

Miscibility Improvement in PP and EPDM Blends via Introducing Specific Interaction

Young-Wook Cho, Jin-Hwan Go*, Won-Ki Lee

Jin-Kook Lee, Won-Jei Cho, Chang-Sik Ha[†]

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

*Department of Polymer Engineering, Chosun University, Kwangju 501-759, Korea

(Received March 22, 2000)

특정상호작용에 의한 폴리프로필렌/EPDM 블렌드의 상용성 향상

조영욱·고진환*·이원기·이진국
조원제·하창식[†]

부산대학교 고분자공학과 *조선대학교 고분자공학과
(2000년 3월 22일 접수)

ABSTRACT: Miscibility improvement between polypropylene(PP) and ethylene-propylene-diene-terpolymer (EPDM) was studied by introducing specific interaction into both polymers. PP was modified by grafting maleic anhydride(MAH) onto backbone, leading to MAH-grafted PP(PP-g-MAH). Sulfonated EPDM ionomer neutralized with bivalent zinc cation(ZnSEPDM) was used as one component. The blends of PP-g-MAH and ZnSEPDM were prepared at 200°C in Brabender Roller Mixer. Fourier transform-infrared(FT-IR) spectroscopic and dynamic mechanical studies have been performed to investigate the miscibility. FT-IR spectral peak corresponding to carbonyl group in PP-g-MAH and that to sulfonate group in ZnSEPDM were shifted to lower and higher frequency with increasing ZnSEPDM content, respectively, in the blends. Glass transition temperature of ZnSEPDM was increased up to 70wt.% of ZnSEPDM, and again decreased above 70wt.%. It can be concluded from the shift of FT-IR characteristic peaks and the changes of glass transition temperatures that the miscibility between PP and EPDM was improved via introducing specific interaction, i.e., dipole-ion interaction.

요약: 폴리프로필렌(PP)과 에틸렌-프로필렌-디엔 고무(EPDM)의 양쪽 성분에 특정 상호 작용기 도입에 의한 상용성 향상효과를 연구하였다. PP는 무수말레인산으로 그래프트시켰고(PP-g-MAH), 다른 한 성분으로는 황산화 EPDM 이오노머(ZnSEPDM)를 사용하였다. 브라벤더 혼합기를 이용하여 200°C에서 블렌딩을 행하였다. 상용성은 FTIR분광기로 분석하였고 또한, 동적기계적 물성으로 분석하였다. FTIR결과 PP-g-MAH의 카보닐기는 단파장 쪽으로 이동하고, ZnSEPDM의 슬폰기는 장파장쪽으로 이동하는 것을 알 수 있었다. ZnSEPDM의 유리전이온도는 그 조성이 70wt.%가

[†]대표저자(e-mail : csha@hyowon.pusan.ac.kr)

지는 증가하다가 70wt.%이상에서 감소하였다. FTIR 스펙트라와 유리전이온도 결과로부터 특정 상호작용, 즉 쌍극자-이온 상호작용에 의해 PP-EPDM사이의 상용성이 증가하는 것을 알 수 있었다.

Keywords : miscibility, specific interaction, polypropylene, ethylene-propylene-diene terpolymer(EPDM), FTIR spectroscopy, glass transition temperature.

I. Introduction

One of the largest classes of polymer blends in use today are the mixtures of polypropylene(PP) and ethylene-propylene-diene-terpolymer(EPDM). Over almost entire composition ranges, useful materials can be obtained.¹⁻³ A toughened polypropylene can be achievable by blending with a small amount of EPDM, whereas thermoplastic elastomer(TPE) can be produced when EPDM is rich. PP/EPDM TPE has a merit of getting good mechanical strength due to the hard phase in blend, while common elastomers should be crosslinked to increase the strength via vulcanizing process, which forces the materials not to be reprocessible. Moreover, low temperature brittleness of PP can be also improved by the incorporation of EPDM.

