Compatibilization of SAN/EPDM Blends by Grafting EPDM with Methyl Methacrylate

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Poly(styrene-*co*-acrylonitrile) (SAN) is a polar thermoplastic polymer with high transparence, excellent gloss, high mechanical strength, and good chemical resistance.[1] However, SAN has the tendency to yellow and “burn” during its processing. On the other hand, ethylene-propylene-diene terpolymer (EPDM), which is a synthetic rubber having non-polar properties and a low unsaturated content, is superior in weather resistance and thermal stability and it shows good electrical insulation property.[1,2] EPDM, however, has poor oil resistance, weak adhesion property and the products based on EPDM vulcanized by sulfur have low tear strength and tensile strength. Blending of SAN and EPDM can combine their good properties including weatherability and good mechanical strength. In general, however, the poor miscibility of SAN and EPDM or ethylene-propylene rubber (EPR) limits their more versatile uses. Recently, reactive compatibilization of SAN/EPR or SAN/EPDM blends has been investigated by grafting maleic anhydride onto EPR or EPDM.[3-5]

In this work, we report the compatibilization of immiscible SAN/EPDM blends by grafting methyl methacrylate (MMA) onto EPDM. It may be expected that compatibilization of SAN/EPDM blends can be achieved in this way since SAN and poly(methyl methacrylate) (PMMA) was reported to be miscible over the entire blend compositions, when the acrylonitrile content in SAN ranges from 9 to 33 %.[6-9] In our previous works, we have studied on the modification of EPDM by graft copolymerization with various vinyl monomers such as vinyl acetate and acrylamide, etc, as well as MMA[10-14] to improve poor properties of EPDM. It was found that the graft copolymer, for example, EPDM-*g*-methyl methacrylate (EPMMA) improved polarity, adhesion, oil resistance and tensile strength compared to EPDM. The compatibilization of SAN/EPDM blends was investigated by light scattering and FT-IR spectra.

Experimental Section

Ethylene-propylene-diene terpolymer (EPDM), having 5-methylene-2-norbonene as a termonomer (Aldrich Co., USA, 50 wt % ethylene, 8 wt % 5-methylene-2-norbonene, mooney viscosity 50; M_n: 61,500, M_w: 131,500), Poly(styrene-*co*-acrylonitrile) (SAN, Aldrich Co., 30 wt % acrylonitrile; M_n: 152,000, M_w: 287,500), were used as received. Methyl methacrylate (MMA, Junsei Chemical Co., Japan) was purified by standard procedures. Benzoyl peroxide (BPO, Aldrich Co.) was purified by recrystalization from methanol. Toluene and chloroform were distilled prior to use. EPDM-*g*-methyl methacrylate (EPMMA), having graft percentage of 26% was obtained by graft copolymerization of MMA onto EPDM in toluene with EPDM/MMA wt % ratio of 1/2 using 1 wt % BPO as an initiator, at 70 °C for 48 h. Its M_n and M_w were 118,000 and 274,000, respectively.

Preparation of Blends. The 2 wt % solution of SAN was prepared by dissolving SAN in chloroform at 60 °C with stirring continuously for 4h. By the same method, the 2 wt % solutions of EPDM or EPMMA were also obtained. Blends of SAN and EPDM or EPMMA with different compositions were prepared by mixing SAN and EPDM or EPMMA solutions with high speed stirring for 1 h at room temperature. Then, the above solution was poured into shallow glass dish (Petri) with a flat glass cover to control the rate of solvent evaporation. After solvent was removed, the films were dried in vacuum at room temperature to constant weight.

Measurements

The changes of scattered intensity distribution with temperature during the phase separation were analyzed by an automated laser light scattering photometer. The transmitted and scattered light intensity were detected by photodiode and its relative values were stored by P/C data acquisition system. A small piece of film was sandwiched between two glass slides and placed on a hot plate device. The sample was placed in a temperature controlled brass block. The thickness was about 100 μm. He-Ne laser source of 632.8 nm wavelength was applied vertically to the film specimen. The scattered light measured at 30 °C was focused onto the slit of a photomultiplier detector. All measurements were performed at 5 °C/min. The FT-IR spectra of the blend film samples were determined with a Jasco FT/IR-5300 spectro-

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photometer. These samples were prepared from 0.5 wt % solution of the blends with different compositions.

Results and Discussion

Figure 1 demonstrates a cloud point data of SAN/EPDM blends as a function of SAN composition. The chloroform cast blend showed upper critical solution temperature (UCST) behavior. It was clear that SAN and EPDM are not miscible at all blend compositions.

It can be explained by the nature of SAN and EPDM. SAN is a polar thermoplastic with the presence of nitrile group in its molecule. EPDM is a synthetic rubber having non-polar properties and a low unsaturated content. They are difficult to mix or blend to form homogenous mixture. The immiscibility of SAN/EPDM blends films when cast from chloroform was also proved by their opaque nature.

