무수말레산 그라프트 폴리에틸렌과 무수말레산 그라프트 폴리프로필렌과의 용융 블렌드

박 상 진 · 신 춘 환 · 김 창 기 · 김 병 규

부산대학교 고분자공학과

(1988년 12월 26일 접수)

Melt Blends of MAH-g-PE with MAH-g-PP

Sang Jin Park, Choon Hwan Shin, Chang Kee Kim, and Byung Kyu Kim

Dept. of Polymer Science & Engineering, Pusan National University, Pusan 609-735, Korea

(Received December 26, 1988)

요 약 : Brabender plasticoder를 이용, 무수말레산 그라프트 폴리에틸렌과 무수말레산 그라프트 폴리프로필렌과의 용융 블렌딩을 행하였다. 이들 블렌드물에 대하여 capillary형 rheometer 로써 정상상태 전단점도를 측정하고 주사전자 현미경으로 부터 morphology를 관찰해본 결과 그라프트 폴리에틸렌 / 그라프트 폴리프로필렌 블렌드가 폴리에틸렌 / 폴리프로필렌 블렌드에 비하여 상당히 상용성이 증대된 것으로 나타났으며 이는 무수말레산 그라프트가 상간 상호작용인력을 증대시킨데 기인한 것으로 판단되었다.

Abstract : Melt blends of MAH-g-PE with MAH-g-PP were prepared from a Brabender plasticoder. Measurements included steady shear viscosity from a capillary rheometer, and morphology from a scanning electron microscopy. Results indicated a significant increase in compatibility over the conventional ungrafted PE / PP blends due probably to the increased interaction between the phases.

INTRODUCTION

Blends of polyethylene (PE) with polypropylene (PP) have widely been encountered in many laboratories and used commercially for over ten years.[1~3] As a matter of fact, many of the commercially available homopolymer grades of PE and PP contain substantial amount of the other to impart high impact strength and low-temperature toughness. However, being as crystalline polymers, the commercial application of these blends has been limited to a narrow composition ratio due to the molcular incompatibility between the two polymers.[1]

In an attepmt to enhance the compatibility of PE / PP blends, this paper considers the blend of modified PE with modified PP. Modification was made from maleic anhydride (MAH) grafting onto the base polymers. In addition to common branches in the grafted polymers, hydrogen bondings leading to interactions between the phases are expected from the MAH grafted polymer blends.

Blend properties measured included viscosity from a capillary rheometer, and morphology by

Sang Jin Park, Choon Hwan Shin, Chang Kee Kim, and Byung Kyu Kim

a scanning electron microscopy(SEM) from a cryogenically fractured surface.

EXPERIMENTS

Commercial grades of HDPE and PP(Daehan Petrochemical Ind. Co.), molecular parameters in Table 1, were used as base polymers. Grafting of MAH onto PE and PP was carried out by following literature[4,5] in xylene with benzoyl peroxide (BPO).

For the preparation of MAH-g-PE, mixture of BPO(0.2 part) and MAH(1) dissolved in xylene (10) was dropwisely added to the solution of PE(10) in xylene(100) during the first 3.5 hrs of the reaction.

For the preparation of MAH-g-PP, PP(10), MAH(1) and xylene(100) were put into a vessel and heated with stirring to homogenize the solution followed by adding the BPO(0.2) at once.

In both cases, the reaction proceeded for 4 hrs at 120℃ in nitrogen atmosphere with agitation. Upon completing the reaction, the reaction mixture was cooled and washed with methanol several times, and dried in vacuum oven.

Blends of MAH-g-PE with MAH-g-PP were prepared from melt mixing using a Brabender plasticoder, L/D=40, 40 rpm and 210℃(die). Blends of ungrafted PE with ungrafted PP(base polymers) were also prepared at the same conditions to give thermal and shear histories identical to those of grafted blends. Identical process of extrusion was also applied to blend components for the same reason.

Steady shear viscosities were measured from a capillary-type rheometer (Capirograph) with L/D=40, D=1mm at 210℃. Bagley correction

was neglected by using a capillary of large L/D ratio. However, wall shear rate was corrected following Rabinowitsch procedure.[7]

The morphological texture of the blend was observed using a scanning electron microscopy (SEM, JEOL JSM-840A) from the cryogenically fractured(at liquid nitrogen temperature) surfaces, sputtered with gold before viewing.

