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Interparticle distance–temperature–strain rate equivalence for the brittle–tough transition in polymer blends

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From the angle of energy transformation an equation was obtained for the brittle transition in polymer blends. The effects of interparticle distance, temperature and strain rate on the brittle–tough transition in polymer blends were characterized by this equation. The calculations show that, for this transition: (1) increasing temperature and decreasing interparticle distance are equivalent and the shift factor increases with increasing temperature; (2) decreasing strain rate and decreasing interparticle distance have equivalent effects on the transition; (3) the strain rate must be optimum in order to find the brittle–tough transition phenomena for a given temperature region. © 1998 Published by Elsevier Science Ltd. All rights reserved

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Introduction

Since 1985, when the interparticle distance (*ID*) model shown in *Figure 1* for the brittle–tough transition (BTT) in nylon 66/rubber blends was first proposed by Wu[1], this subject has been extensively studied. ID can be obtained from equation (1) for the cubic packing of spherical particles:

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

where d is the rubber particle diameter and V_r is the rubber volume fraction. But there are still many outstanding experimental phenomena that have not been interpreted. First it was found that the critical interparticle distance (ID_c) increases nonlinearly with increasing temperature[2]. It was then found that ID_c not only depends on the matrix materials[3–5] but also on the mechanical properties of the dispersed phase[6,7], strain rate[8], plasticizer[9] and so on. This study aims to study the effects of interparticle distance, temperature and strain rate on the brittle–tough transition in polymer blends and to give quantitative relations between these three factors.

Model and theory

As the elastic moduli and Poisson's ratio of the dispersed phase are different from those of the matrix, when a force is applied to a sample of the polymer blend a stress concentration will form around particles of the dispersed phase. Its scope can be described as a stressed volume, in which the diameter of the stressed volume $S = d + ID$, where d is the diameter of the dispersed particle phase and *ID* is the interparticle distance, as shown in *Figure 2a*. There are a great many experimental and theoretical results which confirm that, during impact or tensile fracture of polymer

blends, the rubber particles will be greatly deformed until cavitation of the rubber particles occurs, relieving the triaxial dilative stress[10–13]. This leads to shear yielding in those ligaments which are thinner than the critical value(ID_c), and the polymer blend is tough. This process was described as the percolation model by Wu and Margolina[14,15]. According to this model, the stressed volumes will yield and propagate during the process of BTT, and the critical point corresponds to the percolation threshold, which refers to the onset of first-path connectivity as shown in *Figure 2b*. If the brittle–tough transition is a percolation phenomenon, one may expect a scaling law above the percolation threshold ϕ_s as in equation (2):

$$G \propto (\phi_s - \phi_{sc})^\beta \qquad (2)$$

where G is the toughness, ϕ_s and ϕ_{sc} are the stressed volume fraction and critical stress volume fraction, and β is the critical exponent. The experimental results show that $\beta = 0.45$ for nylon/rubber blends[14] and $\beta = 0.42$ for PP/rubber blends[4]; these values are close to the theoretical value $\beta = 0.44$ for three dimensions[16]. All this supports the idea that the BTT is a percolation process. But the difference from ordinary percolation is that the percolation clusters are the yielded stressed volumes. This suggests that the matrix in a stressed volume is either completely yielding or not at all. *Figure 2b* shows that some rubber particles are not in the percolation cluster; therefore no matrix is yielding around them although the matrix around such particles is stressed, otherwise BTT would not take place sharply and the critical exponent β would not be close to the theoretical value $\beta = 0.44$. So we must consider the matrix in a stressed volume as a whole.

Now we consider that equal-sized elastomer particles are randomly distributed in thermoplastic matrix. No matter how high the elastomer content in the matrix, we can draw the stressed volumes which refer to the onset of first-path connectivity shown in *Figure 3*. The lower the elastomer content, the larger the size of the stressed volume at the onset of first-path connectivity. As mentioned above, only
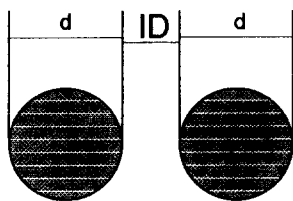
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Figure 1 Model for (surface to surface) interparticle distance *ID* and rubber particle diameter *d*

when these connected stressed volumes yield can the BTT take place. So it is very important to give a criterion of the matrix yielding in a stressed volume.

