

# Polypropylene/Metallocene Ethylene–Octene Copolymer Blends with a Bimodal Particle Size Distribution: Mechanical Properties and Their Controlling Factors

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**ABSTRACT:** Blends of polypropylene homopolymer (PP) and metallocene produced ethylene–octene copolymer (EOR) with a bimodal particle size distribution were investigated. The aim of the work was to study the influences of EOR characteristics and its concentration on the tensile and impact properties of the blends. The matrix ligament thickness between rubber particles was measured and compared to those predicted using the theoretical models. The relationships between blend morphology and impact property were reported. It was found that the content of comonomer and molecular weight of the EOR as well as its concentration in the blends were the major factors controlling the tensile and impact properties of the blends. These factors became ineffective to impact property when the ligament thickness of the matrix was larger than the critical value ( $T \sim 0.3\text{--}0.4 \mu\text{m}$ ). To achieve blends of high impact strength, the ligament thickness between rubber particles should be smaller than the critical value, and for a certain ligament thickness, EOR with high octene content and high molecular weight was preferred. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2412–2418, 2002

**Key words:** polypropylene (PP); rubber; mechanical properties

## INTRODUCTION

Polymer blends are important industrial materials. Their properties can be altered to satisfy a wide range of applications. Improving mechanical properties such as toughness is usually the main reason for the development of thermoplastic blends. Mechanical properties of the blends, to a great extent, are controlled by their morphology. For rubber-toughened polymers, the average size of the rubber particles and their size distribution have a major effect on properties of the blends.<sup>1–5</sup> In high-impact polystyrene, a dual rubber particle size distribution is effective for enhanced

toughness.<sup>6</sup> In styrene copolymers, the usefulness of a rubber phase with a bimodal distribution has been reported.<sup>7,8</sup> However, the cases of polypropylene (PP) with a bimodal distribution of rubber particle size have not been extensively reported in the literature.<sup>9</sup>

Apart from morphology, other factors determining the blend properties include blend composition, rheological properties, and physical characteristics of the components such as their melt viscosity, molecular weight (MW), and molecular weight distribution (MWD). Generally, these parameters are interrelated. Study of the effect of each parameter independently is rather difficult. In recent years, the discovery of a new class of catalysts called metallocene made this type of study possible. The most distinguishing characteristic of metallocene-based polymers is that

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**Table I** Material Characteristics

Properties	Materials			
	PP	EOR1	EOR2	EOR3
Grade	P400S	E8150	E8003	E8200
Octene content (% mol) <sup>a</sup>	—	10.9	7.6	10.0
Molecular weight (g/mol) <sup>b</sup>	458,385	213,110	151,139	111,056
Molecular weight distribution	5.9	2.5	2.3	3.0
Density (g/cm <sup>3</sup> )	0.903	0.868	0.885	0.87
Mooney viscosity (ML 1+4 @121°C)	—	35	22	8

<sup>a</sup> determined by <sup>13</sup>C-NMR.

<sup>b</sup> determined by GPC.

they are not restricted by the current immutable property relationships that are commonly affected for Ziegler-Natta catalyst products.<sup>10</sup> Density, MW, and long chain branching can be controlled independently.<sup>10</sup> It is reported that long chain branching has little effect on density of polyethylene copolymer,<sup>11</sup> whereas short chain branching mainly controls the density,<sup>11–14</sup> as the content of short chain branching increases, the density of the copolymers decreases.<sup>11–14</sup>

Blends of polypropylene and metallocene-produced ethylene–octene copolymers (EORs) are the focus of this study. Three grades of EOR were selected to investigate the effects of EOR characteristics including the content of octene comonomer, MW and MWD, and the viscosity ratio between EOR and PP phases, and of the EOR concentrations on the tensile and impact properties of the blends. All blends of this study showed a morphology where a bimodal distribution of EOR particles of approximately 0.1 and 0.3  $\mu\text{m}$  was observed. Details on the blend morphological study have been reported elsewhere.<sup>15</sup>

## EXPERIMENTAL

### Materials

Polypropylene (PP) (grade P400S) was supplied by Thai Polyethylene Co. Ltd., Thailand. Three grades of metallocene-catalyzed ethylene–octene copolymer (EOR) (ENGAGE 8150, ENGAGE 8200, and ENGAGE 8003) supplied by DuPont Dow Elastomer Co. were used. The molecular characteristics of these polymers are shown in Table I.

