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# Miscibility and Properties of Ethyl-Branched Polyethylene/ Ethylene-Propylene Rubber Blends( I )

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# 에틸 가지화된 폴리에틸렌과 에틸렌-프로필렌 고무 블렌드의 혼화성과 물성( I )

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**ABSTRACT** : Ethyl-branched polyethylene[PE(2)] containing 2mole% ethyl branch and three ethylene-propylene rubbers(EPR's) having the same ethylene(E)-propylene(P) molar ratio(E/P=50/50) with different stereoregularity, that is, random EPR(r-EPR), alternating-EPR(alt-EPR) and isotactic-alternating-EPR(iso-alt-EPR) were mixed for the investigation of their properties depending on the stereoregularity. The three blends were immiscible at room temperature, and showed the simple additivity effect in density behavior. The melting point depression with blend composition increased in order of PE(2)/r-EPR>PE(2)/alt-EPR>PE(2)/iso-alt-EPR. In the tensile test, this blend systems have the lowest value of the breaking strength at PE(2) fraction of 0.5. This phenomenon results from the greastest separated phase morphology at this blend composition.

요 약 : 2몰% 에틸가지를 포함하는 에틸 가지화 폴리에틸렌[(PE(2)]과 에틸렌-프로필렌 몰비가 50:50으로 같지만 입체규칙성이 서로 다른 랜덤-에틸렌-프로필렌 고무(r-EPR), 교호-에틸렌-프로필렌 고무(alt-EPR) 및 이소탁틱-교호-에틸렌-프로필렌 고무(iso-alt-EPR)를 에틸렌-프로필렌 고무의 입체규칙성에 대한 혼화성과 물성의 차이를 조사하기 위하여 혼합하였다. 이 세가지 블렌드들은 상온에서 상호간에 혼화성이 없었고, 밀도 측정에서 단순한 첨가 효과를 보여 주었다. 블렌드 조성에 따른 폴리에틸렌의 녹는점 감소는 PE(2)/r-EPR>PE(2)/alt-EPR>PE(2)/iso-alt-EPR의 순서로 증가하였다. 인장시험에서 이 블렌드계는 혼합 조성이 50:50 일때 가장 낮은 파단강도의 값을 보여 주어 이 블렌드 조성에서 두 고분자 상(phase)이 가장 분리된 형태학(morphology)을 가지고 있음을 알았다.

*Keywords : ethyl-branched polyethylene, ethylene-propylene rubber, stereoregularity, density, melting point.*

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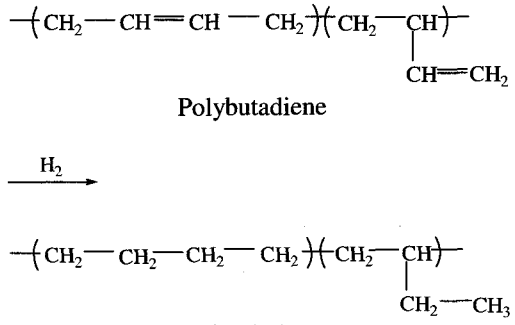
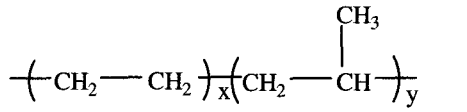
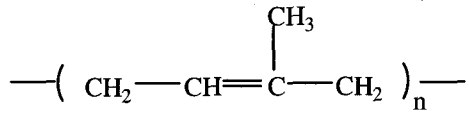
# Ⅰ. Introduction

