Interphase transfer of plasticizer between immiscible rubbers

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Nawaphorn Kuhakongkiat [a], Viyada Wachteng [b], Shogo Nobukawa [a], Masayuki Yamaguchi [a, *]

[a] School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan
[b] Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Ratchthewee, Bangkok 10400, Thailand

ARTICLE INFO

ABSTRACT

Interphase transfer of di-2-ethylhexyl adipate (DOA) between ethylene-propylene copolymer (EPR) and polyisobutylene (PIB) in the laminated sheets was studied. It was found that the amount of DOA in each phase is determined by the ambient temperature. DOA moved to EPR from PIB at $-20\,°C$ and vice versa at $40\,°C$, when the DOA content before lamination was 10 phr. This is attributed to the change of interaction parameters between DOA and each rubber as a function of temperature. Because of the DOA transfer, the glass transition temperature of each rubber phase changes with the ambient temperature. The phenomenon can be applicable to an all-season tire, when a matrix polymer contains more plasticizer at low temperature and vice versa in a blend with sea-island structure.

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1. Introduction

The addition of a third component in an immiscible polymer blend is often carried out in polymer industries to obtain a high-performance polymeric material. When a low molecular weight compound is used as a third component, it is usually dissolved into polymers due to the contribution of mixing entropy, in which the content of a third component in each phase is not the same in general. In fact, uneven distribution occurs owing to the difference in the miscibility of a third component with each polymer [1–5]. The miscibility of polymer blends is expressed by the Flory–Huggins equation, in which the Flory–Huggins interaction parameter represents the contribution of the mixing enthalpy and other factors except for the combinatorial entropy [6,7]. Furthermore, the interaction parameter is known to be a function of temperature, which affects the phase diagram [8–10]. As similar to a polymer blend, the interaction parameter between a low molecular weight compound and a polymer is also dependent upon the temperature. Since a low molecular weight compound tends to be dissolved more in a polymer due to the large contribution of mixing entropy, the distribution state of a third component in an immiscible polymer blend could be controlled by the ambient temperature. This phenomenon occurs with the migration of a third component from one phase to another through the boundary of phases, which has been confirmed by several researchers using laminated sheets and/or blends composed of immiscible polymer pairs containing a third component, such as nanofiller, tackifier, and curative for rubbers [11–16]. Here, we propose a novel material design using the plasticizer transfer in an immiscible rubber blend, in which a matrix shows low glass transition temperature T_g in winter and high T_g in summer season. In this study, amorphous polyolefins, such as polyisobutylene (PIB) and ethylene-propylene copolymer (EPR), were employed. As a third component, di-2-ethylhexyl adipate (DOA), known as a plasticizer, was employed because it can decrease T_g greatly. The interaction parameter between PIB and EPR has been studied at various temperatures and found to decrease with increasing the temperature [17,18], indicating that the difference in the interaction parameter between each rubber and DOA also changes with the ambient temperature. This will lead to the interphase transfer of DOA in the blend and change the distribution state in each rubber phase. Since the amount of a plasticizer greatly affects T_g, it can be used for a material design of an all-season tire.

2. Experimental

2.1. Materials

Ethylene-propylene rubber (EPR) (JSR EP11, ethylene content 52 wt.%, JSR, Japan), polyisobutylene (PIB) (Sigma–Aldrich, USA),

* Corresponding author.
  E-mail address: m_yama@jaist.ac.jp (M. Yamaguchi).

and di-2-ethylhexyl adipate (DOA) (New Japan Chemical, Japan) were used in this study. The molecular weights of the rubbers were evaluated using a gel permeation chromatography (HLC 8020, Tosoh, Japan) with polystyrene standard and found to be $M_n = 3.4 \times 10^6$ and $M_w = 4.7 \times 10^6$ for EPR and $M_n = 5.6 \times 10^6$ and $M_w = 7.5 \times 10^6$ for PIB, respectively.

2.2. Sample preparation

A rubber and 10 phr of DOA were blended in a mixed solvent of dichloromethane and toluene (8:2). After slowly evaporating the solvent, the obtained mixture, i.e., a rubber with DOA, was compressed into a flat sheet with 1 mm thickness using a compression-molding machine at 100 °C under 20 MPa. The EPR and PIB sheets containing 10 phr of DOA were laminated together under an applied slight pressure by manual operation. Then the samples were annealed without pressure at −20 and 40 °C for 5 days. Fig. 1 shows the experimental procedure for the interphase transfer experiment. In order to confirm the reversibility of the DOA transfer phenomenon, one set of the laminated sheets annealed at 40 °C (or −20 °C) was further annealed at −20 °C (or 40 °C). The separated sheets were kept at room temperature for 3 days to homogenize the DOA distribution in a sheet prior to the characterization.

