

Reactive Compatibilization of Polyketone/Ethylene-Octene Rubber Blends by Diaminodecane

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Abstract: The reactive compatibilization of polyketone (PK) and maleic anhydride (MA)-grafted ethylene-octene rubber (mEOR) blends by addition of 1,10-diaminodecane (DA) was studied. Effects of DA were evaluated through the Fourier transform infrared (FTIR) spectroscopy, melt flow index (MFI), morphology, thermal, and mechanical properties. FTIR spectra indicated that DA reacted with PK and mEOR during melt blending and produced the PK-mEOR inter-polymers at the interface. The addition of DA was found to decrease the MFI value, diminished the size of the dispersed phase, and enhanced its adhesion with PK matrix. For PK/mEOR/DA system, while the tensile properties were changed little, the impact strength was three times those of PK/mEOR blends. SEM observations of the blend morphology indicated that the impact strength of PK/mEOR blend was primarily controlled by the matrix ligament thickness.

Keywords: polyketone, ethylene-octene rubber, blend, compatibilizer, diamine.

Introduction

Polyketone (PK) is an alternating copolymer of carbon monoxide and ethylene, to which a small amount of propylene is added as the third monomer. PK is a semicrystalline engineering plastic with comparable mechanical properties as nylons and polyesters. Properties distinguishing of PK include good chemical and wear resistance, very low permeability, and fast crystallization.¹⁻³ To employ PK in the applications requiring higher impact strength, blending or toughening with other polymer is a natural approach.⁴

PK has been blended with rigid polymers like polyurethane, amorphous polyamide, nylon 6 (PA6), PA6/maleic anhydride (MA) grafted high density polyethylene.⁵⁻⁸ While the incorporation of the rigid polymers into PK resulted in increases in stiffness, it gave no or little increase in impact strength. Various elastomers including copolyester (Hytel[®]), ethylene/methacrylic acid copolymer (Surlyn[®]), and core-shell rubber (CSR) have been incorporated for impact modification of PK.⁹⁻¹² Although there were some increase in impact strength over neat PK, the degrees of increase were not satisfactory in view of toughened polymers. It has been considered that the blends could be further toughened if the interface between PK and rubber had been better.

In the present study, we report the toughening of PK with maleic anhydride (MA)-grafted ethylene-octene rubber (male-

ated EOR, mEOR) as impact modifier and diamine as reactive compatibilizer. Compared with other polyolefin elastomeric copolymers like ethylene-propylene rubbers or ethylene-propylene-diene terpolymers, mEOR has been known to be better miscible to other polymers and of better stiffness/ductility balance due to narrow molecular weight and homogeneous comonomer distribution.^{13,14} However, mEOR was not expected to be compatible enough with PK, a polar polymer, to give the blend of the two good dispersion and interfacial adhesion, which are crucial for effective toughening.¹⁵⁻¹⁷ A method frequently used to improve the compatibility is the incorporation of a third component with appropriate functional groups capable of chemical reaction with the blend components. In the reactive blend system, block or graft copolymer can be formed *in situ* during melt compounding and acts as a surfactant at the interface.^{18,19} An example has been reported for the blend of PK and MA-modified polypropylene (mPP) prepared with polyoxypropylenediamine.²⁰ It was observed that PK-g-mPP copolymer formed by the chemical reaction during the melt blending compatibilized the two polymers, and effectively enhanced the impact strength of PK.

We selected 1,10-diaminodecane (DA) as a reactive compatibilizer for the PK/mEOR blend. It was expected for DA to react with one or both of PK and mEOR resulting in grafting to one polymer or interlinking the two polymers. DA was chosen as it was large enough not to evaporate during the melt blending process and small enough to maximize the number of amine end groups within a given concentration. This work is

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devoted to investigate the compatibilizing effect of DA on the morphology and mechanical properties of PK/mEOR blends.