RESULTS AND DISCUSSION

The grafting of MAH onto PE and PP was confirmed by FTIR measurement. Grafting ratio, determined from weight increase, ranged 2-3% by the formula :

$$\text{grafting ratio}(\%) = \frac{\text{weight of grafted polymer} - a}{\text{weight of base polymer (a)}} \times 100$$

Steady shear viscosities for blend components are shown in Fig. 1. The viscosity of PE is higher than that of PP. However the viscosity ratio that is not far away from the unity should be pointed out in relation to the blend morphology to follow.
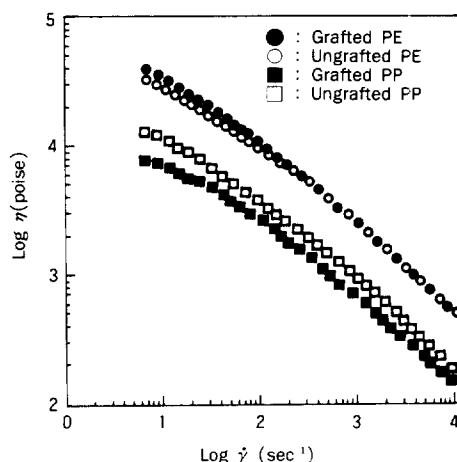
Table 1. Molecular Parameters for the Base Polymers

	M_n	M_w	PDI
PE	21,300	180,250	8.59
PP	39,000	311,700	7.80

Fig. 1. Steady shear viscosity vs. shear rate for blend components.

A larger difference in component viscosity compared to that of base polymers is seen between the grafted PE (MAH-g-PE) and grafted PP (MAH-g-PP). The viscosities of the grafted PE and grafted PP are respectively higher and lower compared to those of corresponding ungrafted ones. This results in a larger viscosity ratio for MAH-g-PE / MAH-g-PP blends compared to PE / PP blends.
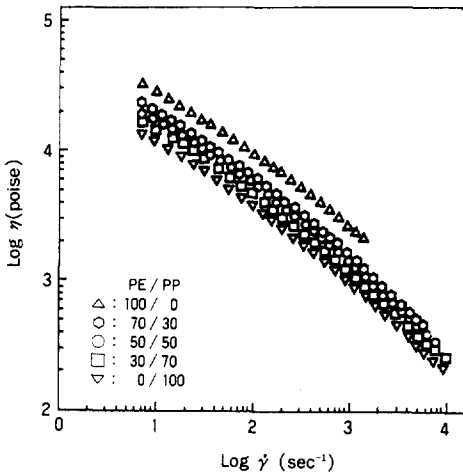
As mentioned earlier, the grafted and ungrafted polymers passed through process of extrusion identical to those of blending, identical thermal and shear histories provided. Short branches, i.e., grafted MAH in this case, do not alter the melt viscosity significantly.[8] Therefore, the notable difference in viscosity between PE and MAH-g-PE, and PP and MAH-g-PP should represent certain structural change druing the grafting process. The BPO-initiated grafting of MAH in xylene should have been accompanied by crosslinking for PE, and degradation for PP like in peroxide-catalyzed melt grafting of MAH onto the same base polymers.[9,10]

Fig. 2 and 3 show the steady shear viscosities for the grafted and ungrafted polymer blends respectively, and comparisons between the two are made in Figs. 4~6 at three different compositions. PE-rich blends show higher viscosity for the grafted one, PP-rich blends show higher viscosity for the ungrafted one, whereas at 50 / 50 composition no distinction is clear.

The viscosity as a function of composition at three different rates of shear is summerized in Fig. 7. The viscosities, for both grafted and ungrafted ones, generally follow the simple additive rule at low rate of shear. Viscosity maxima often
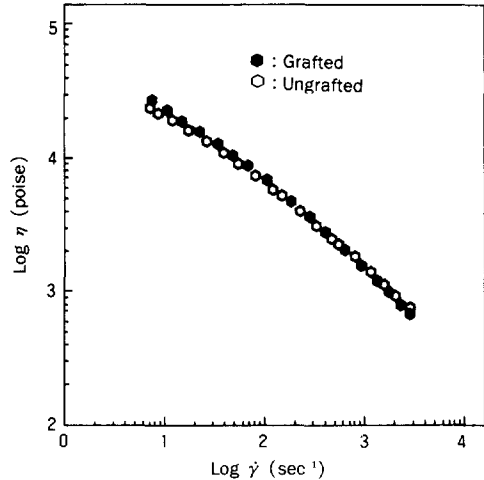

