

# Effect of Octene Content in Poly(ethylene-co-1-octene) on the Properties of Poly(propylene)/Poly(ethylene-co-1-octene) Blends

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Received 8 February 2006; accepted 1 April 2006

DOI 10.1002/app.24644

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Ethylene-octene random copolymer (EOC) is one of the most commonly employed elastomers for PP, and as such its rubber toughening efficiency has been extensively studied. However, most existing studies employ EOC containing an octene comonomer of about 8 mol %. Therefore, in this study, we investigated the effect of EOC octene comonomer content on the morphology and thermal and mechanical properties of PP-ethylene random copolymer (PP-CP)/EOC (80/20 wt %/wt %) blends. It was clearly shown that the properties of the blends are significantly affected by the octene content. The rubber particle size of the blends decreased as the octene content in the EOC was increased, which was a consequence of the reduced interfacial tension between PP-CP and EOC. Impact strength of the blends as a

function of octene content displayed a brittle-ductile transition. The tensile yield strength and modulus of the PP-CP/EOC blends were decreased by addition of EOC, owing to incorporation of the soft EOC into the hard PP-CP. The tensile yield strength and modulus of PP-CP/EOC blends decreased monotonically with the octene content in the EOC. The melting temperature as well as the crystallinity of the PP-CP phase were not affected significantly by the addition of EOC whereas a notable shift in melting and crystallization temperatures was observed for the EOC phase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1133–1139, 2007

**Key words:** blending; compatibility; miscibility; rubber; toughness

## INTRODUCTION

Poly(propylene) (PP) is one of the most versatile commodity polymers. Chemical and moisture resistance, good ductility and stiffness, easy processability, and low cost are a few of its attributes. Although PP has seen widespread application, its limited impact strength, especially at lower temperature due to its relatively high  $T_g$  is an obstacle to broader utilization as an engineering plastic. The impact properties of PP can be considerably improved by incorporation of a rubbery phase. Accordingly, rubber-toughened PP blends with various impact modifiers have been studied, including ethylene-propylene rubber (EPR),<sup>1–3</sup> ethylene-propylene-diene rubber (EPDM),<sup>4,5</sup> and ethylene-propylene-styrene rubber (SEBS).<sup>6–8</sup> Although a variety of elastomers have been studied, EPR and EPDM comprise the majority of commercialized impact modifiers, owing to their low cost. Recently,

impact modification of PP, using metallocene-catalyzed ethylene-octene copolymer (EOC) has attracted attention. EOC provides better efficiency of impact modification than EPR, and is more cost effective than EPDM. Consequently, the conventional EPR and EPDM impact modifiers are currently being substituted with newly developed EOC copolymers.

In rubber-toughened polymers, the morphology (the average size of rubber particles and their size distribution) is a critical factor with respect to the properties of the blends.<sup>9,10</sup> The morphology depends on interfacial interaction, viscosity ratio, shear rate, elasticity of the constituent materials, and processing conditions.<sup>11,12</sup> It is well-known that the interfacial interaction is the most decisive parameter regarding the morphology of the polymer blends. In PP/EOC blends, it is believed that the octene mole percentage changes the number of long side chains [ $-(CH_2)_5CH_3$ ] and the structure of EOC considerably. It may influence the interfacial interaction between PP-CP and EOC phases. In practice, EOC having different octene contents produces PP-CP/EOC blends having different properties. Thus, the effect of octene content in EOC on the properties of PP/EOC blends requires investigation. In spite of EOC's potential importance, however, a systematic study on the effect of octene comonomer content in PP/EOC blends has yet to be reported.

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Contract grant sponsor: RIC/NMR (Regional Innovation Center for New Materials by Recycling), Kongju National University, SBS Foundation; contract grant number: 2005-0187.

