90 (Oil-2), and PW32 (Oil-3). These oils are a mixture of saturated hydrocarbons having different molecular weight, and possess average molecular weights of 750 g/mol (Oil-1),

540 g/mol (Oil-2), and 410 g/mol (Oil-3), according to sample provider.

The SEEPS-1 copolymer and the oil were mixed as a dry blend and left for about 20 h at room temperature. The mixtures were then blended by a batch type mixer (Model: Labo Plastomill, Toyo Seiki Seisakusho Co. Ltd., Japan) and a twin-screw extruder (Model: ULT nano, Technovel Co., Ltd., Japan) from 180 to 240°C at 100 rpm for about 10 min, and subsequently compression molded into a rectangular shape at 180°C and 5 MPa for 10 min by a Mini Test Press-10 (Toyo Seiki Seisakusho Co. Ltd., Japan).

Rheological measurements

Dynamic mechanical measurements were performed using a strain-controlled rheometer (TA Instruments, model: RSA II). The measurements were conducted in tensile mode at a constant frequency of 1.0 Hz over a wide temperature range. The sample dimensions for the tensile oscillatory tests were $5.5 \times 32 \times 1.0$ mm^3. Temperature sweep tests were carried out at a heating rate of 2°C/min from a temperature of (−120°C to the point at which the sample became too soft to be tested. The tensile storage modulus (E') and loss modulus (E'') were measured for each sample. The glass transition temperature (T_g) is specified in this study as the temperature at which E'' shows a maximum.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the dynamic mechanical properties as given by the storage (E') and loss (E'') moduli of the SEEPS-1/Oil-1 blends at various oil contents. For pure SEEPS, the maximum located at (−50°C on the E'' curve [Fig. 1(b)] arises from the glass transition of the PEEP phase. In the temperature range of this transition, the storage modulus E' [Fig. 1(a)] decreases markedly. The T_g of the PS phase is located at 100°C on the E'' curve, at which temperature E' decreases appreciably.

For the SEEPS-1/Oil-1 blends, the peak temperatures of T_gs of PEEP and PS segment are observed at about (−50°C and 100°C, respectively, and have little dependence on the oil content. In the temperature range between the two peaks, E' was observed to be independent of temperature, presumably because the PS phase plays a role in physical crosslinking. The data shown in this study were quite similar both qualitatively and quantitatively to those of SEBS/oil-1 blends reported by Sugimoto et al.[20] We now think that there are not large difference between SEBS and SEEPS. Therefore, solubility parameter of PEEP is similar to that of PEB, because the chemical structure is not so different each other,
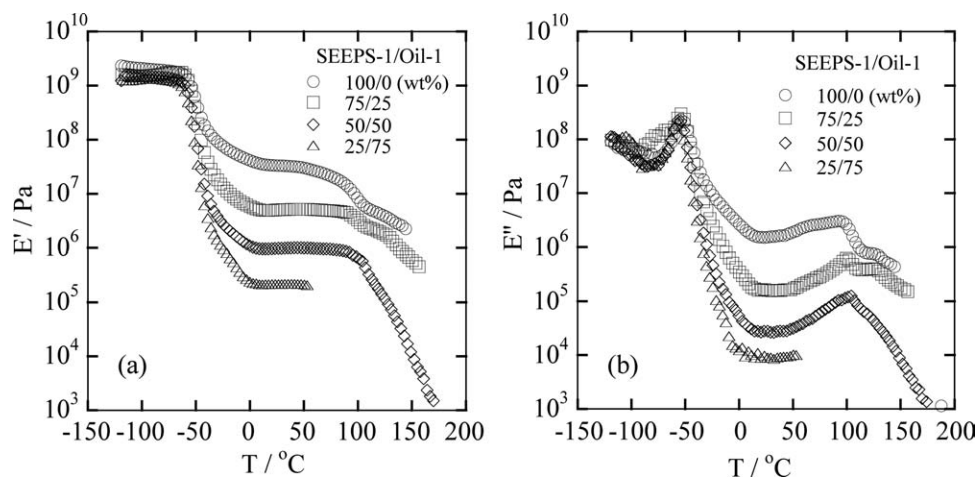
Figure 1 (a) Storage modulus E' and (b) loss modulus E'' as a function of temperature for the SEEPS-1/Oil-1 blends with various oil contents at $f = 1.0$ Hz and a heating rate of 2°C/min.

and the miscibility of PEEP and PEP with hydrocarbon oils is essentially the same. With this similarity, we refer experimental facts of the SEBS system for understanding of the present blends.