We take the stressed volume as a strain energy storage volume. The total strain energy in the matrix in the stressed volume is E, which is dominated by equation (3):

$$E = \int_{V_{shell}} W_s dv \qquad (3)$$

where dv is the differential volume in the spherical shell, W_s is the strain energy density in the matrix and V_{shell} refers to the integral region (spherical shell) of the matrix which is shown in *Figure 2a*. For a uniform stress field, W_s can be expressed as $W_s = \sigma^2/2M$, and $E = (\sigma^2/2M) \times V_{shell}$. At the yield point, W_s tends to $\sigma_y^2/2M$. But for polymer blends the stress field around a dispersed phase is no longer uniform, nor is W_s uniform. Here we would like to emphasize that for a given position this energy density W_s is mainly dominated by the mechanical properties of both the matrix and the dispersed phase, such as the modulus, Poisson's ratio, and brittle strength of the matrix.
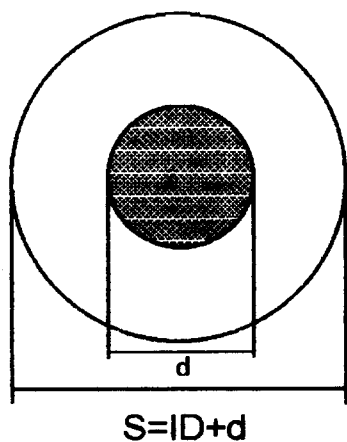
If the matrix in the stressed volume is yielding, the total strain energy E in the matrix in a stressed volume must be greater than W_y, the work required to make the matrix in the stressed volume yield, which can be expressed as:
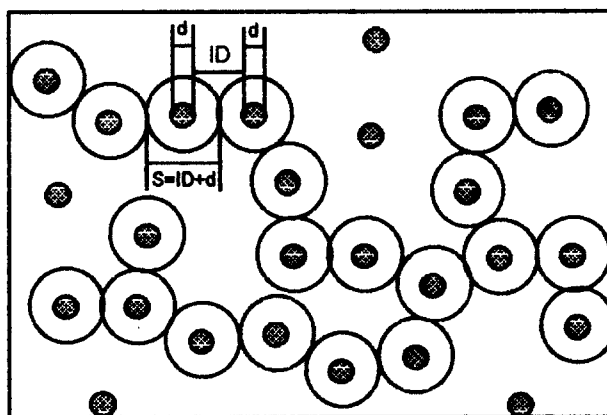
$$W_y = A \times V_s \qquad (4)$$

for ductile fracture

$$E \geq W_y \qquad (5)$$

where V_s is the volume of the matrix spherical shell, and A is the work required to make unit volume of matrix yield. Its

value can be obtained from equation (6):

$$A = \int_0^{\varepsilon_y} \sigma d\varepsilon = \frac{1}{2}\sigma_y \varepsilon_y \qquad (6)$$

where σ_y is the yield stress and ε_y the yield strain of the matrix. V_s can be obtained from equation (7):

$$V_s = \frac{\pi}{6}\left[(d + ID)^3 - d^3\right] \qquad (7)$$

If the fracture is ductile, the stressed volumes must conform to inequality (5). From equations (5)–(7), it is obtained that:

$$E \geq \frac{\pi}{12}\sigma_y \varepsilon_y \left[(d + ID)^3 - d^3\right] \qquad (8)$$

This inequality means not only that the yield stress (σ_y) and yield strain (ε_y) are two important mechanical parameters for polymer materials, but also that their product has a strong influence on the brittle–tough transition in polymer blends. For a given E and d, the smaller the product of yield stress (σ_y) and yield strain (ε_y) for the matrix, the longer is the critical interparticle distance.

