

에틸렌-프로필렌 고무와 에틸렌-아크릴에스터-무수말레산 공중합체로 개질한 Nylon-6의 구조와 물성

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Structure-Property Relationships of Nylon-6 Modified by Ethylene-Propylene Rubber and Ethylene-Acrylic Ester-Maleic Anhydride Copolymer

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요 약 : 에틸렌-프로필렌 고무(EPR)와 에틸렌-아크릴에스터-무수말레산 공중합체(EAM)를 충격 개질제로 사용한 nylon-6/EPR/EAM 블렌드를 용융 혼합하여, 구조와 물성의 상관 관계를 조사하였다. 개질제의 함량이 20%일 때, EAM 함량을 증가시키에 따라 관찰되는 분산상의 크기와 수는 감소하였다. 이것은 EAM과 nylon-6사이에 형성된 그라프트머가 개질제들의 분산을 향상시키기 때문인 것으로 볼 수 있었다. 블렌드의 충격 강도는 EAM 함량의 증가에 따라 최대값을 보이는 바, 크레이즈 형성에 유리한 비교적 큰 EPR 입자와 전단 변형에 효과적인 매우 미세한 분산의 EAM이 동시에 존재하여 상승적인 강인화에 기여하는 것으로 해석하였다. 인장 특성과 nylon-6의 결정화 거동도 블렌드의 형태와 관련지어 고찰하였다.

Abstract : Blends of nylon-6/ethylene-propylene rubber(EPR)/ethylene-acrylic ester-maleic anhydride copolymer(EAM) in which the EPR and the EAM were used as impact modifiers were prepared by melt blending and the structure-property relationships of the blends were studied. It was observed that the size and the number of discrete particles were decreased as the EAM content was increased at the fixed levels of the 20 wt% modifiers. Graftomers seemed to be formed from the reaction between the nylon-6 and the EAM and the dispersion of the modifiers was improved. The impact strength of the blends showed maximum as the EAM content was increased. It is postulated that the synergistic toughening of the nylon-6 by the modifiers is attributable to the relatively large particles of the EPR effective for craze formation as well as the fine dispersion of the EAM favoring shear yielding. Tensile properties and crystallization behaviors of the blends depending on the EAM content are discussed based on the morphology of the blends.

INTRODUCTION

Various rubbers are often employed as impact modifiers of plastics. In order to improve the toughness of brittle plastics efficiently, particle size of the rubber and the rubber-matrix adhesion are reported to be important factors by many researchers.^{1,2} According to Wu, impact energy is dissipated by crazing as well as shear yielding of the matrix in case of nylon-6,6.³ He also pointed out that the distance between rubber particles must be smaller than the critical value for rubber modified nylon-6,6 to dissipate the impact energy efficiently by matrix yielding.⁴ Morphology of rubber modified plastic may be determined by the rheological properties and the compatibilities of the constituents. The compatibility between rubbers and polyamides are reported to be improved by functionalization of the rubber with maleic anhydride which readily forms imide linkage with amine groups of the polyamides during melt mixing.⁵ As an effort to improve the toughness of the nylon-6, ethylene-propylene rubbers (EPR) and ethylene based multifunctional copolymer were employed as impact modifiers and structure-property relationships of the modified nylon-6 are reported in this paper.

EXPERIMENTAL

Commercial polymers were used in this study. Characteristics of the polymers are summarized in Table 1. Both EPR(I) and EPR(II) are immiscible with nylon-6 and the viscosity of the EPR(I) is lower than that of EPR(II). An ethylene based multifunctional copolymer was employed as impact modifiers as well as compatibilizers of the nylon-6/EPR blends. According to the resin maker, the ethylene based multifunctional copolymer is ethylene-acrylic ester-maleic anhydride copolymer (EAM) in which the acrylic ester is ethyl acrylate or butyl acrylate and the comonomer content is 32% and acid value of which is 11 mg KOH/g. The acid value of the EAM corresponds to the maleic anhydride content of 1.0%. Various blends of nylon-6, EPR, and EAM were prepared employing single screw extruder (barrel diameter: 40 mm, ratio of length to diameter: 24). The temperature of the melts in the die head was 240°C. The content of EPR and/or EAM used as impact modifiers was fixed to be 20% by weight in this study and the ratios of EPR and EAM were varied. Compositions of the blends investigated are given in Table 2.