Experimental

Materials and Preparation. PK terpolymer containing 6 mol% of propylene was kindly supplied by Hyosung. EOR and mEOR were commercial products of DuPont Dow Elastomers with the trade name of Engage 8150 and Fusabond MN493D, respectively. DA was purchased from Tokyo Chemical. The polymers and DA were first vacuum-dried at 60 °C for 24 h, and dry-blended prior to melt blending. All blends were prepared by melt mixing using a co-rotating twin screw extruder (Hankook E. M., STS 32HS) with the temperature profile of 210 to 230 °C from hopper to die at the rotating speed of 200 rpm. The blends extruded using a strand die were water-cooled, pelletized, and dried. The pellets were injection-molded (Engel, Victory 650/150) to specimens for the measurements according to ISO 3167 and ISO 179.

The blends were labelled by their compositions. The letter in a sample code denoted the components (M for mEOR, E for EOR, and D for DA), and the number after a letter the amount of the components in phr. For example, M10-D0.1 referred to a sample of PK blended with 10 phr of mEOR and 0.1 phr of DA.

Characterization and Measurement. The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded using a FTIR spectrometer (Thermo Scientific, Nicolet 6700) equipped with an ATR accessory in the range from 4000 to 650 cm^{-1} . When one or both of the components should be removed from the blends for analysis, hexafluoroisopropanol (HFIP) and hexane were used as the solvents for the PK and mEOR, respectively. The remaining insoluble fraction was centrifuged, filtered, dried, and hot-pressed to film sample for ATR-FTIR. Melt flow index (MFI) was determined using a Tinius Olsen MP600 melt flow indexer according to ASTM D1238-90b. A load of 2.16 kg at 230 °C was employed in the measurement.

Thermal properties including onset crystallization temperature (T_c), melting temperature (T_m), and melting enthalpy (ΔH_m) were determined using a differential scanning calorimeter (DSC, TA Instruments, DSC2920) at heating and cooling rates of 10 °C/min under nitrogen atmosphere. The crystallinity of PK matrix in the blend was calculated from the ratio of the measured melting enthalpy to that of 100% crystalline PK (227 J/g).²¹

The morphological analysis of the blend specimens was carried out using a field emission scanning electron microscope (FE-SEM, JEOL, JSM-6701F). The fracture surface was obtained by breaking the specimen after immersion in liquid nitrogen for 5 min. The size and size distribution of rubber phase were analyzed by using Image Pro Plus 6.2 software.

Young's modulus, tensile strength, and elongation at break were determined during the tensile tests conducted accord-

ing to ISO 527. The tests were carried out at a crosshead speed of 50 mm/min using a universal testing machine (UTM, Lloyds Instruments, LR10K). The notched Charpy impact strength was measured using an impact tester (Tinius Olsen, 92T) in accordance with ISO 179 at 25 °C. Notched specimens were prepared using the Tinius-Olsen Model 899 specimen notcher. Prior to testing, all samples were dried in a vacuum oven at 60 °C for 24 h. All mechanical tests were done in five replicates and the values reported were an average of the five tests.

Results and Discussion

Reactive Compatibilization. To identify the chemical reactions that took place during the reactive melt blending, we investigated the FTIR spectra of PK and the blends, which were shown in Figure 1. The carbonyl stretching of PK appeared at 1691 cm^{-1} , which was rather low compared with that of aliphatic ketones at 1715 cm^{-1} . This has been ascribed to the extensive intra- and intermolecular dipole-dipole interactions between the carbonyl groups in PK.² The spectrum of M20 (PK with 20 phr of mEOR) was identical to that of PK except for the bands at around 2900 cm^{-1} owing to the stretching of methylene groups of mEOR. The carbonyl band did not move upon blending, which indicated that there was no interaction between PK and mEOR. The third spectrum of Figure 1 (for D0.2) was actually for the sample prepared by melt-mixing PK with 0.2 phr of diamine followed by extracting unreacted PK with HFIP. The spectrum exhibited a new characteristic band at around 1657 cm^{-1} due to the stretching vibration of C=N, which was formed by the reaction between the carbonyl group of PK and the amine end group of DA during the melt blending. The same band was observed for the cellulose treated with polyethylenimine.²²

