

Compatibilizing Effect of Poly(methyl methacrylate-co-maleic anhydride) on the Morphology and Mechanical Properties of Polyketone/Polycarbonate Blends

Ikseong Jeon
Seung Woo Lee
Jae Young Jho*

School of Chemical and Biological Engineering, Seoul National University, Seoul 08826, Korea

Received December 24, 2018 / Revised January 9, 2019 / Accepted January 10, 2019

Abstract: For the purpose of enhancing the impact resistance of polyketone (PK) without lowering the stiffness, PK was blended with polycarbonate (PC). As a compatibilizer for the blend, poly(methyl methacrylate-co-maleic anhydride) [poly(MMA-co-MA)] was synthesized and introduced. The structure and maleic anhydride content of poly(MMA-co-MA) were investigated by spectroscopy analysis and titration method. In the compatibilized blends, it was observed that the particle size decreased with increasing amount of poly(MMA-co-MA) compatibilizer, and that the compatibilizer encapsulated the PC particles. Among the tensile and impact properties examined, elongation at break and impact strength were greatly enhanced by the compatibilization, while modulus and yield strength were not much affected. The amount of compatibilizer and the resulting particle size giving the highest impact strength were different from those for the highest elongation at break. It was observed that there existed an optimum particle size of about 1 μm that caused the maximum crazing to toughen the blend most effectively.

Keywords: impact strength, polyketone, polycarbonate, compatibilizer, particle size.

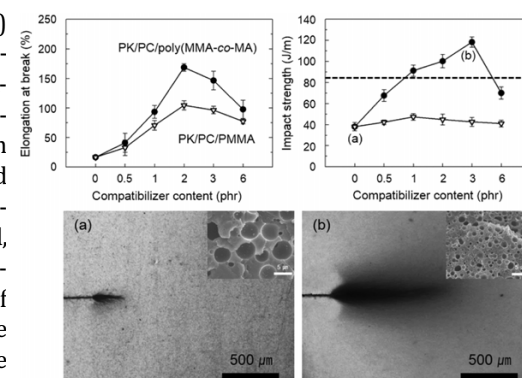
1. Introduction

Aliphatic polyketone (PK) is a thermoplastic polymer composed of carbon monoxide and olefins. As an engineering plastic, PK has mechanical properties comparable to polyamides and polyesters, while the barrier property, chemical resistance, and abrasion resistance are superior to those of the average engineering plastics.¹⁻³ Despite these attractive properties, relatively low impact strength compared to polycarbonate (PC) or poly(acrylonitrile-butadiene-styrene) (ABS) needs to be further enhanced for use in a wide range of applications.

It is well known that the toughness of thermoplastic polymers can be effectively enhanced by blending with rubber. Despite the enhancement in impact strength or toughness, the accompanying drop in stiffness or strength is unavoidable in rubber-toughened thermoplastic polymers. In order to overcome the drawback, the rigid-rigid polymer toughening concept has been introduced and studied steadily. In this concept, the addition of thermoplastic polymers may improve both the modulus and toughness of materials. As examples of rigid-rigid polymer blends, polystyrene (PS)/poly(phenylene oxide) (PPO), polyamide66 (PA66)/PPO, PA66/ABS, and poly(butylene terephthalate) (PBT)/

Acknowledgments: This work was supported by a grant from the Fundamental R&D Program for Technology of World Premier Materials funded by the Ministry of Trade, Industry, and Energy, Republic of Korea. This work was also supported by the Institute of Chemical Processes (ICP) at Seoul National University.

*Corresponding Author: Jae Young Jho (jyjho@snu.ac.kr)



PC have been reported.⁴⁻⁷ The rigid-rigid polymer blends exhibit balanced mechanical properties of stiffness and toughness on the premise of a good miscibility. However, most of the blends except PS/PPO are not miscible and have a low impact strength when blended. Thus, rigid-rigid polymer toughening depends on how effectively the compatibility of the blends can be improved.

