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# Brittle–tough transition in elastomer toughening thermoplastics: effects of the elastomer stiffness

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**Abstract**

The effect of the elastomer stiffness on brittle–tough transition in elastomer toughening thermoplastics was quantitatively studied. A correlation between brittle–tough transition temperature and the elastomer stiffness was obtained. The calculation from this correlation showed that the brittle–tough transition temperature ($T_{bt}$) of elastomer toughening thermoplastics slowly increased up to one tenth of the modulus of matrix, thereafter it increased rapidly with increasing the modulus of elastomer. The results indicated that the modulus of the elastomer must be one-tenth or less of that of the matrix in order to be effective at low temperature. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Toughening thermoplastic; Brittle–tough transition; Stiffness

## 1. Introduction

Toughness is one of the most important parameters that determine whether a polymer can be used as an engineering material. Therefore, toughening polymer is always an attractive topic in polymer physics and polymer materials sciences. From brittle to ductile, it is known that a polymer can undergo a sharp transition. This brittle–tough transition of polymer plays a key role in toughening polymer, and becomes a subject of interest for the polymer scientists.

In general, it is known that this transition depends on temperature, deformation speed, the morphology of dispersed phase, the mechanical properties of matrix and dispersed phase for elastomer toughening thermoplastic. The effects of temperature, strain rate and interparticle distance on the brittle–tough transition in elastomer toughening thermoplastic were quantitatively studied in the previous paper [1]. On the other hand, the experimental studies show that the toughness of elastomer toughening thermoplastics strongly depends on the mechanical properties of the elastomer. In patents of Du Pont [2,3], it is suggested that the modulus of the impact modifier must be one-tenth or less of that of the nylon matrix in order to be effective. The experimental results of Borggreve and Gaymans [4] show that the impact behavior improves with decreasing modulus of the impact modifier. Van der Sanden reported that the brittle–tough transition temperature of polycabonate (PC)/ethylene–propylene–diene monomer rubber (EPDM) blends increases with increasing irradiation dose (i.e. increasing the modulus of EPDM rubber) [5]. Similar results were also found in poly(butylene terephthalate) (PBT)/EPDM rubber blends by Jiang et al. [6] These phenomena were discussed in terms of the mechanical properties and the cavitation ability of the elastomers [5,7,8]. However, to the best of our knowledge, the correlations among brittle–tough transition temperature, the stiffness of the elastomer, and critical interparticle distance remain unclear up to now.

## 2. Theory and model

Based on the elastic viscous theory of polymer and percolation model, the brittle–tough transition equation for elastomer toughening polymer is given as [1]:

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

This equation can be rearranged in the following form:

$$T_{BT} = T_{BT}^{m} - \sqrt{\frac{QE}{[(ID + d)^3 - d^3]}} \tag{2}$$

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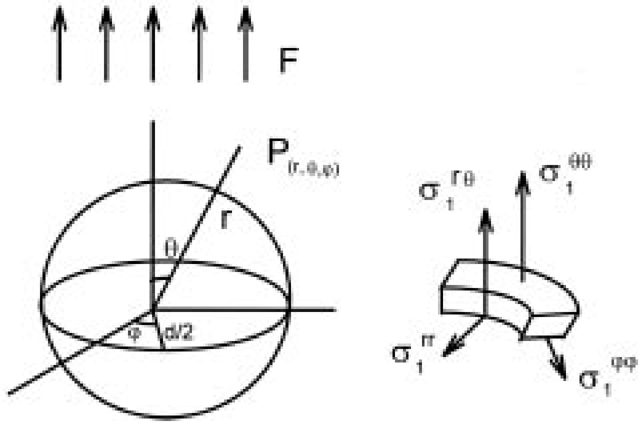

Fig. 1. Stress analysis for the model of composites containing spherical inclusion.

