

Structure Formation and Mechanical Properties of Thermoplastic Elastomer and Oil System Having a Microcellular Porous Structure

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ABSTRACT: A novel microcellular porous structure, the product of a small proportion of a semicrystalline thermoplastic elastomer and a large proportion of low molecular weight oil, was examined. The system exhibited a unique three-dimensional continuous polymer network, consisting of interconnected spherical cells of a few tens of micrometers in diameter. In this report, details of morphology and stress-strain relationship of the system, which is made from hydrogenated poly[butadiene-*b*-(styrene-*random*-butadiene)] (H-SBR) as a semicrystalline thermoplastic elastomer and straight asphalt as an oil, were investigated and analyzed. The system exhibited inverse S-shape type stress-strain curves, but was characterized by extension rate and polymer concentration dependency. It was demonstrated that the

stress-strain curves of the system can be described by a simple combination of that of two phases: asphalt-rich phase and H-SBR-rich phase. Calculations of a simple parallel model quantitatively agreed with experimental data, especially in the case of higher polymer concentrations (about 12 to 20 vol %) where uniform polymer network is formed over the whole system. Disagreement between calculation and experimental data was, however, found in the cases of very small proportions of H-SBR (< ~ 8 vol %), where the polymer network structure in the system was imperfect. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 107–112, 2005

Key words: elastomers; networks; phase separation; morphology; structure-property relations

INTRODUCTION

Over the past few decades large numbers of studies about polymer miscibility and compatibility have been reported¹ and many types of phase-controlled polymers have been developed and put to practical use. Studies that focused on physical properties, based on morphological considerations of phase-controlled polymers, have been carried out.^{2,3} An important issue is how to estimate the physical properties of materials from that of constituents, like design on architecture.

Recently we proposed novel nonaqueous physical gels prepared with small proportions of semicrystalline thermoplastic elastomers (TPEs) and large proportions of oils of low molecular weight.^{4–8} Observed with optical microscope, the systems consist of three-dimensional continuous polymer networks constituted by spherical open cells of a few tens of micrometers in diameter. We call this a “microcellular porous structure.” The structure is obtained by a phase-separation process of a homogeneous mixture of TPE and oil from an elevated temper-

ature to room temperature. The systems are quite stable, both thermally and dynamically, and are currently used in industrial products.⁹

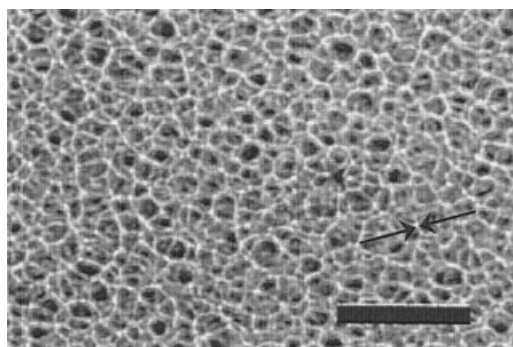
In this report, a system of a hydrogenated semicrystalline thermoplastic elastomer and straight asphalt is examined. At first, the unique polymer network morphology of the system is investigated. The condition of the polymer network in the system is estimated, and appearance of the network under deformation is observed. Next, details of the stress-strain relationship of the system are investigated and analyzed. It is demonstrated that the stress-strain curves of the system can be described by a simple combination of that of two phases: asphalt-rich phase and H-SBR-rich phase.

EXPERIMENTAL

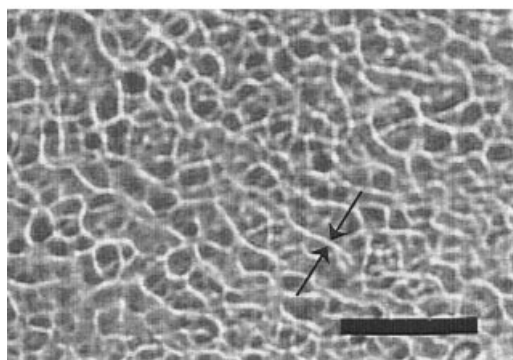
A semicrystalline thermoplastic elastomer, hydrogenated poly[butadiene-*b*-(styrene-*random*-butadiene)] (H-SBR, $M_w = 250,000$, $T_m = 98^\circ\text{C}$) was used. The polymer was synthesized by a conventional living anionic polymerization process.¹⁰ A straight asphalt (product of Nisseki Corp., Tokyo, Japan, penetrating index 40–60) was used as oil. A homogeneous mixture was prepared by mixing with a homogenizer or a conventional rubber mixer for 1 h at an elevated temperature (~ 200°C). The mixture was placed an appro-

