

비상용성의 Nylon 6/EPR 고분자 블렌드 시스템에서
나노 클레이를 이용한 새로운 상용화 방법

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**New Method of Compatibilizing Nylon 6/EPR Incompatible
Polymer Blend System by using Nano Clay**

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Abstract

The effect of nano clay on the compatibilization of incompatible polymer blends consisting of nylon 6 and poly(ethylene-ran-propylene rubber) (EPR) without or with an in-situ compatibilizer of EPR-g-maleic anhydride (EPR-M) prepared by an internal mixer has been studied. The average domain diameter size of EPR in Nylon 6 matrix decreases significantly by the addition of nano clay. The enhanced compatibility in nylon 6/EPR blend system by addition of nano clay may be due to the restricted coalescence of EPR domains that favors the formation of smaller domains.

1. Introduction

Mixing two or more polymers together to produce blend is a well-established strategy for achieving a specified portfolio of physical properties, without the need to synthesize specialized polymer systems (1-2). But because of general immiscibility of the polymers associated with the inherent thermodynamic incompatibility, the use of polymer blends in wide spectrum of industry is limited. Among many compatibilization techniques, reactive compatibilization method has been demonstrated to be effective way and cost efficient route in controlling properties of various immiscible blend systems (3). In our present work, efforts have been put forward to enhance the compatibility of an incompatible polymer blend, consisting of nylon 6 and ethylene propylene rubber (EPR), by using ethylene propylene grafted maleic anhydride, and nano clay. Many works have been published regarding the synthesis of nanocomposites, by different polymerization techniques, melt processing, and the mechanical properties of these nanocomposites have been studied (4-6). However, to the best of our knowledge, reports on use of nano clay as a compatibilizer in incompatible polymer blend system are relatively rare (7,8). Based on this, our present article focuses on the effects of EPR-g-MA and nano clay as compatibilizer in nylon 6/EPR blend system.

2. Experimental and Characterizations

Nylon 6 used in this study was a commercial grade (LG chemical company) with the number-average (M_n) and weight-average (M_w) molecular weights of 12,000 and 47,000 respectively. The glass transition temperature (T_g) of the nylon 6 was 127 °C, determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. Ethylene Propylene

Rubber (EPR) was a commercial grade (KUMHO Polychem Co., Korea) with Mn and Mw 65,000 and 120,000 respectively. The ethylene content in the EPR was 40 wt% and the glass transition temperature (T_g) of the EPR was 45 °C. Ethylene Propylene Rubber Grafted Maleic Anhydride (EPR-M) was a commercial grade (MF-416D, Du Pont Co.). According to the producer, the amount of grafted maleic anhydride in EPR-g-MA was 0.5 ~1.0 wt%. The clay employed in this study was Cloisite 20A (Southern Clay Product Inc) which is a montmorillonite modified with dimethyl dihydrogenatedtallow ammonium. The cation exchange capacity (CEC) of Cloisite 20A is 95 mequiv/100 gm.

Blends were prepared by using an internal mixer (Brabender Co.), at 250 °C and 60 rpm, 20 min, by gradual replacement of the EPR phase with different amount of EPR-g-MA and Cloisite20A. For comparative study, blends were also prepared without EPR-g-MA, and clay, under the same processing condition. Phase morphology of the toluene-extracted samples was studied with a Field Emission Scanning Electron microscope (S-4200, Hitachi). The cross sectional area (A_i) of each particle in the SEM micrograph was measured with a Quantimet 570 image analyzer and then converted into the diameter (D_i) of a circle having the same cross sectional area. The number average (D_n) and surface area average (D_s) domain diameters were calculated. The layer structure of the clay was measured by wide angle x-ray diffraction study (WAXD). The possible location of the nano clay in the composites was investigated through TEM analysis.

3. Results and Discussion

From morphological analysis, it is evident that the extraction of the EPR phase by toluene is easier in nylon 6/EPR blend system. This is reflected by the broad distribution and larger domains in the micrograph (Fig. 1a). In case of the composites containing grafted maleic anhydride as compatibilizer, the domain size of the EPR phase in the micrographs decreases (Fig. 1b, 1c). This is due to the enhanced phase adhesion between nylon 6 and EPR polymers in presence of grafted maleic anhydride. Interestingly, addition of organically treated nano clay in the nylon 6/EPR blend system enhances the phase adhesion between the blend partners to a remarkable extent (Fig. 1d).