*Journal of Applied Polymer Science*, Vol. 103, 1133–1139 (2007)  
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However there have been many studies on PP/EOC blends,<sup>13–26</sup> most of the reported works to date employed EOCs have octene content of about 8 mol %. In the present study, we investigate the effect of octene comonomer content in EOC on the morphology and thermal and mechanical properties in PP/EOC blends. We employ four different EOCs having various octene comonomer content ranging from 4.1 to 12.5 mol %, but the same rheological properties.

## EXPERIMENTAL

### Materials

Four metallocene-catalyzed poly(ethylene-*co*-octene) copolymers (EOCs) were investigated in this study. All EOCs show the same rheological properties but have different octene comonomer content. The PP used is a random copolymer containing ethylene unit of 2.5 wt %. Hereafter, we denote the random PP used in this study as PP-CP. The relevant properties of these resins are tabulated in Table I.

### Sample preparation and characterizations

PP-CP and EOC with a 4/1 ratio in weight were dry blended at 200°C prior to melt blending on a micro compounder developed by our group. The detailed features of the compounder have been reported elsewhere.<sup>29</sup> Blended samples were compression-molded to impact and tensile specimens. Fracture surfaces of the blend were prepared in liquid nitrogen. The fractured surfaces, after etching in xylene at 60°C for 30 s, were platinum-coated. Pure PP-CP was also treated by the same procedure as employed for the blends. This procedure was adopted to ensure that no polymeric component of the PP-CP phase is etched. Phase morphologies were studied with a JEOL JSM-6335F. ImageJ (which is a public domain Java image processing program inspired by NIH Image, <http://rsb.info.nih.gov/nih-image/>) was used to measure the diame-

ter of the EOC domains. About 200 to 300 particles were averaged for each blend.

Tensile properties were tested using a universal mechanical testing machine (Model Hounsfield H25KS) at a crosshead speed of 50 mm/min (ASTM-D638). Notched Izod impact tests were carried out at –20°C according to the ASTM-D256 standard method with specimens 3.2 mm in thickness.

## RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs of PP-CP/EOC blends with various octene comonomer content in EOC. The micrographs clearly show phase-separated structures, reflecting the immiscibility of the blends. To provide a quantitative assessment of number, weight, and volume average sizes of rubber particles were measured using an image analyzer, and the results are shown in Table II. It is observed that the size of rubber particles decreases with increased octene content. In this study, we observed that the rheological properties (storage modulus,  $G'$ , loss modulus  $G''$ , and steady shear viscosity) of all EOCs investigated are nearly identical, regardless of octene content. The rheological properties of all PP-CP/EOC blends are also found to be the same.

It is well-known that the morphology of polymer blends depends on interfacial interaction, viscosity ratio, shear rate, elasticity of the constituent materials, and processing conditions. Because all other properties and processing conditions except the interfacial interaction are the same for all blends, the interfacial interaction is expected to play a key role in the morphological features of the blends investigated in this study.