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(a)



(b)

Figure 1 Optical micrographs of (a) H-SBR/asphalt system, of which the asphalt phase was washed out by xylene and dried; (b) thin film of H-SBR/asphalt system directly observed (polymer concentration $\phi = \sim 12$ vol %). Bar = 100 μm . Arrows point to typical thickness of polymer-rich phase.

appropriate mold (i.e., 2 mm thickness slab sheet mold) after which it was compressed and cooled to room temperature to obtain sample sheets of the mixture. The cooling rate was about 3°C/min. A similar process was also used to obtain asphalt sheet. A similar process was also used to make conventional (without microphase structure) asphalt-extended-polymer compounds consisting of large proportions of polymer (about 90 to 50 vol %) and small proportions of asphalt (about 10 to 50 vol %). Observation of morphologies of the system was performed by conventional optical microscopy.^{5,6} Samples for the extension test were cut to DIN-3-type dumbbells from the sheet. Stress-strain curves were measured by conventional rubber testing equipment at 23°C. Extension rates used were 5, 50, 300, and 500 mm/min.

RESULTS AND DISCUSSION

Polymer network morphology

Figure 1(a) shows an optical micrograph of the H-SBR/asphalt system (polymer concentration $\phi =$ about 12 vol %). Asphalt was washed out by xylene and dried as reported in previous article.⁶ The bright

area corresponds to the polymer-rich phase, and the dark area corresponds to the extracted asphalt-rich phase. The polymer-rich phase forms a three-dimensionally continuous network structure. As we reported,⁴ in TPE/oil systems, the polymer network consists of interconnected spherical cells of a few tens of micrometers in diameter and thus the oil-rich phase (here the asphalt-rich phase) is also continuous. Figure 1(b) shows a directly observed optical micrograph of a very thin film of the H-SBR/asphalt system (polymer concentration $\phi =$ about 12 vol %). The polymer-rich phase in the system slightly swells by asphalt. Comparing Figure 1(b) directly observed with Figure 1(a) in which asphalt was extracted, the polymer-rich phase in the system appears to be swollen to approximately double the size in its cross-sectional area. We believe that such swelling is plausible because the phase diagram of the polymer/oil system is generally highly asymmetric⁸ and the polymer-rich phase includes oil.

Figure 2 also shows a directly observed optical micrograph of a very thin film of H-SBR/asphalt system that includes an extended crack. It is clearly observed that both the polymer-rich and the asphalt-rich phases are deformed toward an extended direction. Further, no void is observed, which suggests that an assumption of *affine* deformation is admissible; that is, macrodeformation might be equal to microdeformation, such that the strain of the polymer-rich phase and that of the asphalt-rich phase might be generally comparable.

Stress-strain relationship

Figure 3 shows a typical stress-strain curve of the H-SBR/asphalt system (Line A: polymer concentration ϕ about 12 vol %). The H-SBR/asphalt gives an inverse S-shape-type stress-strain curve. Stress of the material rapidly increases at small deformation, after

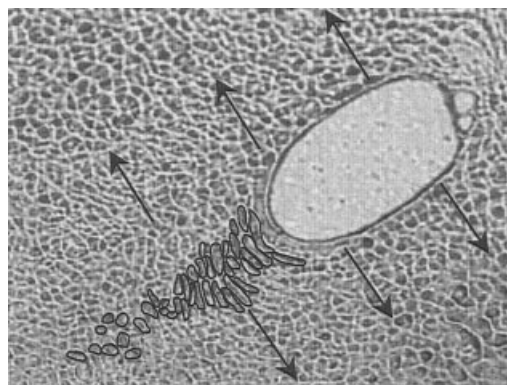


Figure 2 Optical micrograph of thin film of H-SBR/asphalt system near an extended crack. Arrows indicate extension direction. Typical cells of polymer-rich phase near crack are indicated by black line.

