

Effect of morphology on the brittle ductile transition of polymer blends: 5. The role of CaCO_3 particle size distribution in high density polyethylene/ CaCO_3 composites

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The effect of particle size distribution on the brittle ductile transition of high density polyethylene (HDPE)/ CaCO_3 composites is studied. Fu and coworkers reported that the brittle ductile transition curves of HDPE/ CaCO_3 composites obtained by plotting impact strength against matrix ligament thickness do not give a master curve. In this work, the splitting of brittle ductile transition master curve of the composites as matrix ligament thickness is smaller than its critical value at brittle ductile transition is demonstrated to be attributable to the effect of CaCO_3 particle size distribution on matrix ligament thickness. The critical matrix ligament thickness criterion proposed by Wu is thus valid for the brittle ductile transition of HDPE/ CaCO_3 composites when the effect of particle size distribution on matrix ligament thickness is considered. The relations of critical particle size and of critical particle volume fraction at brittle ductile transition to particle size distribution are analyzed, respectively. A narrow particle size distribution is favourable to the enhancement of the toughness of polymer composites. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: particle size distribution; brittle ductile transition; CaCO_3 toughened high density polyethylene)

INTRODUCTION

The brittleness of plastics is one of the major problems that limit their applications in engineering. The toughening of polymers through the incorporation of spherical rubber particles has been proved to be an effective way to improve the impact toughness of plastics¹. Interestingly the enhancement of impact properties of some pseudoductile polymers by introduction of non-elastomers, i.e. plastics^{2–8} and inorganic fillers^{9–15}, has been achieved. The spherical particle filled plastics constitute an important class of polymer blends and composites. Therefore, the toughening mechanisms of these systems have attracted much attention.

In general, the spherical particles act as the stress concentrators to initiate and terminate crazes in the brittle polymer matrices and to initiate shear bands in the pseudoductile polymer matrices, which are responsible for the enhanced energy absorption^{1,16}. The morphology is a key factor determining the toughening efficiency. However, the morphological parameters as well as other factors influencing toughness are interrelated. The understanding of the effects of morphological parameters on toughness is very important not only for optimizing them to attain tough blends but also for the further investigation of the effects of other factors, i.e. the intrinsic ductility, interfacial adhesion and modulus of spherical particles.

The brittle ductile transition of polymer blends arising from the change in morphological parameters has been widely observed. It occurs when the rubber particle size (d) is smaller than a critical value (d_c) of d ^{17,18} or the rubber

volume fraction (ϕ) is larger than a critical value (ϕ_c) of ϕ at brittle ductile transition^{11–13}. d_c increases with ϕ . On the other hand, ϕ_c increases with decreasing d . So, the brittle ductile transition depends not only on ϕ but also on d . However, neither the plot of impact strength against d nor the plot of impact strength against ϕ give the master curves of brittle ductile transition. Wu proposed the criterion of critical matrix ligament thickness (T_c , or critical surface-to-surface interparticle distance) for rubber toughening^{17,18}. The brittle ductile transition occurs when matrix ligament thickness (T , or surface-to-surface interparticle distance) equals T_c ; a blend is tough when $T < T_c$; a blend is brittle when $T > T_c$. The interrelated effects of d and ϕ on impact strength of polymer blends are thus assumed to be separated based on the criterion. T has been suggested to be a single morphological parameter determining the brittle ductile transition in the rubber toughened pseudoductile matrices, for instance, polyamide (PA)^{17,18}, polypropylene (PP)^{19,20}, polyoxymethylene (POM)²¹ and polyethylene terephthalate (PET)²², polymethyl methacrylate^{23,24}, polyvinyl chloride (PVC)^{25,26} and in high density polyethylene (HDPE)/ CaCO_3 composites^{11–13}.

An interesting phenomenon is that the brittle ductile transition master curves obtained by plotting impact strength against T were observed in rubber toughened PP^{19,20}, POM²¹ and PVC^{25,26}, but not in PA/rubber blends^{17,18} and HDPE/ CaCO_3 composites^{11–13}. The brittle ductile transition curves of PA/rubber blends and HDPE/ CaCO_3 composites are divorced from each other when $T < T_c$. While T is a single morphological parameter determining the critical behaviour. So, it would be interesting to clarify the splitting.