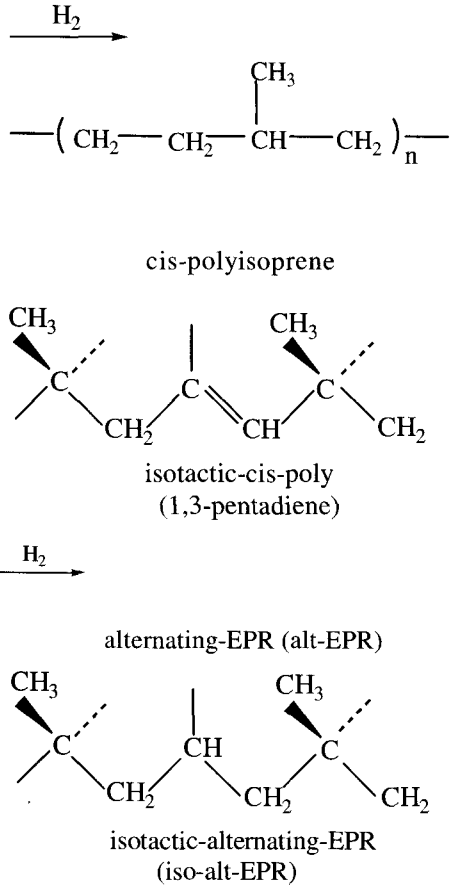
Blends of a rubber with a crystalline polymer are of commercial and technological interest in providing an inexpensive method to enhance physical properties without sacrificing performance. In addition, blending a crystalline with a rubbery polymer results in materials having a two-phase structure with physical properties different from the constituent homopolymers. An interesting example has been reported by Batiuk and coworkers.[1-3] They discovered that by blending certain rubbers of ethylene-propylene-diene(EPDM) with polyethylene, they obtained commercially interesting polyblends with a tensile strength that is surprisingly greater than that of either of the components. As an another example, a commercial blend of rubbery high cis-1,4-polybutadiene with crystalline syndiotactic-1,2-polybutadiene (UBEPOL-VCR) combines good mechanical properties with excellent processability.[4] There are close relationships between morphology, crystal structure and physical properties. The morphology, crystal structure and physical properties for crystalline-amorphous polymer blends may be controlled by both the thermodynamic segment interaction and also the chain stiffness between two polymers. As a result, blend morphology and physical properties are governed by chain rigidity,[5-10] exothermic heats of mixing,[11] and crystallization.[12,13] It is believed that specific molecular interactions, such as ion-dipole, acid-base, charge transfer and hydrogen bonding often contribute strongly toward enhancing miscibility in many polymer blends. However the influence of weaker molecular interactions such as random dipole-dipole and/or dipole-dipole effects on polymer miscibility is less clear.[14] Several efforts[14-22] have been made in recent years to elucidate the effect of these weak molecular forces on polymer miscibility using blends of polyethylene/ethylene-propylene copolymer,[21] polyethylene/ethylene-butadiene,[22] cis-polybutadiene/trans-polybutadiene,[23] and natural rubber/trans-polyisoprene.[24] In the previous papers,[25,26] the research results about the three binary blend mixtures of cis-polybutadiene with three different polyethylenes which differ in ethyl branch content were reported. The system of main interest in this study is to examine behavior of three binary blend mixtures of polyethylene[PE(2)] having 2mole% ethyl branch with three different ethylene-propylene rubbers(EPR's) having the same ethylene(E)-propylene(P) molar ratio (E/P=50/50) with different stereoregularity, namely, random EPR(r-EPR), alternating-EPR(alt-EPR) and isotactic-alternating-EPR(iso-alt-EPR). As shown the Scheme Ⅰ and Ⅱ, PE(2) was obtained by hydrogenation of cis-polybutadiene(cis-PBD).[27] r-EPR was supplied by Exxon Co., alt-EPR and iso-alt-EPR were obtained from hydrogenation of cis-polyisoprene and isotactic-cis-poly(1,3-pentadiene), respectively.[28] Scheme Ⅲ shows three PE(2)/EPR blend system for the research.



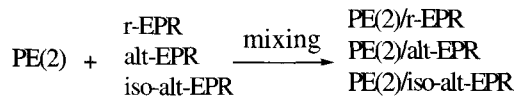

Scheme 1. Formation of polyethylene by hydrogenation of polybutadiene.






Scheme 2. Chemical structure and synthesis of ethylene-propylene rubbers.




Scheme 3. Blending system of PE(2)/EPR.

## Ⅱ. Experimental

### 1. Materials

PE(2) was obtained from hydrogenation of cis-PBD(Goodyear, Budene 1208). r-EPR(Vistalon 404) was supplied by Exxon Co.. alt-EPR was obtained from hydrogenation of cis-polyisoprene(Goodyear, Natsyn 2210). iso-alt-EPR was obtained from hydrogenation of isotactic-cis-poly(1,3-pentadiene) (Goodyear).