In the present study, we report the toughening of PK with PC. PC is an engineering thermoplastic with high stiffness and superb toughness, making it suitable for enhancing the impact strength of PK without a reduction in modulus. However, as PC is not expected to be compatible with PK, their compatibility needs to be improved for effective toughening. A method frequently used for improving compatibility is to add a third component having functional groups capable of chemically reacting with the blend components.^{8,9} In a study on PK/maleic anhydride (MA)-modified polypropylene (mPP) blends compatibilized with polyoxypropylenediamine, the PK-g-mPP copolymer was formed through the chemical reactions. The formation of PK-g-mPP reduced the interfacial tension between PK and mPP.¹⁰

The addition of the compatibilizer changes the state of the dispersed phases by reducing interfacial tension between the blend components. The size of the dispersed phases and interfacial adhesion greatly affects impact resistance of blends.¹¹⁻¹³ As an example, PK blended with MA-grafted ethylene-octene rubber (mEOR) and polyamide6 (PA6) has been reported.¹⁴ The size of the mEOR phase was remarkably reduced due to the chemical reaction between the MA of mEOR and the amine end groups of

PA6 that occurred during melt compounding, which affected the impact strength of the blends. With respect to the particle size, it is known that there are appropriate particle sizes for effective toughening in polymer blends.^{15,16} Therefore, it is necessary to control the particle size to be suitable for toughening by introducing an appropriate compatibilizer.

The compatibilizer we prepared and used for PK/PC blend was poly(methyl methacrylate-*co*-maleic anhydride) [poly(MMA-*co*-MA)]. As PMMA was reported to be partially compatible with the PK¹⁷ and the hydroxyl end groups of PC could react with MA during the melt blending,^{18,19} the copolymer was expected to act as a reactive compatibilizer for PK/PC blends. Through the observation of the morphology and impact-fracture behaviors, the effects of the particle size on the toughness and toughening mechanisms of the blends were investigated.

2. Experimental

2.1. Materials

PK terpolymer containing 6 mol% of propylene was supplied by Hyosung under the trade name of M330A (pellet). The density and melt flow index of PK were 1.24 g/cm³ and 60 g/10 min (240 °C/2.16 kg). PC pellet with a density of 1.20 g/cm³ and a melt flow index of 15 g/10 min (300 °C/1.2 kg) was purchased from Lotte Chemical under the trade name of PC-1150. The polymers mentioned above were used without any purification except for drying at 60 °C for 24 h in a vacuum oven. Methyl methacrylate monomer (MMA, 99%), maleic anhydride (MA, 99%), ethyl acrylate (EA, 99%), and benzoyl peroxide (BPO, 75%) were purchased from Sigma Aldrich. Toluene (99.9%) was obtained from Daejung Chemicals.

2.2. Synthesis and characterization of compatibilizer

Inhibitors of MMA and EA monomers were removed prior to use. MMA (70 g), MA (20 g), and EA (2 mL) were added to 300 mL of toluene in a flask. The EA was added to prevent unzipping depolymerization. Benzoyl peroxide (1 g) was added as an initiator. The polymerization reaction was carried out under nitrogen atmosphere at 80 °C for 18 h with stirring. After the reaction, the mixture was fractionated by precipitation in excess methanol to remove the unreacted monomers. For further purification, the obtained product was added to THF and precipitated in methanol. The final product was obtained after drying in a vacuum oven at 40 °C for 24 h. PMMA was prepared from MMA monomers, following the same procedure described above.

The Fourier transform infrared (FT-IR) spectra of poly(MMA-*co*-MA) was recorded using a FT-IR spectrometer (Thermo Scientific, Nicolet 6700) in the range from 4000 to 650 cm⁻¹. ¹H nuclear magnetic resonance (¹H NMR) spectra was recorded on a Bruker Avance III 400 MHz spectrometer using CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal reference. The titration method was used to determine the MA content of the poly(MMA-*co*-MA). This process involves the reaction of water with MA groups of poly(MMA-*co*-MA). First, poly(MMA-*co*-MA) (1 g) was dissolved in 200 mL of chloroform. Then, 1 mL of water was

added to convert MA to maleic acid by hydrolysis. The solution was maintained at 60 °C for 8 h, with constant stirring. Titration of the maleic acid was carried out using a standardized 0.1 M KOH solution in the presence of phenolphthalein as an acid-base indicator. The number of moles of anhydride groups in poly(MMA-*co*-MA) is equal to half the number of moles neutralized by KOH.