Table 1. Characteristics of Polymers Used in the Preparation of the Blends

| Polymer | Manufacturer (Grade name) | Characteristics |
|---------|-----------------------------------|---|
| nylon-6 | Tongyangnylon (TOPLAMIDE-1021) | Medium viscosity for injection molding, $\bar{M}_n = 25,000$ |
| EPR(I) | Kumho EP Rubber (KEP-070) | Ethylene-propylene copolymer, Moony Viscosity(100°C) : 24 lb. in |
| EPR(II) | Kumho EP Rubber (KEP-570) | Ethylene-propylene-ethylene norbornene copolymer Moony Viscosity(100°C) : 88 lb. in |
| EAM | Ato Chem(LO-TADER 4700) | Ethylene-acrylic ester-maleic anhydride copolymer |

lon-6, EPR, and EAM were prepared employing single screw extruder (barrel diameter: 40 mm, ratio of length to diameter: 24). The temperature of the melts in the die head was 240°C. The content of EPR and/or EAM used as impact modifiers was fixed to be 20% by weight in this study and the ratios of EPR and EAM were varied. Compositions of the blends investigated are given in Table 2.

Table 2. Composition of the Nylon-6/EPR/EAM Blends Studied

| Sample code | Ingredient | Blend ratios (by wt.) |
|-------------|--------------------------|--------------------------|
| A-0 | Nylon-6/EPR(KEP-070)/EAM | 80/20/0 |
| A-4 | Nylon-6/EPR(KEP-070)/EAM | 80/16/4 |
| A-8 | Nylon-6/EPR(KEP-070)/EAM | 80/12/8 |
| A-12 | Nylon-6/EPR(KEP-070)/EAM | 80/8/12 |
| A-16 | Nylon-6/EPR(KEP-070)/EAM | 80/4/16 |
| A-20 | Nylon-6/EAM | 80/20 |
| B-0 | Nylon-6/EPR(KEP-570)/EAM | 80/20/0 |
| B-4 | Nylon-6/EPR(KEP-570)/EAM | 80/16/4 |
| B-8 | Nylon-6/EPR(KEP-570)/EAM | 80/12/8 |
| B-12 | Nylon-6/EPR(KEP-570)/EAM | 80/8/12 |
| B-16 | Nylon-6/EPR(KEP-570)/EAM | 80/4/16 |

The blends were injection molded for tests of tensile strength, elongation at break, and notched Izod impact strength according to ASTM D 638 and D 256. The morphology of the blends was studied with cryogenically fractured specimens followed by etching with xylene. The etched fracture surface were coated with gold in vacuum and observed using scanning electron microscope (SEM : Hitachi X-650). The blends were dissolved in 80% formic acid solution dissolving nylon as well as rubbers to check formation of graftomers by Molau test.⁶ Crystallization of the nylon-6 in the blends was studied employing differential scanning calorimeter (DSC : DuPont 910).

RESULTS AND DISCUSSION

In Fig. 1 and 2, SEM pictures of the fracture surfaces of the nylon-6/EPR/EAM blends are shown. It is believed that the discrete phases are the EPR's and the EAM as they are soluble in xylene and must be etched. It is observed that the size of the discrete domain decreases as the content of the EAM is increased. It is worthwhile to note that the domain size of the discrete phase of the nylon-6/EPR(I)/EAM blends is smaller than that of nylon-6/EPR(II)/EAM. According to Han, the size of discrete phase in polymer blend is determined by the viscosity ratio of the polymers as well as interfacial