### 2. Blending

PE(2) was blended with various EPR's, e.g., r-EPR, alt-EPR, iso-alt-EPR to investigate their mutual compatability. Samples of various compositions were prepared by solution blending in a mutual solvent (p-xylene) followed by solvent evaporation. The evaporation of solvent from the blend solution was carried out at 90℃, at 10 inHg in a vacuum drying oven to prevent polyethylene from precipitating due to crystallization.

### 3. Instruments and Sample Preparation

The melting points of polymer blends were measured by differencial scanning calorimeter(DSC, Dupont 9900 thermal analyzer) with disc memory. DSC analyses were carried out on each polymer sample by placing approximately 10mg of sample into an aluminum sample pan. The dynamic mechanical thermal analysis(DMTA) spectra were obtained by employing a Polymer Laboratories, Mark Ⅱ. Sample specimen having dimensions of 0.5mm×5mm×2cm was prepared by compression molder. The specimens were mounted using a single cantilever clamping frame and a drive shaft clamp. Wide angle X-ray scattering(WAXS) technique was used to measure interplanar crystal spacing by a Rigaku X-ray generator CN40112KI with a stable high voltage and low current power supply(40kV, 20ma). The sample films were made by placing the sample between two pieces of Mylar and compressing the sample with 20tons pressure at 135℃. An ISI SX—40 scanning electron microscope(SEM) was used to obtain scanning electron micrographs of the polymer blend morphology. The samples were prepared as films made from a solution casting method and then compression molded. The samples were immersed in liquid nitrogen for 5 minutes, and then the samples were fractured. The fractured surfaces of the samples were coated with a layor

of gold to enhance the electric conductivity. The density behavior of polymer blends were examined by using a density gradient column filled with water-isopropanol. The density values were obtained from an average of the readings on at least three specimens. The tensile properties were measured using an Instron tensile tester Model 1130. Samples were stamped into a dumbell shape using a micro-die which has a gauge width of 3.054 mm.

## Ⅲ. Results and Discussion

### 1. Melting Point

The melting temperatures of the different PE(2)/EPR blends are plotted in Figure 1 as a function of blend composition. For all PE(2)/EPR systems investigated the melting point depression may be used to describe a single monotonic relationship with respect to composition. The behavior was supported from the results of linear regression analysis of the individual blend systems where similar fitting coefficients for each system were obtained. It is generally believed that the main factor effecting the melting point in polymer blends results from crystal thinning due to the presence of a polymer diluent. In this study, the stereoregularity of EPR increases in the order r-EPR, alt-EPR, iso-alt-EPR. The increase of the stereoregularity in EPR may reduce chain mobility and flexibility. It may affect the interaction between PE(2) and EPR as well as the entropy on mixing to decrease. Thus, the depression of the melting point increases with decreasing the stereoregularity of EPR.

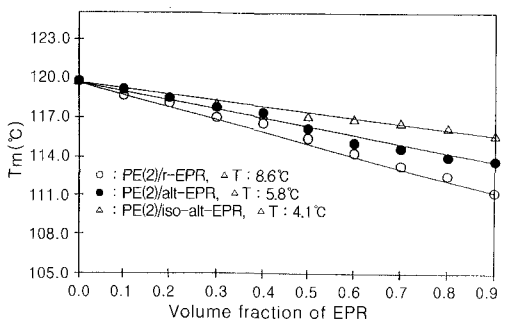



**Figure 1.** Phase diagram for different PE(2)/EPR blends.

### 2. Glass Transition Temperature

For the PE(2)/EPR blends, DMTA technique was used to investigate blend miscibility. As described before,[27] Log E″ peaks for the $\gamma$ and $\alpha$ transitions of PE(2) used here appear around -100℃ and 65℃, respectively. The glass transition temperatures of three EPR's measured by DSC lie between 54℃ and 58℃.[28] $T_g$ values by DMTA technique have shifted to 30℃~40℃. Dynamic mechanical thermal analyzer at 1 Hz for fixed 50/50 composition of different EPR blends with PE(2) are shown in Figures 2 to 4. The glass transition temperature was