Figure 2 demonstrates a cloud point data of SAN/EPMMA blends as a function of SAN composition. The chloroform cast blend showed typical lower critical solution temperature (LCST) behavior. It means that SAN and EPMMA are able to form miscible mixture. It can be explained by the miscibility of SAN and PMMA over the entire composition.[13-15] Therefore, it may be said that PMMA segments in EPMMA plays a role to enhance the miscibility between SAN and EPDM. The data in Figures 1 and 2 were fitted by a binodal curve calculated on the basis of the Flory-Huggins free energy of mixing, given below, with Λ regarded as an adjustable parameter.[15]

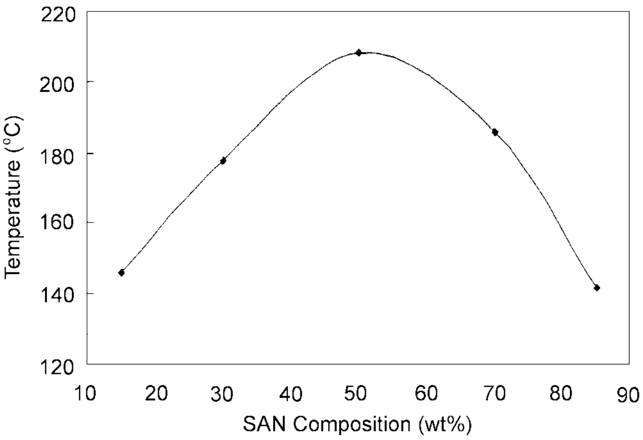

Figure 1. Phase diagram from light scattering of SAN/EPDM blends.

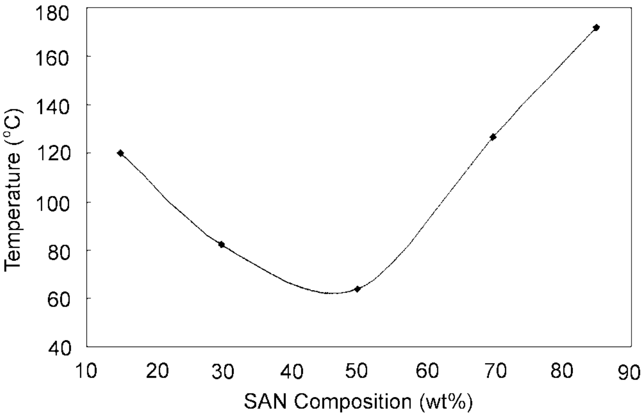

Figure 2. Phase diagram from light scattering of SAN/EPMMA blends.

$$\Delta G = RT\,[(1/V_1)\,\Phi_1 \ln \Phi_1] + [(1/V_2)\,\Phi_2 \ln \Phi_2] + \Lambda\Phi_1\Phi_2 \qquad (1)$$

where ΔG is the free energy per unit volume of the mixture, V_1 and V_2 are the molar volumes of polymer 1 and 2, and Φ_1 and Φ_2 are the volume fractions of two polymers. The quantity Λ, denoting the polymer-polymer interaction energy density, may depend moderately on both the temperature and the composition of the blend. We take the simplest functional form incorporating these dependencies as

$$\Lambda = \lambda_0 + \lambda_1\,\Phi_1 + \lambda_T\,\Phi_T \qquad (2)$$

The values of the constants λ_0, λ_1 and λ_T giving the best fit to experimentally determined cloud points were evaluated by the method of nonlinear least squares. It should be noted that the Λ is related to the traditional Flory interaction parameter χ as follows;[16]

$$\chi = \Lambda\,V_{ref} / RT \qquad (3)$$

where V_{ref} is the volume of a lattice (or a segment). The interaction parameter χ is a dimensionless, and its numerical value depends on the choice of the lattice volume V_{ref} . In the case of polymer solutions, V_{ref} is usually equated to the volume of a solvent molecule and no ambiguity arises, but in the case of polymer blends, the practice of implicitly equating V_{ref} to the volume of a monomer unit is not satisfactory since the monomer volumes of polymers 1 and 2 are usually significantly different from each other. For experimental evaluation the interaction energy density Λ, given in terms of a specific unit such as cal/cm^3, avoids such ambiguity.

The solid curve drawn for SAN/EPDM blend data in Figure 1 was calculated by equation (2) with the following Λ value:

$$\Lambda_{SAN/EPDM} = 1.4796e^{-2} + 1.9635e^{-3}\Phi - 1.2181e^{-5}T \qquad (4)$$

where Λ is in cal/cm^3, Φ is the volume fraction of EPDM, and T is in Kelvin.

For SAN/EPMMA blend based on the data in Figure 2, the following relationship with regard to Λ value was given by

$$\Lambda_{SAN/EPMMA} = -8.8962e^{-3} - 2.3157e^{-3}\Phi + 4.1492e^{-5}T \qquad (5)$$

where Λ is in cal/cm^3, Φ is the volume fraction of EPMMA, and T is in Kelvin.