Fig. 2. Steady shear viscosity vs. shear rate for PE / PP blends.
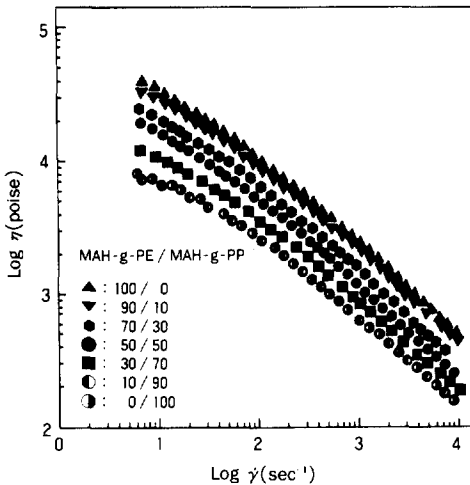
Fig. 3. Steady shear viscosity vs. shear rate for MAH-g-PE / MAH-g-PP blends.

Fig. 4. Steady shear viscosity vs. shear rate for 70 / 30 blends.

reported for PE / PP blends are not appeared. This probably is due to the component viscosity ratio relatively close to unity,[11,12] presently considered. Negative deviation from the additive rule is seen as the rate of shear increases.

When the viscosity is plotted against the composition ratio, a crossover point between the grafted and ungrafted polymer blends is demon-

Fig. 5. Steady shear viscosity vs. shear rate for 50 / 50 blends.
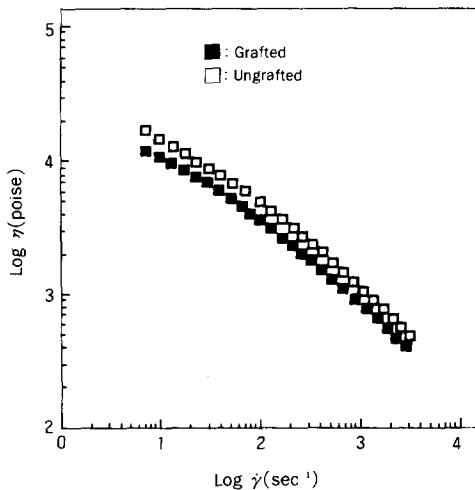
Fig. 6. Steady shear viscosity vs. shear rate for 30 / 70 blends.

strated, and the point moves toward the PP rich region as the rate of shear decreases.

It is natural to expect an improved compatibility and / or increased interphase interaction for the grafted polymer blends over the ungrafted ones, via the hydrogen bonding originated from MAH. However, the results shown in Fig. 7 are apparently unusual, i.e., the extents of deviation from the additive rule do not show any significant difference between the grafted and ungrafted polymer blends.

Due to the difference in viscosity between the two phases, the rate of shear at the interface would be discontinuous. Therefore the use of shear rate in correlating the data may be misleading. Accordingly a better paramerter instead of shear rate should be considered. The continuity of shear stress at the interface is generally assumed,[13,14] and is certainly less vulnerable to commit error compared to shear rate continuity. With the shear stress as the parameter, the viscosity as a function of composition is shown in Fig. 8. As expected, a distinction is made between the grafted and ungrafted polymer blends, especially at low level of shear stress. At low level of shear stress the ungrafted blend gives negative deviation from the additive rule. However, the grafted
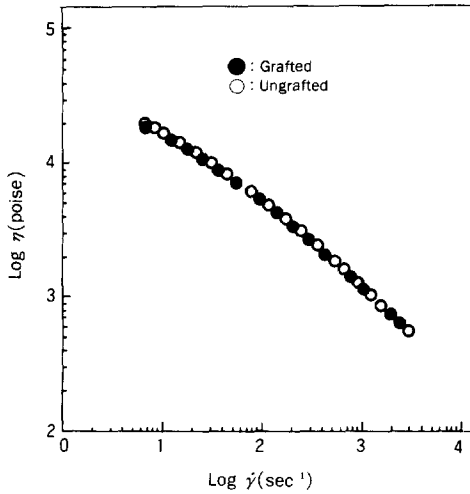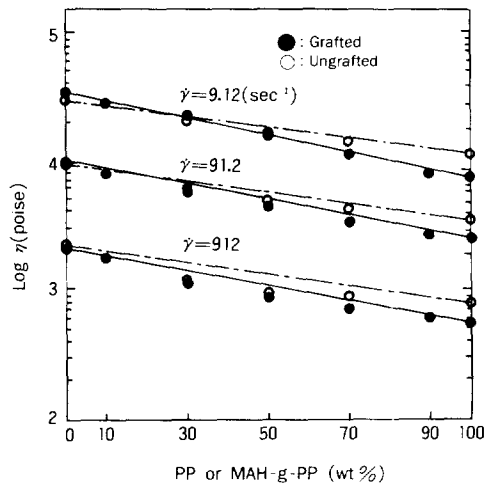