Substituting ε_y by σ_y/M_1, where M_1 is the modulus of the matrix, we have

$$E \geq \frac{\pi}{12M_1}\sigma_y^2\left[(d + ID)^3 - d^3\right] \qquad (9)$$

Applying the Eyring[17] theory of viscosity, the relation between the strain rate, temperature and yield stress can be described as:

$$\dot{\gamma} = B \exp\left[\frac{-(\Delta G - V\sigma_y)}{RT}\right] \qquad (10)$$

where $\dot{\gamma}$ is the strain rate, B is a constant, ΔG is the activation energy, V is the activation volume, R is the gas constant and T is the absolute temperature.

From equations (9) and (10), we obtain the criterion for the brittle–tough transition in polymer blends:

$$T = T_g - \sqrt{\frac{QE}{\left[(ID_c + d)^3 - d^3\right]}} \qquad (11)$$

a

b

Figure 2 Schematic diagram of stressed volume around a dispersed particle
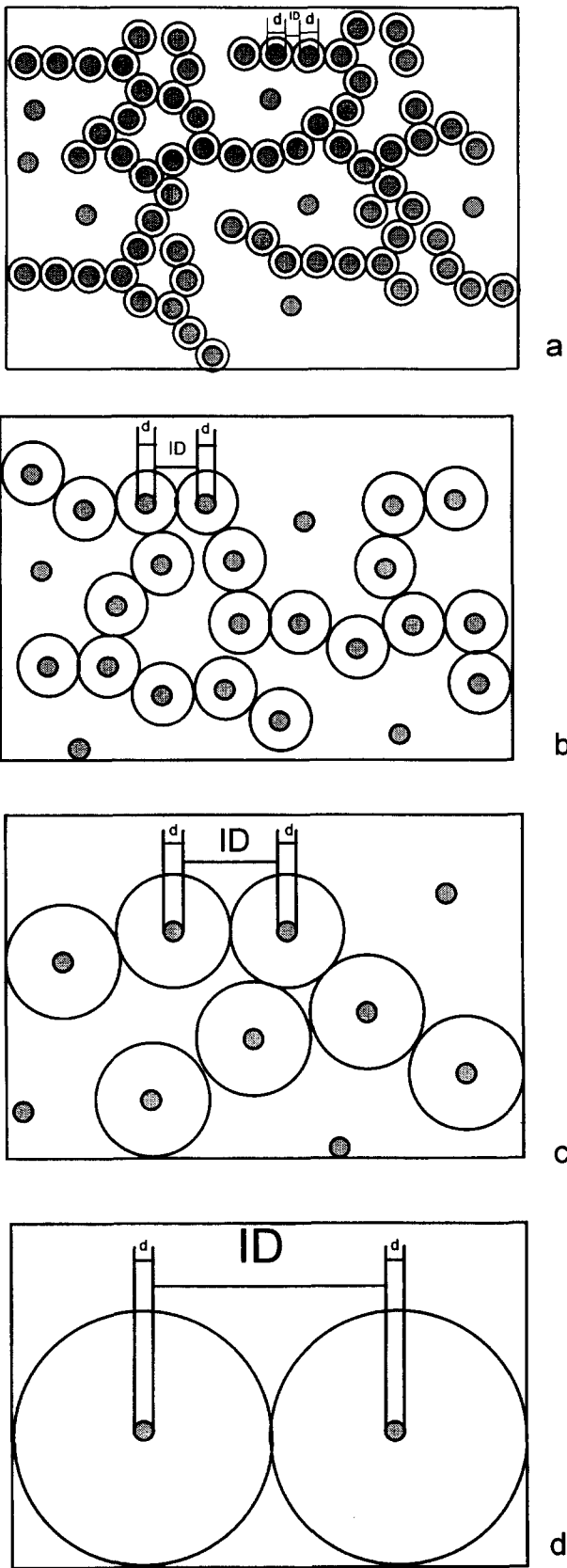
Figure 3 Schematic of the onset of first-path connectivity of the stressed volumes for different elastomer contents