Heck et al.[21] reported that SEBS showed hexagonally packed PS cylinders in a PEB matrix by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). Sugimoto et al.[20] reported the morphology of SEBS/Oil-1 blends by atomic force microscopy (AFM). They observed cylindrical microstructure for the SEBS as the copolymer of symmetric architecture with PS weight fraction of 29%. They also observed regularly aligned sphere domains for SEBS/Oil-1 = 50/50 blend. The spherical domain morphology was stable until 200°C. On the basis of these previous reports, we can speculate that pure SEEPS-1 shows hexagonally packed PS cylinders in a PEEP matrix and SEEP-1/Oil-1 = 50/50 blend has regularly aligned sphere domains. Therefore, the decrease of E' change at rubbery plateau region with an increase in oil content is due to the morphology change from the isolated PS cylinder to particle domains.

Figures 2(a,b) and 3(a,b) show E' and E'' as a function of temperature for the SEEPS-1/Oil-2 blends and/Oil-3 blends at various oil contents. Remarkable difference compared with Figure 1 is that the two peaks corresponding to the T_g of the PEEP and PS phases on the E'' curves shifted toward lower temperatures with increasing hydrocarbon oil. This phenomenon becomes more apparent for the SEEPS-1/Oil-3 blends, as shown in Figure 3, and will be discussed in more detail below. Figure 4 shows the dependence of T_g on the composition of the SEEPS-1/Oil-1, /Oil-2 and/Oil-3 blends and the pure SEEPS-1 of 0 wt % content, as determined by dynamic mechanical measurements. The T_g value of SEEPS-1 is −54°C while the T_g values for the blends gradu-

ally decrease with increasing oil content. These shifts depend on the type of oil. The shift for SEEPS-1/Oil = 25/75 blends, for example, is about 3°C for Oil-1, 10°C for Oil-2, and 22°C for Oil-3. We consider that the T_g of the PEEP phase is decreased because the T_g of the low molecular weight oil is lower than that of the PEEP phase. Oil of smaller molecular weight acts as plasticizer more effectively than larger one.

Let us analyze the composition dependence of the T_g for these blends by using the following Gordon-Tailor equation,[22]

$$T_{g12} = (w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2) \qquad (1)$$

Here, w_1 and w_2 are the weight fraction, and T_{g1} and T_{g2} are the glass transition temperatures of component 1 and 2, respectively. T_{g12} then gives the T_g for the blends. Eq. (1) gives a straight line in the plot of T_{g12} versus $(T_{g2} (T_{g12}) w_2/w_1$ with a slope k and an ordinate intercept T_{g1}. Figure 5 shows plots of T_{g12} versus $(T_{g2} (T_{g12}) w_2/w_1$ for the SEEPS-1/Oil-1, /Oil-2, and/Oil-3 blends. The data was fitted by a least-squares regression technique, and the slope of the straight lines was found to be 1.0, 0.7, and 0.6 for the SEEPS-1/Oil-1, /Oil-2, and/Oil-3 blends, respectively. The k value = 1 for the SEEPS-1/Oil-1 means that blend additively rule is satisfied. The T_g values of the oils, as given by the ordinate intercept, were −59°C, −67°C, and −79°C for the SEEPS-1/Oil-1, /Oil-2, and/Oil-3 blends, respectively.