2.3. Fabrication of blends

PK/PC/poly(MMA-*co*-MA) and PK/PC/PMMA blends were prepared with a co-rotating twin screw extruder. (BA-19, Bautek, Korea). The diameter and length-to-diameter ratio of the screw were 19 mm and 40, respectively. The temperature profiles in the extruder were 260-270 °C from hopper to die zone and the screw rotating speed was 200 rpm. The extruded blends were water-cooled, pelletized, and dried at 60 °C.

The blends were coded with letters and numbers. The letter K and C referred to PK and PC, respectively. The composition of the PK/PC was held at 80/20 (wt%). The letter P and PM after hyphen denoted PMMA and poly(MMA-*co*-MA). The number after the letter P or PM denotes the content of the PMMA or poly(MMA-*co*-MA) in phr. For example, KC-PM2 was composed of an 80 wt% of PK, 20 wt% of PC, and 2 phr of poly(MMA-*co*-MA).

2.4. Characterization and testing of blends

Morphology was examined with a field emission scanning electron microscope (SEM, JEOL, JSM-6701F). The fracture surface was obtained by breaking the specimen chilled in liquid nitrogen. The PC and poly(MMA-*co*-MA) phases were etched with chloroform and acetone, respectively, in order to observe the size of the PC particles and the phase morphology.

The specimens for the tensile and impact tests were prepared with an injection-molding machine (Boy 12A, Boy Machines). Young's modulus, yield strength, and elongation at break were determined using a universal testing machine (UTM, LR10K, Lloyds Instruments). The tests were carried out with a crosshead speed of 10 mm/min and specimens of 63.5×3.18×3.2 mm³ in dimension according to the ASTM D-638 Type V method. The notched Izod impact strength was measured using an impact tester (Tinius Olsen Model 92T) in accordance with ASTM D-256 at 25 °C. The Izod impact test specimen has the dimensions of 63.5×12.7×3.2 mm³ with a 2.54 mm notch depth.

To investigate the fracture behaviors, double-notch four-point-bend (DN-4PB) tests were performed using a rectangular bar of 63.5×12.7×3.2 mm³ in dimension with two notches. The specimen was notched by the Tinius Olsen Model 899 specimen notcher, and a sharp crack was further opened by tapping a razor blade which had been chilled in liquid nitrogen. During the DN-4PB test, one crack was broken while the other was sub-critically damaged, providing information on the fracture behaviors of the specimen. For the transmitted light optical microscopy (TOM) investigation, a thin section of about 50 μm thick including the sub-surface damage zone near the crack tip was obtained by polishing. The damage zone was examined using an optical microscope (Leitz Laborlux 12 POL S, Leica).

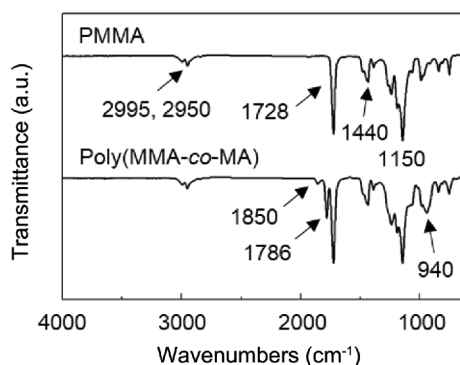


Figure 1. FT-IR spectra of PMMA and poly(MMA-co-MA).

3. Results and discussion

3.1. Structure of poly(MMA-co-MA)

The structures of the synthesized PMMA and poly(MMA-co-MA) were investigated by FT-IR and ^1H NMR spectroscopic analyses. Figure 1 shows the FT-IR spectra of PMMA and poly(MMA-co-MA). In the spectrum of PMMA, the peaks at 2995 and 2950 cm^{-1} were attributed to the stretching of C-H bonds of methyl and methylene groups. Carbonyl stretching appeared at 1728 cm^{-1} . The bending vibration of C-H bonds of the methyl groups and C-O-C stretching vibration appeared at 1440 and 1150 cm^{-1} , respectively.²⁰ The spectrum of poly(MMA-co-MA) was similar to that of PMMA except for the characteristic peaks of MA. The spectrum exhibited the peaks at 1850, 1786, and 940 cm^{-1} due