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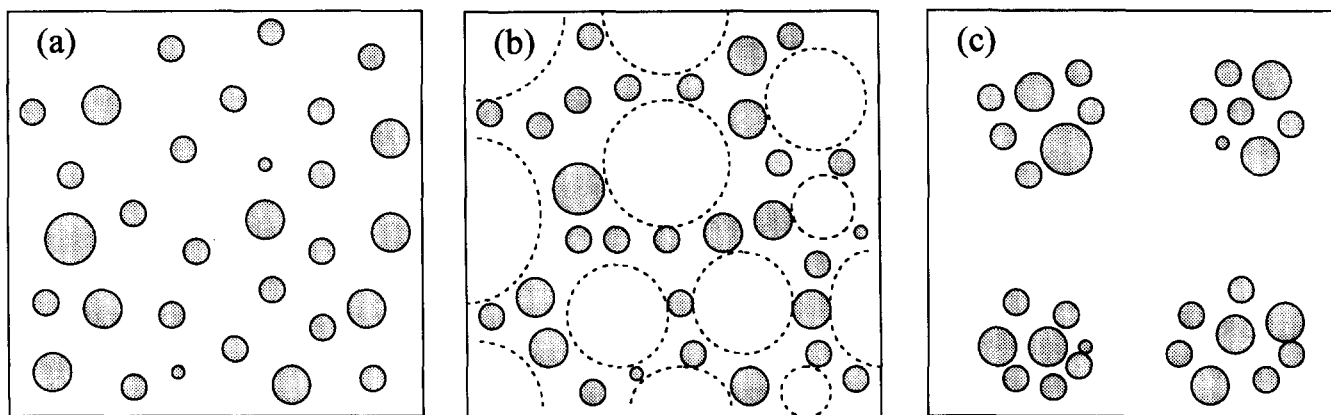


Figure 1 Schematic illustrations of particle configurations (spatial packings): (a) well-dispersed; (b) pseudonetwork; and (c) flocculated. The solid symbols and the dash circles represent the dispersed particles and the pseudonetwork cores, respectively

In addition to d , ϕ and T , the morphological parameters of binary polymer blends include the particle size distribution (σ). We have derived a new equation for relating T to d , ϕ and σ ²⁷. The quantitative relationships between d_c and σ and between ϕ_c and σ for PVC/nitrile rubber (NBR) blends have been established^{25,26}. It has been found that: (1) d_c decreases with increasing σ for a given ϕ . Moreover, the higher the ϕ , the more quickly the d_c reduces with increasing σ . (2) ϕ_c increases with σ for a given d . The larger the d , the more rapidly the ϕ_c increases with σ . Therefore, σ is one of morphological parameters dominating the toughness and the toughening mechanisms of PVC/NBR blends in addition to d , ϕ and T . (3) the T_c criterion is valid for PVC/rubber blends when the new equation is applied.

Although the σ values for PA/rubber blends^{17,18} were not given by Wu, those for HDPE/CaCO₃ composites¹¹⁻¹³ can be found in ref. 13. In this paper, we present the effect of σ on the brittle ductile transition master curve and on d_c and ϕ_c of HDPE/CaCO₃ composites. The influence of T_c on the relationships between d_c and σ and between ϕ_c and σ in binary polymer blends is also discussed.

