Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 44 (2003) 5047–5052
polymer
www.elsevier.com/locate/polymer

Brittle–ductile transition of PP/POE blends in both impact and high speed tensile tests

Jinhai Yang*, Yong Zhang, Yinxi Zhang

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Dongchuan Road, Shanghai 200240, People's Republic of China

Received 24 January 2003; received in revised form 13 May 2003; accepted 28 May 2003

Abstract

Polypropylene (PP)/octene-ethylene copolymer (POE) blends were studied in both impact and high speed tensile tests, in which the practical strain rate was 208/s. With the increase of the POE content, brittle–ductile transition (BDT) of PP/POE blends occurred in both the impact and high speed tensile tests. BDT also occurred with the decrease of the tensile speed when any of the PP/POE blends was drawn. The impact deformation of the notched impact samples was analyzed in details. Most of the strain loading of the notched impact samples is taken by the deformation of the narrow region near the notch tip in impact tests. The microunits of the deformation region deform in two methods: high speed tensile deformation and shear deformation because of the tensile speed gradients in the deformation region. At the beginning of impact tests, the strain rate at the notch tip reaches almost 6000/s. In rubber toughened plastics, the shear deformation decreases greatly because of the rubber particle cavitation. Thus, the impact deformation is really a high speed tensile deformation at the narrow region near notch tips. The BDTs in both impact and high speed tensile tests share the same mechanism. The notch sensitivity of plastics is essentially the tensile speed sensitivity of plastics.

Keywords: Polypropylene; Octene-ethylene copolymer; Brittle–ductile transition; Toughening

1. Introduction

The toughening of polymers has been studied for more than half a century. Since large numbers of thermosetting and thermoplastic polymers have been toughened by rubbers, rigid thermoplastic particles, inorganic particles, and even the microvoids, a great amount of experimental data are available to reveal the toughening mechanism. Many reasonable explanations of the toughening of polymers, such as crazing, shear yielding and critical inter-particle distance, have been put forward [1,12].

Many toughening researches are focused on toughening polypropylene (PP) and polyamide (PA) by rubbers. Brittle–ductile transition (BDT) is usual phenomena in impact tests of PP and PA. Three factors were reported to lead to the BDT: inter-particle distance [2–6]; temperature [5,7,8]; strain rate [9–11]. In rubber toughened semi-crystal polymers, BDT occurs when the inter-particle distance is below to a critical matrix ligament thickness, which is a characteristic parameter of the matrix independent on rubber types and particle diameters (shown as curve 2 in Fig. 1). Semi-crystal polymers have also a BDT temperature, above which BDT occurs (shown as curve 1 in Fig. 1). With the decrease of rubber content, the BDT temperatures move to high temperatures. In other words, with the increase of the test temperature, the critical matrix ligament thickness increases (shown in Fig. 2). Semi-crystal polymers have also a BDT strain rate, below which BDT occurs (shown as curve 2 in Fig. 1). With the increase of rubber content, the BDT strain rates move to high values. In other words, with the increase of strain rates, the critical matrix ligament thickness decreases (shown in Fig. 2).

Based on the micromechanical deformation of plastic materials in impact process, several toughening mechanisms were drawn: matrix crazing, shear yielding, crazing and shear yielding [12]. In rubber toughened semi-crystal polymers such as PP and PA, shear yielding of the matrix is the main methods to absorb the impact energy. Newman and Strella [13] first proposed that shear yielding of the matrix was responsible for rubber toughening. To explain how the rubber particles promote the extensive shear yielding of the

* Corresponding author. Tel.: +86-2154742671; fax: +86-2154741297.
E-mail address: jhyang@sjtu.edu.cn (J. Yang).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00438-5

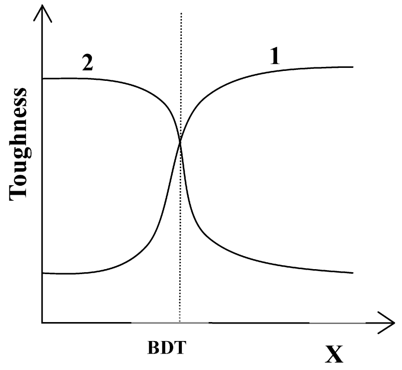


Fig. 1. Three factors lead to the brittle–ductile transition. Curve 1: toughness–temperature; curve 2: toughness–inter-particle distance or toughness–strain rate.