### Blending and Sample Preparation

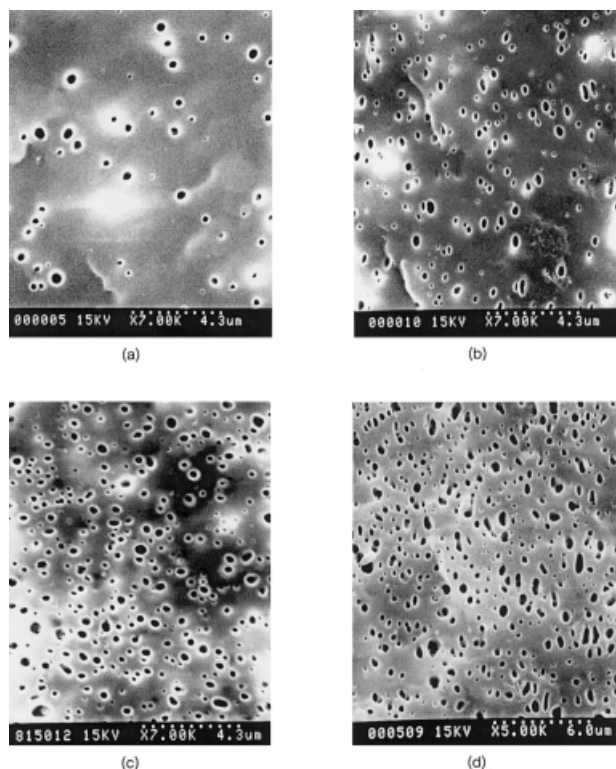
The PP and EOR copolymers were melt-mixed in an intermeshing corotating twin screw extruder (PRISM TSE 16), with a screw diameter of 16 mm. The screws of the extruder were assembled from individual screw elements, including self-wiping screw profile, kneading blocks, and mixing elements for providing good conveying and mixing in the extruder. The temperature profile was controlled at 160, 180, 185, 200, and 200°C from feed to die zones. The screw speed was kept constant at 150 rpm. The concentrations of EOR in the blends were varied in the range of 0–30% vol. All blends were prepared under the same conditions. Test specimens for tensile and impact tests were prepared by injection molding at 200°C.

### Phase Morphology

An Hitachi S2500 scanning electron microscope operating at 15 kV was used to examine the phase morphology of the blends. The samples were cryogenically fractured and etched with heptane vapor for 20 s to remove the EOR phase from the PP matrix. The SEM micrographs were then used for the investigation of the rubber particle size, size distribution, and the surface-to-surface distance between the nearest particles (ligament thickness). The analysis was carried out using a computerized image analyzer with Image-Pro Plus software. Details of specimen preparation and analysis have been reported elsewhere.<sup>15</sup>

### Tensile and Impact Testing

Tensile properties were measured in accordance with ASTM D638-89, using an Instron Model



**Figure 1** Cryogenic fractured and etched surfaces of PP/EOR1 blends. (a) 5, (b) 10, (c) 20, and (d) 30 vol % of EOR.

4301 tensile testing machine with a crosshead speed of 50 mm/min. A load cell of 5 kN was used. Izod impact strength was obtained from notched specimens, using a pneumatic impact tester (Radmana ITR-2000). An impact velocity of 3.4 m/s was used. Fifteen specimens were analyzed for each blend. All mechanical testing was undertaken at 23°C.

