Introduction

Thermoplastic elastomers (TPE) have been receiving much attention in both industrial and academic aspects. A typical commercial TPE is produced by dynamic vulcanization of ethylene-propylene-diene rubber (EPDM) with polypropylene (PP). The dynamic vulcanization yields two-phase material of crosslinked rubber particles with diameter of a few micrometers dispersed densely in crystalline PP matrix\(^1\), even when the volume fraction of the rubber particles is much larger than that of the matrix polymer. In addition to the two polymers, process oils are usually loaded on the TPE. The amount of oil is nearly equal to that of the rubber component and sometimes even larger\(^2\). That is, the TPE is essentially a ternary system consisting of thermoplastic polymer, crosslinked rubber and oil (low molecular liquid).

The effects of process oil on the mechanical properties at ambient temperature have been studied by Coran \textit{et al.}\(^3\). They showed that, increasing the amount of oil, tension set, hardness, elastic modulus and tensile strength decrease while elongation at break remains almost constant. The oil seems to be a softener as in the case of conventional rubber vulcanizates. Further, at higher temperatures the oil is expected to play a role of plasticizer which reduces melt viscosity and improves processability. The viscosity could be reduced only when the oil preferentially migrates into PP matrix at processing temperature. Thus it seems to be of great interest in the industrial aspect to understand the distribution of the oil in TPE, i.e., whether it locates in the rubber particles or in PP matrix. It is also an interesting subject in the scientific points of view, since so far there is no discussion on the phase equilibrium in the ternary system composed of crystalline polymer, crosslinked polymer and solvent (low molecular weight moiety).

In this study, the temperature dependence of the distribution of the oil between thermoplastic polymer phase and crosslinked rubber phase was investigated by the light scattering analysis. As the ternary specimen, a commercial PP/EPDM thermoplastic elastomer was used in this study. The results were compared with the theoretical ones on the basis of the Flory equation of melting point depression\(^4\) and the Flory-Rehner equation for swelling equilibrium\(^5\).

Experimental

The TPE used in this study was Santoprene\textsuperscript{\textregistered} 201-73 (Advanced Elastomer System Co.). A small quantity of the TPE was placed between two cover glasses and melt-pressed to a thin film (ca. 20 \(\mu\)m thick) at 200\(^\circ\)C (>melting point of PP) on a hot stage. The specimen was...
put in a heat chamber set in the light scattering apparatus. The apparatus is schematically shown in Figure 1. The measurement was carried out in two optical alignments. One was the Vv geometry in which the optical axis of analyzer was parallel to that of polarizer and the other was the Hv geometry with a perpendicular set of the two-axis. The radiation of a He-Ne laser of 632.8 nm wavelength was applied vertically to the film specimen. Then the angular dependence of scattered light was observed with photomultiplier tube (PMT) at various temperatures.

The TPE was subjected to solvent extraction to estimate the amount of oil in TPE as well as to prepare a binary system without the oil. The solvent for extraction was a 32/68 (volume ratio) mixture of acetone and chloroform. The ternary system was weighed and put in a soxhlet extraction apparatus. Then the oil was extracted for 48 h boiling the solvent. After removing the TPE specimen and then evaporating the solvent at 70°C for 2 h, the residual was weighed to obtain the weight fraction of oil. Then, the residual was subjected to FT-IR analysis. FT-IR spectrum was recorded by JASCO-FT/IR-8000. The polymer specimen after the extraction, “binary specimen”, was dried in vacuum chamber at 70°C for 24 h. It was also subjected to light scattering measurement as described above.

To measure the melting point of PP, differential scanning calorimetry for both the ternary and the binary systems was performed with DuPont 910 differential scanning calorimeter at a heating rate of 20°C/min.

**Results and Discussion**

By the solvent extraction, it was shown that the weight fraction of the extracted oil from the TPE was 39.6%. Figure 2 is the IR spectrum of the extracted oil from the TPE. This spectrum is almost identical with that of the liquid paraffin with characteristic bands of 2919, 2861, 1458, 1378, and 720 cm\(^{-1}\); assigned to methylene and methyl groups\(^6\). It suggests that the extracted oil is paraffinic process oil generally used in the rubber industry. The DSC thermograms showed that the melting point of PP is 150°C for the ternary system and 162°C for the binary system. It may suggest that the oil plays a role of solvent for PP and causes the melting point depression; see Eq. (10).

In Figure 3 are shown typical examples of light scattering profiles for the ternary system. All light scattering profiles under both Vv and Hv conditions were monotonously decreasing function, \(I\), decreased monotonously with increasing scattering angle, \(\theta\). All scattering patterns were symmetrical with respect to the azimuthal angle. The results suggest that the orientation fluctuations of
crystallites are randomly correlated.

