

Applicability of Wu's Criterion for Brittle-Ductile Transition of Ethylene/1-Octene Copolymer Toughened Polyamide 6

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ABSTRACT: The brittle–ductile transition of ethylene/1-octene copolymer (POE) toughened polyamide 6 (PA6) was studied at various temperatures. The experimental results show that the critical interparticle distance (ID_c) is independent of the POE content, and the POE particle size at lower temperatures, that is, the temperature is much lower than the brittle–ductile transition temperature (T_{BD}^m) of PA6. At higher temperatures, however, especially temperatures close to the T_{BD}^m , the ID_c depends on the POE particle size. This indicates that Wu's criterion for rubber toughening, specifically that “the ID_c is a material property of the matrix, independent of rubber volume fraction and particle size,” is inapplicable at higher temperatures for the brittle–ductile transition of the POE toughened PA6. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polymer blends; toughness; brittle–ductile transition

Received 2 August 2011; accepted 20 April 2012; published online

DOI: 10.1002/app.37935

INTRODUCTION

It is generally known that toughness influences the performance of polymers in various engineering applications. Therefore, polymer toughening has been an important and attractive topic for polymer scientists, as the polymer was used as an engineering material. Great progress has been made in the research of polymer toughening during the past decades,^{1–31} and several model and theories have been proposed.^{5–8} One of the most widely used model and theories is Wu's criterion, that is, the average surface to surface interparticle distance (ID) of rubber particles must be smaller than the critical value (ID_c), and that the ID_c is a material property of the matrix, independent of both the rubber volume fraction and the particle size.^{7,8} This generalized criterion for rubber toughening has been successfully used in rubber or elastomer toughened thermoplastics, including polyamide (PA),^{7,9–13} polypropylene,^{14–18} polybutylene terephthalate,^{19–22} polyethylene terephthalate,^{23,24} polytrimethylene terephthalate,²⁵ and high-density polyethylene (HDPE).²⁶ Aside from rubber toughening, it was found that this criterion is also applicable to rigid particle toughened thermoplastics. For example, Fu et al. and Bartczak

et al. found that the ID_c is independent of calcium carbonate ($CaCO_3$) volume fraction and particle size, when they studied the brittle–ductile transition of $CaCO_3$ particle toughened HDPE.^{27–31} However, we would like to stress here that all results mentioned above were obtained at room temperature.

Experimental and theoretical studies reveal that the ID_c depends on temperature,^{32–34} tensile speed,³⁵ particle properties,^{36–38} and matrix properties.³⁹ It was found that the ID_c increases nonlinearly with increasing temperature.^{32,33} The ID_c approaches infinity when temperature increases and approaches the brittle–ductile transition temperature (T_{BD}^m) of the matrix. To the best of our knowledge, whether or not the ID_c is independent of both particle volume fraction and particle size at higher temperatures, as stated in Wu's criterion, still remains unclear.

In this article, brittle–ductile transition of ethylene/1-octene copolymer (POE) toughened polyamide 6 (PA6) was studied with a wide range of POE particle sizes and content at various temperatures. The purpose of this study is to clarify whether or not Wu's criterion is applicable at higher temperatures.