## RESULTS AND DISCUSSION

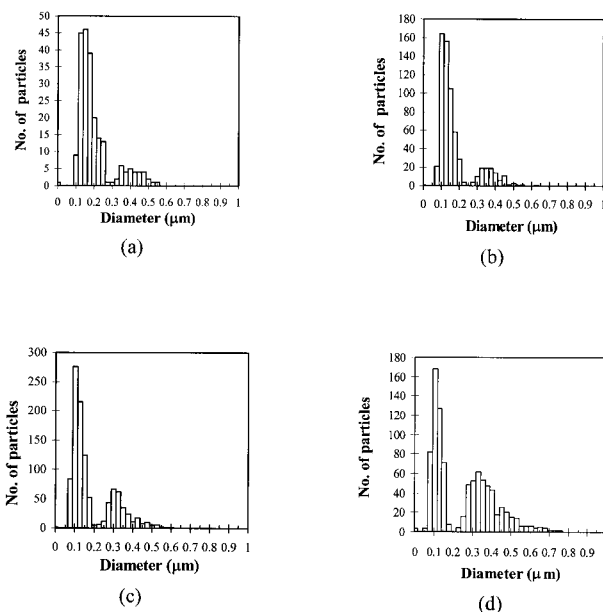
### Morphology of PP/EOR Blends

Qualitative and quantitative analyses of blend morphology were carried out. Details of the investigation and their results are included in ref. 15. Figure 1 shows the morphology of the representative PP/EOR1 blends where a two-phase morphology is clearly seen. EOR droplets are dispersed randomly in the PP matrix. The histograms of Figure 2 show a bimodal distribution of the rubber particle sizes in the PP/EOR1 blends. All compositions show a bimodal distribution of the rubber particle sizes at  $d_1$  of 0.1  $\mu\text{m}$  and  $d_2$  of

0.3  $\mu\text{m}$ . The explanation for the causes of bimodal distribution of rubber particle sizes is unclear at present. Concerning the relationship between the average particle sizes and rubber composition, it was found that, for a given rubber system, the average particle sizes ( $d_n$ ) increased with composition, caused by the presence of populations of larger sizes in the system.<sup>15</sup> However, the majority of the rubber particles still had the same sizes. As seen from Table II, the particle size at the bimodal distribution peaks remained constant at  $d_1$  of 0.1  $\mu\text{m}$  and  $d_2$  of 0.3  $\mu\text{m}$  as the concentration of rubber increased. Varying the EOR used showed no influence on these values. A systematic decrease in the ligament thickness value ( $T$ ) was observed when the rubber concentration increased.

### Tensile Properties of PP/EOR Blends

Figures 3 and 4 show the effects of the concentration of EOR and its characteristics on tensile properties of PP/EOR blends. In this study, all blends exhibited high elongation (>300%). The specimens did not break under the testing conditions. Therefore, the results on elongation and strength at break are not shown here. Figure 3 shows a decrease in modulus as the concentration of EOR increased. This result was simply due to the incorporation of a soft elastomeric phase to



**Figure 2** Histograms of rubber particle sizes in PP/EOR1 blends. (a) 5, (b) 10, (c) 20, and (d) 30 vol % of EOR.

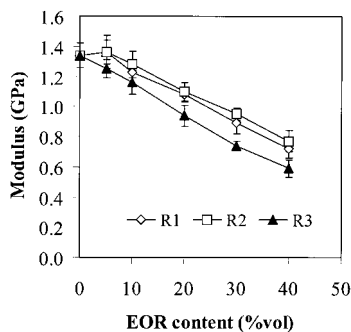
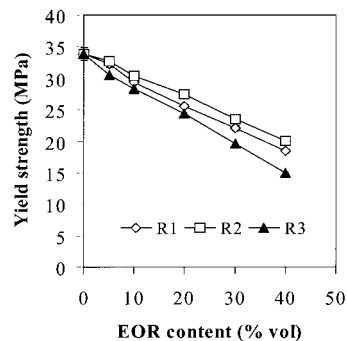
**Table II** Size Range, Frequent Occurring Sizes ( $d_1$ ,  $d_2$ ), Number-Average Rubber Particle Size ( $d_n$ ), Particle Size Distribution ( $d_w/d_n$ ), and Ligament Thickness ( $T$ ) of Various Blends

Blend	Viscosity Ratio ( $\eta_c/\eta_m$ )	% Vol. of Rubber	Size Range ( $\mu\text{m}$ )	Frequent Occurring Size ( $\mu\text{m}$ )		$d_n$ ( $\mu\text{m}$ )	$d_w/d_n$	$T$ ( $\mu\text{m}$ )
				$d_1$	$d_2$			
PP/EOR1	0.9	5	0.10–0.55	0.15	0.33	0.20	1.35	0.60
		10	0.08–0.55	0.10	0.33	0.18	1.33	0.41
		20	0.08–0.60	0.10	0.30	0.19	1.36	0.23
		30	0.08–0.75	0.10	0.33	0.26	1.35	0.15
PP/EOR2	1.0	5	0.08–0.48	0.10	0.33	0.18	1.33	0.50
		10	0.08–0.53	0.10	0.30	0.17	1.29	0.38
		20	0.08–0.70	0.10	0.30	0.25	1.32	0.22
		30	0.08–0.83	0.10	0.30	0.28	1.36	0.16
PP/EOR3	0.5	5	0.08–0.35	0.10	0.30	0.10	1.10	0.48
		10	0.08–0.38	0.10	0.30	0.13	1.23	0.32
		20	0.08–0.57	0.10	0.30	0.19	1.42	0.20
		30	0.08–0.60	0.10	0.30	0.18	1.44	0.13