As shown in Figure 4, the peak temperature of the SEEPS-1/Oil-1 blends at around 100°C was constant irrespective of the oil content, as also reported for SEBS/oil blends in the previous paper.[20] This fact seems to indicate that hydrocarbon oil is nonsolvent for PS, while being a good solvent for SEBS and SEEPS. For the SEEPS-1/Oil-2 and/Oil-3 blends, however, the peak temperatures slightly decreased
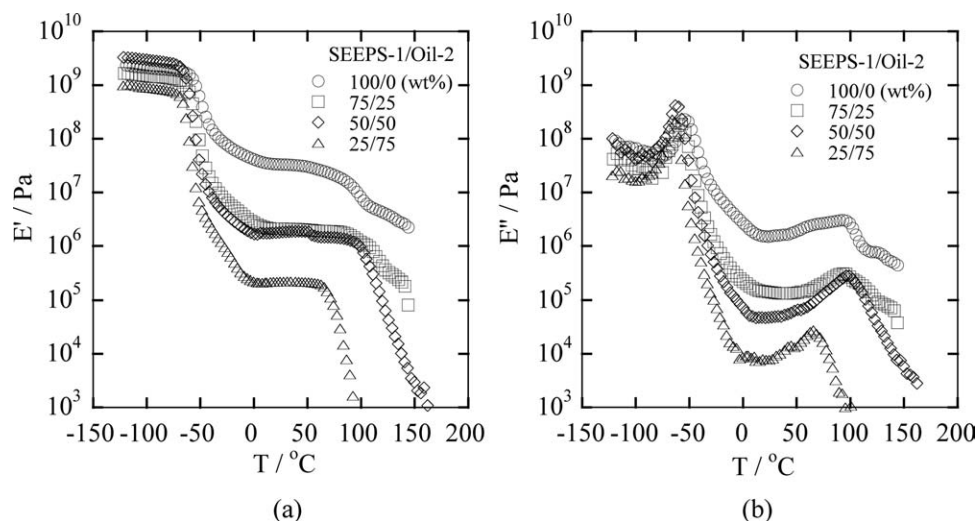
Figure 2 (a) Storage modulus E' and (b) loss modulus E'' as a function of temperature for the SEEPS-1/Oil-2 blends with various oil contents at $f = 1.0$ Hz and a heating rate of 2°C/min.

with increasing oil content. This indicates that the lower molecular weight oils are also mixed into the PS phase.

Kim et al.[23] studied the dynamic mechanical properties of PS/dodecane systems. They reported that addition of dodecane, a low molecular weight hydrocarbon, lowered the T_g of PS and that the maximum loss peak decreased with increasing dodecane content. The T_g for samples with a dodecane content of 5 and 10 wt %, was lower about 30 and 50°C than that of PS, respectively. This result suggests that the lower molecular weight oil dissolves into the PS phase and lowers the T_g of the PS phase. Using the data of Kim et al., the oil content in the PS phase is estimated to be about 6% for the SEEPS-1/Oil-3 = 25/75 blend, which predicts that only

0.45% of Oil-3 dissolves into the PS phase, as the overall PS content of this blend is only 7.5%. The PS phase has lower oil concentration when molecular weight of oil is high and consequently, the SEEPS-1/Oil-1 blends have higher T_g. We consider this effect to be an important factor in depression of the T_g of the PS phase. In addition, the different T_g values of the PS phase may be a result of morphological differences such as the domain size of the PS phase.

Figure 6 shows the storage modulus as E' at (100°C and 25°C as a function of oil content for the SEEPS-1/Oil-1, /Oil-2, and/Oil-3 blends. The value of E' at (100°C is found to be almost constant irrespective of the oil content, because in this case the temperature is below the T_g values of PEEP and PS.
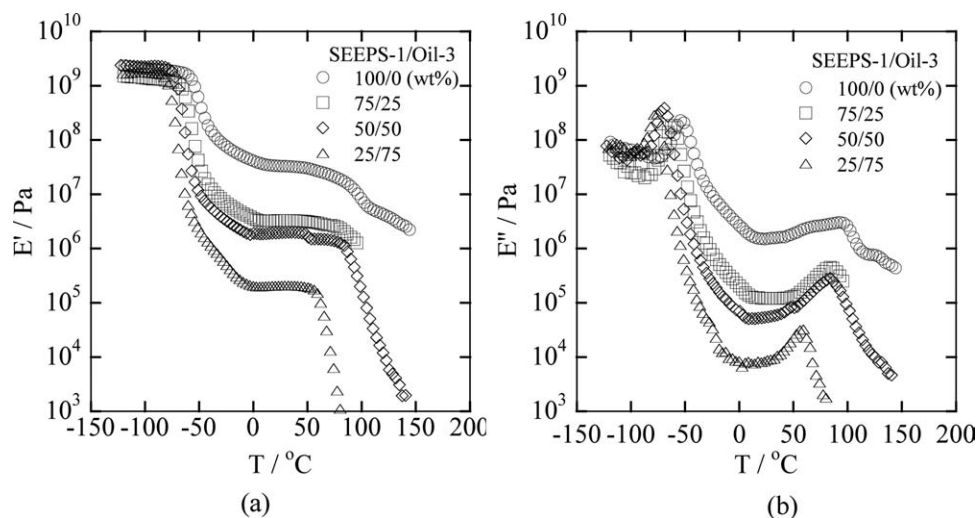