The bottom spectrum was for PK/mEOR/DA after both PK and mEOR that had not reacted with diamine had been removed. This spectrum was similar to that of PK/DA, except for a new absorption band at 1372 cm^{-1} . The band was assigned to the stretching vibration of C-N in imide group, which had been

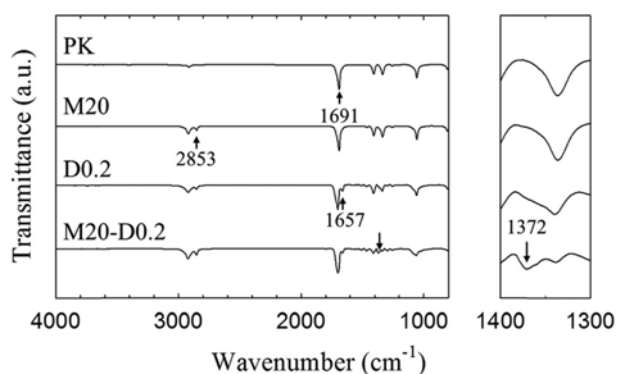


Figure 1. ATR-FTIR spectra of PK, M20, D0.2, and M20-D0.2 blends.

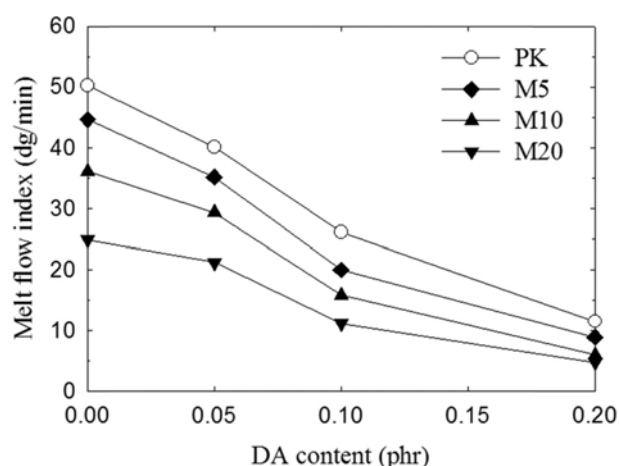


Figure 2. Melt flow index of PK and PK/mEOR blends as a function of DA content.

formed by the reaction of the MA groups of mEOR with the amine end group of DA. Similar results were previously observed in the IR analysis of the preparation of poly(ether imide ester) *via* reaction of pyridine-based ether diamine with trimellitic anhydride.^{23,24} The bottom spectrum showed that both of imine and imide linkages were formed during the melt blending in the extruder. It was then apparent that some PK-mEOR inter-linked polymer molecules were formed, although some other polymers like (lightly) cross-linked PK and mEOR, PK-g-amine, and mEOR-g-amine were also possibly formed.

As the formation of inter-linked and cross-linked polymers should have resulted in the increase in melt viscosity, the MFI was measured. As shown in Figure 2, MFI value of PK/mEOR blends decreased with increasing DA content, which assured the formation of large inter- and cross-linked polymers. It was considered that the interfacial friction caused by the *in situ*-formed copolymers anchoring along the interface also have partially contributed to the observed increase in viscosity of the blends. This effect has often been observed when a strong interfacial interaction between the matrix and the dispersed phase was obtained.²⁵ The reduction in MFI was more drastic for the blends with lower mEOR content. A possible explanation is that more DA could be used for crosslinking of PK, which might be more effective in increasing molecular weight than inter-linking was.