The immiscibility, although the chemical structure of PP and EPDM is similar, is regarded as a major factor degrading several physical properties. So many researches have been carried out to overcome the immiscibility such as adding a third component as a compatibilizer and modifying backbone of PP and/or EPDM to make interaction sites. The compatibilizers, usually block or graft copolymers, reduce the interfacial tension between the incompatible components, PP and EPDM.^{4,5}

A polar group introduced into polymer chain may affect on the polymer-polymer interaction. The kinds of interaction are donor-acceptor,⁶ dipole-dipole,⁷ ion-ion,⁸ acid-base,⁹ ion-dipole,¹⁰⁻¹¹ together with hydrogen bonding.¹²⁻¹³ PP and/or EPDM can be also modified and so has a group to make specific interaction with each other. It has been already reported much enhanced mechanical properties and finer morphology were observed with incorporating small contents of poly(ethylene-co-methacrylic acid) ionomer, which has ionic cluster giving physical crosslinking under dissociation temperature, into PP/EPDM blends.¹⁴ But in case that only one component is ionomer, it is not easy to enhance miscibility due to ionic aggregation in a scale of several nanometers.¹ The ideal picture to utilize ion-ion interaction fully between ionomers is to make one polymer quarternized ionomer having ammonium group, which interacts with another polymer with anionically modified ionomer. Our previous analyses showed that even the modification of either PP or EPDM by maleic anhydride(MAH) in PP/EPDM blends was not effective for improving the miscibility of blends, in part because the unmodified EPDM or PP as a counterpart component in the blends has almost no functional or reactive group to

interact with MAH-modified PP or EPDM.¹⁵

In the present work, PP was grafted with MAH to make PP-g-MAH, and sulfonated EPDM ionomer(ZnSEPDM) neutralized with bivalent cation, Zn^{++} was used, which possess ionic center to work with another functional group. The blend of PP-g-MAH and sulfonated EPDM(ZnSEPDM) may show more improved miscibility than general PP/EPDM blend because at process temperature the zinc cation dissociated from the cluster of ZnSEPDM will be well distributed into two polymer matrices, and ester anion($-COO^-$) from ring-opened maleic anhydride of PP-g-MAH and sulfone anion($-SO_3^-$) of ZnSEPDM will be coulombically attracted to zinc cation. Finally the ionic bond like $(PP--COO^- Zn^{++} SO_3^{--}EPDM)$ may help the miscibility enhancement between PP and EPDM. Contribution of covalent bond($-CO-OSO_2^-$) between PP-g-MAH and ZnSEPDM should be also counted for improving miscibility. FT-IR spectroscopy was utilized to investigate ion-dipole interaction, and the glass transition behavior, which is good and easy method to check the miscibility of polymer blends, was studied using dynamic mechanical thermal analyzer(DMTA).

II. Experimental

Polypropylene(H430; $M_n=87,000$; $M_w=142,000$) was purchased from Honam Oil Refinery Co.Ltd and used as a backbone polymer to synthesize PP-g-MAH. PP-g-MAH was synthesized as follows: 40g of PP was put into a laboratory intensive internal mixer(Brabender

Roller Mixer-w50H) and melted fully for 5 min, and then 10phr of MAH was subsequently added to the molten PP, and finally 0.1 phr of dicumyl peroxide(DCP) was incorporated and reaction was carried out for 15 min. To characterize synthesized PP-g-MAH, 1g of the product was refluxed in 200 ml hot xylene. The washed solution was titrated with 0.05 N n-butanolic KOH using 1% thymole blue as an indicator in DMF. 1 ml excess KOH solution was added, and deep blue color was back-titrated to the point changed to yellowish color by dropping 0.05 N isopropanolic HCl.¹⁶ The characteristic peaks to confirm grafting MAH to PP were found in a wavenumber of 1863 cm^{-1} and 1786 cm^{-1} , which are assigned as asymmetric and symmetric stretching of carbonyl group in anydride, respectively. (see Fig. 1.) Sulfonated EPDM (ZnSEPDM; TP-301; sulfonation level=30meq; $C_3=45\text{wt.}\%$; ethylene-2-norbornene content=5wt.%) was kindly supplied from EXXON Research Center. The PP-g-MAH/ZnSEPDM blends of several compositions(10/90 to 90/10) were pre-

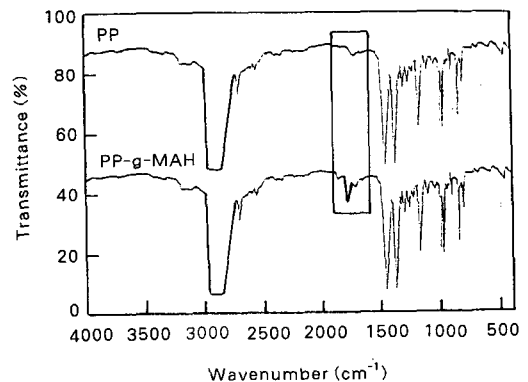


Fig. 1. FT-IR spectra of PP and PP-g-MAH.