matrix is the key to understand the shear yielding mechanism. Bucknall [14], Donald [15], Heckmann [16], Borggreve and Gaymans [17], Yee and Pearson [18,19], Sue [20,21] shared the statement that the cavitation of rubber particles led to the extensive shear yielding of the matrix. After cavitation of rubber particles, the buildup of hydrostatic stress is relieved, and the triaxial stress conditions in the matrix is transformed to the plane stress conditions, which leads the shear yielding of the matrix to occur more readily. Wu and Margolina [22] drew a percolation model to explain the BDT phenomena in rubber toughened Nylon. They proposed that BDT occurs when the yielding process propagates through thin matrix ligaments in which a plane-strain to plane-stress transition takes place. Recently, Muratoglu et al. [23,24] proposed a new morphological explanation to the BDT. In rubber/Nylon 6 blends, specific crystalline lamellae of Nylon, in which the low energy hydrogen-bonded crystallographic planes (001) are parallel to the rubber particle surfaces, are arranged perpendicular to the surfaces of the rubber particles. Such oriented crystalline lamellae extended approximately 0.15 μm away from the rubber particle surfaces. This oriented lamellae show lower shear resistance than the randomly oriented crystallites [25]. When the inter-particle distance is below 0.3 μm, the critical matrix ligament thickness of Nylon 6, the oriented lamellae percolate throughout the matrix, which decreases the shear resistance of the matrix greatly and leads to the BDT.

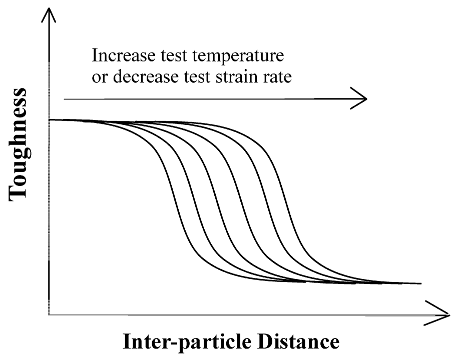


Fig. 2. Effect of temperature and strain rate on critical matrix ligament thickness.

Though a large amount of papers have been published about the BDT in impact tests, the BDT in tensile tests was seldom reported. In this paper, the BDT of PP/POE blends in both impact and tensile tests is studied. The micromechanical deformation of the notched impact samples was analyzed in details. The analysis showed that the deformation of PP/POE blends in notch impact tests is really a high speed tensile deformation at the narrow region near the notch tip. The BDT of the PP/POE blends in impact tests shares the same mechanism with that in high speed tensile tests.

2. Experimental

2.1. Materials and sample preparation

PP Y2600 (Beijing Yanshan Petrochemical Co. Ltd., China), melt flow ratio 10 g/10 min (ASTM D1238), was used as the matrix polymer. POE 8210 (Du Pont Dow Elastermers Co. Ltd., USA) was used to toughen PP.

The PP/POE blends were extruded using a twin-screw extruder at a screw speed of 215 rpm. The temperature profiles of the barrel were 150–180–180–180–180–190 °C from hopper to the die. The extrudate was pelletized, dried in a vacuum oven for 4 h at 80 °C, and injection molded into standard samples. The barrel temperature profiles of the injection molding were 190–210–210–220 °C, and the mold temperature was room temperature.

2.2. Impact tests

Notched Izod impact tests were performed using a RAY-RAN impact tester following ASTM D256, and the sample size was $3.2 \times 12.7 \times 63.5\ mm^3$. The depth of the notch is 2.7 mm and the radius of the notch tip is 0.25 mm. All the tests were performed at 23 °C.

2.3. High-speed tensile test

The tensile samples were injection molded using the PP/POE blends. The size of the narrow section of the sample was $50 \times 4 \times 2\ mm^3$. A two-edge notch was cut in the narrow section. Fig. 3 shows the sketch of the tensile sample. The width between the notches is 2 mm, and the width of the notch is 0.04 mm. In tensile tests of the samples, the deformation occurs in the notched region. The

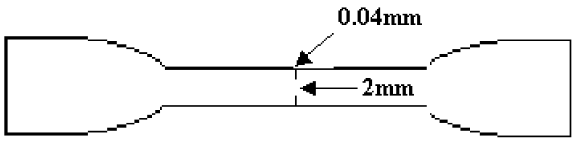


Fig. 3. Sketch of the high-speed tensile sample.