The intensity of scattered light due to the density fluctuation between the matrix and the particles, \( I_p \), can be obtained by subtracting the contribution due to the anisotropy of crystalline phase from \( Vv \) scattered light. When the size and shape of the particles are random, \( I_p \) can be formulated by\(^7\)

\[
I_p(q) = I_{v, p}(q) - \frac{4}{3} I_{h, p}(q)
\]

\[
< \eta^2 > \propto \int_0^\infty \frac{\sin(qr)}{qr} 4\pi r^2 dr
\]

(1)

where \( < \eta^2 > \) is the mean-square average of density fluctuation, \( q \) is the magnitude of scattering vector \( [q=(4\pi/\lambda)\sin(\theta/2); \lambda \text{being the wavelength of the scattered light in the specimen}] \), and \( \gamma(r) \) is the correlation function of the density fluctuation given by Eq. (A-1). The \( < \eta^2 > \) is given by\(^7\)

\[
< \eta^2 > \propto \phi_p(1-\phi_p)(\Delta \alpha)^2
\]

(2)

where \( \phi_p \) is the volume fraction of the particles and \( \Delta \alpha \) is the difference in polarizability between the particle and the matrix. Then, the invariant concerning the density fluctuation, \( Q_{p} \), is given by

\[
Q_p = \int I_p q^2 dq < \eta^2 >
\]

(3)

From the experimental point of view, \( Q_p \) can be calculated from the Debye-Bueche plot (see Appendix). From Eqs. (2) and (3), \( Q_p \) is given by

\[
Q_p = (\Delta \alpha)^2 \phi_p(1-\phi_p)
\]

(4)

Basically Eq. (4) holds for both ternary and binary systems. In the ternary system, however, the oil swells particle phase and/or matrix so that in the ternary system, \( (\Delta \alpha)^{III} \) may differ from that of binary system, \( (\Delta \alpha)^{II} \). When \( (\Delta \alpha)^{III} \) hardly depends on the oil distribution, a ratio of the invariant of ternary system \( Q^{III} \) and that of binary system \( Q^{II} \) is approximated by:

\[
\frac{Q^{III}}{Q^{II}} \propto \phi_p(1-\phi_p)
\]

(5)

In Figure 4 is shown the temperature dependence of the value of \( Q^{III}/Q^{II} \). The value is small at low temperature and increases with increasing temperature, then levels off. According to the electron microscopic observation of the TPE, volume fraction of dispersed phase is around 0.7\(^7\), i.e., \( \phi_p = 0.7 \). Since \( \phi_p(1-\phi_p) \) is a decreasing function of \( \phi_p \) when \( \phi_p \) is larger than 0.5, the higher value of \( Q^{III}/Q^{II} \) at higher temperature in Figure 4 implies that the smaller \( \phi_p \) is expected at the higher temperature. In other words, the oil exists mostly in rubber phase at low temperatures and it migrates into PP matrix at high temperatures.

A thermodynamic consideration on the distribution of oil in TPE may be given as follows. At higher temperatures above the melting of crystalline polymer (PP), a binary solution of PP and oil may coexist with the crosslinked rubber particles swollen with the oil. The phase equilibrium can be described by

\[
\Delta \mu_{SP} = \Delta \mu_{SR}
\]

(6)

where \( \Delta \mu_{SP} \) is the change in the chemical potential of the oil (solvent) with mixing with PP and \( \Delta \mu_{SR} \) is that due to swelling the network. The former is given by\(^3\)

\[
\Delta \mu_{SP} = \ln(1-\nu_{PS}) + \nu_{PS} + \chi_{PS}\nu_{PS}^2
\]

(7)

where \( \nu_{PS} \) is the volume fraction of the polymer in a mixture and \( \chi_{PS} \) is the interaction parameter which may be approximated as

\[
\chi_{PS} = \frac{V_S(\delta_p - \delta_s)^2}{RT}
\]

(8)

where \( V_S \) is the molar volume of the solvent and \( \delta_i \) is the solubility parameter of i-component. \( \Delta \mu_{SR} \) is expressed as\(^3\)

\[
\Delta \mu_{SR} = \ln(1-\nu_{RS}) + \nu_{RS} + \chi_{RS}\nu_{RS}^2 + \nu V_S(\nu_{RS}^{1/3} - \nu_{RS}^2/2)
\]

(9)

where \( \nu \) is the crosslink density, \( \nu_{RS} \) is the volume fractions of the polymer network in the swollen particle and \( \chi_{RS} \) is the interaction parameter between the two components. \( \chi_{RS} \) is approximated in the same manner as in Eq. (8). Combining Eqs. (6)–(9), the value of \( \nu_{RS} \) can be calculated for a given set of the variables: \( \delta_i \), \( T \) and composition.