Thermal Properties. Thermal properties characterized by DSC were listed in Table I. The melting temperature (T_m) and crystallinity (X_c) of the PK phase were almost unchanged by the addition of mEOR or DA. The results indicated that the size and amount of PK crystal were not affected by the addition of immiscible second component or by the formation of inter- and cross-linked polymers. It was considered that the crystallization inside the PK phase were not affected by the addition of the small amount of second phase or by the formation of the small amount of linked polymers. In contrast

Table I. Thermal Properties of PK in Blends with Varying Content of mEOR and DA

Code	T_m (°C)	T_c (°C)	X_c (%)
PK	220.9	186.6	32.9
D0.05	221.5	189.3	32.5
D0.1	221.0	189.6	32.2
D0.2	221.3	191.3	32.0
M5	222.0	186.1	34.1
M5-D0.05	221.1	189.8	33.1
M5-D0.1	221.7	190.6	32.8
M5-D0.2	222.0	190.2	32.4
M10	220.6	186.8	33.6
M10-D0.05	221.0	189.9	34.5
M10-D0.1	221.3	190.0	34.2
M10-D0.2	221.2	189.9	32.6
M20	220.9	186.7	32.0
M20-D0.05	220.6	187.3	31.0
M20-D0.1	220.1	187.7	33.5
M20-D0.2	220.8	191.5	32.6

noticeable, if not large, increases in crystallization temperature (T_c) with increasing DA compatibilizer content was observed. It was conjectured that, although an extensive crosslinking of the chain should disturb the crystallization, crosslinking to some extent might ease the crystallization. It has been explained that light crosslinking often could improve the packing of polymer chains into a crystalline structure even at a higher temperature, since they would restrict the unfolding of polymer chains from packed stack to melt pool.²⁶ Such restrictions would make chain packing possible at a higher temperature, and should lead to the increased crystallization temperature. Similar results were reported in case of PP/natural rubber blend.²⁷

Morphology. Phase morphology of the blends was investigated with SEM on the cryofractured surfaces, which were shown in Figure 3. The number (d_n) and weight-average (d_w) particle size of the second phase and its distribution was determined by analyzing the cryofractured surface and listed in Table II. Figure 3(a) and 3(b), which were for E10 and M10, respectively, showed typical morphology of uncompatibilized blends. Both exhibited distinct phase separation with large rubber particles of a few micrometers in diameter. It was also observed that the interface between the two phases were clean and smooth, indicating the lack of interfacial adhesion. The rubber particles of E10 were larger than those of M10, which reflected the fact that EOR was less polar and less compatible to PK than mEOR was. Comparing M5, M10, and M20, particle size increased with increasing content of mEOR, which was a natural result of higher probability of collision for higher

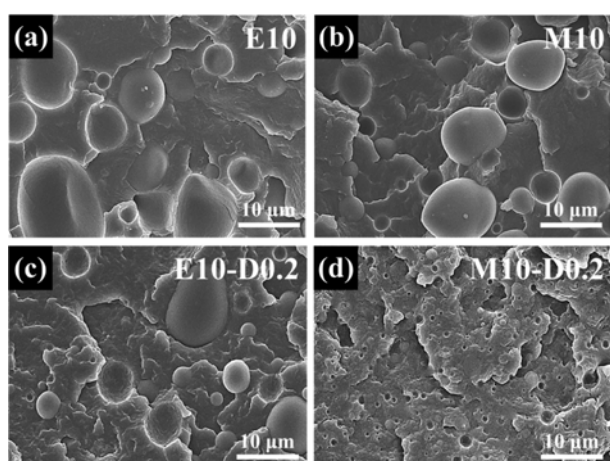


Figure 3. SEM images of the cryofractured surface of (a) E10, (b) M10, (c) E10-D0.2, and (d) M10-D0.2.