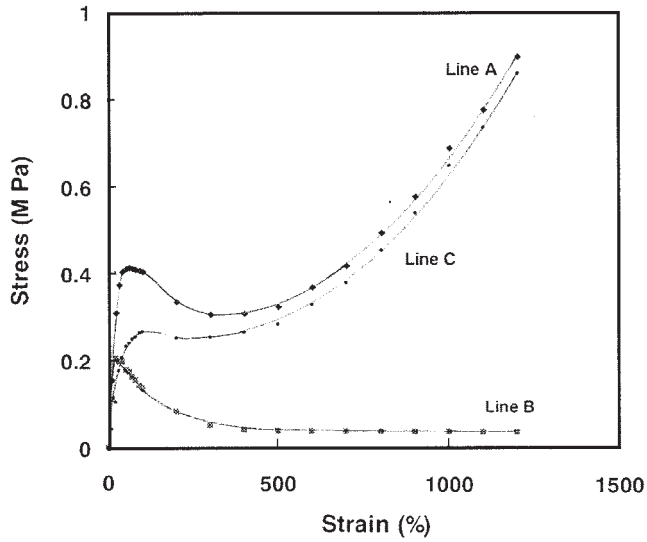


Figure 3 Stress-strain curve of H-SBR/asphalt system. Line A: polymer concentration $\phi = \sim 12$ vol %. Line B: calculated stress-strain relationship attributed to the asphalt phase (~ 88 vol %). Line C: the balance between modulus of H-SBR/asphalt system and calculated modulus of the asphalt phase.

which the stress decreases until about 300% strain. At large strain, the stress of the material increases again, resembling the yield phenomenon of conventional plastic polymers, in which the materials show necking; however, necking was apparently not observed in the system during its deformation.

In Figure 3 two other curves are delineated: one (Line B) is the stress-strain relationship attributed to the asphalt phase (~ 88 vol %) that is calculated from

the stress-strain curve of asphalt; another (Line C) is the balance between the modulus of the H-SBR/asphalt system and calculated modulus of the asphalt phase. We sought to analyze the stress-strain curve to ascertain what controls the relationship of the system. In the next section a simple model is proposed.

Model

Figure 4(a) shows a two-dimensional model of the system, a model of the polymer phase is depicted. In this consideration, we assume the following features, some of which are consequences of morphological observation, although some assumptions are for simple calculation.

- The polymer-rich phase makes continuous polymer network consisting of interconnected spherical cells [Fig. 4(a)].
- Polymer concentration in the polymer-rich phase is about 50 vol % of pure polymer because the polymer is swollen.
- The *effective* volume proportion is half of a polymer-rich phase because about half of a cell could contribute the modulus when the cell was extended [Fig. 4(b)].
- Polymer in the asphalt-rich phase is negligible.
- The asphalt-rich phase is also continuous.
- Both phases can deform freely. A phase does not disturb movement of another phase.
- *Affine* deformation is admissible.
- Mechanical interaction, like friction at the interface between the polymer-rich and the oil-rich phase, is negligible.

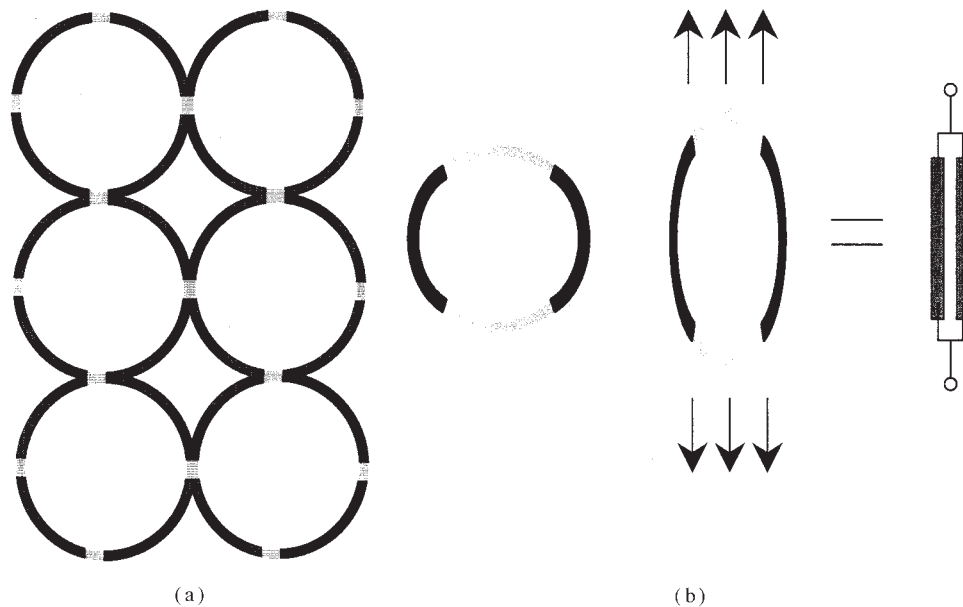


Figure 4 Two-dimensional model: (a) model of the polymer-rich phase; (b) effective volume: about half of a cell (black portion) can contribute the modulus when the cell was extended.

