

BRITTLE-DUCTILE TRANSITION OF POLYMERS AND ITS PERCOLATION MODEL*

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Abstract The brittle-ductile transition (BDT) of particle toughened polymers was extensively studied in terms of morphology, strain rate, and temperature. The calculation results showed that both the critical interparticle distance (ID_c) and the brittle-ductile transition temperature (T_{BD}) of polymers were a function of strain rate. The ID_c reduced nonlinearly with increasing strain rate, whereas T_{BD} increased considerably with increasing strain rate. The effects of temperature and plasticizer concentration on BDT were discussed using a percolation model. The results were in agreement with the experiments.

Keywords Particle toughening polymers, Brittle-ductile transition, Percolation

INTRODUCTION

Toughness is a key parameter that determines whether a polymer can be used as an engineering material. Therefore, polymer toughening has been the subject of interest for polymer scientists and engineers since polymers were first used as engineering materials. In general, the toughness of polymers can undergo a sharp transition with increasing temperature, decreasing strain rate, *etc.* This brittle-ductile transition (BDT) of polymers plays a key role in polymer toughening and application.

The brittle-ductile transition of a polymer can be seen clearly from the schematic diagram as shown in Fig. 1. The regions 1, 2 and 3 in this diagram correspond to brittle, brittle-ductile transition and ductile regimes, respectively. X is a parameter that can induce the brittle-ductile transition of the polymer. It may refer to temperature, rubber content, deformation speed, plasticizer content and so on. X_c is the critical value of X at which BDT occurs. This critical point is a basic reference point for designing ductile polymer materials. It is also the limit point for a polymer to be used as tough material in engineering. On the other hand, critical phenomena are an important subject for scientists. Therefore, studying the BDT of polymers has special meaning both in science and engineering.

THEORETICAL

In general, critical BDT point is a function of temperature, strain rate, dispersed particle size and content, the properties of both matrix polymer and dispersed particle material, test method, and so on. In this case, a function F is expected at the critical BDT point:

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$$F(T, \gamma, d, v, E_m, E_d, \dots) \Big|_{\text{at critical point}} = 0 \quad (1)$$

where T , γ , d , v , E_m , E_d refer to temperature, strain rate, dispersed particle size, the volume fraction of dispersed particle, the modules of matrix polymer, and the modules of dispersed particle. Compared with the dispersed particle size and the volume fraction of dispersed particles, Wu found that interparticle distance (ID) is more important in determining the BDT of polymers^[13]. Therefore, we use ID instead of d and v in the function. Equation (1) can be rewritten as the following form:

$$F(T, \gamma, ID, E_m, E_d, \dots) \Big|_{\text{at critical point}} = 0 \quad (2)$$

The definition of ID is shown in Fig. 2, its value can be determined from equation (3).

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

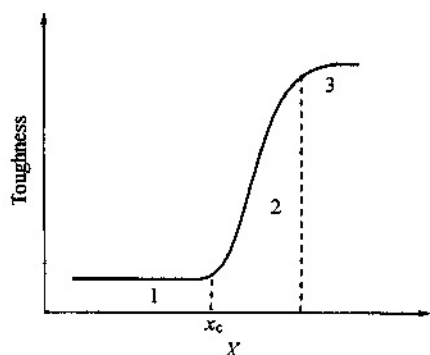


Fig. 1 Schematic diagram showing the brittle-ductile transition of a polymer.

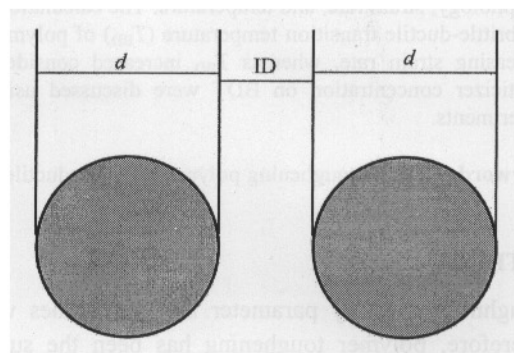


Fig. 2 Schematic diagram showing the definition of interparticle distance (ID)

Based on the elastic viscous theory of polymers and the percolation model^[12], the expression of $F(T, \gamma, ID, \dots)$ at the critical BDT point can be given as:

$$F(T, \gamma, ID, E_m, E_d, \dots) = T_{BD}^m - T - \sqrt{\frac{QE}{[(ID + d)^3 - d^3]}} = 0 \quad (4)$$

where d , ID and T refer to the diameter of dispersed phase, interparticle distance and temperature respectively; E is the strain energy of the matrix in the stressed volume. T_{BD}^m and Q are expressed as:

$$T_{BD}^m = \frac{\Delta G}{R \ln(B/\gamma)}; \quad Q = \frac{12E_m V^2}{\pi R^2 [\ln(B/\gamma)]^2} \quad (5)$$

where ΔG is the activation energy of matrix polymer, R is the gas constant, V is the activation volume of matrix polymer, B is a constant. From Eq. (4), it is easy to obtain the expressions of critical interparticle distance (ID_c) and BDT temperature (T_{BD}) for particle toughened polymers, respectively.