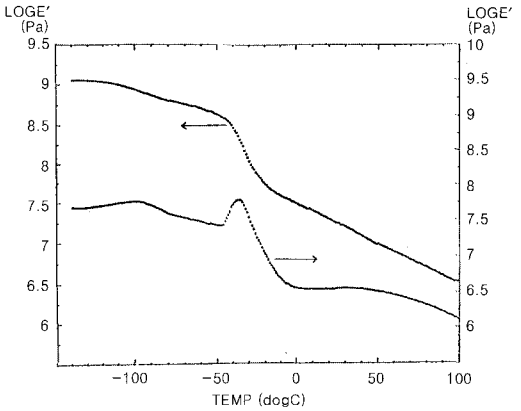



**Figure 2.** DMTA spectra showing the various relaxations of PE(2)/r-EPR(50/50).

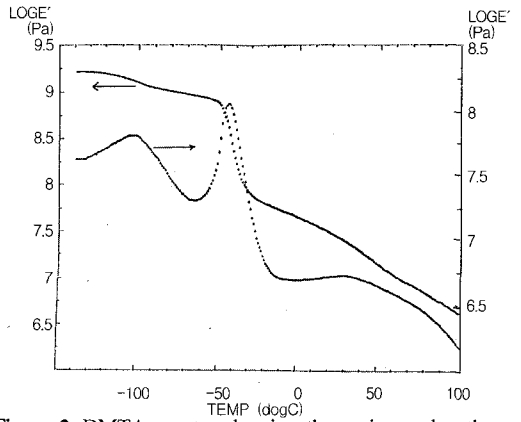



**Figure 3.** DMTA spectra showing the various relaxations of PE(2)/alt-EPR(50/50).

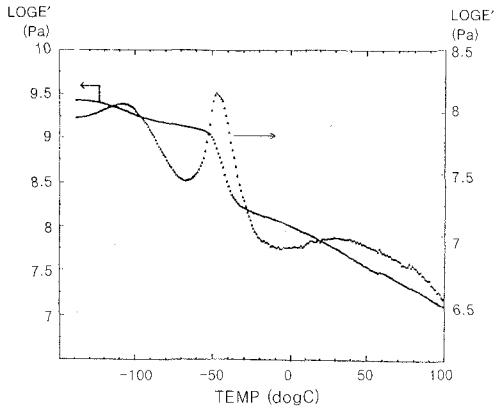



**Figure 4.** DMTA spectra showing the various relaxations of PE(2)/iso-alt-EPR(50/50).

selected as the peak position of the loss modulus (E″) when E″ was plotted vs. temperature. Apparently, $\gamma$, $\alpha$ transitions of PE(2) and $T_g$ of EPR exist for all three blend systems. This means that three blend systems exist as phase-separated state at the ambient temperature. That is, this blend systems imply to be miscible each other at or around melting point of PE(2).

## 3. d-Spacings

The effect of crystalline defects on the crystallization behavior and crystal structure has been previously demonstrated and discussed for cis-PBD/PE blends.[25] Schroeder and Lin[21,22] observed an increase in the d-spacing with increasing the percent ethylene branch of LDPE for LDPE/EPR blends. In general, as the branch concentration is increased or the branch size is decreased, the apparent melting point temperature is lowered and the lattice spacing is expanded. The expansion of the crystal lattice of PE is expected only when co-crystallization of LDPE and EPR takes place. This process is known to be enhanced only when the ethylene content in the EPR is high enough to favor crystallization with PE(2). This study was done to examine if three kinds of EPR's co-crystallize with PE(2). If so, what kind of trend they have dependence on the stereoregularity in EPR. A values of axis d-spacings for the (200), (110) and (020) planes for different weight fractions of various EPR's are shown in Table 1. It is clearly evident that the d-spacings for the different crystal planes are independent of rubber concentration and stereoregularity of EPR. This fact indicates that methyl group of 50% propylene unit in the EPR severely prohibit it from cocrystallizing with PE(2) in the blend.