Table II. Rubber Particle Size and Its Distribution of the Blends

Code	d_n (μm)	d_w (μm)	d_w/d_n
M5	2.8	3.7	1.3
M5-D0.05	1.0	1.2	1.2
M5-D0.1	0.8	0.9	1.2
M5-D0.2	0.6	0.7	1.1
M10	4.3	5.9	1.4
M10-D0.05	1.2	1.5	1.2
M10-D0.1	0.8	1.0	1.1
M10-D0.2	0.6	0.7	1.1
M20	5.5	7.5	1.4
M20-D0.05	2.2	3.0	1.4
M20-D0.1	1.0	1.3	1.3
M20-D0.2	0.6	0.8	1.2
E10	7.6	10.8	1.4
E10-D0.05	6.1	8.2	1.3
E10-D0.1	5.8	7.8	1.4
E10-D0.2	5.5	7.3	1.3

second phase content.²⁸

As DA was incorporated to the blends, rubber particle size decreased. For PK/EOR blends, however, the degree of reduction was minimal as shown in Figure 3(c) and Table II. The decrease in size appeared not to be due to the reactive compatibilization effect of DA, since EOR did not have functional group to react with amine group of DA. The small decreases in size were instead attributed to the increase in viscosity of PK matrix (Figure 2), which was the result of cross-linking of PK chains by added DA.^{28,29} The reactive compatibilization effect of DA was exhibited evidently in

the PK/mEOR blends. As shown in Figure 3(d) and Table II, particle size of mEOR was decreased with the addition of increasing amount of DA. The results were apparently due to the reactive compatibilization of DA. DA reacted with PK and mEOR to form inter-linked copolymers, which lowered the interfacial tension between the phases and suppressed the coalescence of the second phase. The rubber particles were as small as sub-micron in diameter, which was expected to be effective in rubber toughening.

Mechanical Properties. The three tensile properties, modulus, tensile strength, and elongation at break, of PK and the blends were shown in Figure 4. Young's modulus and tensile

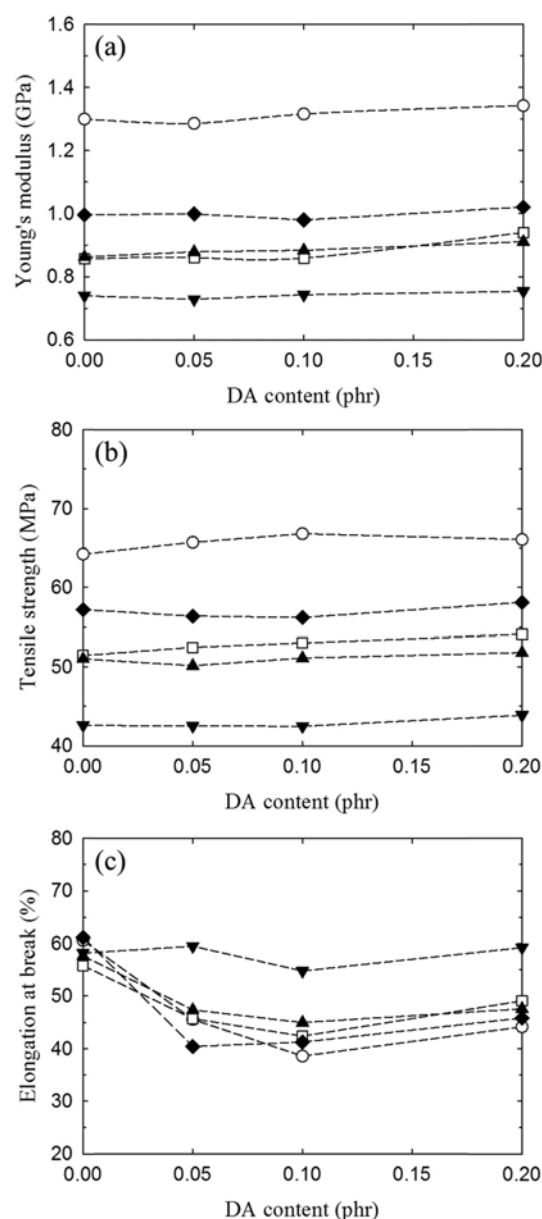


Figure 4. (a) Young's modulus, (b) tensile strength, and (c) elongation at break of PK and its blends as a function of DA content. ○ PK; ◆ M5; ▲ M10; ▼ M20; □ E10.