$$ID_c = \left[\frac{K}{(1 - T/T_{BD}^m)^2} + d^3 \right]^{\frac{1}{3}} - d \quad (6)$$

$$T_{BD} = T_{BD}^m \left[1 - \sqrt{\frac{K}{(ID + d)^3 - d^3}} \right] \quad (7)$$

where $K = \frac{12E_m V^2}{\pi \Delta G^2}$, which is independent of strain rate. From Eqs. (6), (7), it is found that T_{BD}^m is an important parameter that determines the BDT of particle toughened polymers. The calculated results from Eqs. (6) and (7) are shown in Figs. 3 and 4, respectively. Figure 3 reveals that the critical interparticle distance (ID_c) decreases nonlinearly with increasing T_{BD}^m . However, the brittle-ductile transition temperature (T_{BD}) of particle toughened polymers increases linearly with increasing T_{BD}^m (Fig. 4).

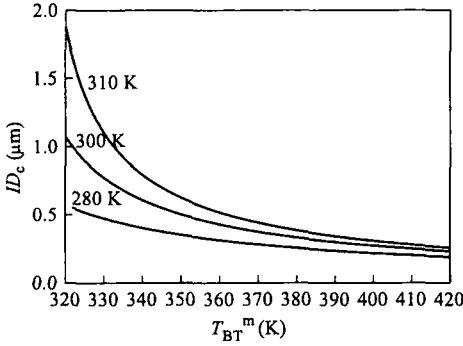


Fig. 3 Variation of critical interparticle distance (ID_c) with T_{BD}^m at various temperatures calculated from Eq. (6), in which $K = 0.01 \mu m^3$, $d = 0.3 \mu m$

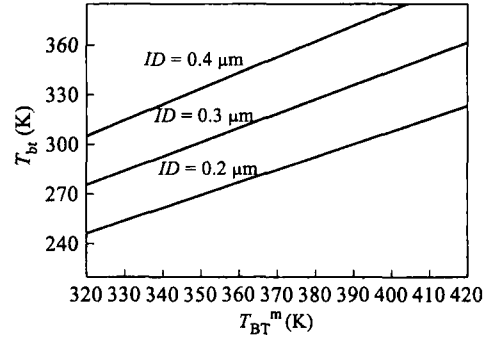


Fig. 4 Variation of brittle-ductile transition temperature (T_{BD}) with T_{BD}^m for various interparticle distances calculated from Eq. (7), in which $K = 0.01 \mu m^3$, $D = 0.3 \mu m$

From Eq. (5), it is known that T_{BD}^m is a function of strain rate ($\dot{\gamma}$) and the activation energy (ΔG) of matrix polymer. The higher the strain rate, the higher the T_{BD}^m is. Thereby, increasing strain rate can lead to a drop of the critical interparticle distance. This prediction is well in agreement with the experiment by Jiang *et al.* The experimental results showed that the critical interparticle distance decreased nonlinearly with increasing strain rate for polypropylene (PP)/ethylene-propylene-diene monomer (EPDM) blends^[3].

On the other hand, from Eq. (5) it is known that T_{BD}^m decreases with decreasing activation energy of the matrix polymer (ΔG). Therefore, the results of Fig. 4 suggest that the brittle-ductile transition temperature reduces with decreasing ΔG . In general, introduction of plasticizer into a polymer can reduce the activation energy of the polymer, and can thus decrease the brittle-ductile transition temperature of the polymer blends. In the nylon 6/EPDM blends, it was found that the brittle-ductile transition temperature is a function of water concentration in the nylon 6 matrix. The brittle-ductile transition temperatures dropped considerably with increasing water concentration in nylon 6 matrix for various nylon 6/EPDM blends^[4]. Water can be considered as plasticizer for nylon. Therefore, these experimental results correlate well with the theoretical prediction.