Figure 3 (a) Storage modulus E' and (b) loss modulus E'' as a function of temperature for the SEEPS-1/Oil-3 blends with various oil contents at $f = 1.0$ Hz and a heating rate of 2°C/min.
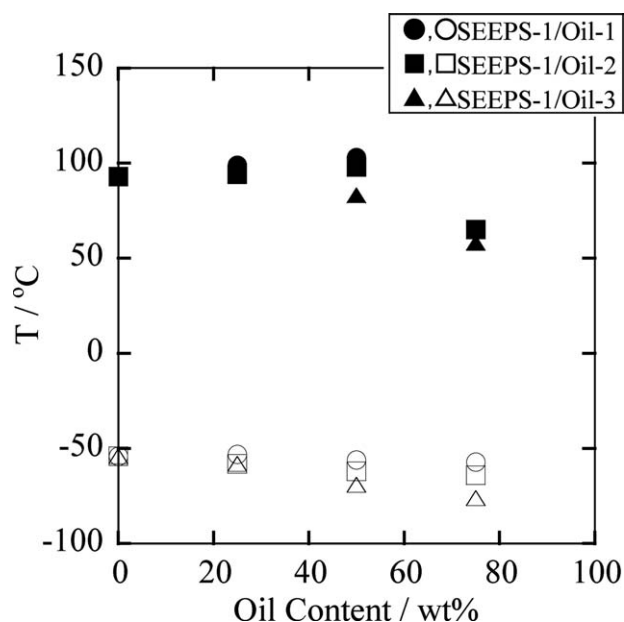
Figure 4 E'' peak temperatures as a function of blend composition for the SEEPS-1/Oil-1 (●,○), SEEPS-1/Oil-2 (■,□), and SEEPS-1/Oil-3 (▲,△) blends. The closed and open symbols show the E'' peak temperature at high and low temperatures, respectively.

In contrast, at 25°C, the value of E' decreases with increasing oil content. This fact indicates that these oils are mainly mixed into the PEEP phase, whereas small amount is also mixed into the PS regions changing the T_g of the PS phase.

Figure 6 shows that at 25°C, the value of E' decreases with increasing oil content. However
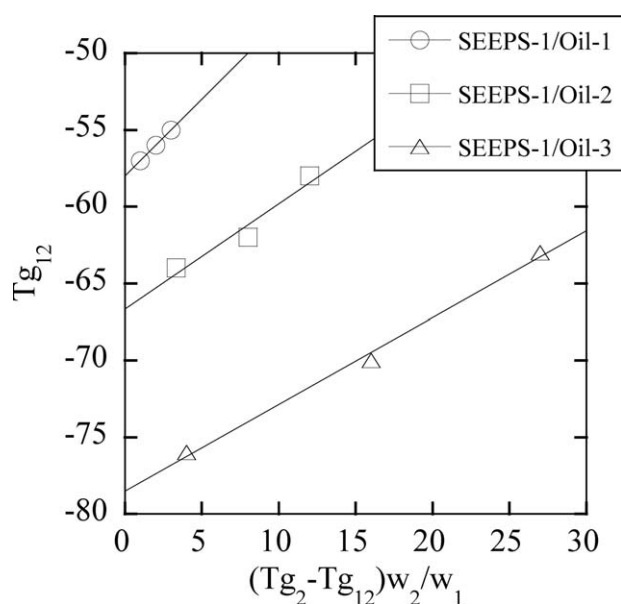

Figure 5 T_g of the SEEPS-1/Oil-1 (○), Oil-2 (□), and Oil-3 (△) blends plotted according to the Gordon-Tailor equation.[13]
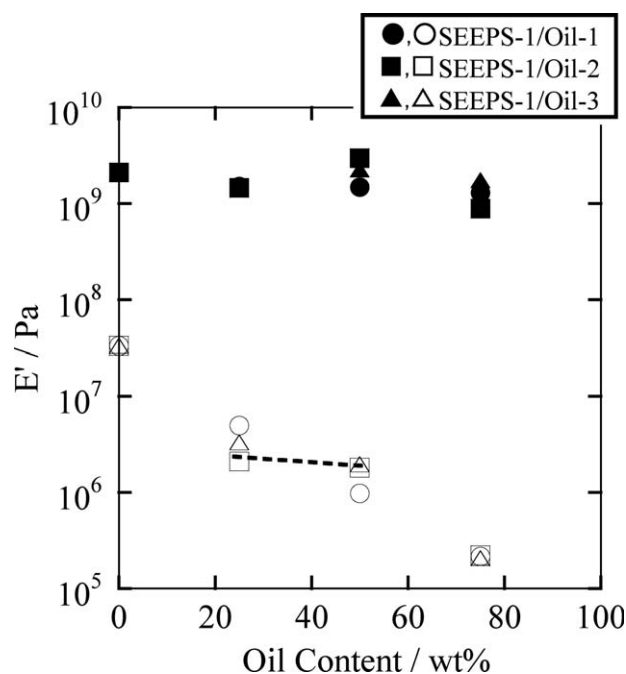