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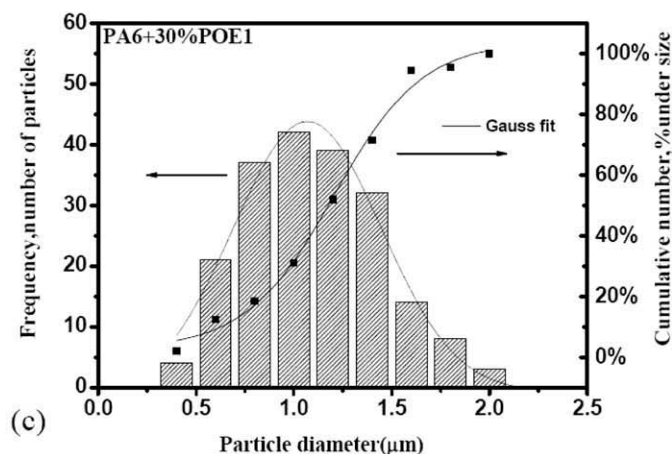
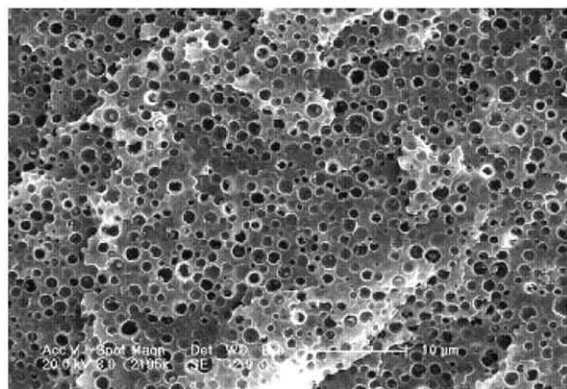
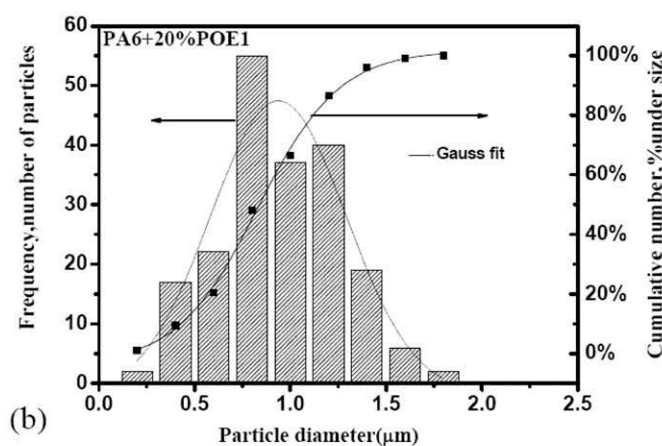
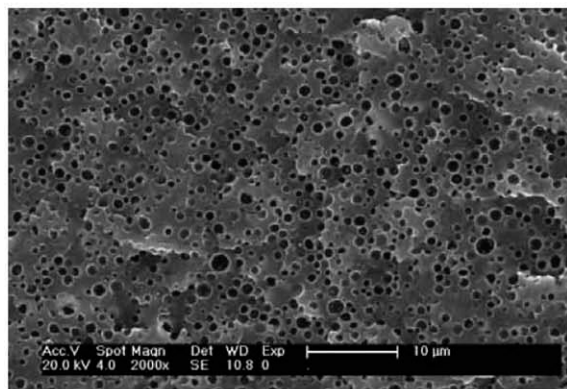
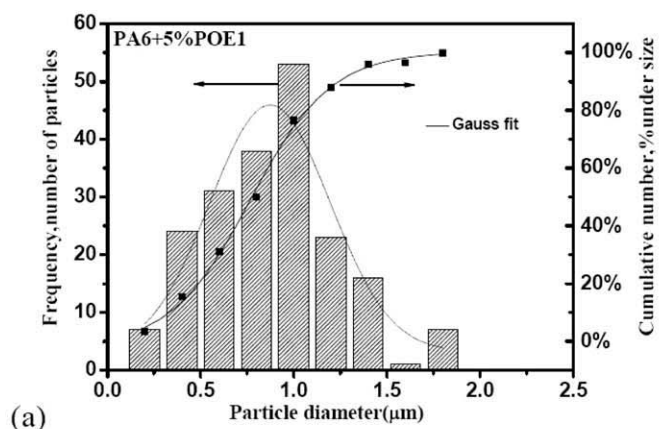
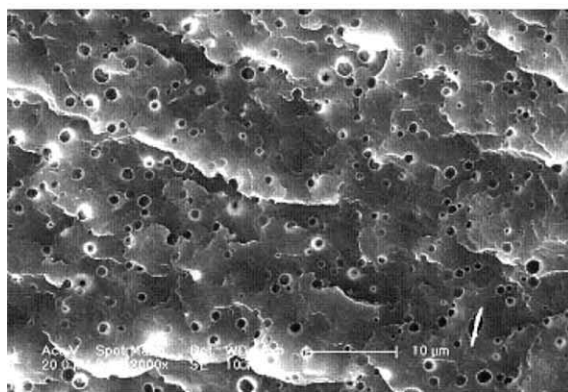


Figure 1. SEM micrographs of cryofractured surfaces for the PA6/POE1 specimens and the corresponding particle size distribution. POE content: (a) 5 wt %, (b) 20 wt %, and (c) 30 wt %.

EXPERIMENTAL

Materials

PA6, commercial grade M2800, was produced by GuangdongXinhui Meida Nylon (Guangdong, China). POE, Engage 8150, was purchased from DuPont[®]Dow Elastomers (Wilmington, DE).