This equation can be rearranged to the following form:

$$ID_c = \left[\frac{QE}{(T_g - T)^2} + d^3 \right]^{\frac{1}{3}} - d \qquad (12)$$

where

$$T_g = \frac{\Delta G}{R \; \ln(B/\dot{\gamma})} \quad \text{and} \quad Q = \frac{12M_1 V^2}{\pi R^2 \left[\ln(B/\dot{\gamma})\right]^2} \qquad (13)$$

and

As equations (11) and (12) are the equations for the brittle–tough transition in polymer blends, *ID*, *T* and $\dot{\gamma}$ in these equations refer to the critical interparticle distance, critical temperature and critical strain rate respectively.

Application of the theory

T, V_r and *d* in equations (11) and (12) can be measured by experiment. *ID* can be obtained from equation (1). In order to obtain the physical meaning of T_g, we let *ID* approach infinity and obtain $T = T_g$ from equation (11). According to equation (1), we know that as *ID* approaches infinity the volume fraction V_r tends to zero; i.e., the sample is the pure polymer without a second phase. Thus the physical meaning of T_g is the brittle–tough transition temperature of the matrix, which can be measured by experiment. *E* is the total strain energy of the matrix in the stressed volume and is difficult to measure directly by experiment. For a given blend system, if we take *QE* as approximately independent of temperature, from equation (12) it is obvious that the critical interparticle distance ID_c increases nonlinearly with increasing temperature.

In the experiments of Borggreve *et al.*[2], the rubber particle size changed from 0.29 to 1.94 μm. The brittle–tough transition temperature for pure dry nylon is 74°C, i.e. $T_g = 74°C$. Thus, from equation (11) and the experimental data for ID_c, it is obtained that *QE* is approximately independent of temperature, as shown in *Figure 4*. When *QE* is taken as 400 μm^3 K^2), the results of the temperature dependence of ID_c calculated using equation (12) are shown in *Figure 5*, from which it is seen that the theory is well in agreement with experiment and that Margolina's empirical formula[18] is the first-order approximate result of equation (12) in the lower temperature region.

Combining equations (11) and (12) with Goodier's equations[19], the effect of the properties of the dispersed phase and the matrix on the brittle–tough transition in polymer blends have been well studied. The detail will be published in a separate paper. Calculations show that: (1) *E* changes much more slowly with changing modulus of both matrix and dispersed phase (*n*) when the ratio of shear modulus of matrix to that of dispersed phase is more than 10; (2) the strain energy density W_s rapidly decreases with increasing interparticle distance *ID*.

When we calculated the temperature dependence of ID_c for nylon/EPDM blends using equation (12), we took *E* as being approximately independent of temperature and *ID*. This is because the temperature region we study is between the glass temperature of the elastomer and the brittle–tough transition temperature of the matrix. In this temperature region, for nylon/EPDM blends, the value of *n* is much more than 10 and remains roughly unchanged and, compared with the yield strength of the matrix (dominating W_y), the brittle fracture strength of the matrix (dominating *E*) changes much more slowly with temperature[20]; on the other hand, the strain energy density W_s rapidly decreases with increasing *ID*; thus increasing *ID* does not make *E* increase significantly.

Interparticle distance–temperature–strain rate equivalence

All that we have mentioned above is focused on the critical transition point; in fact, for tough fracture of a polymer blend, we can obtain the following inequality from

inequality (9) and equation (10).

