Improved Compatibility of Styrene-Maleic Anhydride Copolymer/Polyethylene Blends Through Reactive Mixing

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IMPROVED COMPATIBILITY OF STYRENE-MALEIC ANHYDRIDE COPOLYMER/POLYETHYLENE BLENDS THROUGH REACTIVE MIXING

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ABSTRACT

To improve the compatibility of styrene-maleic anhydride copolymer/low density polyethylene (SMA/LDPE) blends, LDPE grafted with 2-hydroxyethyl methacrylate-isophorone diisocyanate (LDPE-g-HI) was prepared and blended with SMA of which anhydride was converted to carboxylic acid (SMAAc). The infrared spectra of LDPE-g-HI established the presence of isocyanate group. In the blend morphology, some adhesions between the two phases and much finer dispersions were observed in the SMAAc/LDPE-g-HI blends, indicating that chemical reactions took place during the melt blending. The lower heat capacity change at the glass transition temperature demonstrated that chemical bonds were produced in the SMAAc/LDPE-g-HI blends. From the results of the rheological test, it was found that strong positive deviation from the mixing rule occurred in viscosity for the SMAAc/LDPE-g-HI blends, concerning with good adhesion and finer dispersions. In the measurement of tensile property, the improved mechanical properties for the SMAAc/LDPE-g-HI blends were shown.

INTRODUCTION

Reactive mixing process has been widely used for obtaining improved compatibility of blend [1]. Such a process required introduction of some functionality reacting with other functional groups to either of the blend components. Immiscible blends are possible to be compatibilized through the reaction that reduces interfacial tension and promotes adhesion at the interface. The results are a finely dispersed phase, resistance to gross separation, and enhanced overall properties [2].

Several authors [3-15] have reported that one polymer with some functional group reacted with another polymer during blend processing and this resulted in a compatible effect. Most of the functional groups were acid anhydride [3-7], carboxy [8-11], epoxy [12, 13], and oxazoline [14, 15] reacted with the amine or carboxyl group of various thermoplastic resins. Because almost no research work for use of isocyanate (NCO) having a better reactivity over the above mentioned functional groups has been published, we have carried out a study on the preparation of polyolefin with NCO functionality. Also the compatibilizing effect of NCO group on blends of engineering resins and low density polyethylene (LDPE) was shown in our previous paper [16, 17].

Styrene-maleic anhidride copolmer (SMA) has numerous applications in overall industry [18]. Especially, high molecular weight SMA are being used for the engineering plastics area where the high heat distortion temperature is needed, in spite of its brittleness. When blended with other ductile polymers like polyethylene (PE), it may offer an attractive balance of mechanical property and resistance to heat distortion. To attain satisfactory performance in the immiscible SMA/PE blend, it will be important to improve the compatibility. There are few detailed studies on the SMA/PE blends obtained by a reactive processing without using a compatibilizer.

In this study, we carried out a blending of LDPE with NCO functionality and SMA with acid functionality to improve compatibility of SMA/LDPE blends through chemical reaction occurring during the blend process. NCO would react quickly with acid at the high temperature [19] where a melt blend processing is performed. The morphological, thermal, rheological, and mechanical properties of the blends were also examined and discussed.

EXPERIMENTAL

Materials

LDPE (Hanwha Chemicals, melt flow index = 12) and SMA (Aldrich

Chemical, maleic anhydride content = 14 wt%, M_w = 220,000, melt flow index = 1.9) were used as received. A functional monomer with NCO group was prepared by the reaction of 2-hydroxyethyl methacrylate (Junsei Chemical, HEMA) with isophorone diisocyanate (Aldrich Chemical, IPDI), with a molar ratio of 0.95 to 1 at 40°C in nitrogen blowing for 6 hours [16, 17]. To obtain SMA with acid functionality (SMAAc), mild hydrolysis converting of maleic anhydride to maleic acid was carried out in boiling water for 2 hours. The maleic acid content of 1.3 wt% in SMAAc was determined from potentiometric titration according to ASTM D 2930.

Graft Copolymerization

Graft copolymerization was carried out in xylene with dicumyl peroxide (DCP) to introduce of NCO group into LDPE. LDPE (10 parts) and xylene (100 parts) were put into a vessel and heated with agitation, followed by the immediate addition of HEMA combined with IPDI (HI) (2 parts) and DCP (0.1 parts). The reaction was continued at 120°C in nitrogen blowing for 4 hours. The reaction mixture was cooled, washed with pure xylene several times, and dried in vacuum. Evidence for grafting was obtained from Fourier transform infrared (Nicolet, Mahgna IR-550), and the grafting degree of 1.92% was determined from elementary analysis (Yanaco, MT-2 CHN coder).

Blends Preparation

SMAAc and LDPE grafted with HI (LDPE-g-HI) were mixed at 230°C, 50 rpm in an internal mixer (Hakke, Rheocorder 900). After mixing for 5 minutes, the blends were cooled in water. Additionally, the blends of SMA with LDPE were also prepared for comparison purposes. The blend ratios of SMAAc/LDPE-g-HI (or SMA/LDPE) were 10/90, 30/70, 50/50, 70/30, and 90/10 by weight.