MATRIX LIGAMENT THICKNESS

The definition of particle size distribution

The log-normal distribution has been shown to be applicable for many polymer blends^{17,18,20,26-29}. For log-normal distribution, the frequency ($f(d_i)$) of a uniform particle size (d_i) is defined as

$$f(d_i) = \frac{1}{\sqrt{2\pi} \ln \sigma} \exp \left[\frac{-(\ln d_i - \ln d)^2}{2 \ln^2 \sigma} \right] \quad (1)$$

where the average value of particle size d and its distribution σ are given by³⁰

$$\ln d = \frac{\sum_{i=1}^N n_i \ln d_i}{\sum_{i=1}^N n_i} \quad (2)$$

where N is the number of particle grading, n_i the number of particles with a size, d_i , and

$$\ln \sigma = \sqrt{\frac{\sum_{i=1}^N n_i (\ln d_i - \ln d)^2}{\sum_{i=1}^N n_i}} \quad (3)$$

In the case of monodispersity, $\sigma = 1$; and $\sigma > 1$ when polydispersity.

The matrix ligament thickness

We shall show that T is a function of particle configuration (or spatial packing) elsewhere. Three particle dispersions are schematically illustrated in *Figure 1*. The solid symbols in this figure represent the particles of dispersed phase. *Figure 1a* shows the configuration of well-dispersed particles. It consists of a polymer matrix and the well-dispersed particles. *Figure 1b* displays the particle configuration of pseudonetwork morphology. The pseudonetwork cores (the dash circles) and the pseudonetwork bands (consisting of a polymer matrix and the dispersed particles) comprise the pseudonetwork morphology. *Figure 1c* shows the configuration of flocculated particles. The last two types of particle configurations lead to smaller T s.

Wu^{17,18} has proposed an idealized equation for estimating T given by

$$T = d \left[\left(\frac{\pi}{6\phi} \right)^{\frac{1}{3}} - 1 \right] \quad (4)$$

In fact, the particle size in equation (4) is assumed to be uniform-sized. We have pointed out that σ has a great influence on T , and derived a new equation for calculating T given by²⁷

$$T = d \left[\left(\frac{\pi}{6\phi} \right)^{\frac{1}{3}} \exp(1.5 \ln^2 \sigma) - \exp(0.5 \ln^2 \sigma) \right] \quad (5)$$

We have shown that equation (5) is generally applicable to the binary polymer blends with the log-normal distribution of particle size and the particle configuration of well-dispersed particles.

DISCUSSION

The effect of particle size distribution on the master curve of brittle ductile transition

The d values of CaCO₃ particles obtained by Fu *et al.*¹¹⁻¹³ are 6.66, 7.44 and 15.9 μm , respectively. The histograms of the particle size distributions for HDPE/CaCO₃ composites were given in ref. 13. In this work, the accumulative number of particles are plotted against particle size, the data were fitted by least-squares regression, as

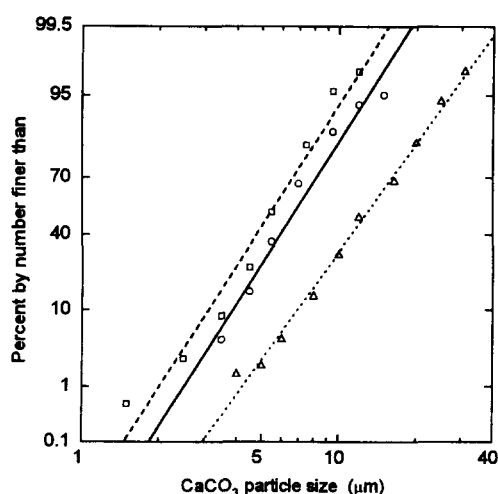


Figure 2 Log-normal distribution plot for CaCO_3 particles

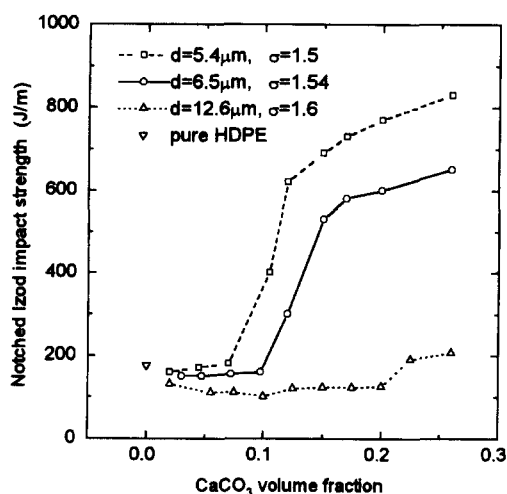


Figure 3 Notched Izod impact strength as a function of CaCO_3 volume fraction

show in Figure 2. Figure 2 shows that the particles fit log-normal distribution. Thus, the d values are actually 5.4, 6.5 and 12.9 μm . The corresponding σ values are 1.5, 1.54 and 1.6. In this study, σ increases with d . Figure 3 shows the plot of notched Izod impact strength versus CaCO_3 volume fraction for the composites. The brittle ductile transitions are found to occur at the different ϕ_c s.