pared through melt mixing in a Brabender Roller Mixer under 200°C for 15 min at 60 rpm. FT-IR spectra of PP, PP-g-MAH, and the blend films were obtained using FT-IR spectrometer(Polaris). DMTA(Gabo-Qualimeter 3031) was used to measure glass transition temperature with a heating rate of 3°C/min and a frequency of 1 Hz.

III. Results and Discussion

A number of works of calorimetric, light or neutron scattering, and other experimental techniques have been reported to investigate the miscibility of polymer blends. Particularly, the application of FT-IR spectroscopy to probe the specific intermolecular interactions in polymer blends is currently attracting wide research interest. Recently, our group has used the FT-IR spectroscopy has been used as a tool for elucidation of specific interaction in a miscible polymer blend.¹⁷⁻¹⁹

FT-IR spectra of PP-g-MAH/ZnSEPDM blends with various compositions are shown in Fig. 2. The wavenumber ranged from 1740 cm⁻¹ to 1900 cm⁻¹ is corresponded to asymmetric and symmetric stretching of carbonyl group in PP-g-MAH.

Since carbonyl group in MAH has a positively charged carbon(δ^+) and negatively charged oxygen(δ^-), this group is vulnerable to the attack or interaction of electron-rich anion in sulfonate group. As a result, the carbon in carbonyl group can be abundant of electron, and then the strength of dipole moment in carbonyl group may be weaker

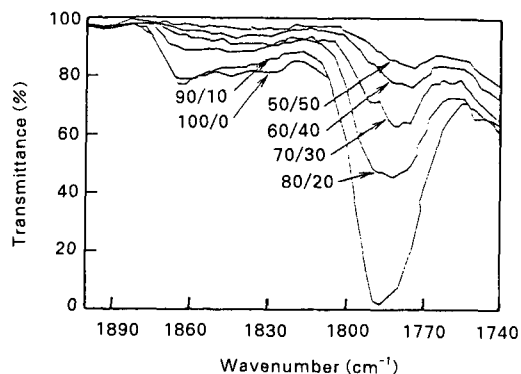


Fig. 2. FT-IR spectra of PP-g-MAH/ZnSEPDM blends around 1750-1850 cm⁻¹.

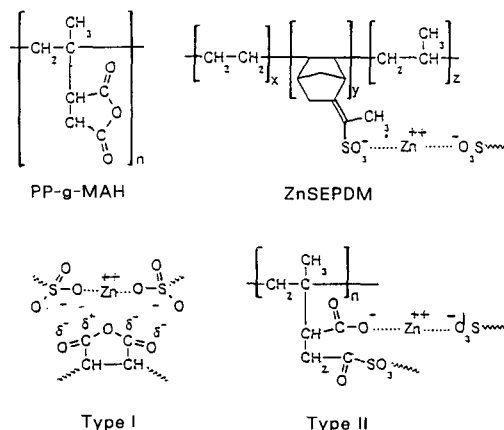


Fig. 3. Chemical structure of PP-g-MAH and ZnSEPDM together with supported mechanism of specific interactions (Type I) and covalent bond (Type II) in PP-g-MAH/ZnSEPDM blends.

than that without any other polar groups. The FT-IR spectra of the blends show that the peak for the carbonyl group shifts to lower wavenumber, meaning low vibrational resonance energy with increasing ZnSEPDM content. From this shift in FT-IR spectra, it is regarded that the above consideration is rational, and a specific interaction is made

between carbonyl group in PP-g-MAH and sulfonate group in ZnSEPDM. The chemical structure of PP-g-MAH and ZnSEPDM, and the supposed mechanism of this interaction is appeared in Fig. 3. It should be noted that there is no further shift of carbonyl group above 50wt.% of ZnSEPDM, indicating that this is a boundary or critical composition affecting to the interaction between carbonyl and sulfonate groups under limit of instrument resolution (Type I in Fig. 3). It is also possible that maleic anhydride is ring-opened, and covalent bond(-CO-OSO₂-) and ionic link(-COO⁻ Zn⁺⁺-) are formed as illustrated in Type II of Fig. 3. This covalent bond and ionic link would play more important roles in enhancing miscibility than the role of dipole-ion interaction.