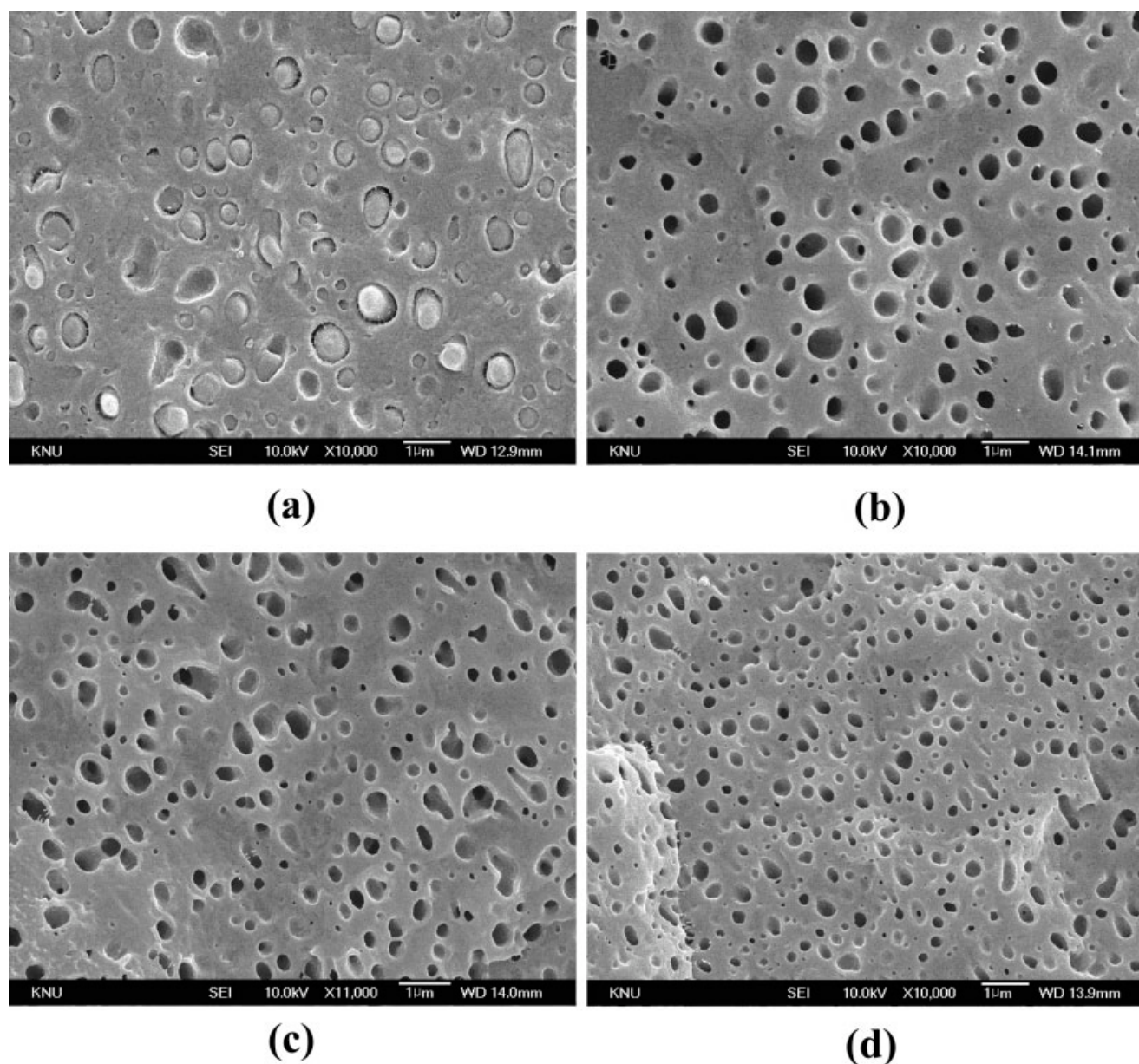
In emulsion models (e.g. Paliarne's model), describing the viscoelastic properties of polymer blends with dispersed morphology, the interfacial energy contribution is represented by the ratio of the interfacial tension and the domain size,  $\sigma/\text{day}$ .<sup>30</sup> Therefore, the interfacial tension, which is a key parameter repre-

TABLE I  
Characteristics of Polymers Used in This Study

Materials	Poly(propylene- <i>co</i> -ethylene)		Poly(ethylene- <i>co</i> -octene)		
	PP-CP	EOC4	EOC7	EOC10	EOC13
Supplier	SK Chemicals	Dow Chemicals	Dow Chemicals	Dow Chemicals	Dow Chemicals
Grade	R900Y	Engage 8480	Engage 8003	Engage 8100	Engage 8842
Octene comonomer content (mol %) <sup>a</sup>	–	4.1	6.8	9.8	12.5
Melt flow index (g/10 min)	0.4	1.0	1.0	1.0	1.0
Density (g/cm <sup>3</sup> )	0.905	0.902	0.885	0.870	0.857
Solubility parameter (MPa <sup>1/2</sup> ) at 166°C <sup>b</sup>	16.4	17.7	17.6	17.4	17.3