## 4. Density Behavior

The density behavior of the blends of PE(2)/EPR was determined by density gradient column filled with water-isopropanol. The density value of each pure polymer was already introduced in the previous paper.[28] According to the result, the higher the stereoregularity, the higher the density of EPR. This means that the free rotation, chain mobility favor in the low stereoregularity. EPR, i.e., Vistalon 404 make much free volume and prevent good chain

**Table 1. d-Spacings of (020) (200) and (110) Planes for Different Blends**

| Composition | d-Spacings(Å) PE(2)/r-EPR | | | PE(2)/alt-EPR | | | PE(2)/iso-alt-EPR | | |
|---|---|---|---|---|---|---|---|---|---|
| | (020) | (200) | (110) | (020) | (200) | (110) | (020) | (200) | (110) |
| 20 / 80 | 2.483 | 3.743 | 4.142 | 2.489 | 3.751 | 4.162 | 2.487 | 3.765 | 4.172 |
| 40 / 60 | 2.485 | 3.746 | 4.152 | 2.484 | 3.742 | 4.142 | 2.848 | 3.738 | 4.139 |
| 50 / 50 | 2.485 | 3.746 | 4.154 | 2.485 | 3.743 | 4.156 | 2.483 | 3.737 | 4.146 |
| 60 / 40 | 2.487 | 3.743 | 4.154 | 2.484 | 3.738 | 4.146 | 2.483 | 3.738 | 4.133 |
| 80 / 20 | 2.487 | 3.743 | 4.146 | 2.485 | 3.742 | 4.148 | 2.483 | 3.734 | 4.139 |

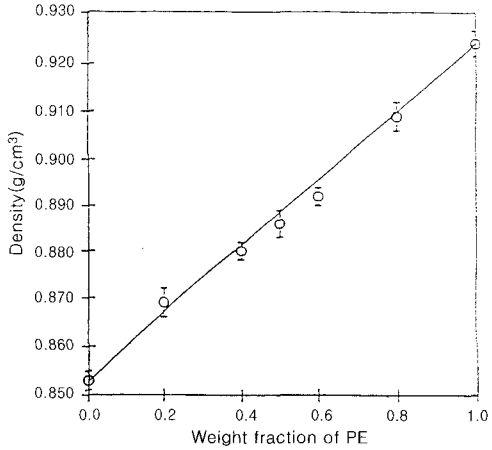



**Figure 5.** Blend densities as a function of composition at 25℃ for PE(2)/r-EPR.

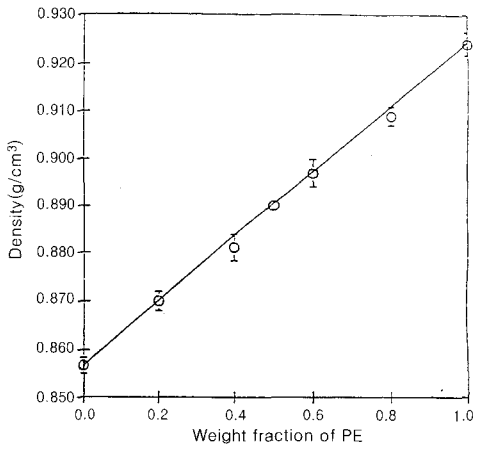



**Figure 6.** Blend densities as a function of composiion at 25℃ for PE(2)/alt-EPR.

packing. Figures 5 to 7 show the change of blend density with blend composition. The PE(2)/EPR blends indicate the linear relation between the density and blend ratio. The data of densities( $\rho_b$) measured for incompatible blends perfectly accord with values calculated from Equation(1).

$$1/\rho_b = w_1/\rho_1 + w_2/\rho_2 \quad (1)$$

Where $w_1$,$w_2$ and $\rho_1$, $\rho_2$ are the weight and the density of two pure polymers, respectively. No volume change of the blends means that this kinds of blends don't show better chain packing from