Finally, from Eq. (6) it is known that increasing test temperature (T) and decreasing value of T_{BD}^m have an equivalent effect on the brittle-ductile transition. Compared with test temperature (T) and T_{BD}^m , $1 - T/T_{BD}^m$ is a more important parameter that determines the brittle-ductile transition of polymers. The brittle-ductile transition curves of ID_c versus $1 - T/T_{BD}^m$ should be independent of matrix polymers for their blends with the same dispersed particle. According to the percolation model, the critical brittle-ductile transition point corresponds to the "first-path" percolation threshold formed by yielded stress volumes^[5]. The effects of test temperature and T_{BD}^m on the "first-path" percolation threshold (critical brittle-ductile transition point) can be seen in Fig. 5. From this figure, it can be found that there is a "first-path" percolation threshold for any test temperature and any T_{BD}^m . The results indicate that test temperature, strain rate, plasticizer concentration, *etc.* depend on each other at the critical brittle-ductile transition point. Ductile fracture of particle toughened polymers can be achieved by decreasing strain rate, increasing plasticizer concentration or increasing test temperature.

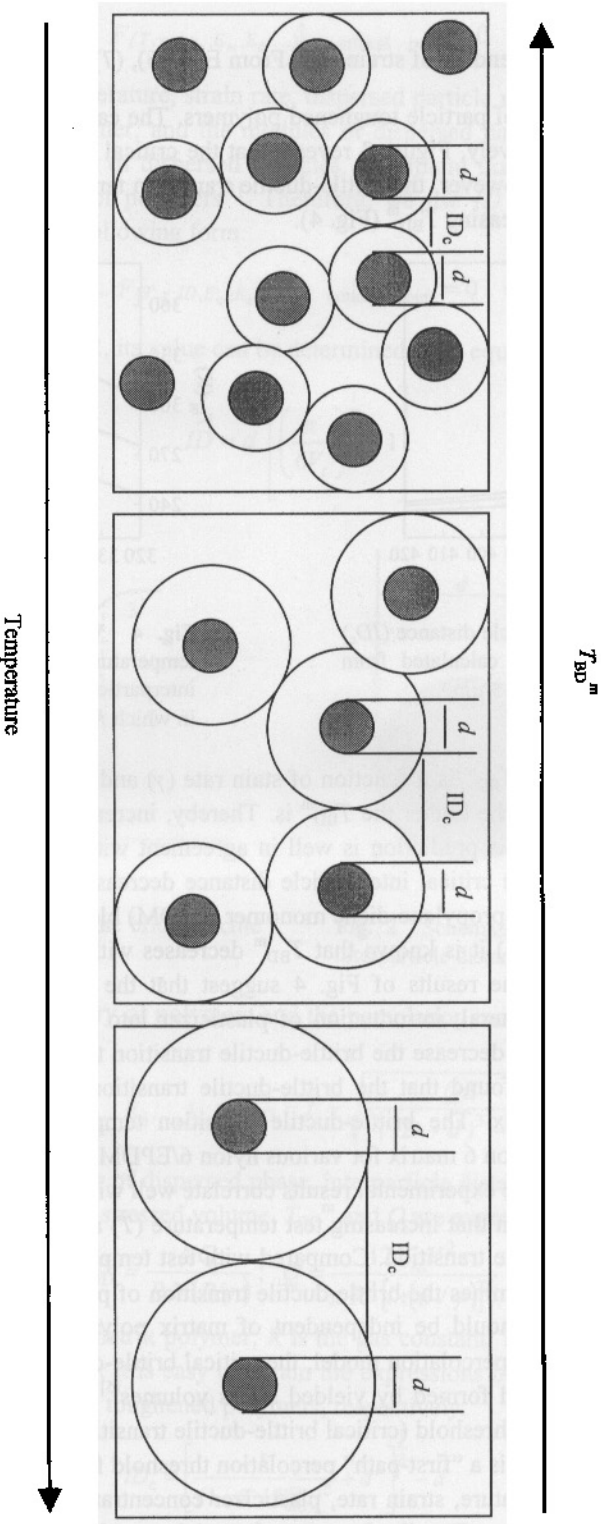


Fig. 5 Schematic diagram showing the “first-path” percolation thresholds at various temperatures and T_{BD}^m

CONCLUSIONS

Effects of test temperature, interparticle distance, strain rate, plasticizer on brittle-ductile transition of particle toughened polymers were studied in theory. The calculation results showed that both critical interparticle distance (ID_c) and brittle-ductile transition temperature (T_{BD}) of polymers were a function of strain rate and plasticizer concentration. The ID_c reduced with increasing strain rate, whereas the T_{BD} increased considerably with increasing strain rate. Furthermore, the theoretical results indicate that test temperature, strain rate, plasticizer concentration, *etc.* depend on each other at the critical brittle-ductile transition point, and the ductile fracture of particle toughened polymers can be achieved by decreasing the value of T_{BD}^m or by increasing test temperature.

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