<sup>a</sup> Octene comonomer contents were estimated from pellet density according to the relation by Bensason et al.<sup>27</sup>

<sup>b</sup> Solubility parameters were obtained from study by Han et al.<sup>28</sup>



**Figure 1** Scanning electron micrographs of (a) PP-CP/EOC4, (b) PP-CP/EOC7, (c) PP-CP/EOC10, and (d) PP-CP/EOC13.

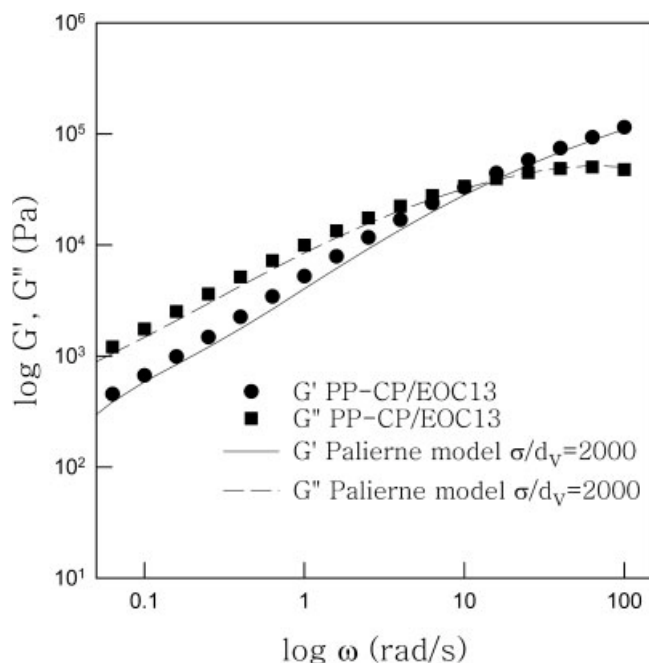
senting the interfacial interaction or compatibility between polymer pairs, is proportional to the reciprocal of the domain size in our blends system, because

the rheological properties of all elastomeric phases (EOCs) are identical and those of all PP-CP/EOC blends are the same. From these interpretations, it is

**TABLE II**  
Average Rubber Particle Size, Matrix Ligament Thickness, and Interfacial Tension Values of the PP-CP/EOC Blends

Blends	Average rubber particle size ( $\mu\text{m}$ )		Matrix ligament thickness ( $\mu\text{m}$ )	Interfacial tension (mN/m)
	$D_n$	$D_v$		
PP-CP/EOC4	0.407	0.579	0.263	2.32
PP-CP/EOC7	0.324	0.462	0.189	1.39
PP-CP/EOC10	0.273	0.399	0.163	1.20
PP-CP/EOC13	0.242	0.350	0.131	0.70





**Figure 2** Palierne model fit for the PP-CP/EOC13 at 200°C.

inferred that the interfacial interaction or the compatibility between PP-CP and EOCs increases as the octene content in EOC increases.