$$QE \geq (T_g - T)^2 \left[(ID + d)^3 - d^3 \right] \qquad (14)$$

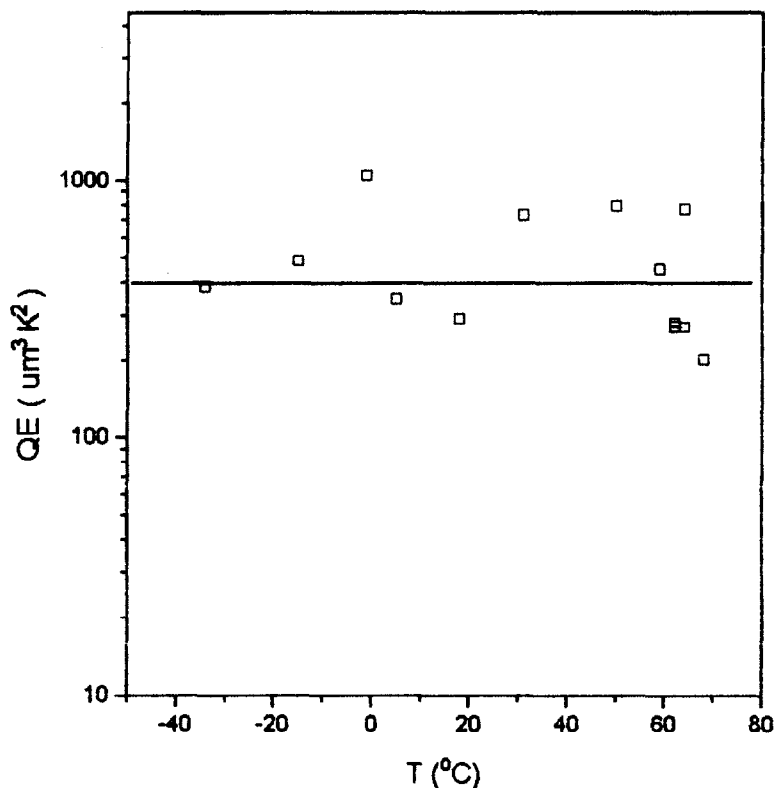The total strain energy in the matrix shell E may be smaller

Figure 4 Temperature dependence of QE in nylon6/rubber blends, obtained from equation (9) by substituting ID_c, d and T by the data in the experiment of Borggreve et al.[2] and $T_g = 74°C$
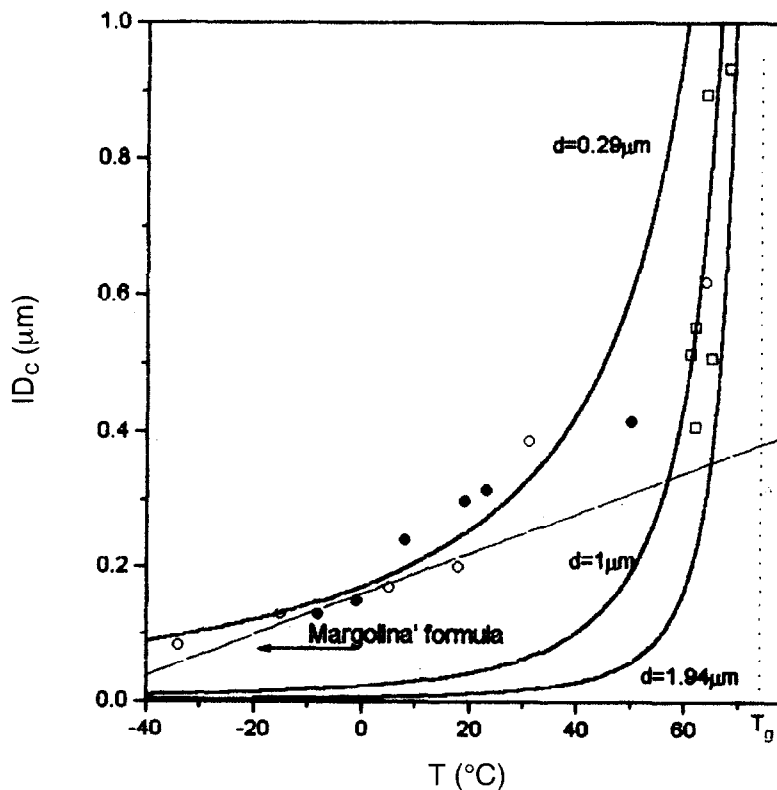