to the asymmetric, symmetric C=O stretching vibrations of MA, and the ring-stretching vibrations of MA.²¹ Figure 2 shows ^1H NMR spectra of PMMA and poly(MMA-co-MA). In Figure 2(a), peaks for $-\text{CH}_3$, $-\text{CH}_2-$, and $-\text{COOCH}_3$ groups appeared at 1.0, 1.8, and 3.6 ppm, respectively. In the spectrum of poly(MMA-co-MA), a new peak appeared at 2.8 ppm due to the methine ($=\text{CH}-$) groups of MA.^{20,22}

The MA content of poly(MMA-co-MA) was confirmed with titration analysis. In the hydrolysis process for poly(MMA-co-MA), two carboxylic acid groups were formed per MA. Twenty milliliters of KOH (0.1 M) was consumed to the neutralization point, meaning that 9.8 wt% of MA was included in the poly(MMA-co-MA). Based on the FT-IR, ^1H NMR, and titration results, it was concluded that the MMA and MA were successfully copolymerized.

3.2. Morphology

Because the state of the dispersed phases affects the mechanical properties of blends, the particle size and phase morphology of the PK/PC blends were examined. The surfaces of the PK/PC and PK/PC/poly(MMA-co-MA) blends after the PC phases had been extracted are shown in Figure 3. KC exhibited the typical morphology of an immiscible blend. The large and polydispersed spherical PC particles were due to high interfacial tension and between the blend components and coalescence. The addition of poly(MMA-co-MA) led to a noticeable reduction in the size of the PC particles by stabilizing the phases and suppressing aggregation. The size reduction and fine dispersion of PC upon incorporation of poly(MMA-co-MA) was related to the decreased interfacial tension. For the PK/PC/PMMA blends, the particle size did not decrease significantly, indicating that the compatibilizing effect of PMMA was insufficient (Figure S1 and Table S1 in the supporting information).

The particle size and size distribution of the PK/PC and PK/PC/poly(MMA-co-MA) blends are listed in Table 1. The weight average particle diameters (d_w) and the d_w/d_n value of KC were 4.30 μm and 1.34, respectively. When 2 phr of poly(MMA-co-MA)

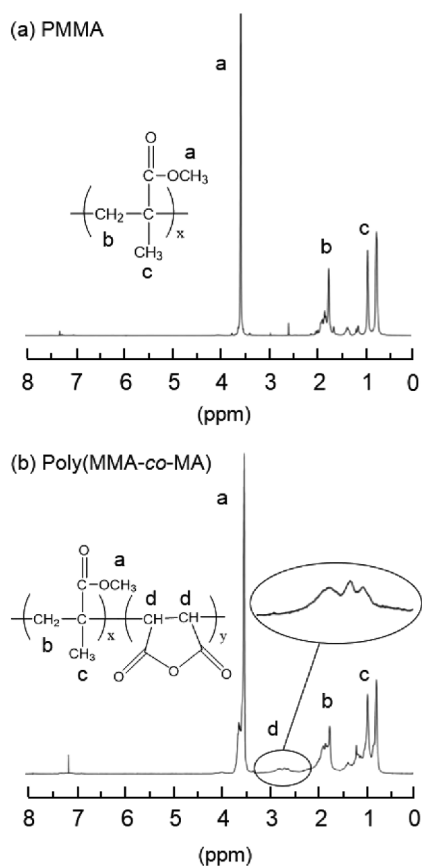


Figure 2. ^1H NMR spectra of (a) PMMA and (b) poly(MMA-co-MA) in CDCl_3 .