Sample Preparation

Prior to melt compounding, PA6 was predried over 24 h in a vacuum oven at 90°C, whereas the elastomers were dried at

65°C. Melt blends were prepared using a Hakke batch intensive mixer (Hakke Rheomix 600, Germany) with a batch volume of 50 mL. Polymers were mixed at a screw speed of 60 rpm for 5 min at 235°C. Plaques were prepared under a pressure of 10 MPa for 5 min at 240°C, and then they were cooled down naturally at room temperature under a pressure of 10 MPa. Izod impact specimens with dimensions of 63.5 × 12.7 × 3.2 mm³ were cut from the plaques. A sharp notch was created on all specimens. The resulting specimens were tested with a XJU-2.75

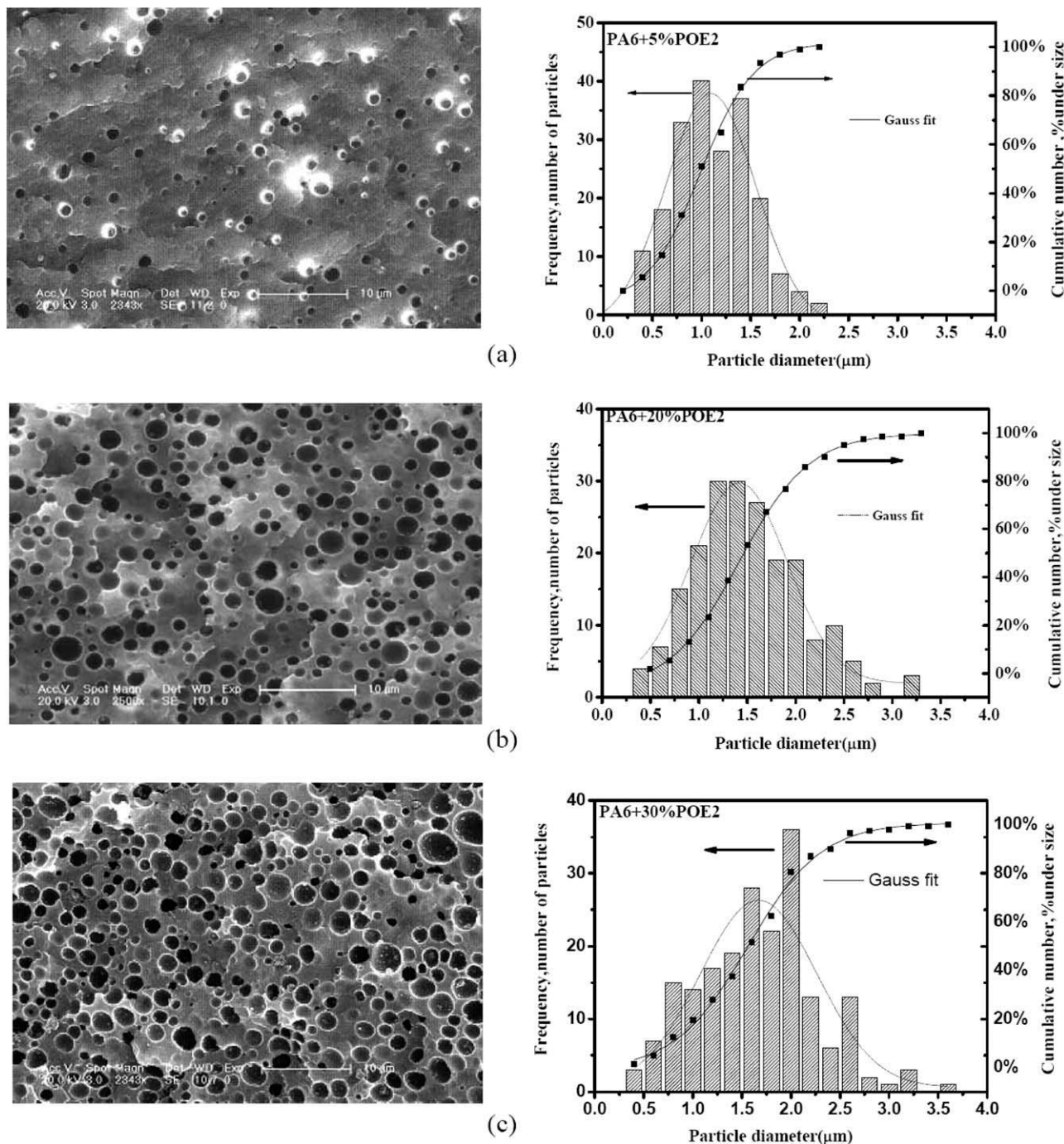


Figure 2. SEM micrographs of cryofractured surfaces for the PA6/POE2 specimens and the corresponding particle size distribution. POE content: (a) 5 wt %, (b) 20 wt %, and (c) 30 wt %.