Figure 5 Comparison, for $T_g = 74°C$ and $QE = 400 \ \mu m^3 \ K^2$, of temperature dependence ID_c calculated from equation (9) with experimental results[2] and results calculated from Margolina's empirical formula[18]

than the work required to make the matrix shell yield. In this situation the fracture of the polymer blend is brittle. In order to obtain ductile fracture, the matrix yield stress σ_y or the interparticle distance ID must be decreased till W_y is smaller than E. The yield stress σ_y can be decreased by increasing the temperature or decreasing the strain rate, and ID can be decreased by adding elastomer to the matrix. In *Figure 3*, if T_{BT}^a is the brittle–tough transition temperature for blend **a**, at this temperature blends **b**, **c** and **d** would be brittle. In order to obtain ductile fracture for these three blends, the temperature must be increased, and it can be obtained that $T_{BT}^a \le T_{BT}^b \le T_{BT}^c \le T_{BT}^d$, which means that tough polymer blends can be obtained either by increasing the temperature or by decreasing ID. We call this phenomenon ID–T equivalence for BTT. It is easy to obtain the shift factor a_T from equation (12) for a small temperature difference:

$$a_T = \frac{2QE}{3\{(T_g - T)^{5/3}[QE + d^3(T_g - T)^2]^{2/3}\}}\Delta T \qquad (15)$$

where ΔT is the difference between two temperatures. From equation (15) it can be obtained that the shift factor a_T increases with increasing temperature for the same value of ΔT. When $\Delta T = 5$ K, QE $= 165\ \mu m^3\ K^2$, $T_g = 15°C$, $d = 0.38\ \mu m$. The results of calculations for shift factor a_T *versus* temperature are shown in *Figure 6*.

As we know, there have been no experimental results to directly verify this principle, but *Figure 7* in van der Sanden *et al.*[7] shows the notched tensile toughness in PC(polycarbonate)/EPDM(ethylene–propylene–diene monomer rubber) blends *versus* temperature for different rubber contents. Now we show toughness *versus* ID for different temperatures, as shown in *Figure 7*. This not only verifies ID–T equivalence, but also confirms that the shift factor a_T increases with increasing temperature for the same temperature difference (5°C).

From inequality (14), it is known that either decreasing the strain rate (i.e., decreasing T_g) or decreasing ID is the other way by which tough polymer blends can be obtained; in other words, decreasing strain rate and decreasing interparticle distance have equivalent effects on the brittle–tough transition in polymer blends.

From equations (11) and (12), it is known that the lower the strain rate $\dot{\gamma}$, the lower is the brittle–tough transition temperature of a polymer blend. If the temperature remains unchanged, the critical interparticle distance increases with decreasing strain rate, which can explain Dijkstra *et al.*'s experimental results[8]: if the strain rate is low, even a very low rubber content (which means a larger ID when d remains unchanged) is capable of toughening the plastic.

According to equation (11), the brittle–tough transition temperature in slow-speed testing should be much lower than that in high-speed testing, which means that for a given polymer blend system the strain rate must be optimum in order to find BTT phenomena in a given temperature region.

Conclusions

(1) An equation for the brittle–tough transition in polymer blends due to matrix shear yielding was obtained, from which the effects of temperature, interparticle distance and strain rate on BTT were correlated.

(2) The results calculated from equation (12) for temperature dependence of interparticle distance are in agreement with experiment over a wide temperature range, including temperatures close to T_g. Margolina's equation is a first-order approximation to our theory in the lower temperature region.