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. $T_{\mathrm{BT}}^{\mathrm{m}}$ is the brittle–tough transition of matrix material itself. $T_{\mathrm{BT}}^{\mathrm{m}}$ and $Q$ are expressed as:

$$T_{\mathrm{BT}}^{\mathrm{m}} = \frac{\Delta G}{\mathrm{R}\ln(B/\gamma)}; \qquad Q = \frac{12M_1V^2}{\pi\mathrm{R}^2[\ln(B/\gamma)]^2} \tag{3}$$

where $\gamma$ is the strain rate, $B$ is a constant, $\Delta G$ is the activation energy, $V$ is the activation volume, R is the gas constant and $M_1$ is the modulus of matrix.

The effects of temperature, strain rate and interparticle distance on the brittle–tough transition in elastomer toughening thermoplastic were well studied by these equations in the previous paper [1]. In order to obtain the effect of the properties of the elastomer on the brittle–tough transition in polymer blends, it is necessary to evaluate the value of the whole matrix strain energy ($E$) in the stressed volume around an elastomer particle. $E$ can be obtained by the following integration:

$$E = \int_{V_{\mathrm{shell}}} W_{\mathrm{s}}\,\mathrm{d}_v \tag{4}$$

where $d_{\mathrm{v}}$ is the differential volume in the spherical shell, $W_{\mathrm{s}}$ is the strain energy density in matrix and $V_{\mathrm{shell}}$ refers to integral region (spherical shell of matrix in the stressed volume). In spherical polar coordinate, as shown in Fig. 1, Eq. (4) can be expressed as:

$$E = 2\pi\int_{d/2}^{ID/2}\int_0^{\pi} W_{\mathrm{s}}r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta \tag{5}$$

The strain energy density in the matrix can be given as [5,9]

$$W_{\mathrm{s}} = \left(\frac{1}{2M_1}\right)[\sigma_1^2 + \sigma_2^2 + \sigma_3^2 - 2\nu_1(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_3)] \tag{6}$$

where $\sigma_1$, $\sigma_2$ and $\sigma_3$ are the three principal stresses, $M_1$ and $\nu_1$ are Young's modulus and Poisson's ratio of matrix, respectively. The three principal stresses can be written as [10]

$$\begin{aligned}
\sigma_1 &= \frac{1}{2}(\sigma_1^{rr} + \sigma_1^{\theta\theta}) + \frac{1}{2}\sqrt{(\sigma_1^{rr} - \sigma_1^{\theta\theta})^2 + 4(\sigma_1^{r\theta})^2}\\
\sigma_2 &= \frac{1}{2}(\sigma_1^{rr} + \sigma_1^{\theta\theta}) - \frac{1}{2}\sqrt{(\sigma_1^{rr} - \sigma_1^{\theta\theta})^2 + 4(\sigma_1^{r\theta})^2}\\
\sigma_3 &= \sigma_1^{\varphi\varphi}
\end{aligned} \tag{7}$$

where $\sigma_1^{rr}$, $\sigma_1^{\theta\theta}$, $\sigma_1^{\psi\psi}$ and $\sigma_1^{r\theta}$ are the stresses inside the composites containing spherical inclusion (elastomer) which are shown in Fig. 1. In order to make quantitative calculations, we neglect the interaction among particles and assume both matrix material and elastomer are homogeneous, isotropic, linear elastic and perfect adhesion between the elastomer and matrix. From Goodier's equations [11], these stresses can be expressed as:

$$\begin{aligned}
\sigma_1^{rr} &= 2\left\{\frac{2A}{r^3} - \frac{2\nu_1}{1-2\nu_1}\frac{C}{r^3} + 12\frac{B}{r^5} + \left[-\frac{2(5-\nu_1)}{1-2\nu_1}\frac{C}{r^3} + 36\frac{B}{r^5}\right]\cos 2\theta\right\}\\
\sigma_1^{\theta\theta} &= 2\left\{-\frac{A}{r^3} - \frac{2\nu_1}{1-2\nu_1}\frac{C}{r^3} - 3\frac{B}{r^5} + \left[\frac{C}{r^3} - 21\frac{B}{r^5}\right]\cos 2\theta\right\}\\
\sigma_1^{\varphi\varphi} &= 2\left\{-\frac{A}{r^3} - \frac{2(1-\nu_1)}{1-2\nu_1}\frac{C}{r^3} - 9\frac{B}{r^5} + \left[3\frac{C}{r^3} - 15\frac{B}{r^5}\right]\cos 2\theta\right\}\\
\sigma_1^{r\theta} &= 2\left\{-\frac{2(1+\nu_1)}{1-2\nu_1}\frac{C}{r^3} + 24\frac{B}{r^5}\right\}\sin 2\theta
\end{aligned} \tag{8}$$

$$\frac{A}{(d/2)^3} = -\frac{F}{8}\frac{n-1}{(7-5\nu_1)n + (8-10\nu_1)} \times \frac{2n(1-2\nu_2)(6-5\nu_1) + (3+19\nu_2-20\nu_1\nu_2)}{2n(1-2\nu_2) + (1+\nu_2)} + \frac{F}{4}\frac{\left[(1-\nu_1)\dfrac{1+\nu_2}{1+\nu_1} - \nu_2\right] - n(1-2\nu_2)}{2n(1-2\nu_2) + (1+\nu_2)}$$

$$\frac{B}{(d/2)^5} = \frac{F}{8}\frac{n-1}{n(7-5\nu_1) + (8-10\nu_1)}$$

$$\frac{C}{(d/2)^5} = \frac{F}{8}\frac{5(1-2\nu_1)(n-1)}{n(7-5\nu_1) + (8-10\nu_1)}$$

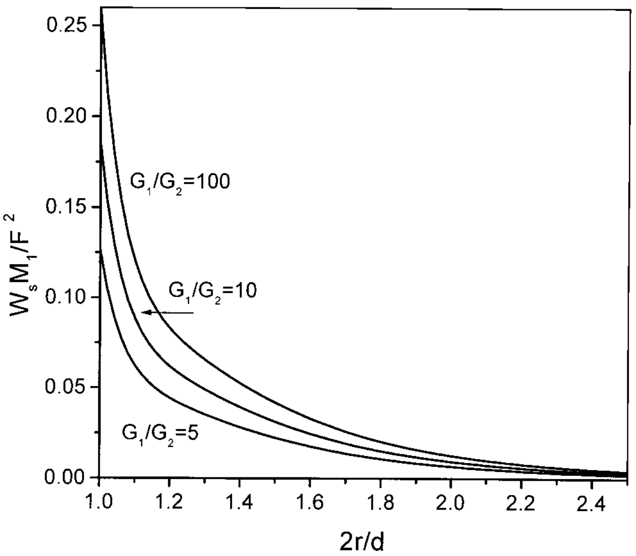

Fig. 2. Strain energy density $W_s$ in the matrix around an elastomer particle versus $r/d$, in which $\nu_1 = 0.43$, $\nu_2 = 0.5$.

where $n$ is the ratio of shear modulus ($G_1$) of the matrix to that ($G_2$) of the elastomer, $\nu_1$ and $\nu_2$ are Poisson's ratios for matrix and elastomer, respectively, $F$ the applied uniaxial tension, $r$ the radius from the center of the inclusion and the superscripts represent the tensorial notation. The effect of the stiffness of elastomer on brittle–tough transition can be calculated from Eqs. (2)–(8).

## 3. Results and discussion

Calculation results for the strain energy density from Eqs. (6)–(8) are shown in Figs. 2–4. Figs. 2 and 3 show the strain energy density distribution along $r$, and $\theta$. Fig. 4 gives the variation of the strain energy density with the ratio of shear modulus ($G_1$) of the matrix to that ($G_2$) of the elastomer ($n$). For the given blend with $d = 0.30$ μm, $ID = 0.30$ μm, the calculation results of the energy $E$ are shown in Fig. 5. From this figure, it is clear that when $n > 10$ the value of $E$ changes much slowly, whereas it changes rapidly with $n$ when $n < 10$. For the single component sample, $n = 1$ and $\nu_1 = \nu_2$. In this case, the energy $E = 0$. From Eq. (2), it is known that the brittle–tough transition temperature equals $T_{BT}^{m}$, i.e. the brittle–tough transition temperature of matrix itself. Therefore, $T_{BT}^{m}$ is also the highest brittle–tough transition temperature for elastomer toughening thermoplastics.