Figure 6 The storage modulus E' at (100°C and 25°C as a function of oil content for the SEEPS-1/Oil-1 (●,○), SEEPS-1/Oil-2 (■,□), and SEEPS-1/Oil-3 (▲,△) blends. The closed and open symbols show the values of E' at (−100°C and 25°C, respectively.

detail of decreasing behavior is different for type of oils. As is also indicated by Figure 1, the value of E' of the SEEPS-1/Oil-1 system decreases simply monotonically. However, Figures 2 and 3 indicates that the E's at 25°C of SEEPS-1/Oil-2, Oil-3 = 75/25 and SEEPS-1/Oil-2, Oil-3 = 50/50 are similar, whereas finally it decreases as we increase the content of oil up to 25/75 fraction. This behavior also appears in Figure 6.

The dependence of E' as a function of oil content is affected by several factors. As a simplification we consider the ideal rubber elasticity described by

$$E' = \nu k_B T, \tag{2}$$

where ν is the number density of crosslinking in the system. When the elasticity of the present system at 25°C is mainly from physical crosslinking between different PS domains, we can propose

$$\nu = (1 - \iota)\rho X_{SEEPS} N_A / M_{SEEPS}, \tag{3}$$

where ρ is the density of the material X_{SEEPS} is the weight fraction of SEEPS in the SEEPS/oil system, N_A is the Avogadro number, M_{SEEPS} is the molecular weight of SEEPS. And ι is the fraction of intramolecular crosslinkings. Intramolecular crosslinkings would not contribute elasticity, if we neglect entanglements between them.

Equation (3) shows that the dependence of E' is mainly estimated by factor $(1-\iota)X_{SEEPS}$. We consider that the number density of PS domains in the system is closely related to ι for the present case. We expect that oil of small M_w goes into the PS region comparably more easily than oil of large M_w affecting the number density of PS domains.

We are now studying the order–disorder transition (ODT) of SEEPS/Oil blends at high temperature. The ODT temperature T_{ODT} was not observed for the neat SEEPS and it was observed for SEEPS-1/Oil = 75/25 blend below 300°C. The T_{ODT} of SEEPS-1/Oil-1 = 50/50 blend was found to be below 220°C. This T_{ODT} behavior is almost the same as that of SEBS/Oil-1 blends reported previously.[20] Therefore, it is concluded that the thermal stability of the morphology is similar for SEBS and SEEPS blends. From the similarity with SEBS, the neat SEEPS-1 and SEEPS-1/Oil = 75/25 blends is considered to form hexagonally packed PS cylinders in the PEEP matrix. However, the morphology of the neat SEEPS-1 and SEEPS-1/Oil = 75/25 blends would be changed by compounding condition, although SEEPS-1/Oil = 50/50 and 25/75 blends have stable sphere domains. In fact, the data of SEEPS-1/Oil = 75/25 blends were scattered, when we measured the blend again. These morphological changes by compounding condition is particularly important. However, morphological study is out of the scope of this article. This is considered as important future work.

CONCLUSIONS

We have studied the dynamic mechanical properties of blends for SEEPS with three types of hydrocarbon oil. Our general focus is on effect of molecular weight of oil as plasticizer on the triblock copolymer system. The T_g values of the PEEP and PS phases were found to be dependent on the molecular weight of oil in the blends. With increasing oil composition, the T_g of the PEEP phase of the SEEPS-1/Oil blends shifts to lower temperature. Analysis by the Gordon-Taylor equation can disclose the difference of oil type as the slope of k in Eq. (1) Oil of smaller molecular weight is related to the smaller value of k. The T_g of the PS phase for the SEEPS-1/Oil blends also shifted to lower temperatures with increasing oil content depending on molecular weight of oils. These results indicate that the lower molecular weight oil is slightly dissolved in the PS phase, although largely dissolved in the PEEP phase. The E' value at (−75°C, at which temperature both phases are in a glassy state, was found to be independent of the oil content. In contrast, at 25°C, at which temperature the PEEP phase is in a rubbery state, the E' value decreases with an increase in oil content. These results allow us that selection of molecular weight of oil is one of the key factors to control rheological properties for triblock type elastomers.

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