strength of the PK decreased with increasing EOR or mEOR content. The results were natural considering the incorporation of the elastomeric phases. The addition of DA did not affect the modulus or tensile strength, despite the change in morphology. The results exhibited that these properties were more dependent on the respective properties of the components, and far less on the size of the phases.

Elongation at break (EB), on the other hand, decreased with the addition of DA, as shown in Figure 4(c). Reduction in size of the rubber phases by compatibilization gave rise to the lower EB compared to those of the uncompatibilized blends. The results indicated that EB is more dependent on the area or number of interfaces rather than on the strength of interfacial adhesion. Although the interfacial adhesion had been improved by DA compatibilization, as long as the adhesion were not perfect or strong enough, every interface could be the weak point at large deformation region. The interfacial area rather than interfacial adhesion appeared thus to be more decisive in the deformation region where EB or ultimate strain was measured. Similar results were reported for EOR rubber-toughened PA6.³⁰ This explanation did not, however, quantitatively describe the results. The similar EB of E10 and M10 blends with different particle size and the higher EB of M20 blends with similar particle size could be addressed with this explanation only qualitatively. Another possible explanation for the decrease in EB with the addition of DA was the formation of cross-linked PK chains, as cross-linking might restrict the extension of chains.³¹ The relative contribution of the effect of cross-linking should be small, since the extent of cross-linking would not be that large. The fact that EB was slightly larger with the addition of 0.2 phr of DA than with 0.1 phr made the cross-linking explanation less important, as more cross-linking should have occurred by more DA.

Figure 5 showed the variation of the notched Charpy impact strength (IS) of PK and its blends. It was found that IS of PK did not increase with the addition of EOR or mEOR without

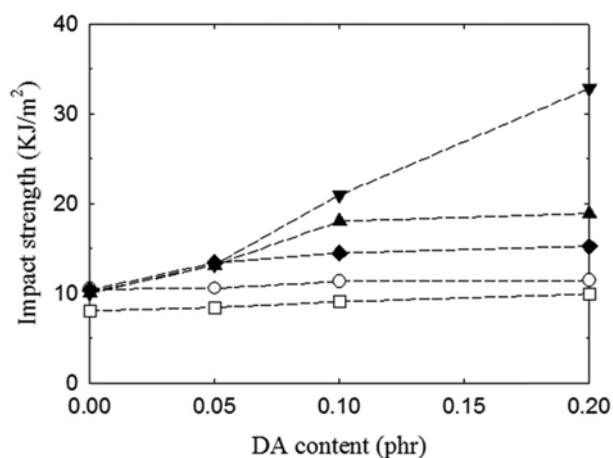


Figure 5. Notched Charpy impact strength of PK and its blends as a function of DA content. ○ PK; ◆ M5; ▲ M10; ▼ M20; □ E10.

compatibilizer. IS of the PK/EOR blends was actually lower than that of PK, even with the addition of DA compatibilizer. The effect of DA reactive compatibilization on IS of PK/mEOR was evident. When 0.2 phr of DA was added to M20, IS of three times higher than that of M20 was obtained, indicating very effective compatibilization and toughening. For M5 and M10, however, the additions of more than 0.05 and 0.1 phr of DA, respectively, were not worthwhile for toughening, as IS did not increase over that amount of DA. It appeared that the amount of compatibilizer should be controlled to that was necessary, since the compatibilizer might exert some adverse effect on the property of the blend.