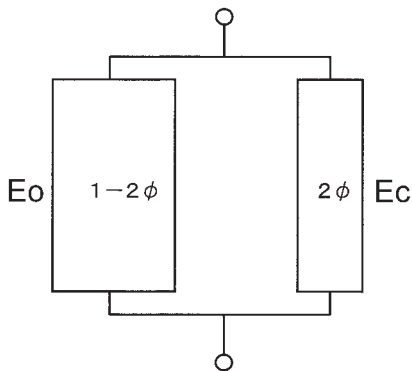


Figure 5 Simple parallel model.

It is possible to simplify the model of Figure 4(a) to a parallel model. Figure 5 shows a simple parallel model. In the figure, ϕ is the volume proportion of pure polymer in the system. As mentioned above, it can be assumed that the polymer-rich phase is swollen to double the size of the unswollen polymer. Therefore, the volume proportion of cells of the polymer-rich phase in the system is 2ϕ , and thus the volume proportion of the oil-rich phase is calculated as $1 - 2\phi$. Young's modulus of the system (E) can be calculated by the following equation¹¹:

$$E = \frac{1}{2}(2\phi)E_C + (1 - 2\phi)E_A \quad (1)$$

Here E_C and E_A are the moduli of swelling cells and the asphalt-rich phase, respectively. Note that in eq.

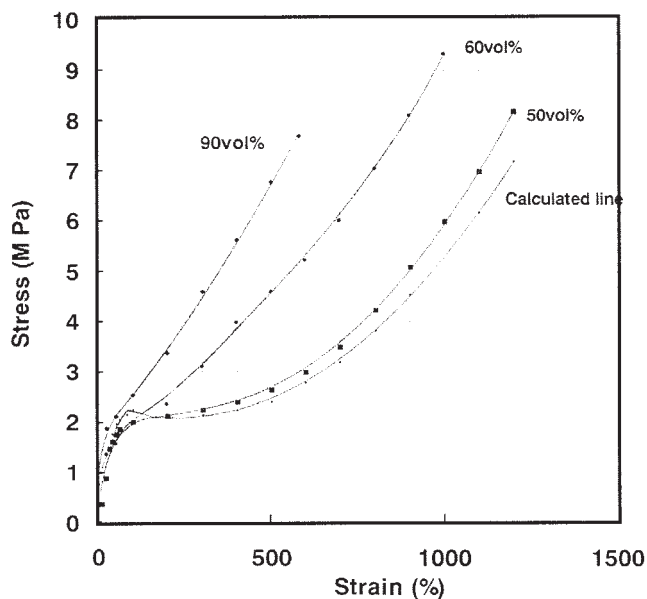
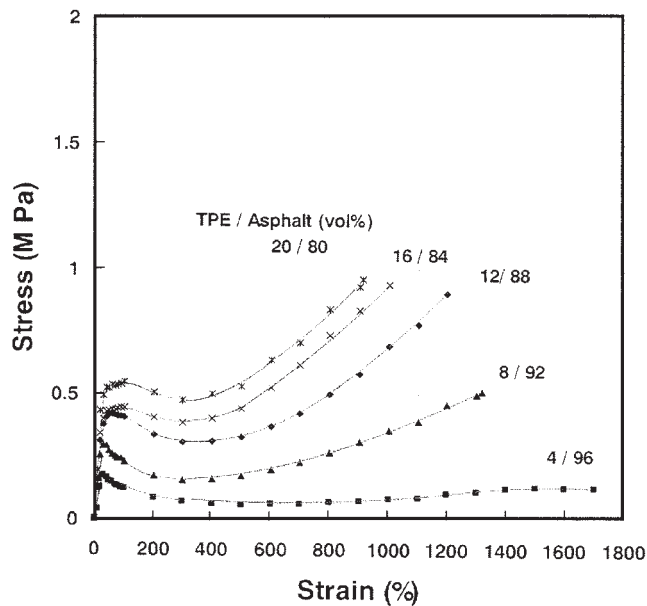