In Fig. 4, FT-IR spectra for S-O stretching of sulfonate group in PP-g-MAH/ ZnSEPDM blends are shown. It can be easily supposed the sulfonate group is in resonant state between S-O and S=O groups, leading to the delocalization of negative charge. In the blends, the shift of S-O peak to lower wavenumber was observed, and the degree of shift was larger with increasing PP-g-MAH contents, which means an interaction of S-O group with other polar group, i.e., carbonyl group. This shift to lower energy in S-O group has originated from the electron deficiency due to the interaction of positively charged carbon in carbonyl group; although for the spectra for the blends above 50 wt.% of ZnSEPDM, the peak location was similar to that of ZnSEPDM(613.3 cm⁻¹). Conclusively, the critical composition of

ZnSEPDM affecting to the interaction between PP-g-MAH and ZnSEPDM was revealed as 50 wt.%. Additionally, the degree of peak shift was much less in sulfonate group than that in carbonyl group. It is considered that the sulfonate group is more stable than carbonyl group because of the delocalization/resonance electron structure. Table 1 summarizes the peak shifts of carbonyl group and sulfonate group.

Table 1. Characteristic FT-IR Vibration Band of Carbonyl and Sulfonate Groups in PP-g-MAH/ZnSEPDM Blends

PP-g-MAH/ZnS EPDM	Carbonyl Group (cm ⁻¹)	Sulfonate Group (cm ⁻¹)
100/0	1788.9	-
90/10	1788.3	-
80/20	1781.2	604.6
70/30	1779.2	604.7
60/40	1774.4	606.5
50/50	1773.4	607.6
40/60	1772.5	607.6
30/70	1772.5	607.6
20/80	1772.5	613.3
10/90	1772.5	613.3
0/100	-	613.3

Loss tangent ($\tan \delta$) of blends was measured to reveal an interaction between PP-g-MAH and ZnSEPDM. Fig. 5 shows the $\tan \delta$ as a function of temperature in PP-g-MAH/ ZnSEPDM blends. Tgs of both PP-g-MAH and ZnSEPDM were observed to be increased with increasing ZnSEPDM compositions. Even though the increasing Tgs of PP-g-MAH with ZnSEPDM composi-

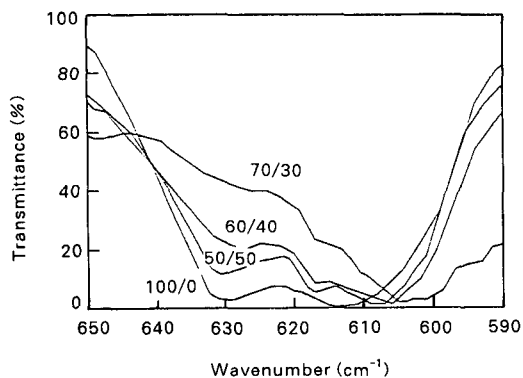


Fig. 4. FT-IR spectra of PP-g-MAH/ZnSEPDM blends around $600\text{--}650\text{cm}^{-1}$.

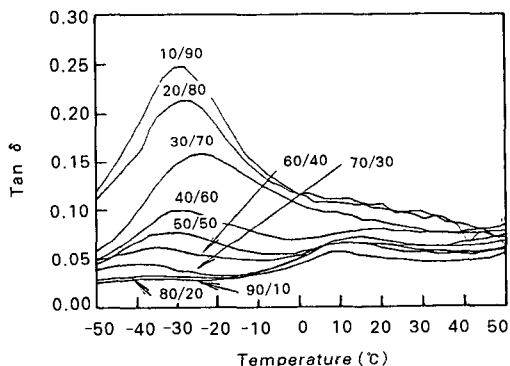


Fig. 5. Loss tangent as a function of temperature for PP-g-MAH/ZnSEPDM blends.

tions up to 60 wt.% seems to be related to the miscibility behavior of the blends, the trend may be due to the increasing amounts of ionic clusters of the ionomer according to the increasing ZnSEPDM compositions. The Tgs of PP-g-MAH were not clearly detected above 70 wt.% of ZnSEPDM compositions.