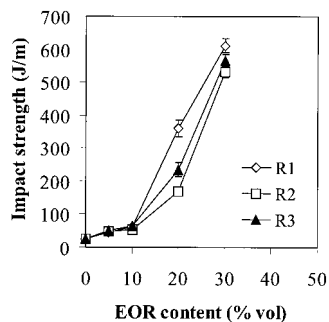
the PP matrix. The same trend was also found for tensile yield strength. In this study, the highest values of modulus and yield strength were observed in the PP/EOR2 system, followed by the PP/EOR1 and PP/EOR3 blends, respectively. The differences in these properties became more pronounced at high rubber loadings. Compared to EOR1 and EOR3, EOR2 has lower comonomer content (7.6% mol). According to Simanke,<sup>16</sup> an increase in the comonomer content generally resulted in difficulty for the chains to crystallise, and as a consequence, tensile yield strength and the resistance to strain (modulus) decreased. In the blends of PP and metallocene based random ethylene/1-butene copolymers (EB), stiffness decreased with increasing 1-butene content, whereas toughness/stiffness synergism was ob-

served at a 1-butene content in EB of 48 wt % (31 mol %).<sup>17</sup>

To study the effects of molecular weight and molecular weight distribution of EOR on tensile properties, a comparison was made between the PP/EOR1 and PP/EOR3 blends. Both EOR1 and EOR3 have a similarity in their octene content (~10 mol %) but EOR1 has relatively high MW and narrow MWD. The tensile results showed that blends of PP and EOR1 gave a higher tensile modulus and yield strength than those containing EOR3. From these results, it can be concluded that the blends of higher modulus and yield strength were obtained by the use of EOR containing low comonomer content, and for a given comonomer content high molecular weight was preferred.

**Figure 3** Effect of EOR content on modulus of various PP/EOR blends.**Figure 4** Effect of EOR content on yield strength of various PP/EOR blends.





**Figure 5** Effect of EOR content on impact strength of various PP/EOR blends.

### Impact Properties of PP/EOR Blends

Figure 5 shows the effect of EOR content on notched Izod impact strength of various PP/EOR blends at room temperature. Under the testing conditions, PP failed in a brittle manner with an impact strength of 26 J/m. An enhancement of impact strength of PP was obtained by the addition of EOR. As the concentration of EOR in the blends increased, the impact strength increased. A sudden jump of impact strength occurred at the rubber concentration of 10 vol %. A sudden change from brittle to ductile behavior or “brittle–ductile transition” has been reported in various polymer blends.<sup>18,19</sup> General observations of brittle–ductile transition for PP occurred when the total content of elastomer was about 20–25%. In the study of Paul and Kale, the transition was observed at the elastomer (Engage 8150) concentration of about 10–15%, instead of 20–25%. It was reported to be due to the fact that the PP used in their work was a copolymer that contained 10% ethylene content.<sup>18</sup> In the present study, the critical concentration of 10% was observed even though the PP used was a homopolymer.

From Figure 5 it can be seen that the curves can be divided into two regions. In the low rubber concentration region (<10%), a slight increase in impact strength was observed. The impact property was independent of the grade of EOR used. A significant difference in impact strength by the use of different grades of EOR was observed in the second region where the concentration of EOR was in the range of 10–30%. The use of EOR1 gave the blends of highest impact strength, followed by EOR3 and EOR2, respectively. In other words, high impact strength was favored by the use of EOR with high octene content and high MW. From these results, it can be concluded that