Measurements

The morphology of blend was observed by scanning electron microscopy (JEOL, JSM-35CF) from a cryogenically fractured (in liquid nitrogen) surface. A differential scanning calorimeter (Perkin Elmer, DSC-7) was used for the thermal analysis of blend specimen, with a heating scan up to 180°C at a 10°C/min scanning rate. Rheological properties were measured by a rotational rheometer (Rheometric Scientific, ARES), with a 20% strain at 230°C under dry nitrogen. Parallel plates, 25 mm in diameter and a gab height of 2 mm, were used for the steady rate sweep. All of the specimens for mechanical test were prepared by injection molding (Toshiba, IS-60B) at 230°C with the mold temperature of 80°C. Tensile measurements were done on an Instron machine at room temperature, following the procedure described in ASTM D638.
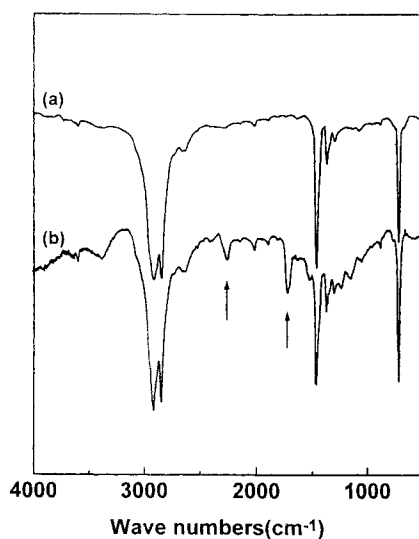
Figure 1.   IR spectra: (a) LDPE, (b) LDPE-*g*-HI.


RESULTS AND DISCUSSION

LDPE with NCO Functionality

Grafting of HI, a monomer with NCO group, on to LDPE was confirmed by IR spectroscopy. Figure 1 (b) shows the IR spectra for LDPE incorporated with the monomer. It is possible to observe the carbonyl absorption band of HEMA at 1730 cm^{-1}. Additionally, the peak due to NCO group is appeared at 2270 cm^{-1}. The figure gives clear evidence for the presence of NCO functional group in LDPE.

Morphology

It has been known that the blend volume ratio plays a predominant role in determining which of the two components forms the dispersed phase and which the matrix phase. This also gives us the indication that, in the LDPE-rich (by volume) blends, SMA forms the dispersed phase in the LDPE matrix and that the reverse is true in the SMA-rich blends.

Figure 2 shows representative SEM photomicrographs of the cryogenically fractured surfaces of the SMA/LDPE blends, and they are typical morphologies of incompatible blends. As above mentioned, the dispersed SMA phases are shown in the 10/90, 30/70, and 50/50 SMA/LDPE blends (Figure 2 (a), (b), and (c)), and LDPE is the dispersed phase in the 90/10 SMA/LDPE blend (Figure 2 (d)). The
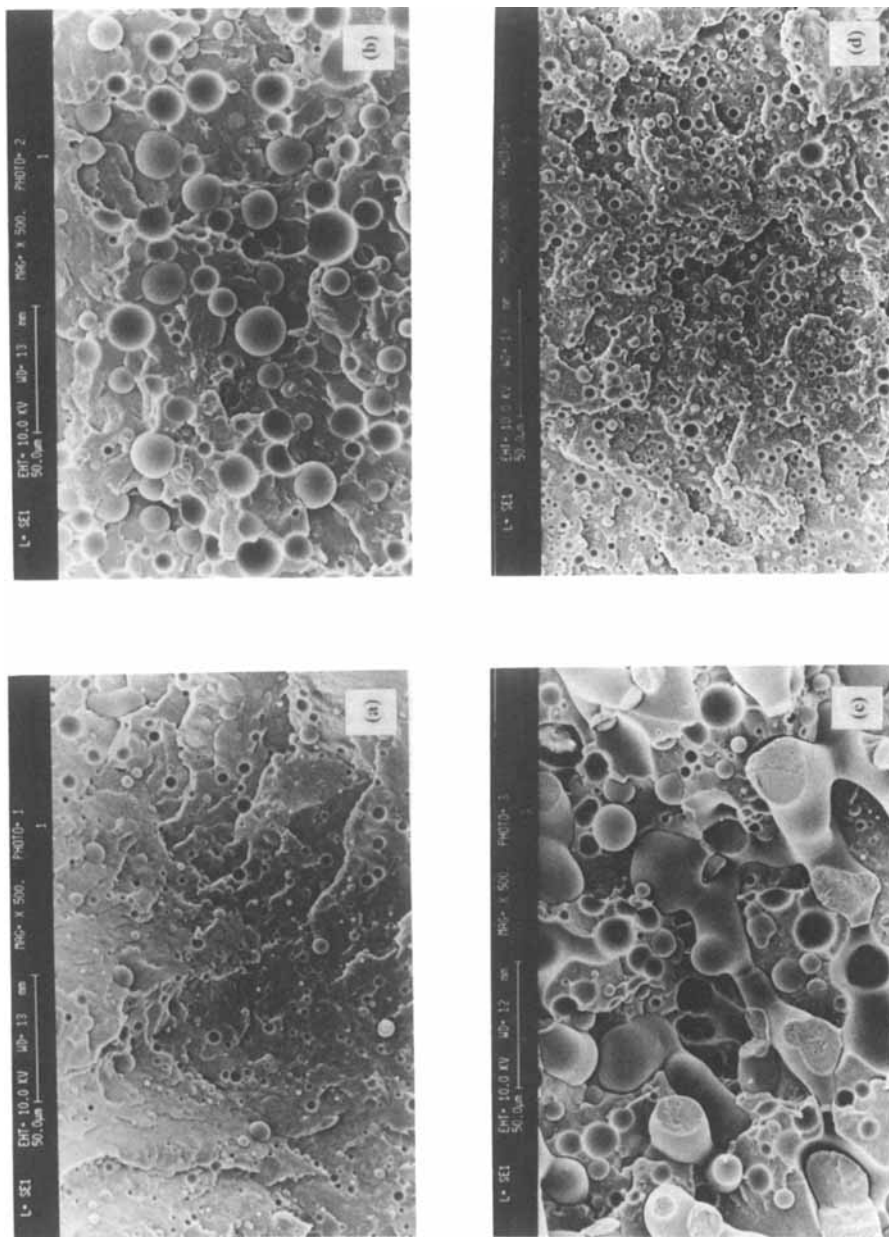
Figure 2. SEM micrographs of the cryogenically fractured surfaces of the SMA/LDPE blends: (a) 10/90, (b) 30/70, (c) 50/50, (d) 90/10.