Although the rubber particle size is a result of interfacial strength between the phases, examining the relation between IS and particle size, the size did not appear to be the sole factor determining IS. For example, IS of the M5, M10, and M20 blends with 0.2 phr of DA all differed, despite the similar particle size of 0.6 micrometer as shown in Table II. Wu suggested a factor governing the toughness of the immiscible polymer blends, the inter-particle distance or ‘matrix ligament thickness.’^{15,16} If the distance between the second phase particles was smaller than the critical value, the ‘critical matrix ligament thickness,’ the matrix could be deformed in a ductile manner to give high IS of the blend. The transition from below to above the critical thickness should be that from plane stress to plane strain condition and from ductile to brittle transition.

In Figure 6, IS of the blends were plotted as a function of inter-particle distance, which was determined from the SEM micrographs. The steep increase in IS below the inter-particle distance of about 0.4 micrometer, which was thought to be the critical matrix ligament thickness of PK. As far as we knew, this was the first time the critical thickness of PK obtained. The thickness of 0.4 micrometer was slightly larger than 0.3 micrometer of nylon 66¹⁶ and smaller than 0.6 micrometer of polyethylene.³² In addition to good interfacial adhesion

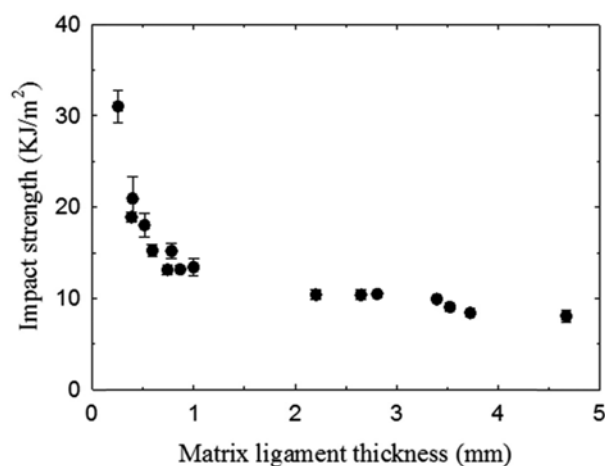


Figure 6. Notched Charpy impact strength of PK/mEOR/DA blends as a function of the matrix ligament thickness.

and small particle size, low inter-particle distance below the critical ligament thickness was achieved by DA compatibilization to give high IS.

Conclusions

PK/mEOR blends were prepared using a DA as the reactive compatibilizer *via* melt-blending. ATR-FTIR spectroscopy indicated that DA was able to react with both PK and mEOR simultaneously at the interface to form the desired PK-mEOR inter-polymer. The formation of inter-polymer and the improved interfacial adhesion were confirmed also by the increase in melt viscosity of the blends. Compared to the PK/mEOR blends, the PK/mEOR/DA blends had smaller particle size with narrower distribution. Modulus and tensile strength of the compatibilized PK/mEOR blends remained the same as those in the corresponding uncompatibilized blends. Elongation at break of the compatibilized blends were lower than the uncompatibilized blends due to the larger interfacial area. Impact strength was enhanced only in the blends where interface modification was carried out using DA. A direct correlation between the impact strength and the inter-particle distance could be established. The critical matrix ligament thickness of PK was established experimentally as 0.4 micrometer. Below this value, a decrease in the matrix ligament thickness resulted in the significantly enhanced impact strength.

