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Effect of cavitations on brittle–ductile transition of particle toughened thermoplastics

Wei Jiang*, Qiang Yuan, Lijia An, Bingzheng Jiang

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

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Abstract

In this study, we established a correlation between cavitations volume and the brittle–ductile transition (BDT) for particle toughened thermoplastics. The brittle–ductile transition temperature (T_{BD}) was calculated as a function of T^* and interparticle distance (ID), respectively, where T^* was a parameter related to the volume of cavitations. The results showed that the smaller the cavitations volume, the higher the brittle–ductile transition temperature. The calculations correlated well with the experimental data. With respect to rubber particle, the rigid particle was too hard to be voided during deformation, thereby the T_{BD} of the blend was much higher than that of rubber particle toughened thermoplastic. This was a main reason that rubber particle could toughen thermoplastics effectively, whereas rigid particle could not. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer toughening; Brittle–ductile transition; Cavitations

1. Introduction

From brittle to ductile, it is known that a polymer or its blend can undergo a sharp transition. This transition plays a key role in polymer toughening and application. The critical transition point is a reference point for designing a supertough polymer. Moreover, this point is also a limit point that a polymer material can remain ductile fracture behavior. For examples, the brittle–ductile transition temperature (T_{BD}) is the lowest temperature that a polymer can be used as a ductile material, whereas the critical brittle–ductile strain rate is the highest strain rate that a tough polymer material can sustain. On the other hand, transition and its critical phenomenon is always an attractive field with challenge in sciences. Therefore, the brittle–ductile transition (BDT) of polymer and its blend has been attracting much interest from both sciences and technologies [1–10].

It is generally known that the brittle–ductile transition of polymer and its blend depends on temperature, deformation speed, the morphology of dispersed phase, the mechanical properties of dispersed phase and matrix for particle toughened thermoplastic. The effects of temperature, strain rate and interparticle distance on the brittle–ductile transition in elastomer toughening thermoplastic were theoretically studied in the previous paper [11]. The calculated results imply that the critical interparticle distance (ID_c) is a function of temperature and strain rate. More recently, the effect of the elastomer properties on brittle–ductile transition in elastomer toughened thermoplastics was also studied from this theory. It is concluded that the modulus of an elastomer must be one-tenth or less of that of the matrix in order to be effective to toughen the thermoplastic [12].

However, it is found that some elastomers cannot be used to toughen thermoplastic effectively although their moduli are one-tenth or less of the modulus of the matrix [13]. Further experimental study suggests that this phenomenon was caused by cavitation ability of the elastomer [14]. The lower cavitation ability of the elastomer, the higher the T_{BD} of the blend is. Similar phenomena were observed by van der Sanden etc. In their experiment, the T_{BD} increased markedly with increased irradiation dose for polycarbonate (PC) and ethylene–propylene-diene monomer rubber (EPDM) blends [15]. Irradiation can lead to crosslink of EPDM molecules, thereby decreasing the cavitations ability of the EPDM rubber.

Until now, the greater part of the research effort in theory was directed towards the formation of cavitations [16–20]. For an example, Bucknall etc gave an energy-balance criterion for cavitations of rubber particles [16–18]. Their model related the critical volume strain at cavitations to the radius

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* Corresponding author. Tel.: +86-431-526-2151; fax: +86-431-568-5653.

E-mail address: wjiang@ciac.jl.cn (W. Jiang).

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of the rubber particle, and to the shear modulus, surface energy and failure strain of the rubber [16]. However, to the best of our knowledge, the relation between the BDT of particle toughened thermoplastic and cavitations effect remains unclear up to now. The purpose of this paper is to establish a correlation among cavitations effect, T_{BD} and $\mathrm{ID_c}$ for particle toughened thermoplastic.

2. Theory

First of all, the Eyring equation including additional stress should be studied in order to evaluate the effect of cavitations on the BDT. According to the references, the modified Eyring equation including the effect of pressure may be very simply given [21,22]

$$\gamma = B\exp[-(\Delta G + PV^{*} - V\sigma_{\mathrm{y}})/RT] \tag{1}$$

where γ is the stain rate, σ_{y} is the yield shear stress, B a constant, ΔG the activation energy, V the activation volume, R the gas constant, P the hydrostatic component of stress and V^{*} is the pressure activation volume, respectively. From Eq. (1), it is known that the yield shear stress increases with increasing pressure.