dispersions of the SMA/LDPE blends are fairly large and coarse. It is also seen that, upon fracture, the particles were pulled off clean from the matrix phase, showing no evidence that any adhesion is produced between SMA and LDPE.
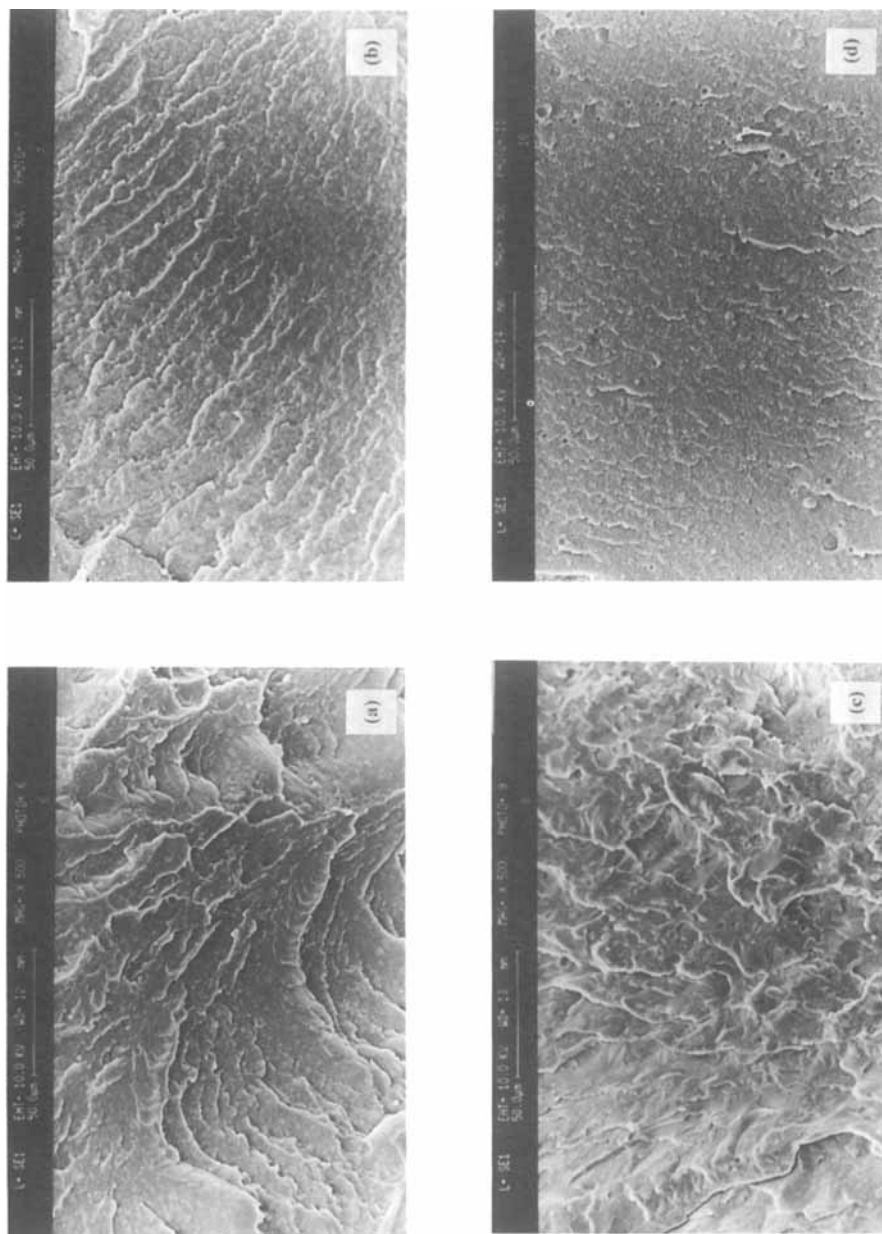
The photomicrographs of the cryogenically fractured surfaces of the SMAAc/LDPE-g-HI blends were represented in Figure 3. The dispersions of the SMAAc/LDPE-g-HI blends were much finer than those of the SMA/LDPE blends. Additionally, it is seen that some adhesions between the dispersed and matrix phases are present in the blends where SMAAc dispersed phase formed, although are insufficient to observe in the 90/10 blend forming the LDPE-g-HI submicrodispersions. These adhesions obviously indicate that chemical bonds between the two phases are produced by reactions occurred during the melt blending. NCO of LDPE-g-HI would react with carboxylic acid (COOH) of SMAAc to form amide.