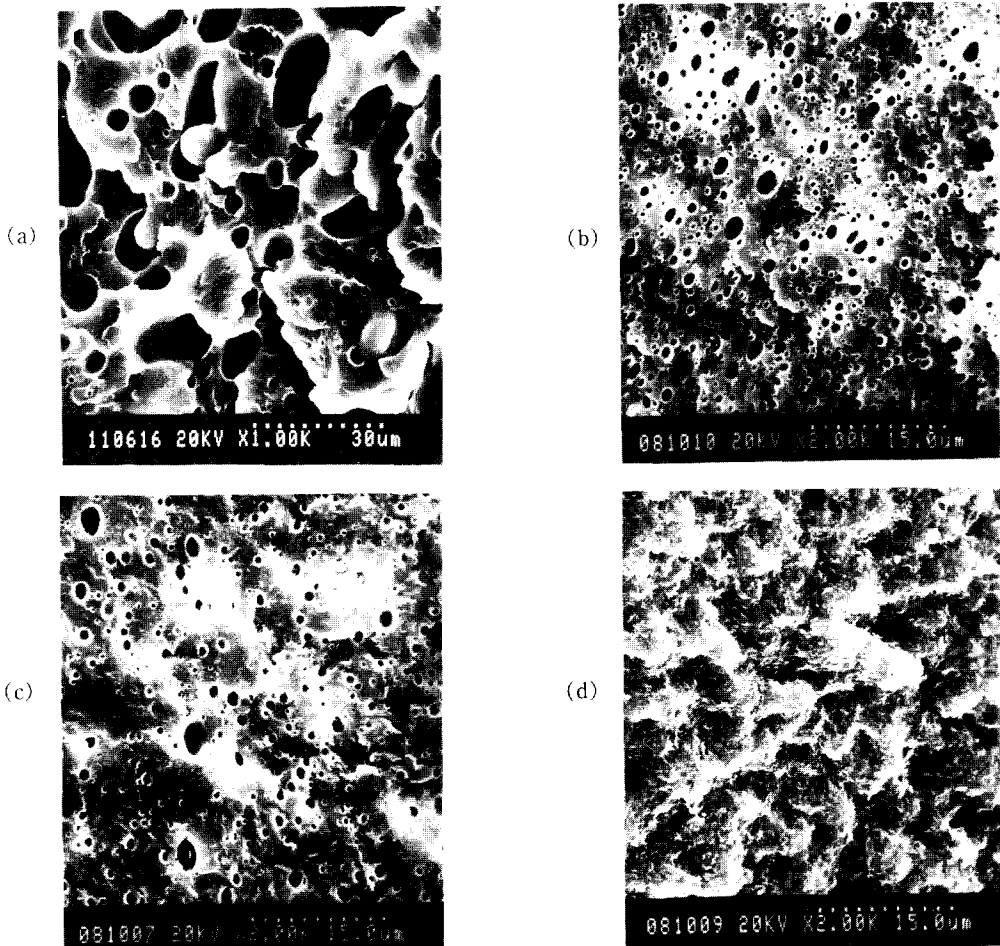


Fig. 1. SEM micrographs of cryogenically fractured surface of various nylon-6/EPR(I)/EAM blends : (a) A-0 ; (b) A-4 ; (c) A-12 ; (d) A-20.