Moreover, crosslinked rubbers were also prepared to predict the difference in the interaction parameter between EPR-DOA and PIB-DOA. As a curing agent, 2 phr of sulfur (Kanto Chemical, Japan) was added with 2 phr of *N-tert*-butyl-2-benzothiazole sulfenamide (Alfa Aesar, UK) as an accelerator for each rubber. Furthermore, 3 phr of zinc oxide (Kanto Chemical, Japan) and 1.5 phr of stearic acid (Sigma Aldrich, USA) were also added as activators. They were mixed together at 60 °C in an internal batch mixer (Labo-Plastomill, Toyoseiki, Japan) with a blade rotation speed of 40 rpm. The curing was performed using a compression-molding machine at 170 °C under 20 MPa for 15 min and subsequently cooled at 15 °C for 10 min. The thickness of the film was 1 mm.

2.3. Measurements

Temperature dependence of the dynamic tensile modulus was measured by a dynamic mechanical analyzer (DVE3, UBM, Japan). The specimen with 5 mm in width and 20 mm in length was employed. The measurements were performed from −100 to 100 °C at a heating rate of 2 °C/min. The frequency was 10 Hz. The

peak temperature in the tensile loss modulus was taken to define T_g.

Thermal properties were evaluated by a differential scanning calorimeter (DSC) (DSC 8500, Perkin Elmer, USA). Measurements were carried out from −100 to 25 °C at a heating rate of 10 °C/min.

The attenuated total reflection (ATR) spectra were measured by a Fourier−transform infrared spectroscopy (FT-IR) analyzer (Spectrum 100, Perkin Elmer, USA) using diamond as an ATR plate. The DOA content is evaluated by the absorption peak at 1740 cm^{-1} ascribed to the C=O=C stretching vibration mode.

The swell ratio of crosslinked rubbers in DOA was measured. The crosslinked rubber films were immersed in toluene at 25 °C to evaluate the crosslink density. Moreover, they were immersed in DOA at −20 or 40 °C for 5 days to measure the weight of the swollen gel W_s. They were then immersed in ethanol several times to remove DOA perfectly. The samples were dried in a vacuum oven to measure the weight of the dry gel W_d. The swell ratio q was defined as follows;

$$q = \frac{W_s}{W_d} \tag{1}$$

3. Results and discussion

Prior to the evaluation of the transfer phenomenon, the effect of the DOA addition on the dynamic tensile modulus is examined. Fig. 2 shows the temperature dependence of tensile storage modulus E' and loss modulus E'' for pure polymers and the polymers with 10 phr of DOA. It is found that the peak temperatures of E'', defined as T_g, shift to lower temperature by the addition of DOA. The T_g shift for EPR is more pronounced than that for PIB, presumably owing to higher T_g for EPR. The peak width is not so affected by the DOA addition, suggesting the narrow distribution of relaxation time, i.e., good miscibility. The rubbery plateau modulus decreases slightly by the DOA addition. This is reasonable because the entanglement density decreases.

The amounts of DOA can be characterized by FT-IR spectra using the peak intensity at 1740 cm^{-1}, ascribed to the stretching vibration mode of the carbonyl group in DOA. At first, the peak intensities are evaluated using the EPR sheets containing various amounts of DOA, as shown in Fig. 3. This peak is appropriate to estimate the DOA amount, because (1) pure EPR does not show any absorbance; and (2) good reproducibility with almost no experimental error.

The laminated samples composed of the EPR and PIB sheets, in which 10 phr of DOA was added into each sheet, were annealed at −20 or 40 °C for 5 days. Assuming that the diffusion constant of a low molecular weight compound in a rubber is 10^{-11} m^2/s [19], it takes 1 day for the diffusion distance of 1 mm, i.e., the thickness of the sheet. Therefore, the annealing time is long enough to be in the equilibrium state from the viewpoint of the DOA distribution. In this experiment, the laminated sheets were separated without any difficulty, suggesting that the interfacial thickness λ, provided by equation (2) [20,21], is too thin to show strong adhesion because of a small number of entanglement couplings at boundary;

$$\lambda = \frac{2b}{(6\chi)^{1/2}} \tag{2}$$

where χ is the polymer−polymer interaction parameter and b is the statistical segment step length.

The weak interface is attributed to the immiscible nature between PIB and EPR. Although Krishnamoorti and Graessley
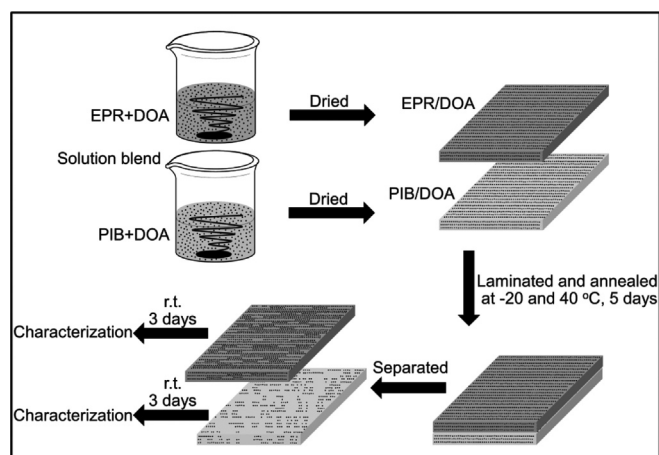

Fig. 1. Schematic illustration of experimental procedure.