For the morphology of immiscible polymer blend, the size of the dispersed phase formed in the blend could be dominated preferentially by the interfacial tension between the polymers. Undoubtedly, chemical reactions between the dispersed and the matrix phases in immiscible polymer blends can bring about adhesion of the phases, or cause the interfacial tension to reduce and result in a finely dispersed phase [20]. That is to say, the compatibility of the blends is improved through chemical reactions. In our experiment, by the interfacial reaction of NCO and COOH in the SMAAc/LDPE-g-HI blends during the melt blending, the interfacial tension of the blends could be lowered over the SMA/LDPE blends where no chemical reaction existed. From this effect, we could observe the finer dispersions as well as some adhesions of the phases in the SMAAc/LDPE-g-HI blends.

Thermal Analysis of Blends

Figure 4 shows the dependence of heat capacity change (ΔCp) at glass transition temperature (T_g) of SMA (or SMAAc) on the blend composition. In the blends where the SMA content was less than 30 wt%, ΔCp were very small and no reliable quantitative estimates can be made. However, sufficiently high ΔCp values were obtained in the blends where the SMA content was more than 30 wt%. At each blend composition, ΔCp for the SMAAc/LDPE-g-HI blend is lower than that for the SMA/LDPE blend.

It is generally known that the increase in the heat capacity at T_g reflects the increase in the molecular motion. For polymer blend, it can be also accepted that the greater the amount of molecules increasing motions at T_g of one polymer compo-

Figure 3. SEM micrographs of the cryogenically fractured surfaces of the SMAAc/LDPE-g-HI blends: (a) 10/90, (b) 30/70, (c) 50/50, (d) 90/10.
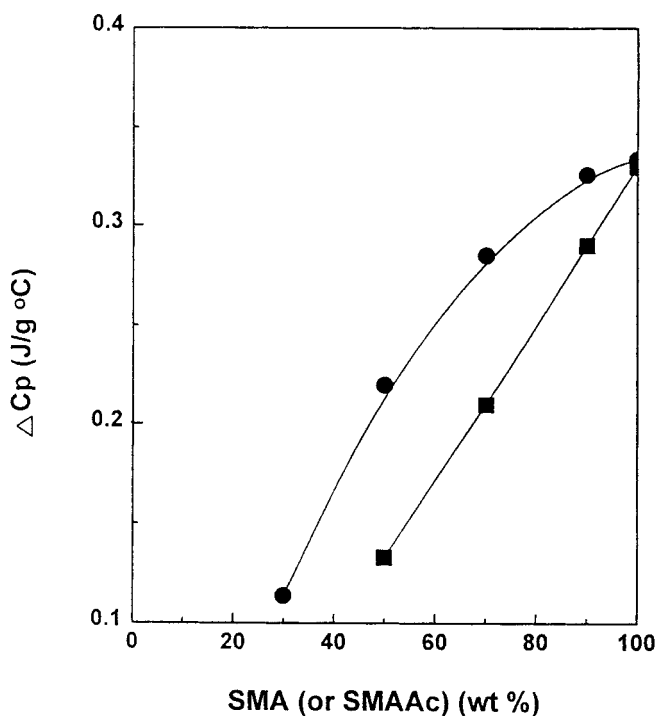
Figure 4.   The dependencies of ΔCp on blend composition:
(●) for the SMA/LDPE blends, (■) for the SMAAc/LDPE-g-HI blends.

nent, the higher ΔCp value. Because chemical reactions took place during the melt blending, some chemical bonds between the interfaces would be produced in the SMAAc/LDPE-g-HI blends. In this case, LDPE-g-HI molecule affects the chain mobility of SMAAc and, then the heat capacities at T_g are relatively diminished. The lower ΔCp for the SMAAc/LDPE-g-HI blend over the SMA/LDPE blend is attributed to chemical bond.

Rheology

It has been understood that the type of dispersion deformation, continuous or periodic, greatly influences the rheological properties of heterogeneous polymer blends or emulsions [21, 22]. A spherical droplet suspended in a continuous medium can be subjected to either a steady shearing flow or an oscillatory shearing flow. Under the steady shearing flow, the droplet is deformed in the direction of the shearing plane, and the greater the shear rate, the longer the droplet will be stretched (continuous deformation). On the other hand, under the oscillatory shearing flow,
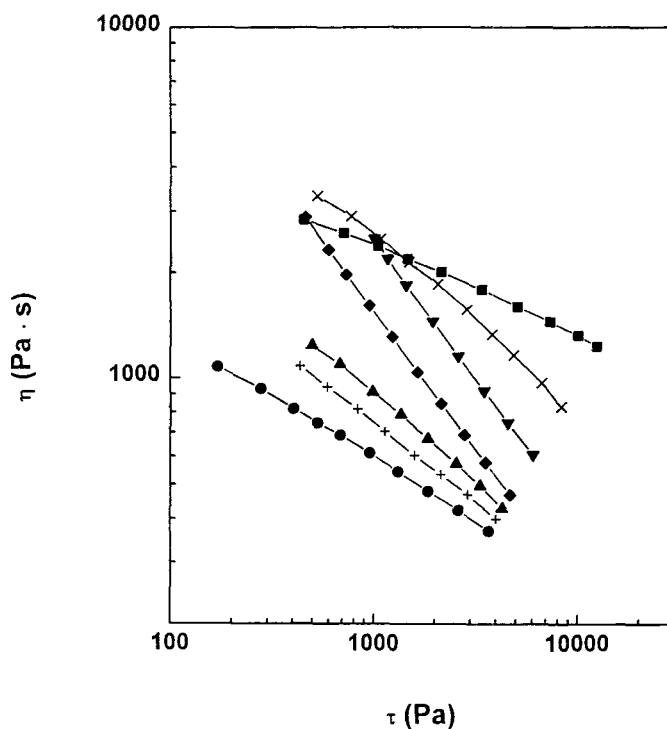
Figure 5 (a). η vs. τ   for the SMA/LDPE blends: (●) 0/100, (+) 10/90, (▲) 30/70, (◆) 50/50, (▼) 70/30, (✕) 90/10, (■) 100/0.