Izod impact tester (made in Chengde, China) at various temperatures. Eight specimens were measured and the average values reported for each experimental datum. All specimens were dried for over 24 h in a vacuum oven at 90°C prior to testing. One purpose was to ensure that the specimens were dried enough under such treatment, because PA6 absorbs water. The other purpose was to ensure that the specimens were experienced same thermal history. It is generally known that the crys-

tallization for PA depends on thermal history, and the crystallization can affect the impact behavior of PA/rubber blends. For an example, Leibler and coworkers⁴⁰ found that crystalline orientation, size of crystalline grains, and molecular organization at grain boundaries play a determinant role in rubber toughening PA12, and differences in crystalline organization of PA12 matrix can induce dramatic changes in toughening efficiency.

Table I. Summary of Rubber Particles and ID for PA6/POE1 Blends

Sample No.	Weight fraction of POE (%)	Volume fraction of POE (%)	\bar{d}_n (μm)	\bar{d}_w (μm)	$\frac{\bar{d}_w}{\bar{d}_n}$	ID (μm)
POE1-1	1.0	1.3	0.62	0.96	1.6	2.33
POE1-2	2.0	2.6	0.68	0.85	1.3	1.46
POE1-5	5.0	6.5	0.79	0.95	1.2	0.95
POE1-8	8.0	10.2	0.74	0.91	1.2	0.66
POE1-10	10.0	12.7	0.78	0.93	1.2	0.56
POE1-12	12.0	15.2	0.74	0.91	1.2	0.46
POE1-15	15.0	18.8	0.85	1.00	1.2	0.41
POE1-18	18.0	22.3	0.86	0.98	1.1	0.32
POE1-20	20.0	24.7	0.85	0.96	1.1	0.27
POE1-22	22.0	27.0	0.98	1.12	1.1	0.28
POE1-25	25.0	30.4	0.99	1.14	1.2	0.23
POE1-30	30.0	36.0	1.02	1.14	1.1	0.15

POE Particle Size Analysis

The surfaces of cryogenically fractured specimens were observed by a field emission scanning electron microscope (FESEM, XL 30 ESEM FEG, FEI Company) after gold coating. The test specimens were etched with hot xylene for 3 h to remove the POE phase. The particle size of the rubber was measured in representative zones of the cryogenically fractured impact specimens. The number-average particle size (\bar{d}_n) and weight-average particle size (\bar{d}_w) were calculated from a minimum of 200 rubber particles according to the following equations:

$$\bar{d}_n = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

$$\bar{d}_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (2)$$

where n_i is the number of the particle with size d_i .

RESULTS AND DISCUSSION

To examine whether or not the ID_c is independent of particle volume fraction and particle size, we have to obtain blends with different rubber particle sizes. It is generally known that the particle size in a PA matrix can be controlled using different levels of maleation in the rubber phase.^{41–45} POE samples grafted with maleic anhydride (POE-g-MA) were prepared in our laboratory by a twin screw extruder. The amount of grafted MA in the POE is about 0.5%. In this study, two POE mixtures, POE1 and POE2, were prepared by mixing POE-g-MA and POE. The POE1 mixture contained 6 wt % POE-g-MA, whereas the POE2 mixture contained 3.3 wt % POE-g-MA. The POE particle size for both PA6/POE1 and PA6/POE2 blends with various POE contents can be obtained from SEM micrograph measurements. Figures 1 and 2 are the cryogenically fractured surface SEM micrographs for PA6/POE1 and PA6/POE2 blends with different rubber contents, respectively. It can be found that