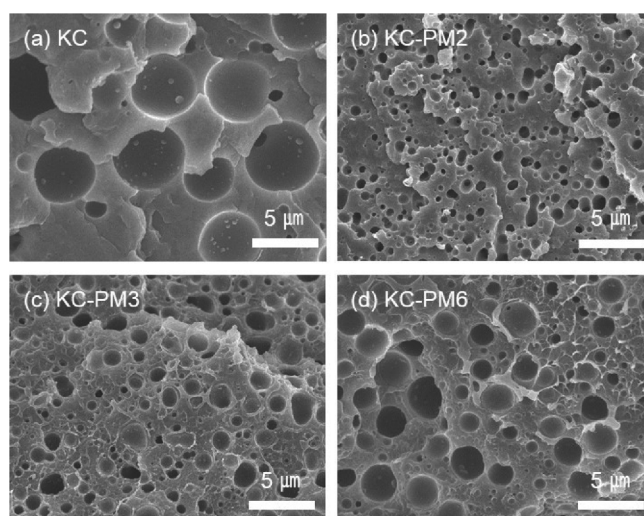


Figure 3. SEM micrographs of the cryofracture surfaces of (a) KC, (b) KC-PM2, (c) KC-PM3, and (d) KC-PM6 after the PC phases were extracted.

Table 1. Particle size and size distribution of the blends

Code	d_n (μm)	d_w (μm)	d_w/d_n
KC	3.22	4.30	1.34
KC-PM2	0.52	0.63	1.21
KC-PM3	0.83	1.02	1.23
KC-PM6	1.61	2.03	1.26

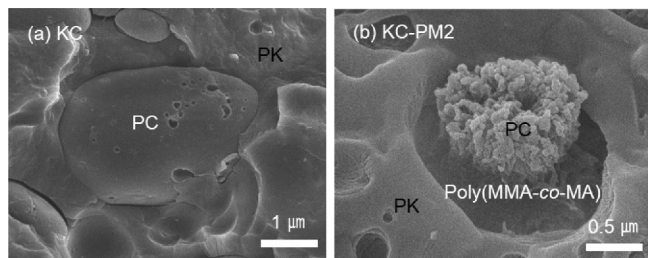


Figure 4. SEM micrographs of the cryofracture surfaces of (a) KC and (b) KC-PM2 after the poly(MMA-co-MA) phases were extracted.

was added, the d_w value was greatly reduced to 0.63 μm and the d_w/d_n value was also decreased. However, when more than 2 phr of poly(MMA-co-MA) was added, the particle size increased again. The d_w of KC-PM3 and KC-PM6 increased to 1.02 and 2.03 μm , respectively. The particle size was dependent not only on the thermodynamics of the interactions between the polymer phases but also on the kinetics of the mixing process. At the same conditions for the shear rate and residence time during melt extrusion, the probability of collision of poly(MMA-co-MA) became greater as its amount was increased. It was considered that the excess poly(MMA-co-MA) forming some aggregated phases made it difficult to function properly as a compatibilizer and

lowered the viscosity of the continuous phase, resulting in an increase in the size of the dispersed phase.²³

Figure 4 shows the phase morphology of KC-PM2. The cryofractured surface of KC-PM2 was observed after the removal of poly(MMA-co-MA). From the observation, it was confirmed that poly(MMA-co-MA) was located at the PK/PC interface and completely encapsulated the PC particle. The phase morphology of KC-PM2 was determined from the balance of the interfacial tensions between the blend components.²⁴⁻²⁶ The interfacial tension between poly(MMA-co-MA) and PK was affected by the interactions between carbonyl groups of the two phases. In addition, the interfacial tension between PC and poly(MMA-co-MA) was reduced by a grafting reaction between MA and PC. The interfacial tension of poly(MMA-co-MA)/PK and interfacial tension of PC/poly(MMA-co-MA), which were lower than that of PC/PK, led to a morphology in which the PC particles were encapsulated by poly(MMA-co-MA).

3.3. Mechanical properties

The results of the tensile and impact tests are summarized in Figure 5. The Young's modulus for both the PK/PC/poly(MMA-co-MA) and PK/PC/PMMA blends was higher than that of PK due to the addition of PC. This reinforcement is an advantage of blending with a rigid polymer. The yield strength of the blends was similar to that of PK. The elongation at break of the blends was lower than that of PK (268%), but it changed significantly with the addition of compatibilizers. As shown in Figure 5(c), the elongation at break of PK/PC/poly(MMA-co-MA) was higher than that of PK/PC/PMMA, which was attributed to the improved interfacial adhesion due to the reactive compatibilization. The