The CaCO_3 particles were well dispersed in the HDPE matrix^{11–13}. Thus, equation (5) can be used in the composites. If neglecting the influence of σ on T and T is calculated by equation (4), the notched Izod impact strength is plotted against matrix ligament thickness given in Figure 4. For the three particle sizes, the brittle ductile transition is found to occur at $T_c = 4.5 \mu\text{m}$. However, the three curves (dot lines) do not give one master curve (solid line). It is seen that the impact strength increases with the reduction of d when T is identical. This phenomenon becomes more evident when $T < T_c$.

If considering the influence of σ on T and T is calculated by equation (5), the notched Izod impact strength is plotted against matrix ligament thickness given in Figure 5. The data well fall on one master curve. For the three particle sizes, the brittle ductile transition is found to occur at $T_c = 8.6 \mu\text{m}$.

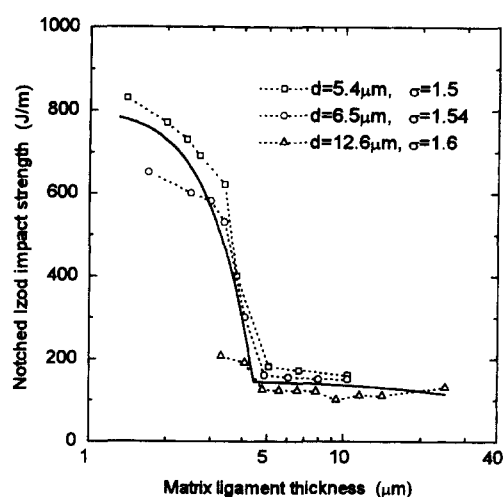


Figure 4 Notched Izod impact strength as a function of matrix ligament thickness by neglecting the influence of CaCO_3 particle size distribution. The dot lines are experimental results. The solid line is fitted by equation (6) in the case of $T < T_c$.

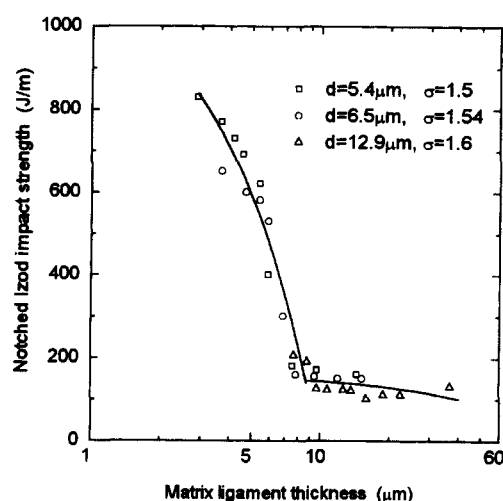


Figure 5 Notched Izod impact strength as a function of matrix ligament thickness by considering the influence of CaCO_3 particle size distribution. The solid line is fitted by equation (6) in the case of $T < T_c$.

A master curve may be drawn by polynomial regression through

$$IS = A_0 + A_1 T + A_2 T^2 \quad (6)$$

where IS is the notched Izod impact strength, and A_0 , A_1 and A_2 are constants.

The effect of σ on the brittle ductile transition of CaCO_3 composites can be quantitatively analyzed by correlation coefficient and standard deviation. The parameters of equation (6) used for fitting data in Figures 4 and 5 when $T < T_c$ are listed in Table 1. A_0 , A_1 and A_2 are different for the two figures. Therefore, two equations are obtained. Table 2 gives the correlation coefficient and standard deviation of the two equations. Compared with Figure 4, Figure 5 shows a master curve with much larger correlation coefficient and markedly smaller standard deviation because of the consideration of the influence of σ on T .