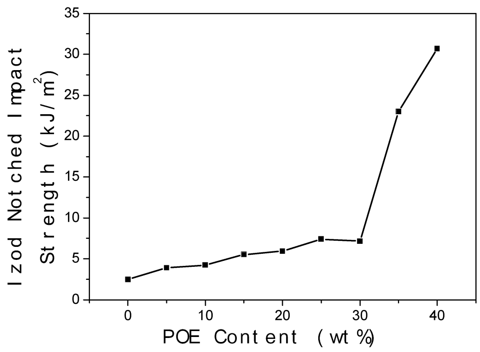
tensile speed of cross head is 500 mm/min, thus, the practical strain rate of the notched region is about 208/s at the beginning of the test.

3. Results

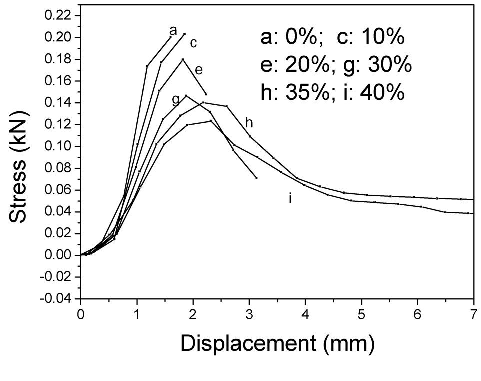
3.1. Brittle–tough transition in both impact and high speed tensile tests

Fig. 4(a) shows that an obvious brittle–tough transition of the PP/POE blends occurs in the notched Izod impact tests with the increase of POE content. The polypropylene used in the experiment had high melt flow index (MFI), thus, a very high POE content was needed to initiate the brittle–tough transition.

Fig. 4(b) shows the tensile curves of the PP/POE blends obtained in the high-speed tensile tests. The samples with the POE contents of 0, 10, 20 and 30 wt% all fractured at the notched region in a brittle manner. Slight whitening on the fracture surfaces showed that only little yielding deformation occurred (shown in Fig. 5(a)). However, the samples with the POE contents of 35 and 40 wt% deformed largely at the notched region without fracture, and the deformation extended into the material on both sides of the notch (shown in Fig. 5(b)). Thus a BDT also occurred in the high-speed tensile tests when the POE content reached 35 wt%. Though, the BDT in impact tests has been reported largely, the BDT in tensile process is seldom reported. It is meaningful to explain whether the BDT in both impact and tensile tests shares the same mechanism.



(a)



(b)

Fig. 4. Effect of POE content on the toughness of PP/POE blends. (a) Impact toughness; (b) tensile toughness.

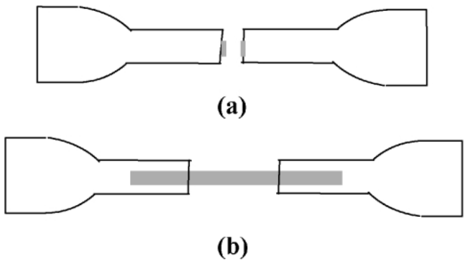


Fig. 5. Sketches of fractured samples in high speed tensile tests. (a) Brittle fracture. (b) Tough fracture.

3.2. Effect of tensile speed on toughness

Fig. 6 shows the effect of tensile speeds on the tensile toughness of the PP/POE blends. The samples were the same as that shown in Fig. 3. Four cross head speeds, 50, 100, 300 and 500 mm/min, were used, which led to four practical strain rate of the notched region, 20.8, 41.6, 124.8 and 208/s. The neat PP fractured in brittle manner at all the tensile speeds. The PP/POE (10 wt%) blend fractured in brittle manner at tensile speeds of 500, 300 and 100 mm/min, and showed ductile deformation at the tensile speed of 50 mm/min. The PP/POE (30 wt %) blend showed ductile deformation at tensile speeds of 100 and 50 mm/min, and fractured in brittle manner at tensile speeds of 500 and 300 mm/min. The PP/POE (35 wt%) blend showed ductile deformation at all tensile speeds. Fig. 6 shows that with the decrease of the tensile speeds, a BDT occurs in tensile tests of the samples. The more the POE content is, the higher the BDT tensile speed is. Both Jiang [10] and Gaymans [9] have also gotten the same conclusion.