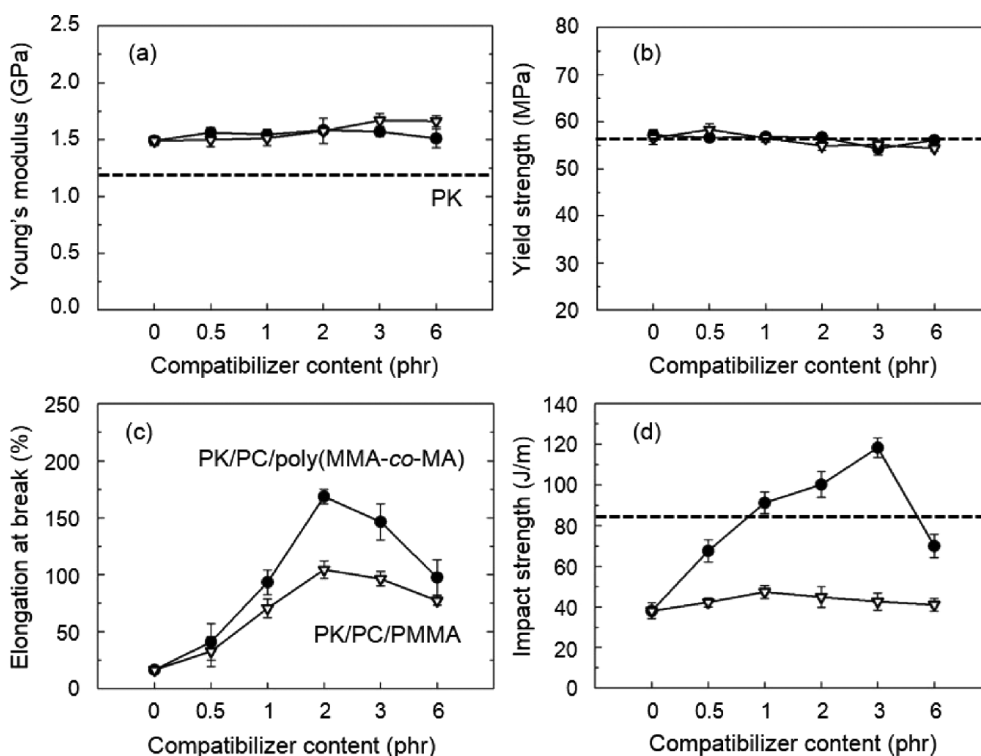


Figure 5. (a) Young's modulus, (b) yield strength, (c) elongation at break, and (d) impact strength of the blends as a function of compatibilizer content: ∇ PK/PC/PMMA, \bullet PK/PC/poly(MMA-co-MA), and (---) PK.

maximum value of elongation at break was achieved in the blend with 2 phr of poly(MMA-*co*-MA), which had the smallest particle size. As excess poly(MMA-*co*-MA) was added, the elongation at break was reduced again, which was accompanied by an increase in the particle size.

The result of the impact test clearly demonstrated the effect of compatibilization. The impact strength of PK/PC/poly(MMA-*co*-MA) was higher than those of PK/PC and PK/PC/PMMA. KC-PM3 showed an impact strength of about 38% higher than that of PK. For the PK/PC/poly(MMA-*co*-MA) blends, the particle size of PC was considered to have a great influence on the impact strength. As confirmed by morphological observations, KC-PM2 was the most compatible and had the smallest diameter of PC particles (d_w of 0.63 μm). However, KC-PM3, whose PC particle diameter (d_w of 1.02 μm) was larger than the minimum value, showed a higher impact strength. This indicated that there was an appropriate particle size to effectively enhance the impact strength.

3.4. Toughening mechanism

In order to investigate the toughening mechanisms of the PK/PC/poly(MMA-*co*-MA) blends, the DN-4PB test was performed. The sub-surface damage zone around the surviving crack tip of the DN-4PB specimen was analyzed by TOM observation. The dark damage zone of the bright-field TOM image was due to the light scattering from the crazes created during the crack-opening process.²⁷ In Figure 6(a), KC showed a small and narrow damage zone around crack tip. The level of crazing in KC was insufficient to relieve the triaxial stress constraint. Large PC particles were easily detached from the PK matrix due to poor interfacial adhesion when an external force was applied. Because of the early detachment, the particles did not function properly as stress concentrators and as a result intense crazing could not be generated.¹⁴ On the other hand, wide and intense damage zones were observed in KC-PM3.