The present study clearly shows that the T_c criterion is valid for the brittle ductile transition of HDPE/ CaCO_3 composites when the effect of σ on T is evaluated. In an independent study we have already obtained a master curve

Table 1 The results of polynomial regression for Figures 4 and 5 in the case of $T < T_c$.

Parameter	Value		Standard deviation	
	Figure 4	Figure 5	Figure 4	Figure 5
A_0	745	1177	377	200
A_1	98	-116	283	72
A_2	-52	-0.344	50	6.2

Table 2 The correlation coefficient and standard deviation of equation (6) used to fit data of Figures 4 and 5 in the case of $T < T_c$.

Parameter	Figure 4	Figure 5
Fitting equation	$745 + 98T - 52T^2$	$1177 - 116T - 0.344T^2$
Correlation coefficient	0.85	0.96
Standard deviation	121	65

for PVC/NBR blends based on equation (5). As a result, T is a critical morphological factor dominating the brittle ductile transition of polymer blends.

The effect of particle size distribution on the critical particle volume fraction and the critical particle size

For the given d and σ , the impact strength of HDPE/CaCO₃ composites is a function of CaCO₃ content. The brittle ductile transition is found to occur at varying ϕ_c s (0.07, 0.098 and 0.22, respectively). Because σ increases with d , ϕ_c increases with d , as shown in Figure 3. Rearranging equation (5) we have

$$\phi_c = \frac{\pi}{6} \left[\frac{\exp(1.5 \ln^2 \sigma)}{\frac{T_c}{d} + \exp(0.5 \ln^2 \sigma)} \right]^3 \quad (7)$$

Figure 6 shows the calculated variations of ϕ_c as a function of σ at constant d and T_c for the composites. Clearly ϕ_c is not a constant for a given d , and increases with σ . The larger the d , the more rapidly the ϕ_c increases with σ . A small σ does not possess a significant impact on ϕ_c . However, this effect is marked in the range of large σ . For a very larger σ , the brittle ductile transition cannot take place. For instance, if $d = 12.9 \mu\text{m}$ and the phase inversion occurs at $\phi = 0.5$, the maximum value (σ_{max}) of σ for the onset of brittle ductile transition is 1.9. The brittle ductile transition disappears when $\sigma \geq \sigma_{\text{max}}$. The dependence of ϕ_c on σ is found to be associated with T_c as predicted by equation (7). Figure 7 schematically displays the influence of T_c on the dependence of ϕ_c on σ when $d = 5 \mu\text{m}$. It is seen that the larger the T_c , the less remarkable the effect of σ on ϕ_c . For a given σ , the larger the T_c , the lower the ϕ_c . A low ϕ_c means that the brittle ductile transition takes place more easily. Consequently, a large T_c is favourable to the brittle ductile transition.

According to equation (5) the relation of d_c to ϕ , σ and T_c is

$$d_c = \frac{T_c}{\left(\frac{\pi}{6\phi}\right)^{\frac{1}{3}} \exp(1.5 \ln^2 \sigma) - \exp(0.5 \ln^2 \sigma)} \quad (8)$$

If experiments are done to obtain the plot of impact strength as a function of d at constant $\phi = 0.07, 0.098$ and 0.22 , the corresponding d_c values, $5.4, 6.5$ and $12.9 \mu\text{m}$, are expected. Figure 8 shows the calculated variations of d_c as a