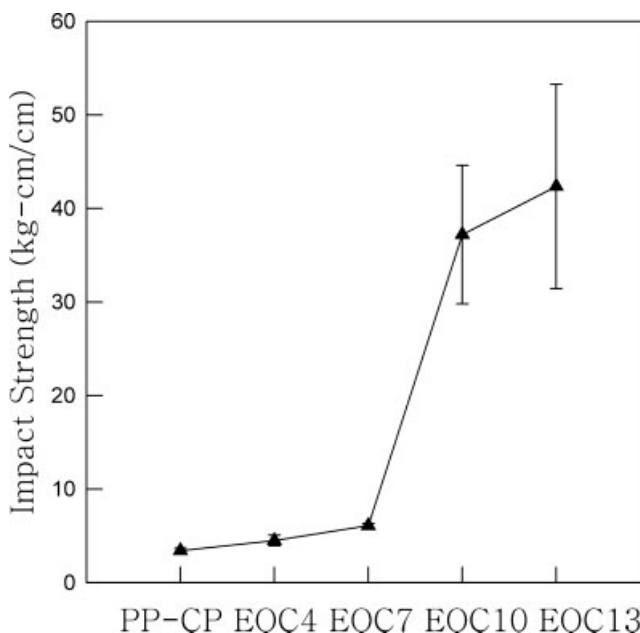
The Palierne emulsion model was used to obtain the interfacial tension values between PP-CP and various EOCs. A representative fit is shown in Figure 2. The resulting values of interfacial tension,  $\sigma$ , for PP-CP/EOC blends at 200°C are summarized in Table II. We first attempted to measure the interfacial tension by the drop retraction method, a direct approach.<sup>31</sup> However, measurement was not possible because the interface between PP-CP and EOCs becomes indiscernible as soon as the PP-CP phase melts. This is not because PP-CP and EOC are miscible, but most likely because the refractive indexes of PP-CP and EOC are the same.

We investigated the appearance of homo-PP/EOC blends at the melt state. The blends are opaque, indicating the homo-PP and EOC have different refractive indexes, whereas the mixture of EOC and PP-CP used in this study is transparent during the melt state. Surprisingly, only a small amount of ethylene unit alters the optical properties of homo PP to a large extent. As expected from the morphological observations, the interfacial tension values between PP-CP and EOC decrease monotonically with the octene content in EOC. The values are in reasonably good agreement with those measured from the direct method by Carriere and Silvis.<sup>24</sup>

It is known that the presence of chain end reduces the interfacial tension.<sup>12</sup> The effect of molecular weight on interfacial tension below the plateau region is interpreted to be due to the increased number of chain end

present at the interface (“known as loose packing theory”). The effect of the side chains can be interpreted by the loose packing theory. As the octene comonomer content increase in EOC, the amount of side chains increases, and consequently the interfacial tension between PP-CP and EOC decreases.

Figure 3 shows the effect of octene content in EOC on the Izod impact strength of PP-CP/EOC blends at  $-20^{\circ}\text{C}$ . The impact strength increases with the addition of EOC. A rapid increase in impact strength of PP-CP/EOC blends was observed when the octene content in EOC is greater than 6.8 mol %. It is well-known that the rubber particle size and dispersion are critical factors for obtaining optimal material performance in rubber-toughened plastics.<sup>9,10</sup> The matrix ligament thickness is also an important factor, having a strong effect on the toughness of rubber-toughened plastics. The matrix ligament thickness was defined by Wu<sup>10</sup> as the surface-to-surface distance between rubber particles in the matrix. The relationship between impact strength and morphology was reported by Wu.<sup>10</sup> He observed that the ligament thickness in the rubber-toughened plastics increases with average rubber particle size at a constant elastomer volume fraction. He also found that the impact strength increases gradually as the rubber particle size decreases, and suddenly jumps to a much higher value at a critical rubber particle size. This critical rubber particle size depends on the volume fraction of the rubber phase. However, in a plot of the impact strength versus matrix ligament thickness, instead of rubber particle size, the sudden jump occurs at a constant matrix ligament thickness regardless of the volume fraction. This sudden jump