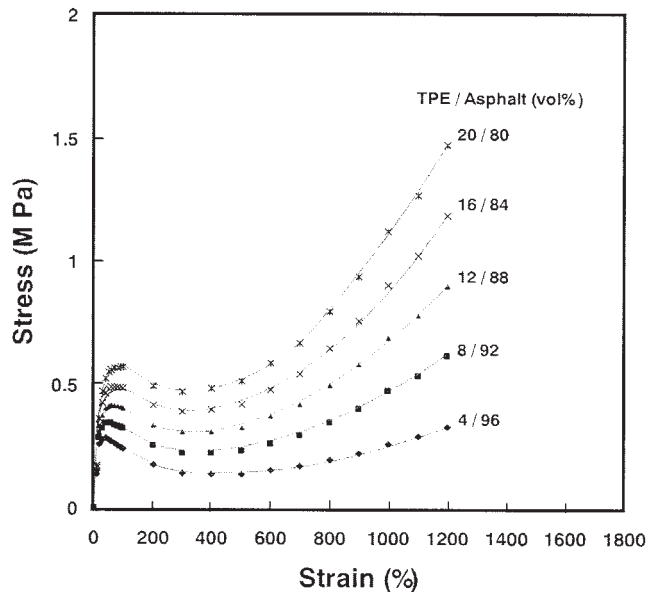
Figure 6 Stress-strain curves of asphalt-extended-polymer compounds. Polymer concentration $\phi = 90, 60,$ and 50 vol %. Calculated stress-strain curve (polymer concentration $\phi = 50$ vol %).

(1) we apply $12(2\phi)$ as the effective volume proportion of the polymer-rich cell because we assumed that about half of a cell could contribute the modulus when the cell was extended [Fig. 4(b)].

Incidentally, we assumed that the polymer-rich phase is swelling and polymer concentration in the phase is estimated to be about 50 vol %. We next evaluate this assumption. Figure 6 shows the stress-strain curves of asphalt-extended-polymer com-



(a)



(b)

Figure 7 Polymer concentration dependency of stress-strain relationships: (a) experimental data of H-SBR/asphalt system (extension rate is 300 mm/min, room temperature); (b) calculated curves.

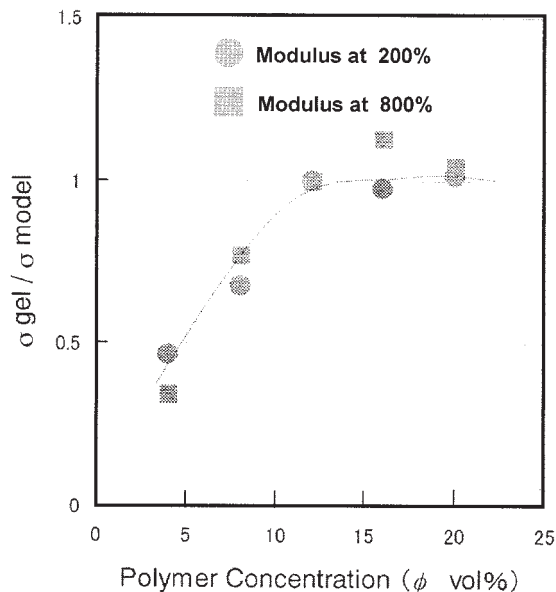


Figure 8 Comparison between experimental data [Fig. 7(a)] and calculation of the model [Fig. 7(b)].

pounds, in which we cannot see any cell structures. The modulus of the compound decreases as the proportion of asphalt increases. On the other hand, the stress-strain relationship of polymer swollen with oil can be estimated from the balance between the H-SBR/asphalt system and the calculated asphalt phase (Line C in Fig. 3). That is, the stress-strain relationship of the swelling polymer itself can be obtained by the calculation: the balance multiplied by $1/\phi$. [Here we considered again that the polymer proportion is ϕ ; the cell swells to double 2ϕ , but the effective volume proportion of the polymer-rich cell is half $1/2$. That is, the effective polymer concentration is $1/2(2\phi) = \phi$.]