The Λ values can be utilized as a semiquantitative tool to estimate the interaction energy density between polymer pairs interacting not only through non-polar forces but also through other types of forces, such as polar or hydrogen bonding forces. In general, blends exhibiting an LCST behavior have either a negative or a small positive Λ value at low temperature, which increases rapidly with increasing temperature. On the other hand, blends exhibiting a UCST behavior have a positive Λ value at low temperature, which in general decreases as the temperature is increased.[15-18] The temperature dependence of the interaction energy density ($\lambda_T/\Lambda = d \ln \Lambda/dT$) for both SAN/EPDM and SAN/EPMMA blends were estimated as $-1.0032\ e^{-3}$ and $1.8020\ e^{-2}$ at room temperature, and $-1.1214\ e^{-3}$ and $6.2040\ e^{-3}$ at 403 K, respectively from the equations (4) and (5). The inverse temperature dependence of the interaction energy density for SAN/EPDM and SAN/EPMMA blends, therefore, proves that the former blends exhibit UCST behavior and the latter blends exhibit LCST behavior. The temperature dependence of Λ was described in more detail by Roe and Zin using the Flory equation-of-state theory.[15] It is well known that the strong concentration dependence of χ, often found with dilute polymer solutions, is not encountered with polymer mixtures, due to the fairly satisfactory mean-field approximation, and as is, the concentration dependence of Λ is not large in comparison to its temperature dependence by the relationship of equation (3).[16]

The FT-IR spectra have been used for evaluation of specific interaction in a miscible polymer blend. When two polymers are completely miscible, there is a chemical interaction between the two different polymers. This interaction leads to considerable difference between the spectrum of the polymer in the blend.[19,20] Figure 3 presents the FT-IR characteristic peaks of carbonyl group (C=O) in EPMMA of the blends as a function of blend composition.

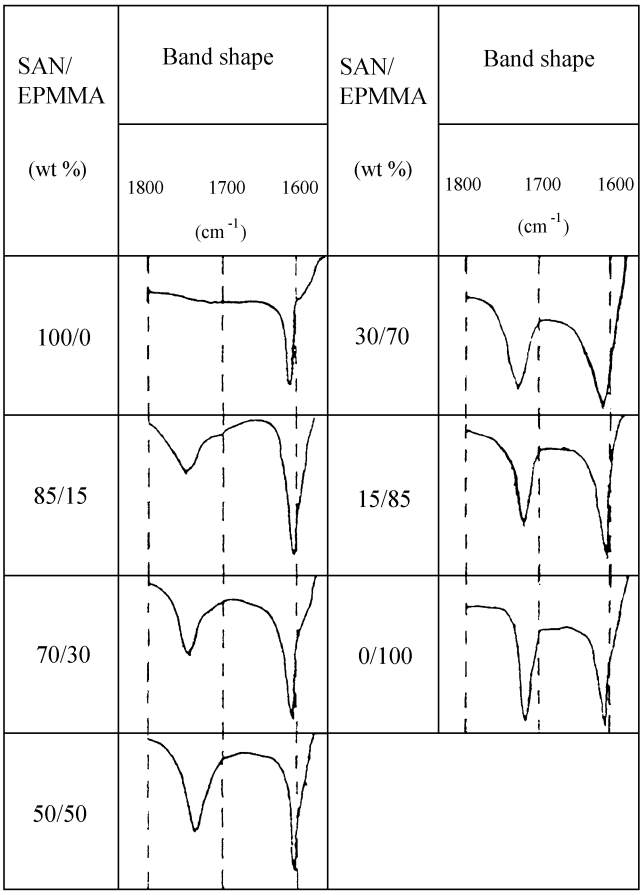

Figure 3. Relative intensity of the peak around 1700 cm^{-1} of SAN/EPMMA blends on FT-IR spectra as a function of blend compositions.

It is clear that, when the composition of EPMMA in the blends increased, the peak of C=O group in EPMMA was shifted to shorter wavenumber. The frequency shift of this peak was about 10 cm^{-1}. The peak shift can be explained by the interaction between functional groups of EPMMA and SAN. It is suggested this interaction is dipole-dipole interaction between C=O group in EPMMA and nitrile group (CN) in SAN, and the interaction may vary with the composition of the blend.[19] For immiscible SAN/EPDM blends, the peak shift on the FTIR spectra was not observed over the entire blend compositions.

In summary, the SAN/EPDM blends were found to be immiscible and exhibited UCST behavior over the entire composition ranges. In order to improve the miscibility of the blends, EPDM was grafted with methyl methacrylate (MMA). The blends of the graft copolymer of EPDM and MMA (EPMMA) with SAN were found to be miscible and showed LCST behavior at all blend compositions when they were cast from chloroform. The result proves that compatiblization of the immiscible SAN/EPDM blends was achieved by grafting EPDM by methyl methacrylate. The intermolecular interaction in the miscible SAN/EPMMA blends was interpreted by the shift in the peak due to C=O group to shorter wavenumber on FT-IR spectra with increasing the EPMMA composition in the blends. Further works are underway to reveal how the compatibilization affects the properties of the SAN/EPDM blends and how the compatibilities of the SAN/EPDM or the SAN/EPMMA blends are related to the copolymer composition of SAN, *i.e.* whether the SAN/EPMMA blends exhibit some miscibility window behaviors depending on the copolymer composition in SAN in more detail and will be reported elsewhere.

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