the shape of droplet will be oscillate, commensurate with the frequency of the oscillation imposed on the fluid (periodic deformation). Therefore, one must not expect any correlation between the steady shearing flow properties and the oscillatory shearing properties for heterogeneous polymer blends. In this work, the steady shearing flow was used for the measurements of viscoelastic properties, namely viscosity (η), first normal stress difference (N_1), and shear stress (τ).

Observations concerning N_1 vs. τ have been reported by Han [23] and White [24]. According to them, the dependence of N_1 on temperature is suppressed when N_1 is plotted against τ, instead of shear rate. Because this is considerably valid, plots of N_1 vs. τ will provide more universal rheological information capable of being disregarded for temperature effect. Figure 5 (a) gives plots of η vs. τ and Figure 5 (b) gives plots of N_1 vs. τ for the SMA/LDPE blends. The plots of η vs. τ and N_1 vs. τ for the SMAAc/LDPE-g-HI blends are represented in Figure 6 (a) and (b), respectively.
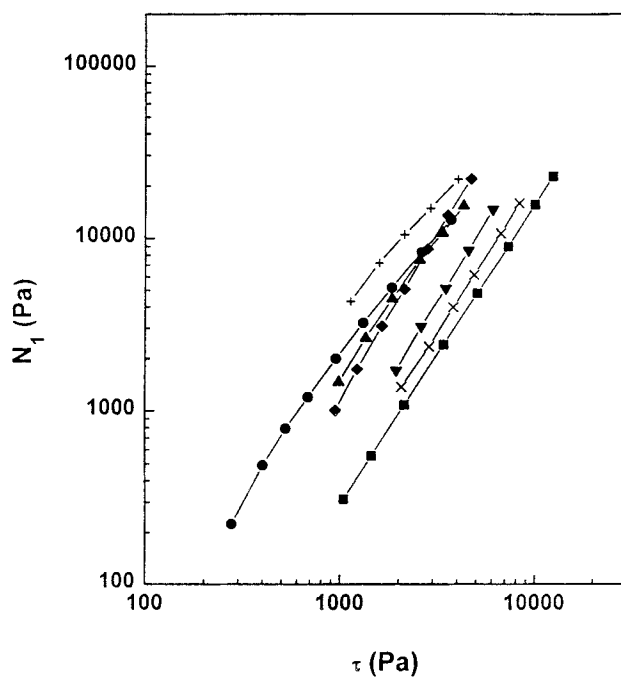
Figure 5 (b). N_1 vs. τ for the SMA/LDPE blends: ($\bullet$) 0/100, (+) 10/90, ($\blacktriangle$) 30/70, ($\blacklozenge$) 50/50, ($\blacktriangledown$) 70/30, ($\times$) 90/10, ($\blacksquare$) 100/0.
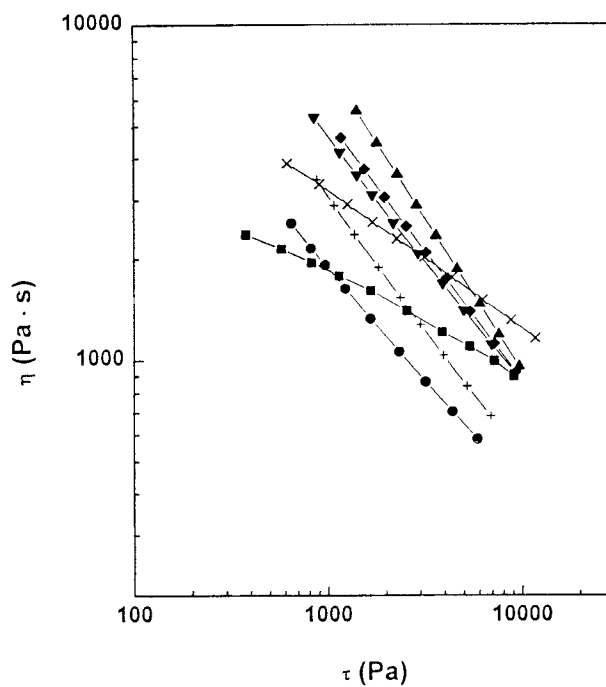
Figure 6 (a). η vs. τ for the SMAAc/LDPE-g-HI blends: ($\bullet$) 0/100, (+) 10/90, ($\blacktriangle$) 30/70, ($\blacklozenge$) 50/50, ($\blacktriangledown$) 70/30, ($\times$) 90/10, ($\blacksquare$) 100/0.
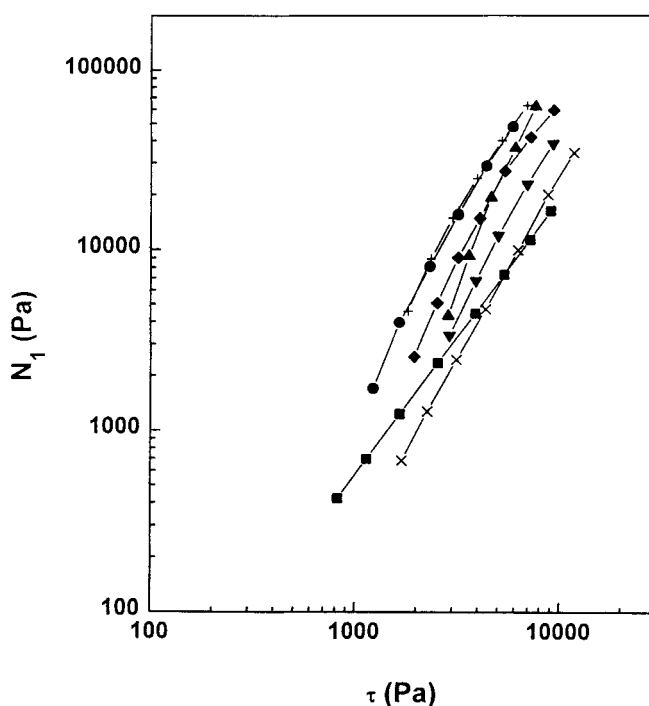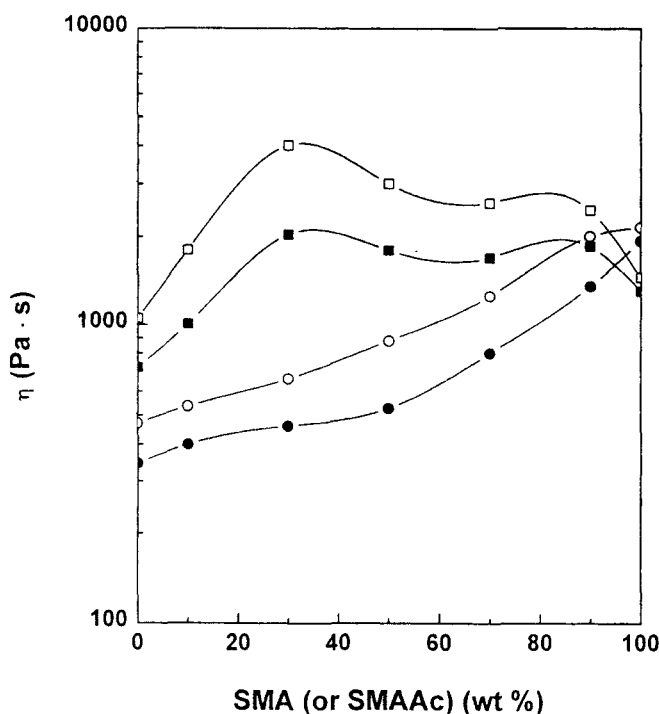
Figure 6 (b). N_1 vs. (for the SMAAc/LDPE-g-HI blends: (●) 0/100, (+) 10/90, (▲) 30/70, (◆) 50/50, (▼) 70/30, (✗) 90/10, (■) 100/0.