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References

- (1) M. A. Del Nobile, G. Mensitieri, and A. Sommazzi, *Polymer*, **36**, 4943 (1995).
- (2) A. Sommazzi and F. Garbassi, *Prog. Polym. Sci.*, **22**, 1547 (1997).
- (3) G. P. Belov and E. V. Novikova, *Russ. Chem. Rev.*, **73**, 267 (2004).
- (4) W. C. J. Zuiderduin, J. Huétink, and R. J. Gaymans, *J. Appl. Polym. Sci.*, **91**, 2558 (2004).
- (5) R. L. Danforth, W. P. Gergen, D. L. Handlin Jr, and R. G. Lutz, US Patent 4,851,482 (1989).
- (6) W. P. Gergen and W. W. Hart, US Patent 4,960,838 (1990).
- (7) A. Asano, M. Nishioka, Y. Takahashi, A. Kato, S. Hikasa, H. Iwabuki, K. Nagata, H. Sato, T. Hasegawa, H. Sawabe, M. Arai, T. Suda, A. Isoda, M. Mukai, D. Ishikawa, and T. Izumi, *Macromolecules*, **42**, 9506 (2009).
- (8) W. P. Gergen, J. M. Machado, D. G. Waters, and R. P. Gingenrich, US Patent 5,043,389 (1991).
- (9) W. P. Gergen, US Patent 4,818,798 (1989).
- (10) W. P. Gergen and R. G. Lutz, US Patent 5,071,916 (1991).
- (11) W. C. J. Zuiderduin, D. Vlasveld, J. Huétink, and R. J. Gaymans, *Polymer*, **46**, 10321 (2005).
- (12) W. C. J. Zuiderduin, D. Vlasveld, J. Huétink, and R. J. Gaymans, *Polymer*, **45**, 3765 (2004).
- (13) S.-L. Bai, G.-T. Wang, J.-M. Hiver, and C. G. Sell, *Polymer*, **45**, 3063 (2004).
- (14) K. Premphet-Sirisinha and S. Chalearmthitipa, *Polym. Eng. Sci.*, **43**, 317 (2003).
- (15) S. Wu, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 699 (1983).
- (16) S. Wu, *Polymer*, **26**, 1855 (1985).
- (17) D. Dompas, G. Groeninckx, M. Isogawa, T. Hasegawa, and M. Kadokura, *Polymer*, **35**, 4760 (1994).
- (18) B. D. Favis, *Can. J. Chem. Eng.*, **69**, 619 (1991).
- (19) T. T. M. Phan, A. J. DeNicola Jr, and L. S. Schadler, *J. Appl. Polym. Sci.*, **68**, 1451 (1998).
- (20) E. Marklund, U. W. Gedde, M. S. Hedenqvist, and G. Wiberg, *Polymer*, **42**, 3153 (2001).
- (21) P. Gupta, J. T. Schulte, J. E. Flood, and J. E. Spruiell, *J. Appl. Polym. Sci.*, **82**, 1794 (2001).
- (22) M. U. de la Orden, M. C. Matias, and J. Martinez Urreaga, *Polym. Degrad. Stab.*, **85**, 697 (2004).
- (23) S. Mehdipour-Ataei and A. Amirshaghghi, *J. Appl. Polym. Sci.*, **96**, 570 (2005).
- (24) K. Faghihi and M. Shabaniyan, *Int. J. Polym. Mater.*, **60**, 505 (2011).
- (25) C. R. Chiang, C. R. Tseng, and F. C. Chang, *J. Polym. Res.*, **4**, 91 (1997).
- (26) A. W. Birley, B. Haworth, and J. Batchelor, in *Physics of Plastics*, Hanser, Munich, 1991, pp 12-13.
- (27) L. K. Yoon, C. H. Choi, and B. K. Kim, *J. Appl. Polym. Sci.*, **56**, 239 (1995).
- (28) U. Sundararaj and C. W. Macosko, *Macromolecules*, **28**, 2647 (1995).
- (29) B. D. Favis and J. P. Chalifoux, *Polymer*, **29**, 1761 (1988).
- (30) J. J. Huang, H. Keskkula, and D. R. Paul, *Polymer*, **47**, 639 (2006).
- (31) C. Han, X. Su, K. Zhang, N. Liu, and L. Dong, *Polym. Int.*, **56**, 593 (2007).
- (32) Z. Bartczak, A. S. Argon, R. E. Cohen, and M. Weinberg, *Polymer*, **40**, 2331 (1999).