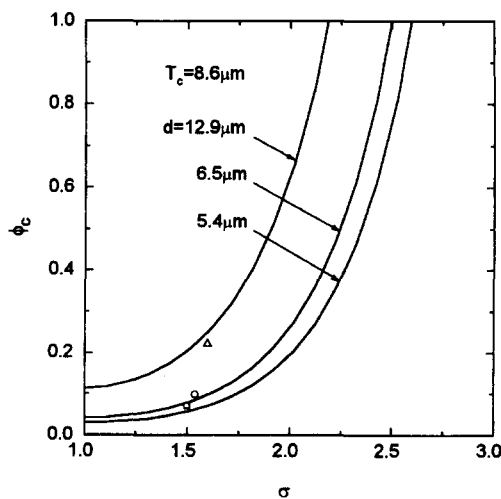


Figure 6 Calculated variations of ϕ_c as a function of σ at a constant T_c and the various d values for the HDPE/CaCO₃ composites

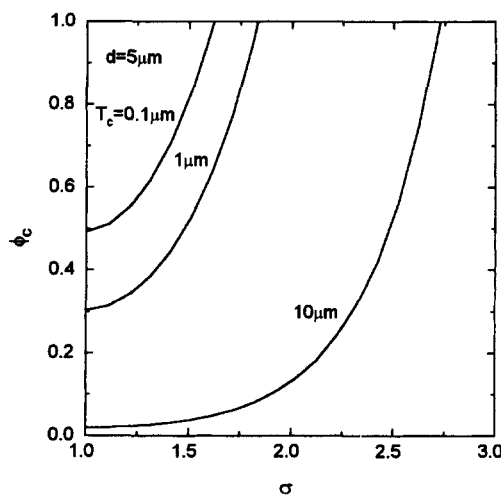


Figure 7 Calculated variations of ϕ_c as a function of σ at a constant d and the various T_c values for binary polymer blends

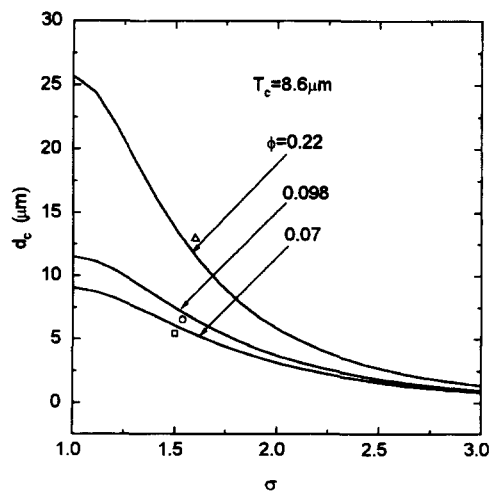


Figure 8 Calculated variations of d_c as a function of σ at a constant T_c and the various ϕ values for the HDPE/CaCO₃ composites

function of σ at constant ϕ and T_c for the composites. The expected experimental d_c s are indicated in this figure. For a given ϕ , d_c is not a constant too, and decreases with increasing σ . The higher the ϕ , the more significant the influence of

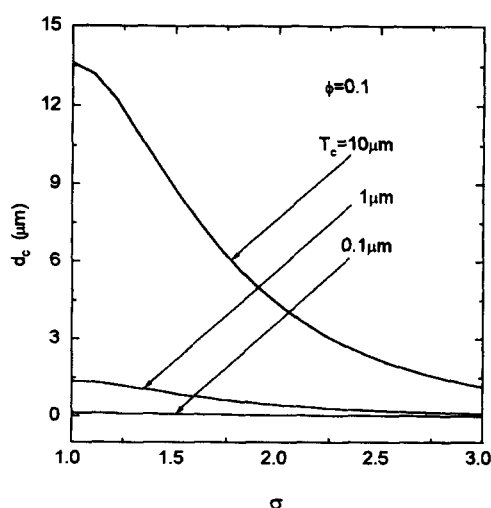


Figure 9 Calculated variations of d_c as a function of σ at a constant ϕ and the various T_c values for binary polymer blends

σ on d_c . Even a small σ will considerably reduce d_c . Nevertheless, the effect resulting from ϕ tends to disappear in the range of larger σ . d_c will be very small for blends with very large σ . While very small particles cannot toughen a matrix^{31–44}. It is thus expected that the brittle ductile transition cannot be observed for blends with very large σ . When $\phi = 0.1$, the effect of T_c on the relation of d_c to σ is schematically illustrated in Figure 9. The calculated variations indicate that the larger the T_c , the more significant the effect of σ on d_c . Clearly a large T_c results in a large d_c for a given σ , which favours the brittle ductile transition.