the elastomer characteristics, such as octene content, MW, and MWD, showed a strong influence on impact property of PP/EOR blends only in the high concentration region (conc. ~10–30%). In the low concentration region, the use of EOR of different characteristics gave similar impact property. Many explanations have been proposed for the brittle–ductile transition mechanisms. Wu demonstrated that the distance between rubber particles or “matrix ligament thickness” is the key parameter for rubber toughening. Regardless of particle size and rubber concentration, the blend is tough if the matrix ligament thickness is kept lower than a critical value.<sup>20, 21</sup> The ligament thickness value of 0.3  $\mu\text{m}$  was reported for polyamide 6,6<sup>21</sup> and 0.6  $\mu\text{m}$  for polyethylene.<sup>22</sup> In the PP blended with EPDM, Wu et al. reported the value of 0.15  $\mu\text{m}$ ,<sup>23</sup> whereas that of 0.8  $\mu\text{m}$  was found for PP/EPR blends.<sup>24</sup> Although the criterion of toughening by Wu is generally accepted, and can be applied to various blend systems, some conflicting results still remain. Van der Waal found that the brittle–ductile transition, as measured by notched Izod impact strength for PP/EPR blends, cannot be described with a ligament thickness parameter. For blends containing 5 and 20% of EPR, data did not fall on one line, and the data of 10% rubber were in between.<sup>1</sup> In blends of PVC and NBR, one brittle–ductile transition master curve was not attained, owing to the effect of rubber particle spatial distribution on impact property. The dependence of toughening efficiency on the spatial distribution was reported to be stronger than on the matrix ligament thickness.<sup>25,26</sup>

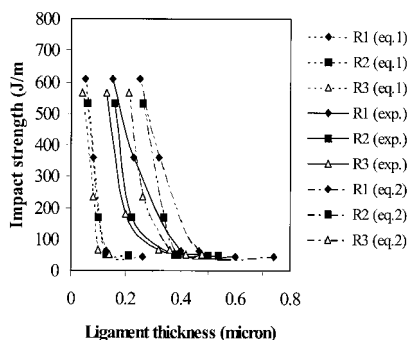
In this study, it was of interest to find out whether the concept of ligament thickness and percolation theory can be applied to the studied PP/EOR blends. The values of matrix ligament thickness between EOR particles ( $T$ ) were obtained from both experimental measurement and theoretical calculations using the equation proposed by Wu<sup>20</sup> and the modified equation by Liu et al.<sup>27</sup> as follows.

$$T = d[(\pi/6\phi)^{1/3} - 1] \quad (1)$$

$$T = d[(\pi/6\phi)^{1/3} \exp(1.5\ln^2\sigma) - \exp(0.5\ln^2\sigma)] \quad (2)$$

where  $d$  is the average rubber particle diameter and  $\phi$  is the rubber volume fraction.

The particle size distribution parameter ( $\sigma$ ) can be calculated from eq. (3).



**Figure 6** The plot of impact strength against matrix ligament thickness for various PP/EOR blends. The experimental data (exp.) were compared to those calculated using the equation proposed by Wu and that by Liu.

$$\ln \sigma = \sqrt{\frac{\sum_{i=1}^N n_i (\ln d_i - \ln d)^2}{\sum_{i=1}^N n_i}} \quad (3)$$

where  $n_i$  is the number of particles with diameter  $d_i$  and  $N$  is the total number of particles. In the case of monodispersity, the value of  $\sigma$  is equal to 1; and when there is polydispersity,  $\sigma$  is greater than 1.

Figure 6 shows the plot of impact strength against the matrix ligament thickness for PP/EOR blends. One brittle–ductile transition master curve cannot be attained. The experimental data (solid lines) were in between those calculated from eqs. (1) and (2). It can be seen that the impact strength decreased sharply with increasing the matrix ligament thickness and then leveled off when the ligament thickness was greater than  $\sim 0.3\text{--}0.4 \mu\text{m}$ . This implies that the critical matrix ligament thickness for the studied PP/EOR blends was about  $0.3\text{--}0.4 \mu\text{m}$ . Above this critical value, the experimental data points fell on one line. This suggested that the characteristics of rubber have no effect on toughening efficiency in that situation, but show a significant role on impact strength improvement as the matrix ligament thickness was smaller than the critical value.

## CONCLUSIONS

Qualitative and quantitative analyses of phase morphology of PP/EOR blends showed a morphol-

ogy where a bimodal distribution of the EOR particle sizes at  $0.1$  and  $0.3 \mu\text{m}$  was observed. The particle size at the bimodal distribution peaks remained constant on changing the type and concentration of EOR in the blends. Increasing the EOR concentration resulted in an increase in the number of EOR particles and, as a consequence, a systematic decrease in the matrix ligament thickness values.