Table II. Summary of Rubber Particles and ID for PA6/POE2 Blends

Sample No.	Weight fraction of POE (%)	Volume fraction of POE (%)	\bar{d}_n (μm)	\bar{d}_w (μm)	$\frac{\bar{d}_w}{\bar{d}_n}$	ID (μm)
POE2-1	1.0	1.3	0.97	1.24	1.3	3.01
POE2-2	2.0	2.6	0.98	1.23	1.2	2.12
POE2-5	5.0	6.5	1.02	1.17	1.2	1.17
POE2-8	8.0	10.2	1.10	1.29	1.1	0.93
POE2-10	10.0	12.7	1.21	1.35	1.1	0.81
POE2-12	12.0	15.2	1.13	1.27	1.1	0.65
POE2-15	15.0	18.8	1.16	1.30	1.1	0.53
POE2-18	18.0	22.3	1.26	1.42	1.1	0.47
POE2-20	20.0	24.7	1.51	1.72	1.1	0.48
POE2-22	22.0	27.0	1.38	1.57	1.1	0.39
POE2-25	25.0	30.4	1.41	1.57	1.1	0.31
POE2-28	28.0	33.8	1.57	1.86	1.2	0.30
POE2-30	30.0	36.0	1.55	1.79	1.2	0.23
POE2-32	32.0	38.1	1.61	1.81	1.1	0.20

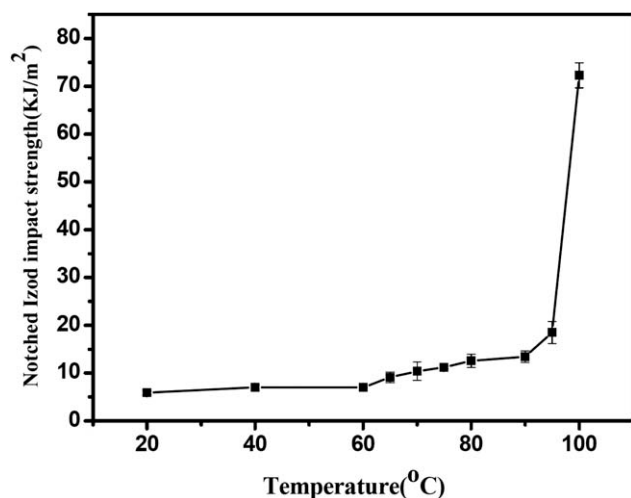


Figure 3. Variation of notched Izod impact strength for the PA6 with temperature.

the POE2 particles are clearly larger than the POE1 particles in PA6 matrix due to the lower level of maleation in the POE2 phase. The statistic results for particle size are also given in

Figures 1 and 2. They show that both POE1 and POE2 particle size distributions in PA6 matrix follow a lognormal distribution.^{46,47} Similar results are obtained for other blends. The related results for all blends are listed in Tables I and II.

From the particle volume fraction and particle size, we can calculate the ID using eq. (3)⁷:

$$ID = \bar{d}_w \left[\left(\frac{k\pi}{6V_r} \right)^{\frac{1}{3}} - 1 \right] \quad (3)$$

where V_r is the rubber volume fraction, $k = 1$ is the cubic packing, and \bar{d}_w is the weighed average rubber particle size. The volume fraction V_r of the POE is given by

$$V_r = \frac{W_r \rho_m}{W_r \rho_m + (1 - W_r) \rho_r} \quad (4)$$

where W_r , ρ_r , and ρ_m refer to the weight fraction of POE, density of the POE, and density of the matrix, respectively. For PA6/POE blends, $\rho_r = 0.87$ (g/cm³) and $\rho_m = 1.14$ (g/cm³). The calculated results from eqs. (3) and (4) are also listed in Tables I and II.