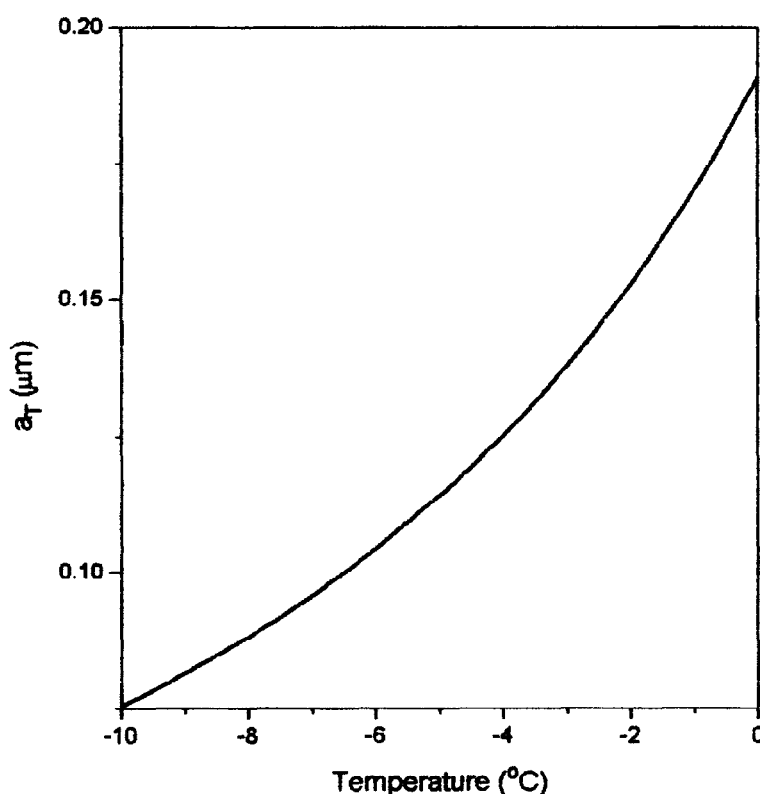(3) Interparticle distance–temperature equivalence is proposed in this paper. The shift factor increases with

Figure 6 Temperature dependence of shift factor a_T in which $\Delta T = 5$ K, $QE = 165\ \mu m^3\ T_g$, $T_g = 15°C$, $d = 0.38\ \mu m$
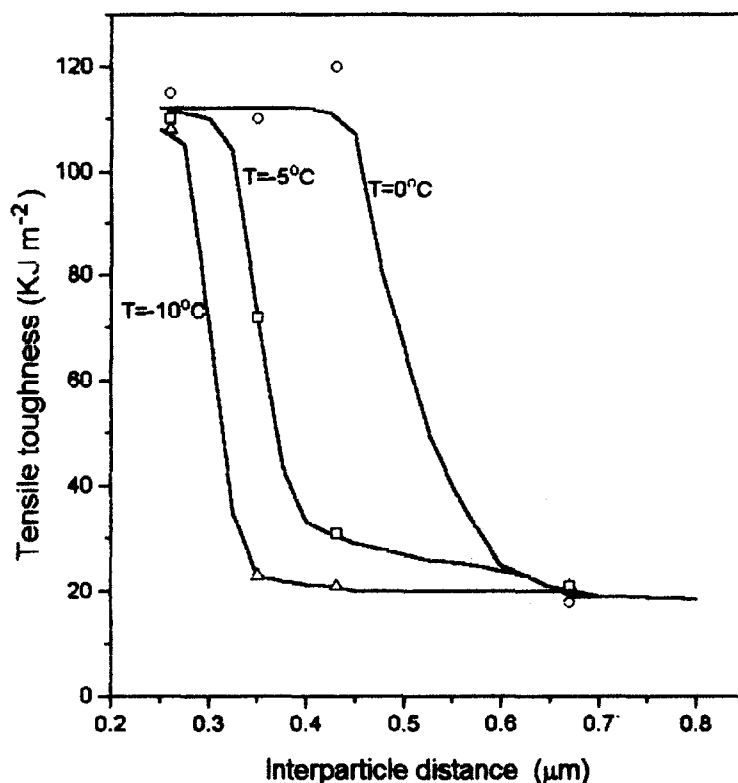
Figure 7 *ID–T* equivalence for PC/EPDM, taken from *Figure 7* in van der Sanden *et al.*[7].

increasing temperature. It is suggested that the dependence of toughness on interparticle distance shopuld be measured for different temperatures, in order to directly verify this equivalence for the brittle–tough transition in polymer bends.

(4) The critical interparticle distance increases with decreasing strain rate: the lower the applied deformation rate, the lower the brittle–tough transition temperature of the polymer blend; the strain rate must therefore be optimum in order to find brittle–tough transition phenomena for a given temperature region.

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