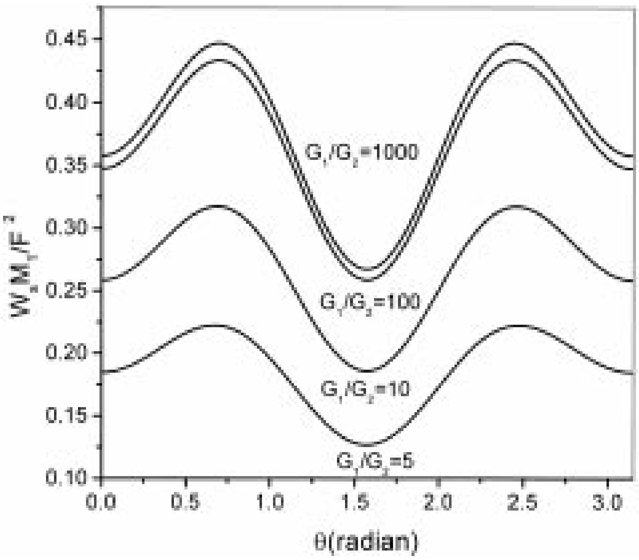

Fig. 3. Strain energy density $W_s$ in the matrix around an elastomer particle versus $\theta$, in which $r = d/2$, $\nu_1 = 0.43$, $\nu_2 = 0.5$.

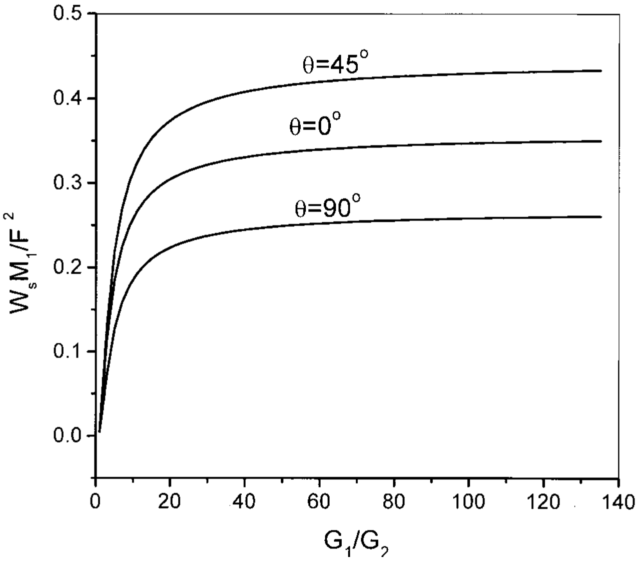

Fig. 4. Strain energy density $W_s$ in the matrix around an elastomer particle versus $n$, in which $r = d/2$, $\nu_1 = 0.43$, $\nu_2 = 0.5$.

The purpose in this paper is to study the effect of dispersed phase on BTT. In this case, the matrix material