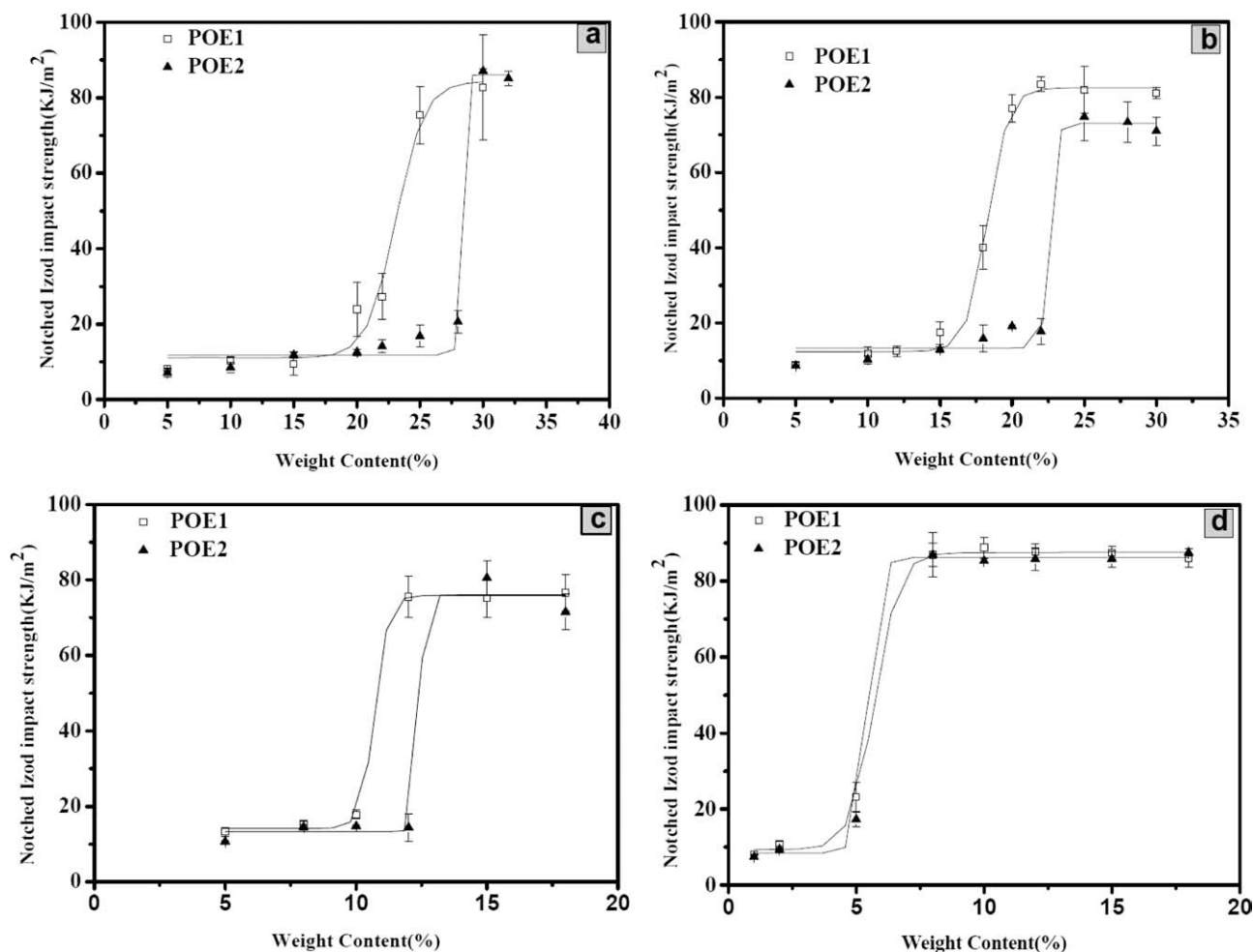


Figure 4. Variation of notched Izod impact strength for PA6/POE blends with POE weight content at 20°C (a), 45°C (b), 65°C (c), and 80°C (d).