In Figure 6 we delineated the result of calculation (calculated line). The result of calculation generally agrees with the experimental result of the asphalt-extended-polymer compound (about 50 vol %). This means that the initial assumption—the polymer-rich cell is swelling and the polymer concentration in the polymer-rich phase is about 50 vol % of pure polymer—is generally reasonable.

Polymer concentration dependency

Now, we apply the model to analyze the stress-strain relationship of the system. Figure 7(a) shows a polymer concentration dependency of stress-strain relationships of the H-SBR/asphalt system (extension rate 300 mm/min). The modulus increases as the proportion of polymer increases. We next estimate those experimental data by the model that we proposed. Figure 7(b) exhibits the calculated curves of each polymer proportion. In the case of relatively higher poly-

mer concentration, about 12 to 20 vol %, the estimated lines generally agree with those of experimental data. Disagreement between calculation and experimental data is, however, found in cases of very small proportions of H-SBR (<8 vol %). Figure 8 illustrates the comparison between calculation of the model and experimental data. It is clearly shown that the modulus

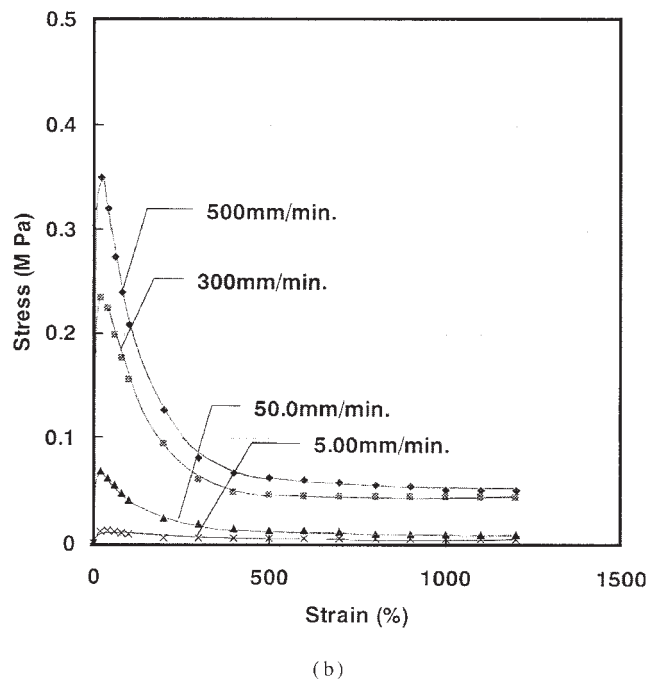
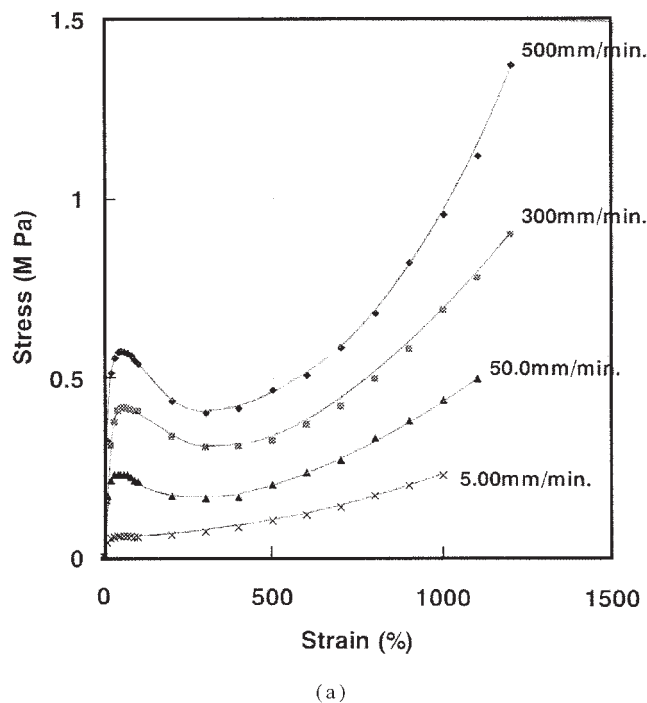


Figure 9 Extension rate dependency of stress-strain curves: (a) H-SBR/asphalt system (polymer concentration $\phi = \sim 12$ vol %, room temperature); (b) asphalt (room temperature).

in the experimental data is smaller than that estimated by the model in the cases of 8 and 4 vol %. We reported in a previous article⁶ that the polymer network structure over the system was imperfect in such a small proportion of polymer. The polymer network is not uniform over the system in those cases, and thus the disagreement of those cases is thought to be somewhat defective in real materials.