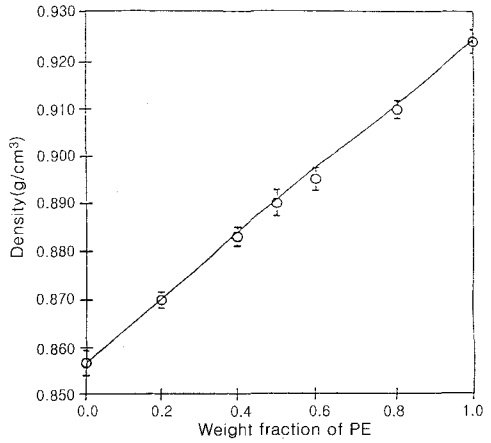



**Figure 7.** Blend densities as a function of composiion at 25℃ for PE(2)/alt-EPR.

increased molecular interaction.[29,30] We can expect that no molecular interaction between PE(2) and EPR exist for all three blend systems.

## 5. Stress-Strain Measurement

The tensile deformation properties of three pure EPR's prior to PE(2)/EPR blends were studied at a cross-head speed of 10cm/min. Figure 8 shows the stress-strain curves for r-EPR, alt-EPR, and iso-alt-EPR. An increase in the stereoregularity of the EPR increases the breaking strength and decreases the elongation at fracture. Probably, the higher stereoregularity may suppress the chain mobility, and the chain rotation due to the fixed molecular configuration. Thus, the iso-alt-EPR needs more energy to be broken. On the other hand, the r-EPR has low strength and high elongation at the breaking point due to the high chain flexibility and the easy chain disentanglement against the external force by the low stereoregularity. If we compare r-EPR with cis-PBD, their strengths are almost the same. But r-EPR has a greater extension than cis-PBD. Likewise, this difference may result from existence and non-existence of double bond in two polymer main backbone. The cis-PBD which possesses the double bond is less elongated due to limitation of rotation by the double bond than the

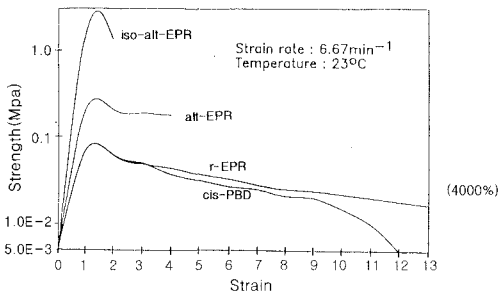



**Figure 8**. The stress-strain curves for the three pure EPR's and cis-PBD.

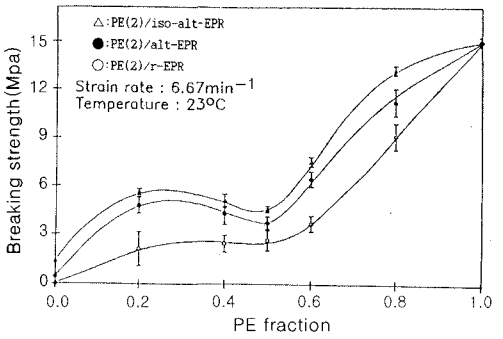



**Figure 9**. The breaking strength vs. PE fraction for the three PE(2)/EPR blends.

r-EPR. Figure 9 shows the stress-strain curves for PE(2)/EPR blends. The data represent that the breaking strength doesn't behavior according to the simple additivity relationship. This blend systems have the lowest value of the breaking strength at PE(2) fraction of 0.5. Such behavior may derive from the greatest separated phase morphology at this blend composition. This immiscible blend systems at room temperature is expected to have a poor degree of interfacial adhesion between components that provides a multiplicity of defects for early failure at the 50/50 ratio.

## Ⅳ. Conclusions

In the research, the melting point depression of polyethylene increases with the decrease of stereo-regularity in EPR. The measured dimensions of the unit cell of a semi-crystalline polyethylene are not affected by the introduction of an amorphous component for PE(2)/EPR blends. According to the measurement of $T_g$ by DMTA these blend systems were determined to be immiscible regardless of blend composition. The three blends show a linear relationship in the density behavior with the change of blend ratio. This trend means that these blends have very weak or no interactions between the two component chain segments. From the measurement of stress-strain behavior for these blends, a blend composition(50/50) has the lowest breaking strength.

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