The tensile results showed that blends having high modulus and yield strength were obtained by the use of EOR containing low comonomer content and for a given comonomer content high molecular weight was preferred. Increasing the EOR concentration in the blends led to a drop of tensile properties. Unlike the results of tensile properties, a sudden jump of impact strength was observed at the EOR concentration of 10%. The EOR characteristics such as MW, MWD, and octene content showed a strong influence on impact property only when the concentration of EOR in the blends was higher than 10%. High impact strength was achieved by the use of EOR with high octene content and high molecular weight. By plotting the impact strength against the matrix ligament thickness, one brittle–ductile transition master curve cannot be attained. The critical ligament thickness of approximately  $0.3\text{--}0.4 \mu\text{m}$  was observed for the PP/EOR blends. The impact strength increased dramatically with decreasing the ligament thickness below this critical value. Above this critical value, the characteristics of rubber showed no role on toughening efficiency.

## REFERENCES

1. Van der Waal, A.; Verheul, A. J. J.; Gaymans, R. J. *Polymer* 1999, 40, 6057.
2. Margolina, A.; Wu, S. *Polymer* 1988, 29, 2170.
3. Borggreve, R. J. M.; Gaymans, R. J.; Schuijjer, J.; Ingen Housz, J. F. *Polymer* 1987, 28, 1489.
4. Speri, W. M.; Patrick, G. R. *Polym Eng Sci* 1975, 15, 668.
5. Dao, K. C. *Polymer* 1984, 25, 1527.
6. Hobbs, S. Y. *Polym Eng Sci* 1986, 26, 74.
7. Fowler, M. E.; Keskkula, H.; Paul, D. R. *J Appl Polym Sci* 1988, 35, 1563.
8. Fowler, M. E.; Keskkula, H.; Paul, D. R. *J Appl Polym Sci* 1987, 28, 2145.
9. Jang, B. Z.; Uhlmann, D. R.; Van der Sande, J. B. *Polym Eng Sci* 1985, 25, 643.
10. Gupta, V. K. In *Handbook of Engineering Polymeric Materials*; Cheremisinoff, N. P., Marcel Dekker: New York, 1997, chapt 12.

11. Kim, Y. S.; Chung, C. I.; Lai, S. Y.; Hyun, K. S. *J Appl Polym Sci* 1996, 59, 125.
12. Minick, J.; Moet, A.; Hiltner, A.; Baer, E.; Chum, S. P. *J Appl Polym Sci* 1995, 58, 1371.
13. Bensason, S.; Nazarenko, S.; Chum, S.; Hiltner, A.; Baer, E. *Polymer*, 1997, 38, 3513.
14. Bensason, S.; Nazarenko, S.; Chum, S.; Hiltner, A.; Baer, E. *Polymer*, 1997, 38, 3913.
15. Premphet, K.; Paechareonchai, W. *J Appl Polym Sci* 2001, 82, 2140.
16. Simanke, A. G.; Galland, G. B.; Baumhardt Neto, R.; Quijada, R.; Mauler, R. S. *J Appl Polym Sci* 1999, 74, 1194.
17. Mader, D.; Thomann, Y.; Suhm, J.; Mulhaupt, R. *J Appl Polym Sci* 1999, 74, 838.
18. Paul, S.; Kale, D. D. *J Appl Polym Sci* 2000, 76, 1480.
19. Choudhary, V.; Varma, H. S.; Varma, I. K. *Polymer*, 1991, 32, 2534.
20. Wu, S. *Polymer*, 1985, 26, 1855.
21. Wu, S. *J Appl Polym Sci* 1988, 35, 549.
22. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. *Polymer*, 1999, 40, 2331.
23. Wu, X.; Zhu, X.; Qi, Z. In 8th International Conference on Deformation, Yielding and Fracture of Polymers; The Plastics and Rubber Institute: London, 1991, p. 78/1.
24. Jancar, J.; DiAnselmo, A.; DiBenedetto, A. T.; Kucera, J. *Polymer*, 1993, 34, 1684.
25. Liu, Z. H.; Zhang, X. D.; Zhu, X. G.; Qi, Z. N.; Wang, F. S.; Li, R. K. Y.; Choy, C. L. *Polymer*, 1998, 39, 5027.
26. Liu, Z. H.; Zhang, X. D.; Zhu, X. G.; Qi, Z. N.; Wang, F. S.; Li, R. K. Y.; Choy, C. L. *Polymer*, 1998, 39, 5047.
27. Liu, Z. H.; Zhang, X. D.; Zhu, X. G.; Qi, Z. N.; Wang, F. S. *Polymer*, 1997, 21, 5267.