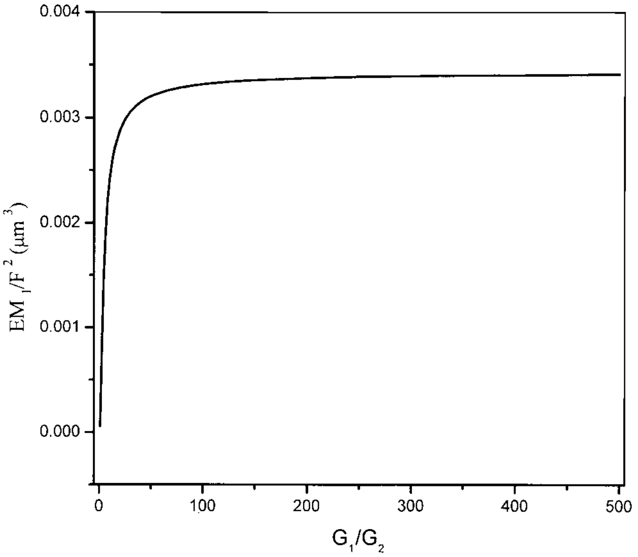

Fig. 5. $n$ dependence of strain energy $E$, in which $d = 0.30$ μm, $ID = 0.30$ μm, $\nu_1 = 0.43$, $\nu_2 = 0.5$.

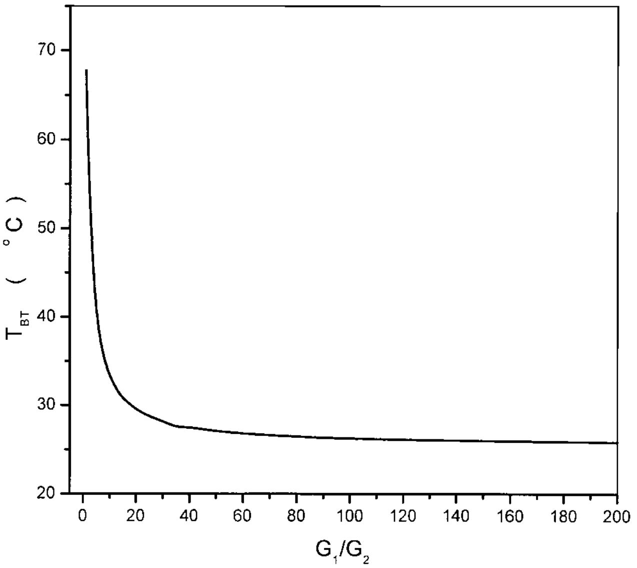

Fig. 6. *n* dependence of BTT temperature of the blend with $d = 0.30$ μm, $ID = 0.30$ μm, $T_{BT}^{m} = 74$(°C).

and strain rate remain unchanged. Thus, the brittle–tough transition temperature of matrix material itself ($T_{BT}^{m}$) and the shear modulus ($G_1$) of the matrix can be taken as constant during calculation. From Eq. (2), it is known that raising the value of $E$ lowers the brittle–tough transition temperature for the blends with constant $ID$ and $d$. Combining Fig. 5 with Eq. (2), we can obtain that the higher the modulus of the elastomer, the higher the brittle–tough transition temperature of the blend is. The calculations of the variation of the brittle–tough transition temperature with $n$ are shown in Fig. 6. From this figure, it is seen that the brittle–tough transition temperature decreases very rapidly with increasing $n$ (namely decreasing the modulus of elastomer) up to 10, thereafter, it decreases very slowly with increasing $n$. The results imply that the modulus of the elastomer must be less than one-tenth of that of the matrix, otherwise, the brittle–tough transition temperature will be relatively high, and the blend is brittle at low temperature for elastomer toughening thermoplastic. This conclusion is in agreement with Du Pont patents [2,3] that the modulus of the impact modifier must be one-tenth or less of that of nylon matrix (or an elastic modulus below 140 MPa) in order to be effective to toughen nylon.

## 4. Conclusions

Combining the brittle–tough transition equation with Goodier's equations, the effect of the stiffness of elastomer on brittle–tough transition in elastomer toughening thermoplastics was quantitatively studied. The calculation results showed that the brittle–tough transition temperature ($T_{bt}$) of elastomer toughening thermoplastics slowly increased up to the one-tenth of the modulus of matrix, thereafter, it increased rapidly by increasing the modulus of the elastomer. The results indicated that the modulus of the elastomer must be one-tenth or less of that of the matrix in order to obtain tough thermoplastic/elastomer blends at low temperature.

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