Fig. 7. Viscosity as a function of composition at three different rates of shear.

blend follows the additive rule at low level of stress.

Han,[13] Wu,[12] Beger et al.[11] and several others[15~17] address the effect of component viscosity and elasticity ratios on the phase morphology of polymer blends, and vice versa. This so-called rheology-morphology feedback actually works especially

Fig. 8. Viscosity as a function of composition at two different levels of shear stress. a : $\tau = 3.75 \times 10^5$ dyne / cm^2, b : $\tau = 1.17 \times 10^6$.

for multiphase flow. This, in short, dictates a fine breakup of dispersed phase when the viscosity of dispersed phase approaches that of continuous phase, and the idea is easily understood by simply assuming the continuity of stress at interface.

Phase morphologies of the grafted and ungrafted polymer blends are given in Fig. 9. Presently obtained SEM micrographs for the ungrafted polymer blends(PE / PP) show island / sea structure at PE10 / PP90 composition(Fig. 9a). Discontinuous structure of PE with short lamella (1μ or less) is obvious. Following Lovinger and Williams,[3] blends of 50% PP or more are typified by PE island dispersed in a PP matrix. Present blend of PE50 / PP50 does not confirm this(Fig. 9b). This is presumably due to a component viscosity ratio close to unity leading to a fine breakup of the dispersed phase. The present blends of PE50 / PP50 as well as PE90 / PP10 show co-continuous morphology.

Completely different blend morphologies are created from MAH grafting onto the base polymers. A finely dispersed co-continuous phase with improved spatial distribution is observed from MAH-g-PE90 / MAH-g-PP10 blend(Fig. 9f). Extensive fibrillations bridging the PE spherulites
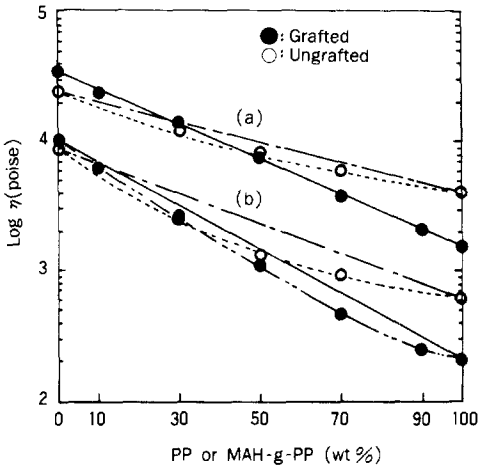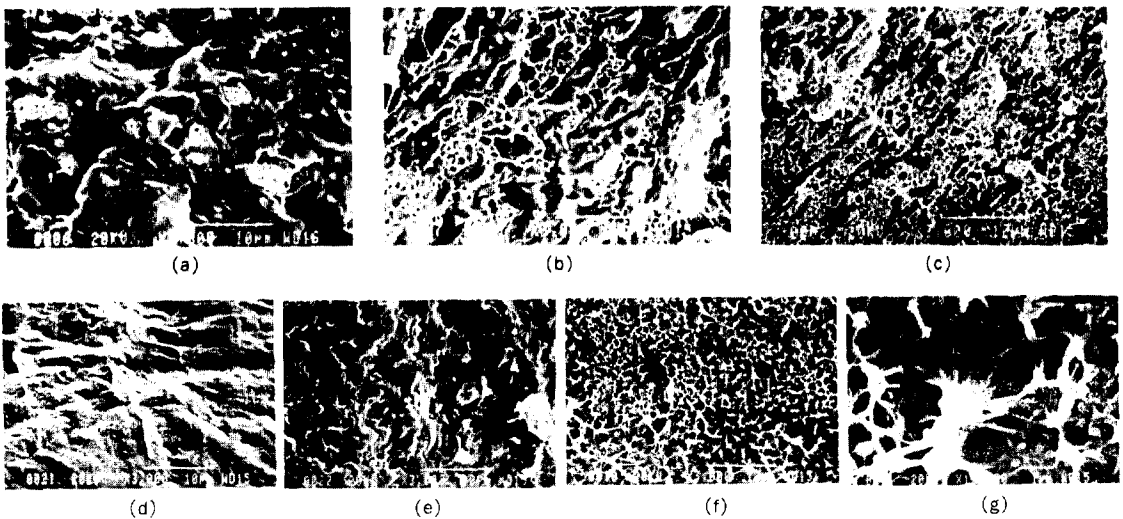