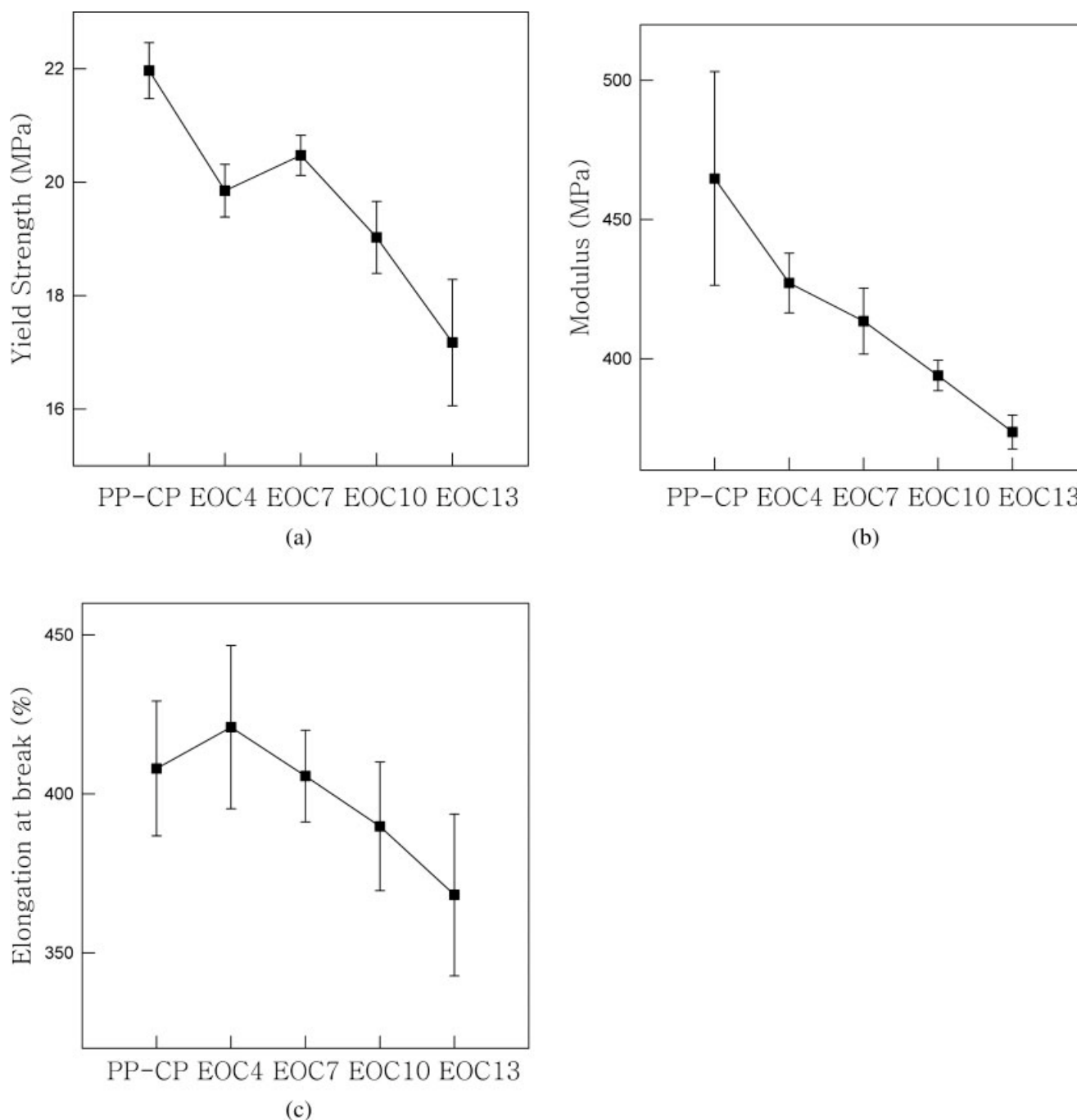


**Figure 3** Izod impact strength of PP-CP/EOC blends.

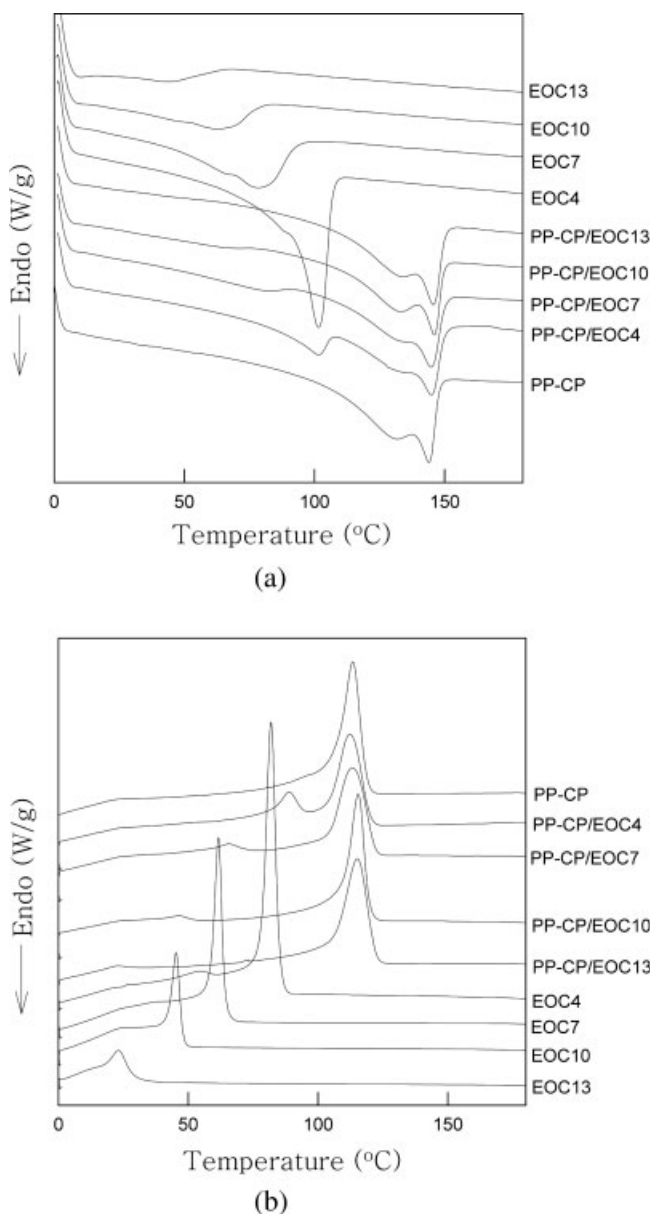
might be due to reinforcing effect at the particular critical point of the system by stabilization of the phase. It is known that this brittle-ductile transition occurs when the interparticle distance is lower than a critical matrix ligament thickness, which is a characteristic parameter of the matrix irrespective of the volume fraction, rubber type, or particle diameter.

Similar phenomena have been reported in PP/EOC blends.<sup>15,26,32</sup> Premphet and Paecharoenchai reported that the critical matrix ligament thickness for PP/EOC blends is between 0.23  $\mu\text{m}$  and 0.32  $\mu\text{m}$  at room tem-

perature.<sup>15</sup> The matrix ligament thicknesses for the PP-CP/EOC in this study are calculated and listed in Table II. The critical matrix ligament thickness of the matrix used in this study is estimated to be between 0.163  $\mu\text{m}$  and 0.189  $\mu\text{m}$ , which is lower than that evaluated by Premphet and Paecharoenchai.<sup>15</sup> This discrepancy is likely a result of the impact test being performed at  $-20^\circ\text{C}$  in this study. The differences in the interfacial interaction values between PP-CP and various EOCs are considered to be responsible for the differences in matrix ligament thicknesses, which are in



**Figure 4** Tensile properties of PP-CP/EOC blends: (a) yield strength, (b) tensile modulus, and (c) elongation at break.



**Figure 5** DSC thermograms of PP-CP/EOC blends: (a) heating scan and (b) cooling scan.

turn a decisive factor for the impact strength of the PP-CP/EOC blends.

Figure 4 shows the effect of octene content in EOC on the tensile properties of PP-CP/EOC blends. All blends show high elongation ( $\gg 350\%$ ). The tensile yield strength and modulus of the PP-CP/EOC blends are lower than those of pure PP-CP, and decrease with octene content. This is simply due to the incorporation of a soft elastomeric phase to the relatively hard PP-CP matrix. Simanke et al. reported that an increase in comonomer content produces soft ethylene ethylene- $\alpha$ -olefin copolymers due to the difficulty of chain crystallization.<sup>33</sup> Several authors attributed this decrease in tensile properties and increase in impact strength to the lowered crystallinity of PP-CP resulting from the addition of EOC.<sup>18,19,22</sup> However, it is observed that the crystallinity of PP-CP is not affected by the presence of EOCs in this study, as will be shown subsequently.