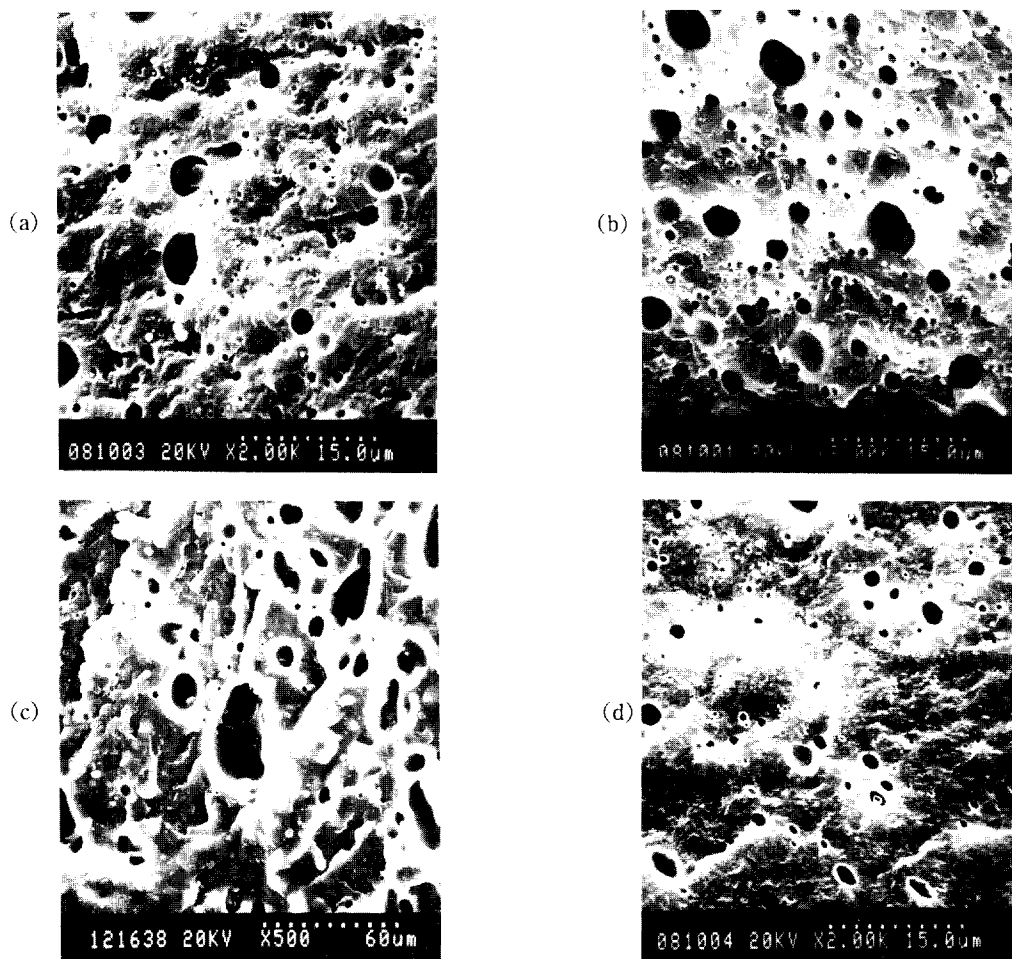


Fig. 2. SEM micrographs of cryogenically fractured surface of various nylon-6/EPR(II)/EAM blends : (a) B-0 ; (b) B-4 ; (c) B-12 ; (d) B-16.

properties.⁷ It seems that the larger discrete domain of the nylon-6/EPR(II)/EAM blend resulted from the higher viscosity of EPR(II) than that of EPR(I). In Molau test, the blends without EAM formed clear supernatant solution of nylon-6 while the blends containing the EAM formed milky supernatant. Cinnamon and his coworkers reported that the milky colloids are due to graftomers formed by the reaction between amine groups of polyamide and maleic anhydride of maleated modifier.⁵ It is postulated that the graftomers were formed from the in-situ reaction between the EAM and the nylon-6 during blending and reduced the

size of dispersed modifiers acting as compatibilizers of the nylon-6/EPR/EAM blends. It is also observed that the number of relatively large discrete particles in the SEM pictures decreases as the EAM content is increased in the blends. It seems that the EPR forms relatively large particles the size of which is reduced as the EAM content is increased while the EAM forms graftomers and is dispersed finely in the blends. However, it is not clear if EPR and EAM form separate domain at this moment. In order to elucidate the dispersion of the EPR and the EAM, further morphological studies may be required.

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In Fig. 3, notched Izod impact strength(NI) as a function of EAM content of the blends is given. It is observed that the NI's of the nylon-6/EPR(I)/EAM blends are higher than those of nylon-6/EPR(II)/EAM blends. It seems that the NI's of the nylon-6/EPR(I)/EAM blends are higher than those of nylon-6/EPR(II)/EAM blends due to the smaller size of discrete particles and shorter interparticle distance of the nylon-6/EPR(I)/EAM blend which is effective for energy dissipation by shear yielding. It is of interest to note that the NI's of the blend show maximum as the EAM content of the blends are increased. Paul and his coworkers reported that synergistic toughening effect was observed for styrene-acrylonitrile copolymer with mixture of fine emulsion particles of methyl methacrylate-butadiene-styrene copolymer and relatively large particles of styrene-butadiene-styrene block copolymer.⁸ Such synergistic toughenings were attributed to the presence of relatively large particles and fine particle which are efficient for craze formation and shear yielding respectively. It is speculated that the NI's of the nylon-6/EPR/EAM blends also show maximum due to synergistic toughening effects by the presence of relatively large particles of the EPR as well as fine

dispersion of the EAM in the blends.

In Fig. 4, tensile strength(TS) of the nylon-6/EPR/EAM blend as a function of EAM content is shown. It is observed that the TS's of the blends increased and leveled off as the EAM content was increased. The increase of TS is attributable to the improved dispersion and adhesion between the discrete phase and the nylon-6 matrix in the blends by the graftomers formed. In Fig. 5, elongation at break(EL) of the nylon-6/EPR/EAM blend as a function of EAM content is given. In case of the nylon-6/EPR(I)/EAM blends, the EL's did not change very much depending on the EAM content. However, significant increase of EL was observed in the nylon-6/EPR(II)/EAM blends. It was observed from the morphology that the dispersion of EPR(II) in B-0 is coarser than that of EPR(II) in A-0 and seems that the graftomers from the reaction between the EAM and the nylon-6 acting as compatibilizers were very effective and the increase of EL was significant for the B-0.