For particle toughening thermoplastic, the matrix thermoplastic will be subjected to an aditional triaxial dilative stress field when a force is supplied to the particle toughed thermoplastic sample. Marglina and Wu pointed out that the rubber particles cavitate to relieve the triaxial dilative stress during impact fracture [23]. Comparing with the hydrostatic component of stress, the dilative stress is more complicated. It varies with position and time. For simplifying, we use an average dilative stress $\bar{P}$ to stand for the real stress during cavitating. Replacing P with $\bar{P}$ in Eq. (1), we can obtain

$$\gamma = B\exp[-(\Delta G - \bar{P}V^{*} - V\sigma_{\mathrm{y}})/RT] \tag{2}$$

Because the direction of the dilative stress is in opposition to the hydrostatic stress, the sign before $\bar{P}V$ term is negative in this equation, and the definition of V^{*} is the average dilative stress activation volume, which is related to the effect of cavitations. Bucknall et al. pointed out that the real importance of cavitations is that it reduces the resistance of the polymer to volumetric expansion in response to dilatational applied stress fields which occur, especially, at crack tips [17]. Based on this conclusion, it is suggested that the larger the cavitations volume, the bigger value of the V^{*} is. In this study, we assume that they follow the simple relation

$$V^{*} = \alpha V_{\mathrm{c}} \tag{3}$$

where α is a non-dimension constant parameter, V_{c} is the cavitations volume, respectively. From Eq. (3), it is known that the V^{*} becomes zero if the cavitations volume V_{c} goes to zero. According to the conclusions of Bucknall et al. [17], it is known that the resistance of the polymer to volumetric expansion in response to dilatational applied stress fields should be extremely high when the cavitations volume V_{c} becomes zero. This can lead to the average dilative stress activation volume V^{*} approaching to zero.

Combining Eqs. (2) and (3) with Eq. (9) in the previous paper [11], we can obtain the brittle ductile transition equations including the effect of cavitations

$$T_{\mathrm{BD}} = T_{\mathrm{BD}}^{\mathrm{m}} - T^{*} - \sqrt{\frac{QE}{(\mathrm{ID}+d)^3 - d^3}} \tag{4}$$

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

where d and T refer to the diameter of dispersed phase and test temperature, ID and $\mathrm{ID_c}$ refer to the interparticle distance and critical interparticle distance defined by Wu [24], respectively; E is the strain energy of the matrix in the stressed volume; $T_{\mathrm{BD}}^{\mathrm{m}}$ and T_{BD} refer to the brittle–ductile transition temperature of matrix material itself and BDT temperature of the particle toughed thermoplastic; Q is a constant for given matrix thermoplastic and strain rate; T^{*} is expressed as

$$T^{*} = \frac{\bar{P}\alpha V_{\mathrm{c}}}{R\ln(B/\gamma)} \tag{6}$$

Comparing these equations with the brittle–ductile transition Eqs. (11) and (12) in the previous paper [11], it is found that an additional item T^{*} appears in Eqs. (4) and (5). These equations imply that the T_{BD} of particle toughened thermoplastic linearly decreases with increasing T^{*}, whereas the $\mathrm{ID_c}$ increases nonlinearly with increasing T^{*}. From Eq. (6), it is known that T^{*} is a function of cavitations volume V_{c}, and possesses temperature dimension. Therefore, the real significance of cavitations is that it reduces T_{BD} of the blend directly through T^{*}. The higher the cavitations volume, the higher value of the T^{*} is, and the lower the T_{BD} of the blend.