Tg of ZnSEPDM was moved to higher temperature with increasing ZnSEPDM content up to 70 wt.%, and then decreased above 70 wt.%. The blend having 70 wt.% of

ZnSEPDM showed higher Tg than ZnSEPDM itself by 17.2°C . It can be explained that the increase in Tg of ZnSEPDM up to 70 wt.% is due to dipole-ion interaction, including the effect of covalent bond and ionic link formed. That is, the dipole-ion interaction between PP-g-MAH and ZnSEPDM played significant role in improving their miscibility, resulting in that Tg of ZnSEPDM was shifted toward higher temperature, caused by the interaction of PP-g-MAH of higher Tg.

IV. Conclusions

Introduction of specific interaction into both polymers, polypropylene and ethylene-propylene-diene-terpolymer, was successful to improve their miscibility in the present study. Shift of carbonyl and sulfonate group peaks on FT-IR spectra, toward lower and higher frequency, respectively, although the degree of shift was different, proved an interaction between PP-g-MAH and ZnSEPDM. The composition limit of the peak shift, which can be considered as a critical boundary between excess and necessary amount for participating in the dipole-ion interaction, is around 60 wt.% of ZnSEPDM. This excess ZnSEPDM without interaction should affect on the loss tangent behavior of the blends. As the amount of excess ZnSEPDM increased, Tg of ZnSEPDM was again lowered, and finally the same as that of ZnSEPDM homopolymer. It can be concluded that the miscibility between ZnSEPDM and PP-g-MAH is enhanced by introducing possible specific interaction group into both

polymers. The effect of covalent bond between PP-g-MAH and ZnSEPDM, and ionic link between carboxylic anion and zinc cation, however, should be investigated in more detail.

Acknowledgement

This work is financially supported by the Korea Science and Engineering Foundation (Grant # 931-1100-011-2) and Brain Korea 21 Project.

References

1. P. Galli, S. Danesi, T. Simonazzi, *Polym. Eng. Sci.* **24**, 544 (1984).
2. C. S. Ha, Y. W. Cho, Y. Kim, W. J. Cho, and T. Inoue, *Polym. Eng. Sci.*, to appear.
3. K. B. Anil and H. L. Stephensn, "Handbook of Elastomers-New Developments and Technology", Marcel Dekker, NY (1988).
4. S. Nakahama, T. Inoue, and T. Chiba, "High Performance Polymer Alloys," Maruzen Press, Tokyo (1991).
5. T. Fukui and T. Inoue, *Polymer*, **32**, 2369 (1991).
6. J. M. Rodriguez-Parada and V. J. Percec, *J. Polym. Sci., Part A: Polym. Chem.* **24**, 579 (1986).
7. G. Belorgey and R. E. Prud'homme, *J. Polym. Sci.: Part B: Polym. Phys. Ed.* **20**, 191 (1982).
8. A. Domard and M. Rinaudo, *Macromolecules*, **14**, 620 (1980).
9. Z. L. Zhou and A. Eisenberg, *J. Polym. Sci.: Part B: Polym. Phys. Ed.*, **21**, 595 (1983).
10. M. Hara and A. Eisenberg, *Macromolecules*, **17**, 1335 (1984).
11. A. Eisenberg and M. Hara, *Polym. Eng. Sci.*, **24**, 1306 (1984).
12. M. M. Coleman, D. J. Skrovanek, J. Hu, and P. C. Painter, *Macromolecules*, **21**, 59 (1988).
13. J. Y. Lee, P. C. Painter, and M. M. Coleman, *Macromolecules*, **21**, 954 (1988).
14. Y. Kim, C. S. Ha, T. K. Kang, Y. Kim, W. J. Cho, *J. Appl. Polym. Sci.* **51**, 1453 (1994).
15. H. Whang, M. S. Thesis, Pusan National University, Pusan, Korea (1993).
16. N. G. Gaylord and M. K. Mishra, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 23 (1983).
17. J. H. Ryou, C. S. Ha, and W. J. Cho, *J. Polym. Sci. Polym. Chem.*, **31**, 325 (1993).
18. S. W. Lee, C. S. Ha, and W. J. Cho., *Polymer*, **37**, 15, 3347 (1996).
19. C. S. Ha, M. G. Go, and W. J. Cho, *Polymer*, **38**, 5, 1243 (1997).