The level of crazing was significantly affected by the particle size. The particles were not able to generate massive crazes

when their size was large, as in KC-PM6, but also when the size was very small such as KC-PM2. It has been previously reported that particle size has an important role in generating crazes.^{28,29} In the isotactic polypropylene (iPP)/Noryl (PPO/PS) blend compatibilized with styrene-ethylene-propylene (SEP), the particle size of iPP/Noryl/2% SEP was 0.8 μm , while the particle size of the blend with 5% SEP was 0.3 μm . Through the TOM investigation of the DN-4PB test specimens, it was confirmed that a high level of crazing was observed in the iPP/Noryl/2% SEP blend but not in the blend with 5% SEP.¹⁶ It is known that the stress concentrated at the interface drops as the distance from the center of the particle increases. As the particle size decreases, the stress drops more rapidly to a level that is not enough to promote crazing.^{29,30} Therefore, very small particles are not effective for crazing. For the PK/PC/poly(MMA-*co*-MA) blends, KC-PM3 with a particle size (d_w) of about 1 μm was more suitable for generating crazing than KC-PM2 with very small particles of less than 1 μm .

4. Conclusions

Poly(MMA-*co*-MA) containing about 10 wt% MA was synthesized by radical polymerization and used as the compatibilizer for PK/PC blends. Comparing the mechanical properties of the blends, elongation at break and impact strength were greatly enhanced by compatibilization, while Young's modulus and yield strength were not much changed. For the compatibilized blends, poly(MMA-*co*-MA) located between the PK matrix and the PC particles played an important role in changing the size of the PC particles. The PK/PC blend with 2 phr of poly(MMA-*co*-MA) had a very small particle size of less than 1 μm and showed the highest elongation at break. The highest impact strength, however, was recorded in the PK/PC blend compatibilized with 3 phr of poly(MMA-*co*-MA), in which the PC particle size was about 1 μm . The largest damage zone by crazing also was observed for the blend with 3 phr of compatibilizer. The results indicated that there is an optimum particle size for effective toughening, which appeared to be 1 μm in the PK/PC blend of the present study.

Supporting information: Information is available regarding the phase morphology and particle size of PK/PC/PMMA blends. The materials are available *via* the Internet at <http://www.springer.com/13233>.

References

- (1) M. A. Del Nobile, G. Mensitieri, L. Nicolais, A. Sommazzi, and F. Garbassi, *J. Appl. Polym. Sci.*, **50**, 1261 (1993).
- (2) A. Sommazzi and F. Garbassi, *Prog. Polym. Sci.*, **22**, 1547 (1997).
- (3) H. Unal, A. Mimaroglu, and T. Arda, *Appl. Surf. Sci.*, **252**, 8139 (2006).
- (4) J. Yang, L. An, and T. Xu, *Polymer*, **42**, 7887 (2001).
- (5) K. Yang, C. Xin, Y. Huang, L. Jiang, and Y. He, *Polym. Eng. Sci.*, **57**, 1090 (2017).
- (6) S. V. Nair, A. Subramaniam, and L. A. Goettler, *J. Mater. Sci.*, **32**, 5347 (1997).
- (7) J. Wu, Y.-W. Mai, and B. Cotterell, *J. Mater. Sci.*, **28**, 3373 (1993).
- (8) S. J. Yoo, S. H. Lee, M. Jeon, H. S. Lee, and W. N. Kim, *Macromol. Res.*, **21**,