3. Application of the theory

Firstly, an evaluation is made of the value of T^{*} of PC/EPDM blends. It is known that the number average molecular weight of the PC used in the experiment [15] is 18.5 kg/mol. Assuming $\bar{P} = 40$ MPa, $\ln B/\gamma = 2$, the density of the PC is 1.1 g/cm^3, and $\alpha V_{\mathrm{c}} = 0.1\% V_{\mathrm{o}}$ where V_0 is the sample volume without the dilative stress. The value of T^{*} calculated from Eq. (6) is 40.5 K, i.e. the T_{BD} will reduce 40.5 K.

In the experiments of Borggreve and Gaymans for nylon 6/elastomer blends [13,14], it is found that the T_{BD} of the nylon 6/elastomer Arnitel (E315) blend is considerably higher than that of the nylon 6/EPDM blend although the modulus of Arnitel (E315) is less than one-tenth of the modulus of the nylon 6. Further experimental results show that the volume changing due to cavitations at 10% strain of the nylon 6/Arnitel (E315) blend is only one fifth of that of

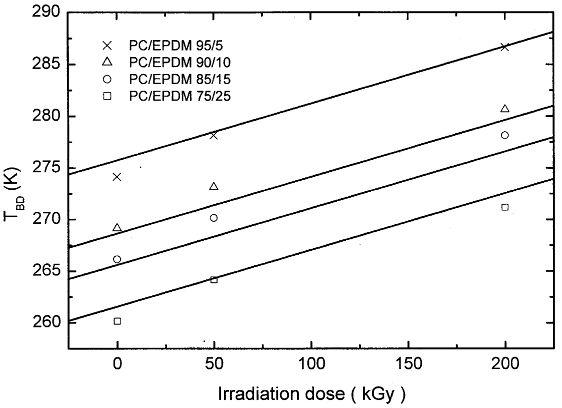

Fig. 1. Variation of T_{BD} with irradiation dose for various PC/EPDM blends, in which $QE = 170$ (μm^3 K^2); the values of d for various PC/EPDM blends are from the experiment [15], i.e. $d = 0.38$ μm) for PC/EPDM 95/5; $d = 0.36$ μm) for PC/EPDM 95/10; $d = 0.38$ μm) for PC/EPDM 95/15; $d = 0.42$ μm) for PC/EPDM 95/25.

the nylon 6/EPDM blend. From Eq. (6), it can be known that the value of T^* of the nylon 6/Arnitel (E315) blend should be one fifth of that of the nylon 6/EPDM blend. Therefore, its T_{BD} is markedly higher than that of the nylon 6/EPDM blend.

Similar results were observed by van der Sanden et al. In their experiment, the T_{BD} of the PC/EPDM blends increased markedly with increasing irradiation dose [15]. Irradiation can lead to the increase of the modulus of EPDM rubber due to the crosslink of EPDM molecules. From the results of dynamic mechanical thermal analysis (fig. 6 in Ref. [15]), it is known that the flat modulus of EPDM rubber increases from about 20 to 70 MPa with increasing irradiation dose from 0 to 200 kGy. However, these moduli are much lower than that of PC (about 3500 MPa). According to the results in the previous paper [12], the value of the E in Eq. (4) can remain roughly unchanged during the modulus of EPDM rubber increases from 20 to 70 MPa. This indicates that the great change of the T_{BD} caused by irradiation comes from the change of T^*. Irradiation can lead to the crosslink of EPDM molecules, thereby decreasing the cavitations ability of the EPDM rubber. In order to make qualitatively calculation, we assume T^* linearly decrease with increasing irradiation dose, and take $QE = 170$ (μm^3 K^2). The values of EPDM particle size and ID for various blends are from the measurement of the experiment [15]. The variation of the T_{BD} with irradiation dose calculated from Eq. (4) is shown in Fig. 1. It is seen that the calculated results are well in agreement with the experiment, indicating that the assumption of the linear relation between T^* and irradiation dose is reasonable within the region of 0–200 kGy irradiation dose.