Notably, the elongation-at-break is decreased by the addition of EOC whereas the impact strength is increased. A few studies have reported the elongation at break of PP/EOC blends. Huneault et al. reported that the elongation at break of Talc/PP/EOC blends increases with the amount of EOC<sup>34</sup> whereas Manchado et al. reported that it is decreased by the addition of EOC.<sup>23</sup>

Figure 5 shows DSC heating and cooling curves of the pure components and their blends. Table III summarizes the thermal properties of the blends. DSC heating curves show that neither the melting temperature nor the shape of the melting endotherm of the PP-CP phase is affected by the addition of EOC, suggesting that lamellae thickness is not altered by EOC. The level of crystallinity of the PP-CP in the PP-CP/EOC blends appears to be independent of the octene content in EOC. The small variations in crystallinity are considered to be insignificant. Therefore, it is assessed that the change of mechanical properties by the addition of EOC is not relevant to the level of crystallinity of the PP-CP phase. Even though the melting temper-

**TABLE III**  
Thermal Properties of the PP-CP/EOC Blends

Materials	Melting temperature $T_m$ (°C)		Crystalline peak temperature $T_c$ (°C)		Heat of fusion $\Delta H_m$ (J/g) of PP-CP	Crystallinity, $X_c$ (%), of PP-CP
	$T_{m, PP-CP}$	$T_{m, EOC}$	$T_{c, PP-CP}$	$T_{c, EOC}$		
PP-CP	143.9	–	113.4	–	78.58	37.60
PP-CP/EOC4	144.9	101.8	112.2	89.0	78.91	37.76
PP-CP/EOC7	144.8	78.5	113.2	65.7	77.98	37.11
PP-CP/EOC10	146.0	63.0	115.4	46.6	76.51	36.61
PP-CP/EOC13	145.6	–	115.0	23.3	78.58	37.60
EOC4	–	101.5	–	81.9	–	–
EOC7	–	78.0	–	61.6	–	–
EOC10	–	62.1	–	45.3	–	–
EOC13	–	43.1	–	23.1	–	–

ature of the PP-CP phase remains relatively constant irrespective of the octene content, indicating the absence of any interaction such as cocrystallization within the PP-CP phase, a notable shift in melting and crystallization temperatures is observed for the EOC phase. The observed shift is attributed to nucleation effects caused by the presence of PP-CP crystals during crystallization of the EOC phase. A similar nucleation effect has been reported previously in PP/ethylene-butene copolymer blends.<sup>13</sup>

### CONCLUSIONS

The effect of octene comonomer content in EOC on the morphology and thermal and mechanical properties of PP-CP/EOC (80/20 wt %/wt %) blends was investigated. It was clearly shown that the level of octene content considerably influences the properties of the PP-CP/EOC blends. The rubber particle size of the blends decreases as the octene content in the EOC increases, which is a consequence of the reduced interfacial tension between PP-CP and EOC. The impact strength of the blends as a function of octene content shows a brittle-ductile transition. A rapid increase in impact strength was observed when the octene content in EOC is greater than 6.8 mol %. The tensile yield strength and modulus of the PP-CP/EOC blends were decreased by addition of EOC, owing to the incorporation of the soft EOC into the hard PP-CP. The tensile yield strength and modulus of PP-CP/EOC blends decrease monotonically with the octene content in the EOC. Neither the melting temperature nor the crystallinity of the PP-CP phase is affected by the addition of EOC, whereas a notable shift in melting and crystallization temperatures is observed for the EOC phase in the PP-CP/EOC blend.

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