Fig. 6 shows the heat of crystallization of the nylon-6(ΔH_c) in the nylon-6/EPR/EAM blends depending on the EAM content. It is observed that the ΔH_c decreases as the EAM content is increased. The ΔH_c was obtained by cooling the sample

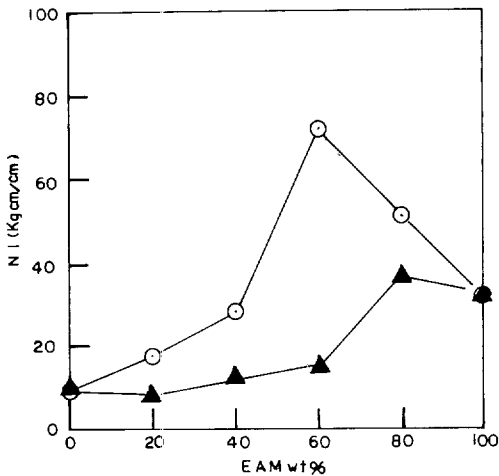


Fig. 3. Notched izod impact strength(NI) vs. EAM content for various nylon-6/EPR(I)/EAM blends(\odot) and nylon-6/EPR(II)/EAM blends(\blacktriangle).

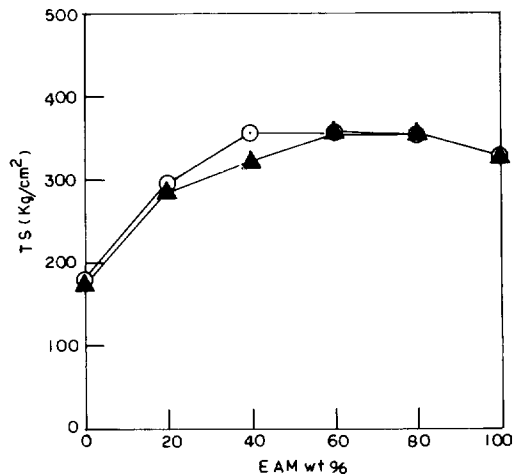


Fig. 4. Tensile strength(TS) vs. EAM content for various nylon-6/EPR(I)/EAM blends(\odot) and nylon-6/EPR(II)/EAM blends(\blacktriangle).

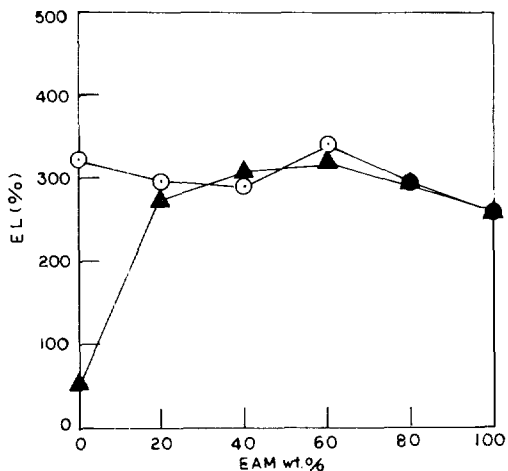


Fig. 5. Elongation at break(EL) vs. EAM content for various nylon-6/EPR(I)/EAM blends(○) and nylon-6/EPR(II)/EAM blends(▲).

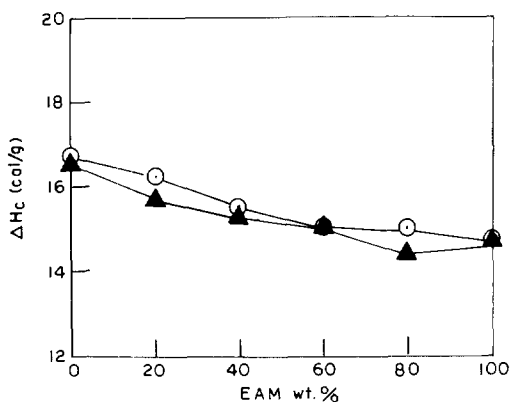


Fig. 6. ΔH_c vs. EAM content for various nylon-6/EPR(I)/EAM blends(○) and nylon-6/EPR(II)/EAM blends(▲).

at 5°C/min, which was initially heated to 240°C and held for 3 minutes in DSC. It seems that the crystallization of the nylon-6 is hindered in the blends due to molecular irregularity introduced by the formation of graftomers from the EAM and the nylon-6.

CONCLUSION

The impact strength of the nylon-6 modified by the EPR and the EAM showed maximum at a certain content of the EAM in the blends. The size and the number of discrete particles decreased as the EAM content was increased. It is speculated from the Molau test that graftomers were formed from the reaction between the nylon-6 and the EAM and improve the dispersion of the modifiers. The synergistic toughening of the nylon-6 by the EPR and the EAM was attributed to the relatively large particles of the EPR and the fine dispersion of the EAM in the blends. Tensile strength and elongation at break of the nylon-6/EPR/EAM blends increased as the EAM content was increased possibly due to the improved dispersion and adhesion of the modifiers in the blends.

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