Rate dependency

Figure 9(a) shows extension rate dependency of stress-strain curves of the H-SBR/asphalt system (polymer concentration ϕ = about 12 vol %) and Figure 9(b) shows that of asphalt itself. Asphalt has very large rate dependency in physical properties; however, a significant rate dependency can be seen even in the H-SBR/asphalt system. To determine the origin of the rate dependency in the system, we calculated the balance between the modulus of the H-SBR/asphalt system and that of the calculated asphalt phase as we performed above. Figure 10 shows the calculated curves of the polymer-rich phase itself. It is suggested that the polymer-rich phase still has a substantial rate dependency. On the other hand, Figure 11 shows the extension rate dependency of stress-strain curves of H-SBR itself. (The sample was made by conventional injection machine.) H-SBR exhibits little rate dependency. This result indicates that the polymer-rich phase includes slight amount of asphalt, as we initially assumed, and asphalt in the polymer-rich phase causes the rate dependency of the stress-strain relationship in Figure 10.

CONCLUSIONS

A novel microcellular porous structure, the product of a small proportion of a semicrystalline thermoplastic

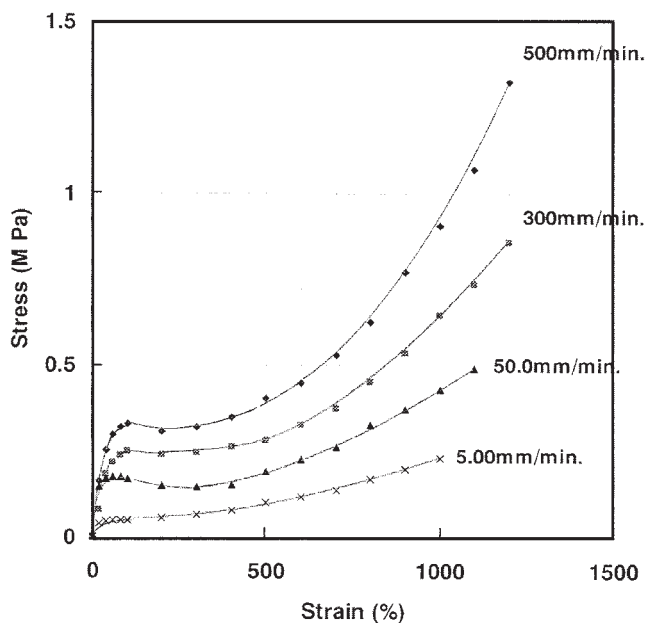


Figure 10 Calculated curves of polymer-rich phase.

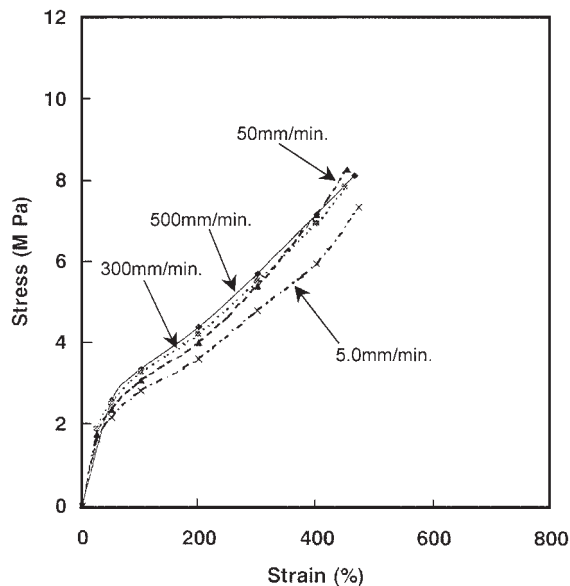


Figure 11 Extension rate dependency of stress-strain curves of H-SBR (room temperature).

elastomer and a large proportion of low molecular weight oil, was examined. Details of the stress-strain relationship of the system were investigated and analyzed. A simple model with some assumptions was proposed and discussed to estimate the stress-strain relationship of the system. The model gives good agreement in relatively higher polymer proportions where the polymer-rich phase forms a uniform network structure over the system.

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