4. Discussion

4.1. Micro deformation of the notched impact samples in impact test

Because of the strain rate concentration of the notch, when being impacted by the pendulum, notched impact samples respond to the pendulum motion by the deformation of the narrow regions near notch tips, the shadow area in Fig. 7, which leads the upper half of the sample to rotate around the point O (shown in Fig. 7). In the process, the microunits of the deformation region, the shadow area in Fig. 7, deform in two methods: high speed tensile deformation and shear deformation because of the tensile speed gradients in the deformation region (shown in formula 3). At the beginning

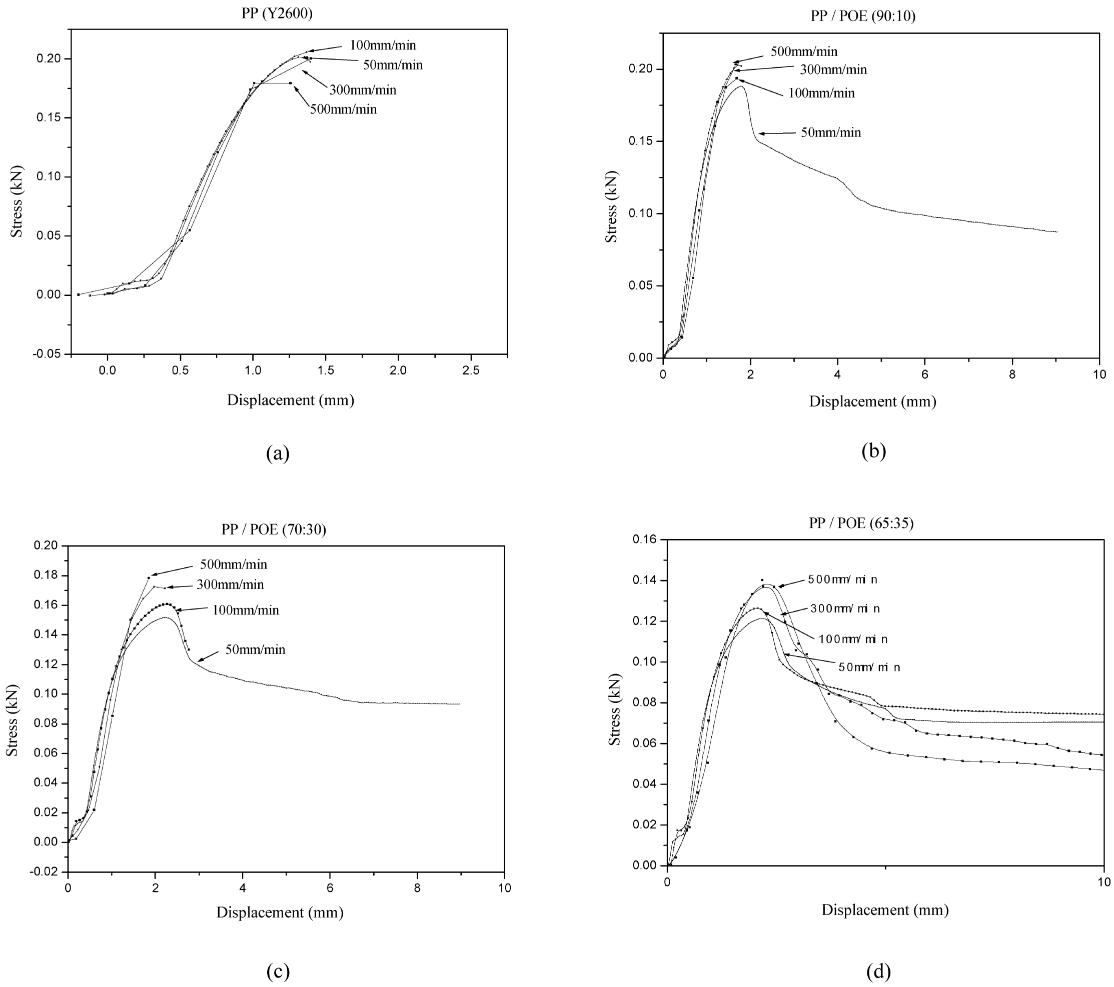


Fig. 6. Effect of tensile speed on the tensile curves of PP/POE blends. (a) PP; (b) PP/POE (90/10); (c) PP/POE (70/30); (d) PP/POE (65/35).

of the impact, the tensile speed at the notch tip, v_1, is perpendicular to the impact speed of the pendulum, v_0. The relationship between v_0 and v_1 is deduced and described as following.

$$v_1 = \frac{ac}{(b^2 + c^2)} v_0 \tag{1}$$

Between the notch tip and point O, the value of the tensile

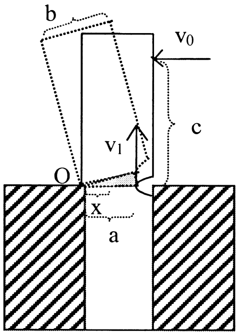


Fig. 7. Sketch of the notched impact sample.