At lower temperatures below the melting point of PP, another phase appears so that one has to take account of...
the phase equilibrium between three phases: the swollen network, PP solution and PP crystal phase.

The phase equilibrium between the PP solution and the crystal phase is described by the Flory theory of melting point depression:

\[
\frac{1}{T} - \frac{1}{T_m} = \frac{R}{\Delta H_{pu}} \left( \frac{V_{pu}}{V_s} \right) \left( \chi_{pu} (1 - \nu_{pu})^2 - (1 - \nu_{pu}) \right)
\]

where \(T\) is the melting temperature, \(T_m\) is the equilibrium melting temperature, \(R\) is the gas constant, \(\Delta H_{pu}\) is the heat of fusion per repeating unit of the polymer, \(V_{pu}\) is the molar volume of the repeating unit of the polymer.

Since the phase equilibrium between the swollen network and the PP solution is given by Eq. (6), \(u_{RS}\) can be obtained by combining Eq. (10) with Eqs. (6) and (9).

Numerical calculation was carried out for a TPE with the particular composition: PP/EPDM = 20/40 in volume ratio, which is close to the composition of commercial TPE in this study. We employed the following values of parameters: \(T_m = 203.5^\circ\text{C}\), \(\Delta H_{pu} = 2.00 \times 10^3\) cal/mol, \(V_{pu} = 42.0\) cm\(^3\), \(V_s = 500\) cm\(^3\), \(v = 2.0 \times 10^{-4}\) mol/cm\(^3\), \(\delta_s = 8.0\) and \(\delta_p = \delta_R = 7.9\) \(\times 10^2\).

The calculated value of \(u_{RS}\) is shown in Figure 5 as a function of \(T\). \(u_{RS}\) is small at ambient temperature. It jumps to higher level above \(T_m\). The results imply that the oil prefer to locate in the rubber phase at low temperatures and in matrix at high temperatures.

Now, if one sets up a composition of TPE as PP/EPDM/oil = 20/40/40 (as the extraction experiment showed), the \(u_{RS}\) is 0.5 as indicated by a chain line in Figure 5. It is larger than the calculated value below \(T_m\), suggesting that the oil is totally located in rubber phase and the third phase does not exist. In other words, the TPE is a two-phase material consisting of swollen rubber particles and PP matrix. Further it implies that the change in the distribution of oil in the real system with such composition (20/40/40) with temperature may be described by a change from the chain line (below \(T_m\)) to the solid line (above \(T_m\)). Based on such temperature dependence of \(u_{RS}\), one can calculate the temperature dependence of \(\phi_p (1 - \phi_p)\). The result is shown by a broken line in Figure 4. The calculated temperature dependence has much sharper transition than the observed one. We believe the deviation is due to by the distribution of \(T_m\) of PP crystals, which is caused by the size distribution of the crystals formed in the real system.

Anyway, the thermodynamic discussion also suggests that the oil would play a role of softener at ambient temperature and that of diluent for PP to reduce the melt viscosity of matrix at processing temperatures.

We also estimated the temperature dependence of \(u_{RS}\) for various \(\delta_s\). The results are shown in Figure 6. When the value of \(\delta_s\) is close to \(\delta_R\), the results are similar; i.e., the third phase does not appear as shown by curves (b), (c) and (d). However, when \(\delta_s\) is very small, e.g., \(\delta_s = 7.0\), the solid line crosses the chain line. It means that at low temperatures the third phase appears, in other words, the oil can be located more in TPE without bleeding so that TPE with higher \(\phi_p\) could be prepared, yielding a better elastic recovery.
Conclusion

Thus, we successfully estimated the distribution of oil in TPE by light scattering to demonstrate that the oil preferentially swells the EPDM particles at ambient temperature and it migrates to PP matrix at processing temperature. The thermodynamic discussion supported the observed results and also provided a guideline for the selection of oil for TPE.

Appendix

For a two-phase system in which the size and shape are at random, \( \gamma(r) \) is approximated as\(^{(1)}\)
\[
\gamma(r) = e^{-r^{1/2}} \tag{A-1}
\]
where \( \xi \) is the correlation length on the density fluctuation. Substituting Eq. (A-1) into Eq. (4),
\[
I_p(q)^{-1/2} = (8\pi < \eta^2 > \xi^3)^{-1/2}(1 + q^2 \xi^2) \tag{A-2}
\]
Then, \( I^{1/2} \) vs. \( q^2 \) plot will result in a straight line with a slope \( B \) and an intercept \( A \) (on \( I^{1/2} \) axis). Hence, the invariant is calculated by the parameters \( A \) and \( B \):
\[
Q_p = \int I_p q^2 dq = \pi \left( 4B \sqrt{AB} \right)^{-1} \tag{A-3}
\]

References