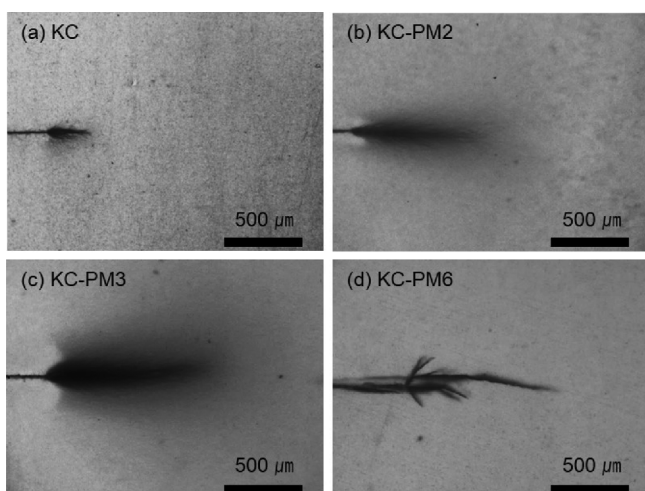


Figure 6. TOM images showing the sub-surface damage zone of the DN-4PB test specimens of the blends: (a) KC, (b) KC-PM2, (c) KC-PM3, and (d) KC-PM6.

- 1182 (2013).
- (9) N. C. Abdul Razak, I. M. Inuwa, A. Hassan, and S. A. Samsudin, *Compos. Interfaces*, **20**, 507 (2013).
- (10) E. Marklund, U. W. Gedde, M. S. Hedenqvist, and G. Wiberg, *Polymer*, **42**, 3153 (2001).
- (11) P. Eskandari, M. M. Mazidi, and M. K. R. Aghjeh, *Macromol. Res.*, **24**, 14 (2016).
- (12) F. Lu, W. J. Cantwell, and H. H. Kausch, *J. Mater. Sci.*, **32**, 3055 (1997).
- (13) S. Horiuchi, N. Matchariyakul, K. Yase, T. Kitano, H. K. Choi, and Y. M. Lee, *Polymer*, **38**, 6317 (1997).
- (14) Y. Kim, J. W. Bae, C. S. Lee, S. H. Kim, H. Jung, and J. Y. Jho, *Macromol. Res.*, **23**, 971 (2015).
- (15) H. Liu, W. Song, F. Chen, L. Guo, and J. Zhang, *Macromolecules*, **44**, 1513 (2011).
- (16) G.-X. Wei, H.-J. Sue, J. Chu, C. Huang, and K. Gong, *Polymer*, **41**, 2947 (2000).
- (17) F. Y. Xu and J. C. W. Chien, *Macromolecules*, **27**, 6589 (1994).
- (18) S. Balakrishnan and N. R. Neelakantan, *Polym. Int.*, **45**, 347 (1998).
- (19) A. Farzadfar, S. N. Khorasani, and S. Khalili, *Polym. Int.*, **63**, 145 (2014).
- (20) W.-W. Yue, T. Xiang, W.-F. Zhao, S.-D. Sun, and C.-S. Zhao, *Sep. Sci. Technol.*, **48**, 1941 (2013).
- (21) D. Becker, E. Hage Jr., and L. A. Pessan, *J. Appl. Polym. Sci.*, **106**, 3248 (2007).
- (22) Y. Huang, X. Y. Ma, G. Z. Liang, and S. H. Wang, *Clay Miner.*, **43**, 405 (2008).
- (23) C. K. Kum, Y.-T. Sung, Y. S. Kim, H. G. Lee, W. N. Kim, H. S. Lee, and H. G. Yoon, *Macromol. Res.*, **15**, 308 (2007).
- (24) H.-M. Chen, X.-F. Wang, D. Liu, Y.-P. Wang, J.-H. Yang, Y. Wang, C.-L. Zhang, and Z.-W. Zhou, *RSC Adv.*, **4**, 40569 (2014).
- (25) S. Horiuchi, N. Matchariyakul, K. Yase, and T. Kitano, *Macromolecules*, **30**, 3664 (1997).
- (26) A. N. Wilkinson, M. L. Clemens, and V. M. Harding, *Polymer*, **45**, 5239 (2004).
- (27) H. J. Sue and A. F. Yee, *J. Mater. Sci.*, **26**, 3449 (1991).
- (28) B. Z. Jang, D. R. Uhlmann, and J. B. Vander Sande, *Polym. Eng. Sci.*, **25**, 643 (1985).
- (29) A. M. Donald and E. J. Kramer, *J. Appl. Polym. Sci.*, **27**, 3729 (1982).
- (30) R. J. Oxborough and P. B. Bowden, *Phil. Mag.*, **30**, 171 (1974).

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.