speed, v_x, is deduced and described as following:

$$v_x = \frac{xc}{(b^2 + c^2)} v_0 \tag{2}$$

Thus, the tensile speed gradients in the deformation region is described as following.

$$\mathrm{grad} v_x = \frac{c}{(b^2 + c^2)} v_0 \tag{3}$$

Where a, b, c are the sample sizes, and x is the distance between the microunits of the deformation area and the point O (shown in Fig. 7). In practical impact tests, $a = 10$ mm, $b = 12.7$ mm, $c = 21$ mm and $v_0 = 3.5$ m/s, thus, $v_1 = 1.2$ m/s. Fig. 8 shows that the notch tip is really a narrow plane, about 0.2 mm in width. In impact tests, if all the deformation of the samples occurs in this narrow region, the strain rate of this region is 6000/s at the beginning of the impact tests. However, the practical strain rate of the notch tip should be lower than the value. Firstly, the regions on both sides of the notch tip are also deformation at some extent. Secondly, the impact speed of the pendulum will decrease because that the kinetic energy of the pendulum is absorbed by the samples. Formula (2) shows that the farther

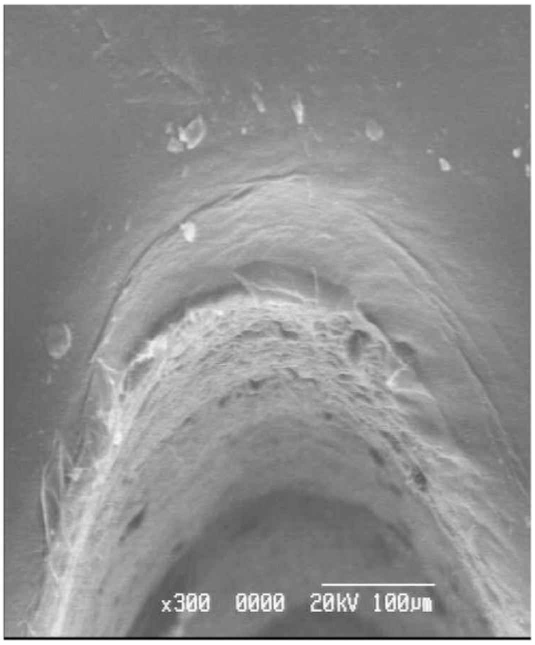


Fig. 8. SEM graph of the notch tip of the impact sample.

the deformation area is away from the notch tip, the lower the tensile speed is.

$$\epsilon = \frac{ac}{(b^2 + c^2)l_0} v_0 \tag{4}$$

In impact tests of the notched samples, the notch has the effect of strain concentrator since the notch tip takes on most of the strain loading of the samples. Formula (4) shows the relationship between the strain rate and the width of the practical deformation region, l_0, which is near to the width of the notch tip. The sharper the notch is, the larger the strain concentration is and the larger the strain rate of the notch tip. When the crack is initiated, the strain concentration will increase sharply because that the width of the crack tip is much less than that of the notch tip, which leads the energy absorbing ability of the samples to decrease greatly.

4.2. Correlation between impact and tensile tests

Figs. 4 and 6 show that BDT occurs with the increase of POE content or with the decrease of the strain rate in tensile tests. The same phenomena have also been reported greatly in impact tests [2–6,9–11]. Even though there is shear deformation of the notched samples in impact tests, the tensile deformation is also an important deformation method. Especially, in rubber toughened plastics, the caviatation of the rubber particles can decrease the shear deformation greatly. In this case, the main deformation method of the notched samples in impact tests is tensile deformation. Thus, the notched impact deformation is really a high speed tensile deformation near the notch tip. The BDT in notched impact tests should share the same mechanism with that in tensile tests.

In none-notched impact tests, all the upper half part of the sample deforms to respond to the pendulum motion. The microstrain rate of the sample is much lower than that of the notched impact sample, which leads the toughness of PP and PA in none-notched impact tests much higher than that in notched impact tests. The notch sensitivity of PP and PA is essentially the tensile speed sensitivity.

5. Conclusions

A high speed tensile test was designed to explore the toughness of PP/POE in high speed tensile tests. The practical strain rate of the sample was 208/s in the test. A BDT occurred when POE content was beyond 35 wt%. With decrease of tensile speeds, all samples showed a BDT. The more the POE contents were, the higher the BDT tensile speeds were.