Several researchers have done experimental studies of the rheological properties of polymer blends [25, 26]. These investigators have considered the effects of the blending ratio on the viscosity and elasticity of blends. Since the viscoelasticity of a polymer melt exhibits large shear dependence, the respective dependence can be evaluated either at constant stress or at constant shear rate. As pointed out by Han [21], the use of shear stress is appropriate for correlating the rheological properties of multiphase polymer systems.

The effect of blend composition on η at two different τ was given in Figure 7. It is seen that η increased monotonically with blend composition for the SMA/LDPE blends, whereas η fluctuated with blend composition for the SMAAc/LDPE-g-HI blends. Also, η shows a strong positive deviation from the mixing rule [27] for the SMAAc/LDPE-g-HI blends. It has been known that for melts of blends of mutually insoluble polymers, the viscosity grows with an increase in the interaction of the components and a decrease in the dispersed phase

Figure 7. The dependencies of η on blend composition at two different shear stresses: (O,●) for the SMA/LDPE blends, (□,■) for the SMAAc/LDPE-g-HI blends. Open symbols at 2000 Pa and closed symbols at 4000 Pa.

particle size [28]. We believe that the strong positive deviation for the SMA/LDPE - g-HI blends resulted from good adhesion between the interfaces and finer dispersions.

The effect of blend composition on N_1 at two different τ is shown in Figure 8. It has been widely realized that, for the polymer blend, the deformation of dispersed droplet essentially dominates elastic characteristics [21, 22]. The larger the deformation, the more the recoverable elastic energy. The force required to deform a droplet is approximately inversely proportional to its size, and, therefore, for a given external force, the smaller the droplet size, the less likely the droplet will deform. For the SMA/LDPE blends, N_1 shows strong positive deviation from the mixing rule over the full composition range investigated, indicating that the large droplet highly deformed. On the other hand, such positive deviation is not observed for the SMAAc/LDPE-g-HI blends. In view of the fact that much finer dispersions were
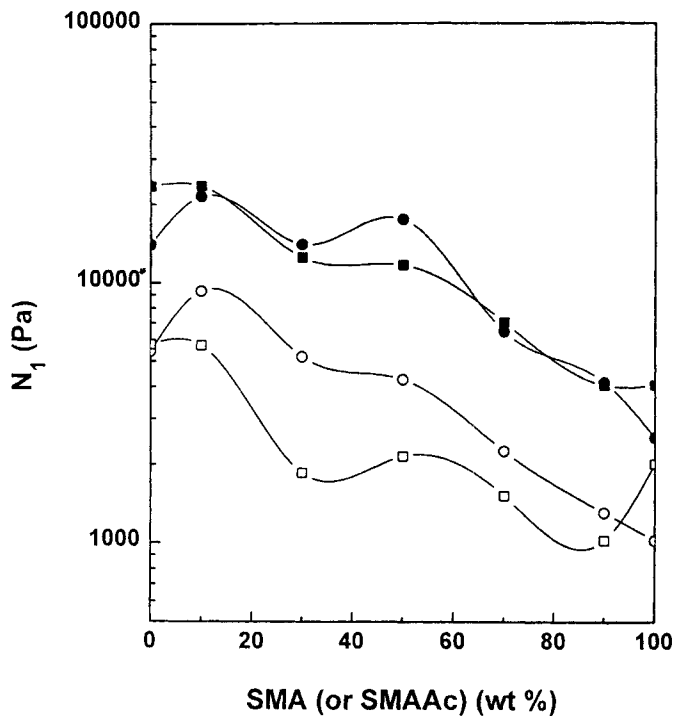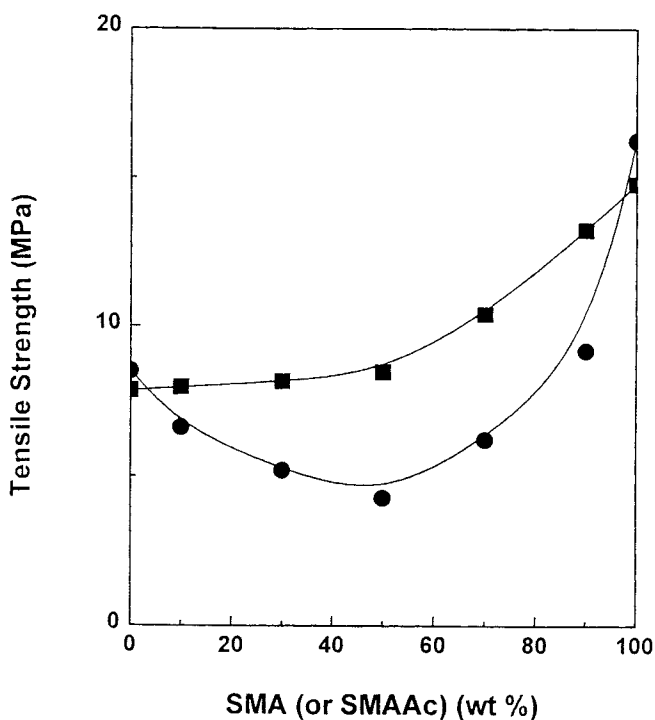
Figure 8.   The dependencies of N_1 on blend composition at two different shear stresses: (○,●) for the SMA/LDPE blends, (□,■) for the SMAAc/LDPE-g-HI blends. Open symbols at 2000 Pa and closed symbols at 4000 Pa.

formed in the SMAAc/LDPE-g-HI blends, it is not considered that strong positive deviation of N_1 for the blend system occurred.

Tensile Properties

The tensile strengths of the blends investigated are given in Figure 9. In the SMAAc/LDPE-g-HI blends, the tensile strengths monotonically increased as the amount of SMAAc increased. On the other hand, the tensile strengths of the SMA/LDPE blends decreased as the amount of SMA increased in the SMA-lean blends, indicating little or no adhesion between the dispersed SMA particles and the continuous LDPE matrix. Also, the tensile strengths dramatically decreased as the amount of SMA decreased in the SMA-rich blends, unlike those of SMA/LDPE-g-HI. As Kunori [29] and Nielsen [30] pointed out, the tensile failure of a blend is attributable to the failure of the adhesion between the dispersed phase and the matrix

Figure 9. The dependencies of tensile strength on blend composition: (●) for the SMA/LDPE blends, (■) for the SMAAc/LDPE-g-HI blends.

phase, through crazing or a dewetting effect. In this work, the dramatic decrease is also thought to be due to the failure of the adhesion between SMA and LDPE.

Elongation at break of the SMA/LDPE and the SMAAc/LDPE-g-HI blends were measured over the full composition range. As shown in Figure 10, a substantial increase in elongation occurs when the LDPE-g-HI more than 50 wt% has been added to the blend. The improvement in mechanical properties is the result of chemical reaction between SMAAc and LDPE-g-HI.