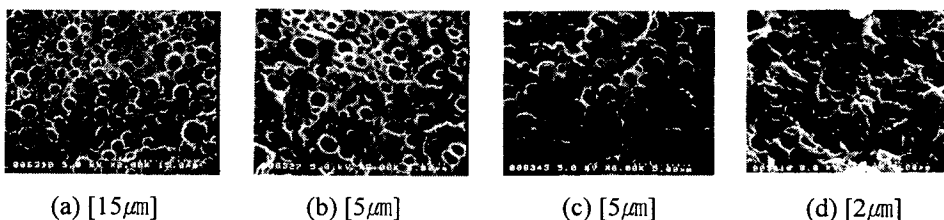


Fig.1. SEM micrographs:(a) Nylon 6/EPR (80/20) (b) Nylon 6/EPR/EPR-g-MA (80/18/2) (c) Nylon 6/EPR/EPR-g-MA (80/16/4), (d) Nylon 6/EPR/clay (80/20/5)

With increasing the amount of grafted maleic anhydride, both the number average (D_n) and surface area average (D_s) domain diameter of the blend decreases rapidly at lower amount of grafted maleic anhydride (Fig.2 a). Addition of nano clay in the blend decreases the average diameter of dispersed domains (D_n and D_s). A rapid decrease in domain diameter (D_n and D_s) was found at lower percentage of clay loading (Fig. 2b).

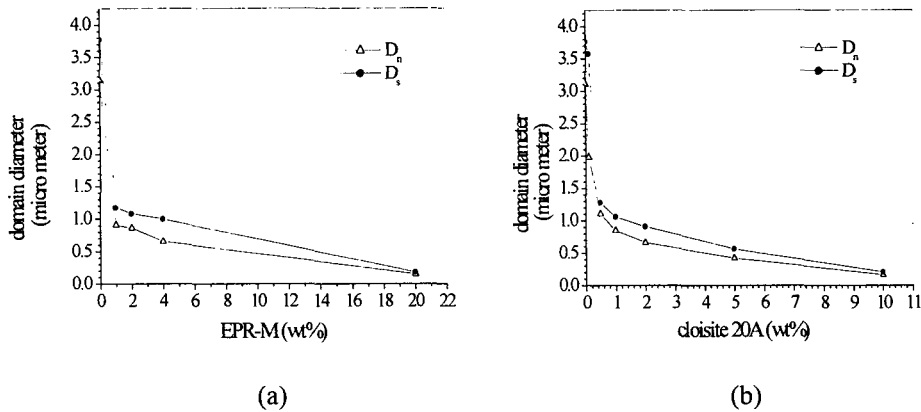


Figure 2. Plot of number average (D_n) and surface area average (D_s) domain diameter of (80/20) nylon 6/EPR blend vs weight percentage of (a) EPR-g-MA (b) cloisite 20A

The increased compatibility in Nylon 6/EPR blend, in presence of nano-clay may be explained by the followings. The competitive adsorption of nylon 6 and EPR produces *in-situ* grafts on the clay platelet surfaces. The platelets, which migrate to the interface, act as effective graft copolymer. Since, the grafts are formed directly at the interface, there is no competition with micellization and a sufficient copolymer to reduce the interfacial tension can be formed. Thus, the interface hardening effect of the clay suppressed the extraction of the rubber phase by solvent. Hence, the bending energy of the interfaces is high. This favors formation of small domains, further aiding the compatibilization process. Again, the electro-statically bound surfactants (organic small molecules) in cloisite 20A may also be extracted during processing, and act as a low quality-nucleating agent (plasticizing effect). WAXD and TEM analysis reveals the exfoliated clay morphology in these composites. Thus, presence of exfoliated clay platelets in the matrix phase may prevent the coalescence of EPR domains. Thus, the clay platelets can act as a barrier to the assembly of EPR chains. This favors the formation of small dispersed domains.

Giannelis et.al. (9) reported that the presence of layered silicates not only affects the enthalpy, but also the dynamics of the polymer blends. Hence, they can further reduce the size of the micro domains in immiscible blend of nylon 6 and EPR.

The domain size of EPR phase in nylon 6/EPR blend decreased to a greater extent in presence of EPR-g-MA and nano clay. The compatibility of the composites, containing grafted maleic anhydride, depends only on the amount and conformation (wet-brush behavior) of *in situ* grafted copolymers (EPR-g-nylon 6) at the interface (10). The *in situ* graft copolymers of conventional reactive polymers (EPR-g-MA) may be moved out of the interface during mixing. In case of nylon 6/EPR/EPR-g-MA/clay composites, the improved compatibility of EPR-g-MA and clay depends on amount, high molecular pseudo wet-brush behavior (interactions of reactive polymers, clay and *in situ* copolymers), and interface hardening effect (combined layered silicates) of *in situ* graft copolymers at the interface. Thus, the combination of grafted maleic anhydride and clay will suppress the move out of *in situ* grafted copolymers at the interface due to the synergic compatibility of polymer-clay interaction and interface hardening effect of the clay at the interface.

4. Conclusion

In this investigation we report a new method of compatibilizing incompatible polymer blend systems by using nano clay. The average domain diameter of the dispersed EPR phase was found to decrease significantly by introducing nano clay into nylon 6/EPR blend system. TEM study reveals that the exfoliated clay platelets are mostly located in nylon 6 polymer. Thus, we may propose that the dispersion of exfoliated clay platelets in the matrix polymer prevents the coalescence of dispersed domains. This leads to the formation of very small dispersed domains in the matrix polymer. The organo clay layers act as barrier to the assembly of EPR chains, and may slow down the phase segregation process.

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