The microdeformation of the notched impact samples was analyzed in details. Since, in impact tests, only a narrow region near the notch tip deforms to respond the pendulum motion, the notch leads to strong strain concentration. The narrow region deforms in two methods: high speed tensile deformation and shear deformation. In rubber toughened plastics, the shear deformation can decrease greatly because of the cavitation of the rubber particles. Thus, in rubber toughened plastics, the deformation of the notched impact samples is really a high speed tensile deformation in the narrow region near notch tips. So the rubber toughened plastics share similar deformation and fracture mechanism in both the impact and tensile tests. The notch sensitivity of plastics is attributed to the strain concentration effect of the notch. In other words, the notch sensitivity of plastics is essentially the tensile speed sensitivity of the plastics.

Appendix A

Relationship between v_0 and v_1

The impact speed, v_0, can be decompose at two directions, parallel to $O''O$ and $O'O''$ (shown in Fig. 9).

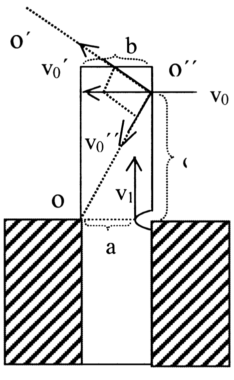


Fig. 9. Sketch of decomposition of impact speed.

v_0' and v_0'' are the two component force of v_0. The value of v_0' can be deduced and described as following.

$$v_0' = \frac{c}{\sqrt{b^2 + c^2}} v_0 \quad \text{(A1)}$$

v_0' leads the upper half of the impact sample to rotate around the point O. The angular velocity of the upper half of the impact sample, ω, can be deduced and described as following.

$$\omega = \frac{c}{(b^2 + c^2)} v_0 \quad \text{(A2)}$$

Thus, the tensile speed of the notch tip, v_1, can be deduced and described as following.

$$v_1 = \frac{ac}{(b^2 + c^2)} v_0 \quad (1)$$

References

[1] Pearson RA, Sue HJ, Yee AF. Toughening of plastics. Washington DC: American Chemical Society; 2000.
[2] Wu S. Polymer 1985;26:1855.
[3] Wu S. J Appl Polym Sci 1988;35:549.
[4] Borggreve RJM, Gaymans RJ, Schuijer J, Housz JF. Ingen. Polymer 1987;28:1489.
[5] Bartczak Z, Argon AS, Cohen RE, Weinberg M. Polymer 1999;40:2331.
[6] Bartczak Z, Argon AS, Cohen RE, Weinberg M. Polymer 1999;40:2347.
[7] Jiang W, Liu CH, Wang ZG, et al. Polymer 1998;39:3285.
[8] van der Wal A, Nijhof R, Gaymans RJ. Polymer 1999;40:6031.
[9] van der Wal A, Gaymans RJ. Polymer 1999;40:6045.
[10] Jiang W, Tjong SC, Li RKY. Polymer 2000;41:3479.
[11] Gensler R, Plummer CJG, Grein C, Kausch HH. Polymer 2000;41:3809.
[12] Collyer AA. Rubber toughened engineering plastics. London: Chapman and Hall; 1994. p. 45.
[13] Newman S, Strella S. J Appl Polym Sci 1965;9:2297.
[14] Bucknall CB. Adv Polym Sci 1978;27:121.
[15] Donald AM, Kramer EJ. J Mater Sci 1982;17:1765.
[16] Ramsteiner F, Heckmann W. Polym Commun 1985;26:199.
[17] Borggreve RJM, Gaymans RJ, Eichenwald HM. Polymer 1989;30:79.
[18] Yee AF, Pearson RA. J Mater Sci 1986;21:2462.
[19] Pearson RA, Yee AF. J Mater Sci 1986;21:2475.
[20] Parker DS, Sue HJ, Huang J, Yee AF. Polymer 1990;31:2267.
[21] Sue HJ, Yee AF. Polym Engng Sci 1996;36:2320.
[22] Margolina A, Wu S. Polymer 1988;29:2170.
[23] Muratoglu OK, Argon AS, Cohen RE, Weinberg M. Polymer 1995;36:921.
[24] Muratoglu OK, Argon AS, Cohen RE, Weinberg M. Polymer 1995;36:2143.
[25] Lin L, Argon AS. Macromolecules 1992;25:4011.