Fig. 9. SEM micrographs of cryogenically fractured surface. a : PE10 / PP90, b : 50 / 50, c : 90 / 10, d : MAH-g-PE10 / MAH-g-PP90, e : 50 / 50, f,g : 90 / 10.

should indicate intensive yielding upon fracture (Fig. 9g). A most striking effect of grafting upon morphological texture is found at MAH-g-PE10 / MAH-g-PP90 blend, i.e., the domain of PE, order of up to 7-8μ in ungrafted blend(Fig. 9a), has almost completely disappeared in grafted blend(Fig. 9d).

With improved compatibility, the viscosity of the mixture should tend to follow the simple additive rule, and highly interlocked morphology should make the mixture more resistance to flow because of the strong interaction between the phases. This may give a plausible explanation to the viscosity-composition relationship mentioned earlier.

CONCLUSIONS

Blends of MAH-g-PE with MAH-g-PP were prepared from melt extrusion, and comparison with ungrafted blends were made with respects to rheological property and morphological texture. The grafted polymer blend followed the simple additive rule of compatible blend whereas the ungrafted one showed a negative deviation at low level of shear stress. Island / sea morphology, appeared for PE10 / PP90 blend, almost completely disappeared from grafted polymer blend at the same composition. An extensive interlocked morphology rather than a simple co-continuous morphology for PE90 / PP10 blend, was unequivo-cally demonstrated for the grafted polymer blend at the same composition. A well-mixed, and interlocked morphology should account for the improved rheological compatibility of the grafted polymer blends.

REFERENCES

1. D. R. Paul and S. Newman, "Polymer Blends", Academic, New York, 1978.
2. W. Wenig, *Angew. Makromol. Chem.*, **74**, 147 (1978).
3. A. J. Lovinger and M. L. Williams, *J. Appl. Polym. Sci.*, **25**, 1703(1980).
4. N. G. Gaylord and M. Mehta, *J. Polym. Sci., Part C*, **20**, 481(1982).
5. N. G. Gaylord and M. K. Mishra, *J. Polym. Sci., Part C*, **21**, 23(1983).
6. C. D. Han, "Rheology in Polymer Processing", Academic, New York, 1976.
7. R. Darby, "Viscoelastic Fluids", Marcel Dekker, New York, 1976.
8. J. E. Mark, A. Eisenberg, W. Graessley, L. Mandelkern, and J. Koenig, Ed., "Physical Properties of Polymers", Amer. Chem. Soc., Washington, D. C., 1984.
9. N. G. Gaylord and S. Maiti, *J. Appl. Polym. Sci.*, **33**, 2549(1987).
10. N. G. Gaylord and R. Mehta, *J. Polym. Sci., Part A*, **26**, 1189(1988).
11. W. Berger, H. W. Kammer, and C. Kummerlowe, *Makromol. Chem. Suppl.*, **8**, 101(1984).
12. S. Wu, *Polym. Eng. Sci.*, **27-5**, 335(1987).
13. C. D. Han, "Multiphase Flow in Polymer Processing", Academic, New York, 1981.
14. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena", Wiley, New York, 1960.
15. H. J. Karam and J. C. Bellinger, *Ind. Eng. Chem. Fundamental*, **7**, 576(1968).
16. R. W. Flumerfelt, *Ind. Eng. Chem. Fundamental*, **11**, 312(1972).
17. S. Torza, R. G. Cox, and S. C. Mason, *J. Colloid Interf. Sci.*, **38**, 395(1972).