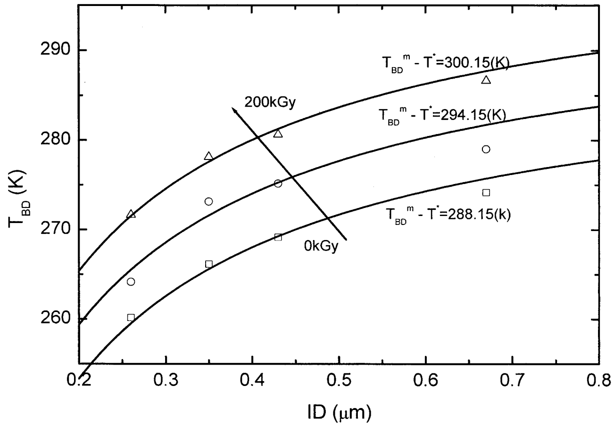

Fig. 2. Variation of T_{BD} with ID for different irradiated PC/EPDM blends, in which $QE = 170$ μm^3 K^2) and the particle sizes for various PC/EPDM blends are with the same values in Fig. 1.

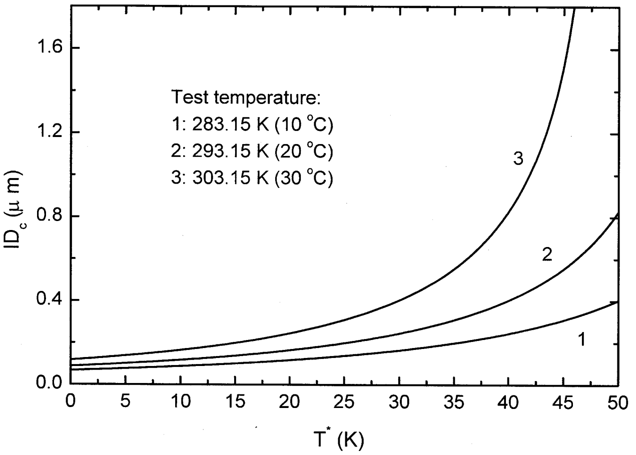

Fig. 3. Variation of ID_c with T^*, in which $d = 0.38$ μm, $QE = 170$ μm^3 K^2), and $T_{BD}^m = 353.15$ K).

Fig. 2 is the variation of the T_{BD} with ID calculated from Eq. (4). The experimental results in Ref. [15] are also shown in this figure for the purpose of comparison. In this figure, we assume that the value of $T_{BD}^m - T^*$ linearly changes from 288.15 to 300.15 K when the irradiation dose changes from 0 to 200 kGy. It is seen that the experimental data correlate well with the theoretical prediction, suggesting that the assumption is reasonable. In this experiment [15], it is found that both the molecular weight and the properties of the PC remains unchanged within the irradiation region from 0 to 200 kGy, implying that the brittle–ductile transition temperature of pure PC (T_{BD}^m) is a constant for all the samples tested with the same strain rate. Therefore, we can conclude that the change of the value of $T_{BD}^m - T^*$ results from the change of the value of T^*, namely the change of the cavitations ability of the EPDM rubber caused by irradiation.

From Eq. (5), it is known that critical interparticle distance (ID_c) is also a function of T^*. The lower value of T^*, i.e. the lower cavitations ability of the particle, the shorter the ID_c is. Further calculation for the ID_c versus T^* is shown in Fig. 3. The result shows that the ID_c non-linearly increases with increasing T^* at constant temperature.

Finally, it is known that the rigid particle is very difficult to be voided during fracture. The voiding can only occurs between polymer matrix and the surface of rigid particles for thermoplastic/rigid particle blends. According to the discussion above, the value of T^* in such blend is extremely low, leading to a very high brittle–ductile transition temperature (T_{BD}) of the blend. Therefore, the rigid particle size must be smaller enough, or the temperature is high enough in order to obtain ductile thermoplastic/rigid particle blends.

4. Conclusions

The brittle–ductile transition equations including cavitations effect was established for particle toughened thermoplastic. It was pointed out that the volume of cavitations was a key parameter that determined the BDT for particle-toughened thermoplastic. The results showed that the larger the volume of cavitations, the lower the BDT temperature. Calculation results correlated well with the experiments. In addition, the cavitations volume was extremely small for thermoplastic/rigid particle blends, leading to an extremely low value of T^*. This was why the rigid particle was much more difficult than elastomers to be used to toughen thermoplastic effectively.

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