CONCLUSION

To improve the compatibility of the SMA/LDPE blends, LDPE introduced NCO functional group by a grafting of HI was blended with SMAAc having acid functionality. IR spectra for LDPE-g-HI provided the evidence for the presence of NCO group. In the blend morphology, some adhesions between the two phases and much finer dispersions were observed in the SMAAc/LDPE-g-HI blends,
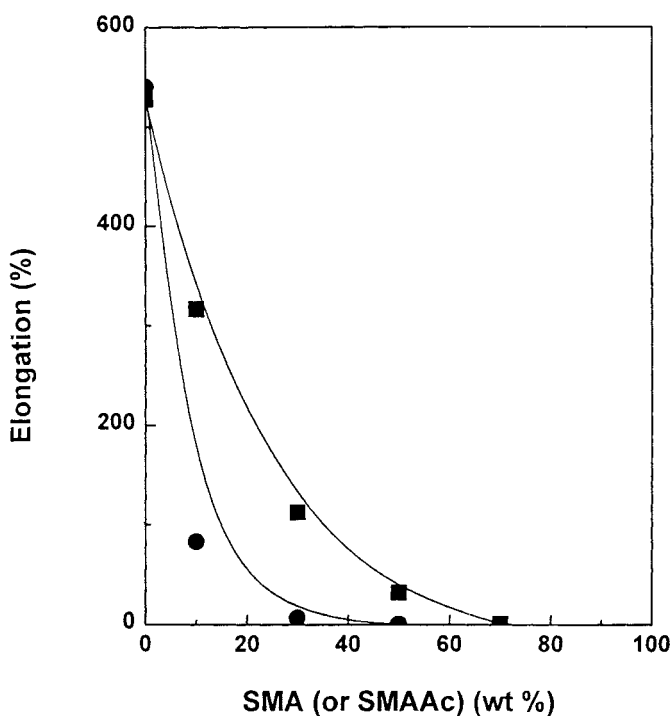
Figure 10. The dependencies of elongation on blend composition: (●) for the SMA/LDPE blends, (■) for the SMAAc/LDPE-g-HI blends.

indicating that chemical reactions took place during the melt blending. Lower ΔCp at T_g for the SMAAc/LDPE-g-HI blend over the SMA/LDPE blend is attributed to chemical bond. The results of rheological test showed that strong positive deviation from the mixing rule occurred in η and not in N_1 for the SMAAc/LDPE-g-HI blends, concerning with good adhesion and finer dispersions. For the SMAAc/LDPE-g-HI blends, the improvement in mechanical properties, resulting from chemical reaction, was produced. With the above-mentioned results, it could be concluded that the compatibility of the SMA/LDPE blend was improved by the reactive mixing.

REFERENCES

[1]   M. Xanthos and S. S. Dagli, *Polym. Eng. Sci.*, 31, 929 (1991).

[2]   D. R. Paul and S. Newman, *Polymer Blends*, Academic Press, Vol. 2, New York, 1978.

[3]   Y. Minoura, M. Ueda, S. Mizunuma, and M. Oba, *J. Appl. Polym. Sci.*, *13*, 1625 (1969).

[4]   F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.*, *18*, 963 (1974).

[5]   M. Narita, M. Akiyama, and M. Okawara, *Kogyo Kagaku Zashi, 70*, 1432 (1967).

[6]   N. G. Gaylord and M. Mehta, *J. Polym. Sci., Polym. Lett. Ed., 20*, 481 (1982).

[7]   S. Cimmino, L. D'Orazio, R. Greco, G. Maglio, M. Malinconico, C. Mancarella, E. Martuscelli, R. Palumbo, and G. Ragosta, *Polym. Eng. Sci., 24*, 48 (1984).

[8]   P. M. Subramanian and V. Mehra, *Polym. Eng. Sci., 27*, 663 (1987).

[9]   G. Fairley and R. E. Prud'homme, *Polym. Eng. Sci., 27*, 1495 (1987).

[10]   W. J. MacKnight, R. W. Lenz, P. V. Musto, and R. J. Somani, *Polym. Eng. Sci., 25*, 1124 (1985).

[11]   P. Bataille, S. Boisse, and H. P. Schreiber, *Polym. Eng. Sci., 27*, 622 (1987).

[12]   M. K. Akkapeddi and B. Vanbuskirk, *Polym, Mater. Sci. Eng., 67*, 317 (1992).

[13]   T. C. Maa and F. C. Chang, *J. Appl. Polym. Sci., 49*, 913 (1994).

[14]   W. E. Baker and M. Saleem, *Polym. Eng. Sci., 27*, 1634 (1987).

[15]   S. Gotoh, M. Fujii, and S. Kitakawa, *S.P.E. ANTEC Tech. Papers, 32*, 54 (1986).

[16]   K. Y. Park, S. H. Park, and K. D. Suh, *J. Appl. Polym. Sci.*, 66, 2183 (1997).

[17]   S. H. Park, K. Y. Park, and K. D. Suh, *J. Polym. Sci., Part B: Polym. Phy., 36*, 447 (1998).

[18]   Y. Ozeki and J. Kim, *Polymeric Materials Encyclopedia,* CRC Press, New York, Vol. 10, 1996.

[19]   C. Hepburn, *Polyurethane Elastomers*, Elsevier Applied Science, London, 1992.

[20]   M. Xanthos, *Polym. Eng. Sci., 28,* 1392 (1988).

[21]   C. D. Han, *Rheology in Polymer Processing,* Academic Press, New York, 1976.

[22]   Y. G. Yanovsky, *Polymer Rheology: Theory and Practice*, Chapman & Hall, London, 1993.

[23]   C. D. Han and K. W. Lem, *Polym. Eng. Rev., 2,* 135 (1982).

[24]   H. Yamane and J. L. White, *Polym. Eng. Rev., 3,* 167 (1982).

[25] S. Wu, *Polym. Eng. Sci., 27,* 335 (1987).

[26] A. P. Plochocki, *Polym. Eng. Sci., 26,* 82 (1986).

[27] D. Klempner and K. C. Frisch, *Polymer Alloys III*, Plenum Press, New York, 1981.

[28] C. D. Han, *Multiphase Flow in Polymer Processing*, Academic Press, New York, 1981.

[29] T. Kunori and P. H. Geil, *J. Macromol. Sci. Phys., B18,* 135 (1980).

[30] L. E. Nielsen, *Mechanical Properties of Polymer and Composites*, Marcel Dekker, Inc., New York, 1974.