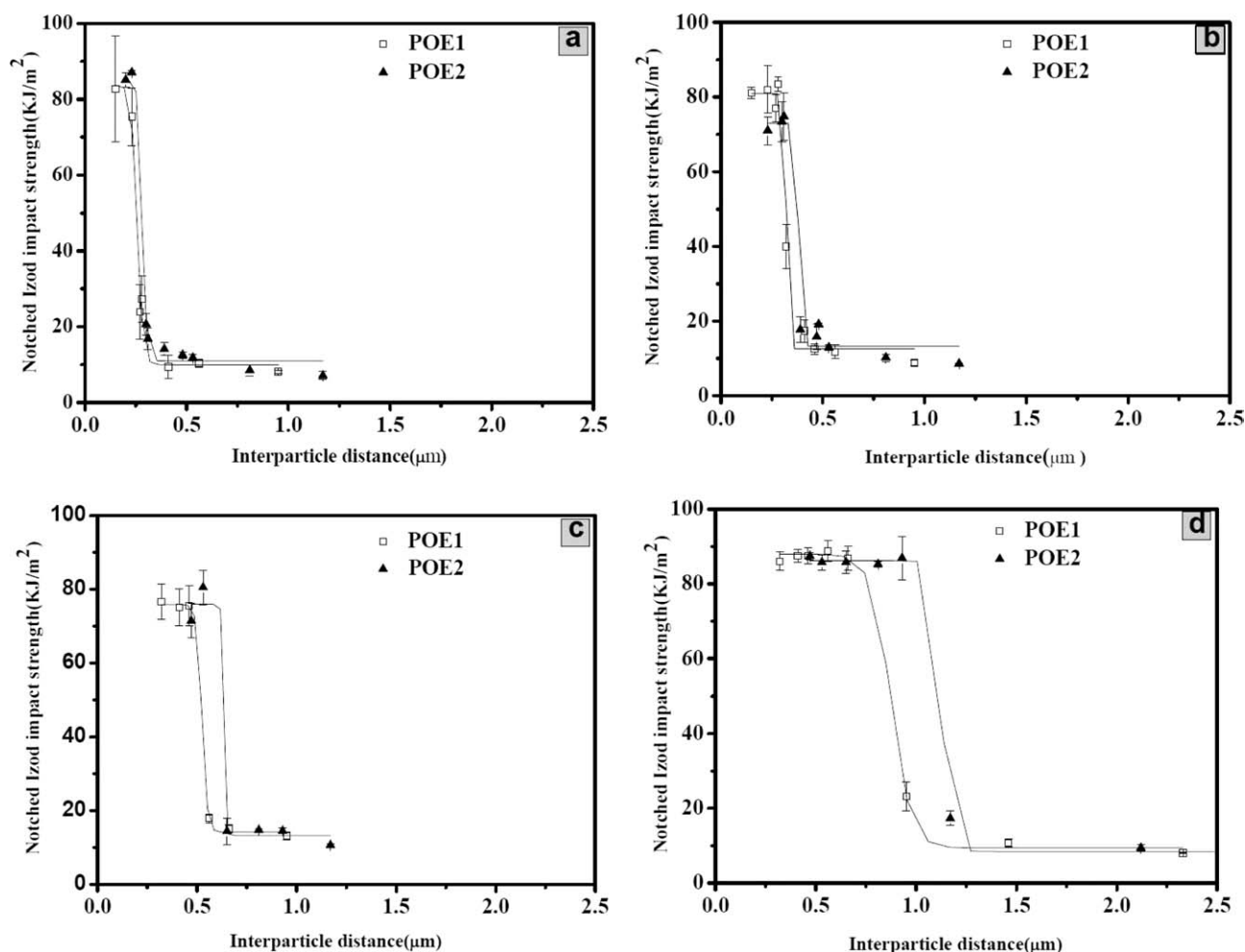


Figure 5. Variation of notched Izod impact strength for PA6/POE blends with ID at 20°C (a), 45°C (b), 65°C (c), and 80°C (d).

Before studying the brittle–ductile transition of the PA6/POE blends, let us look at the results of the brittle–ductile transition temperature of PA6, because it plays a special role in rubber toughening. Figure 3 shows the variation of the notched impact strength of the PA6 with temperature. It can be seen that the notched impact strength increases slowly with increasing temperature up to 95°C, the brittle–ductile transition temperature (T_{BD}^m) of PA6. Over this temperature, the impact strength increases sharply with increasing temperature. 95°C is higher than the brittle–ductile transition temperature (74°C) of PA6 used in the study of Borggreve et al.³³ This difference may result from the different PA6 materials used in the experiment. Figure 3 suggests that the impact test temperature for the PA6/POE blends should be lower than 95°C.

Figure 4 gives the variation of the notched Izod impact strength for PA6/POE blends with POE weight contents at 20°C (a), 45°C (b), 65°C (c), and 80°C (d). The results indicate that increasing POE content can lead to the brittle–ductile transition for both PA6/POE1 and PA6/POE2 blends, and the critical weight concentration (W_c) at which the brittle–ductile transition occurs decreases with increasing temperature. However, the W_c of PA6/POE2 blends are obviously higher than that of PA6/

POE1 blends at lower temperatures. A more interesting observation is that this difference becomes smaller and smaller with increasing temperature.

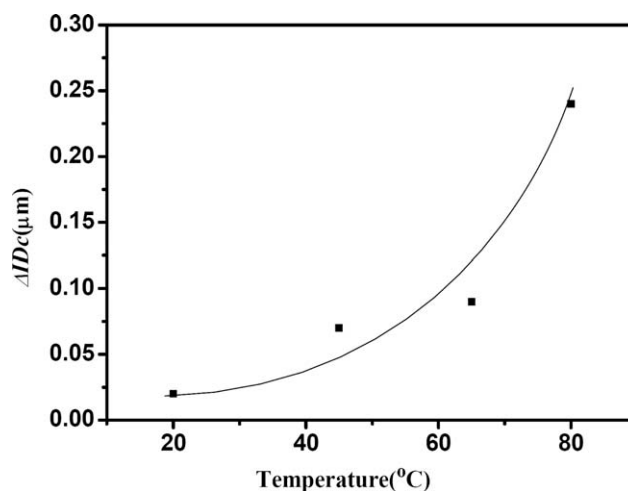


Figure 6. Variation of the ID_c difference (ΔID_c) with temperature.

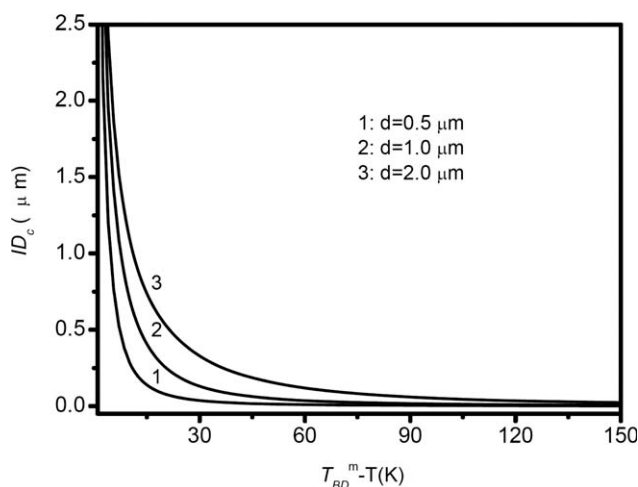


Figure 7. Variation of the ID_c with $T_{BD}^m - T$ calculated from eq. (5) for different particle sizes, in which $QE = 400$ ($\mu\text{m K}^2$) (K is the unit of the absolute temperature).

Figure 5 shows the variation of the notched Izod impact strength for PA6/POE blends with ID at various temperatures. The results indicate that decreasing ID can result in brittle–ductile transitions for both PA6/POE1 and PA6/POE2 blends, and the ID_c at which the brittle–ductile transition occurs increased with increasing temperature. At lower temperatures, that is, at 20°C, it was found that the ID_c difference (ΔID_c) between the two systems is quite small. The ID_c is 0.3 μm and is independent of POE content and POE particle size, indicating that Wu’s criterion is applicable to this case. With an increase in temperature, however, the ID_c difference becomes larger and larger. When temperature increases to 80°C, the ID_c difference can reach 0.24 μm . The results clearly show that ID_c depends on the POE particle size at higher temperatures. For clarity, Figure 6 shows the variation of ΔID_c with temperature. It can be seen that the ΔID_c increases with temperature. Therefore, Wu’s criterion for rubber toughening (“ ID_c is a material property of the matrix, independent of rubber volume fraction and particle size”) is inapplicable at higher temperatures.

In fact, as early as 1998, Jiang et al.⁴⁸ gave a theoretical expression for ID_c :

$$ID_c = \left[\frac{QE}{(T_{BD}^m - T)^2} + d^3 \right]^{\frac{1}{3}} - d \quad (5)$$

where Q and E can be considered as constants for a given rubber and matrix. The calculation results show the variation of the ID_c with $T_{BD}^m - T$ for different particle sizes, as calculated from eq. (5). These results are given in Figure 7. It is clear that the ID_c strongly depends on the particle size when the $T_{BD}^m - T$ is close to zero, that is, the test temperature T is close to the T_{BD}^m . However, the ID_c is almost independent of the particle size, when the temperature is much lower than the brittle–ductile transition temperature (T_{BD}^m) of the matrix. The results are in agreement with the present experiment.

CONCLUSIONS

This study clarified that the applicability of Wu’s criterion for the brittle–ductile transition of POE toughened PA6 is applicable to the case where the temperature is much lower than the brittle–ductile transition temperature (T_{BD}^m) of the matrix. At higher temperatures, especially at the temperatures close to the T_{BD}^m , the criterion is not applicable.

ACKNOWLEDGMENTS

The authors are grateful for the financial support provided by the General Program (50573074), the Major Program (50833005), the Funds for Distinguished Young Investigators (50725312) and Creative Research Groups (50921062) of National Natural Science Foundation of China, and the Research Program (20080506) of Jilin Province. They thank Chen Changjiang and Zhang Weiguang for their kind help in experiment.

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