The understanding of the effect of T_c on d_c and ϕ_c is very important in the toughening of a matrix polymer with the rigid filler. For instance, to supertoughen PE with CaCO_3 a tough matrix that would lead to a large T_c must be employed. If the Izod impact strength of pure PE is small, i.e. smaller than 100 J/m , the brittle ductile transition of the composites has not yet been observed. When a tough matrix is used, for instance, the Izod impact strength is 175 J m^{-1} , the brittle ductile transition of the composites occurs, as shown in Figure 3. Another example is the polypropylene/kaolin composites¹⁵.

Wu proposed that T_c is a material property of the matrix for a given mode, temperature and rate of deformation^{17,18}. Based on this assumption, Wu derived the relationship between T_c and the intrinsic ductility of the matrix polymer given by^{22,24}

$$\log T_c(\mu\text{m}) = 0.74 - 0.22C_\infty \quad (9)$$

where C_∞ is the characteristic ratio for a coiled polymer chain, and is a measure of the intrinsic ductility. The tougher the matrix polymer, the smaller the C_∞ .

However, we have shown that T_c is a function of interfacial adhesion^{44,45}, spatial packing of dispersed particles in the matrix²⁶ and the modulus of the dispersed phase⁴⁶. The T_c of PVC/NBR blends reduces with the enhancement of interfacial adhesion. The T_c of PVC/NBR blends with the morphology of well-dispersed rubber particles is much smaller than that with the pseudonetwork morphology. The T_c of PP/ethylene propylene diene monomer (EPDM) blends is larger than that of PP toughened with the EPDM shell/HDPE core particles. So T_c is not a material property of the matrix. Therefore, these factors influence the relations of d_c to σ and of ϕ_c to σ .

CONCLUSIONS

The understanding of the role of T as a single morphological parameter determining the brittle ductile transition of polymer blends and composites will provide a deep insight into the effects of additional morphological parameters and other factors on the toughness of polymer blends and composites. T_c is a constant for a given blend system along with a given mode, temperature and rate of deformation. The identification of the effects of additional morphological parameters needs the separation of these variables based on equation (5). Moreover, the understanding of the effects of other factors, i.e. the intrinsic ductility, interfacial adhesion and the modulus of spherical particles, requires the separation of the effects of other factors from those of morphological parameters by equation (5).

In this work, the splitting of the brittle ductile transition master curve reported by Fu and coworkers has been attributed to the effect of σ on T . A brittle ductile transition master curve has been obtained by plotting impact strength against T calculated by equation (5). So, the T_c criterion proposed by Wu is valid for the brittle ductile transition of HDPE/ CaCO_3 composites when the effect of σ on T is considered. This further confirms that T is a single morphological parameter determining the brittle ductile transitions of polymer blends and composites.

ϕ_c is not a constant for a given d , and increases with σ . For a given ϕ , d_c is not a constant too, and decreases with increasing σ . Therefore, a small σ is favourable to the toughening of HDPE. The influence of σ on ϕ_c is related to d . The larger the d , the more rapidly the ϕ_c increases with σ . The influence of σ on d_c is also connected with ϕ . The higher the ϕ , the more quickly the d_c decreases with increasing σ .

In general, the tougher the matrix, the larger the T_c . T_c considerably affects the relations of ϕ_c to σ and of d_c to σ in polymer blends and composites. The larger the T_c , the less rapidly the ϕ_c increases with σ , but the more quickly the d_c decreases with increasing σ . The calculated variations indicate that the larger the T_c , the lower the ϕ_c , and the larger the d_c . In other words, a large T_c favours the brittle ductile transition of polymer blends and composites.

ACKNOWLEDGEMENTS

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1. Glossary of symbols and terms

- A_0 Constant of equation (6)
- A_1 Constant of equation (6)
- A_2 Constant of equation (6)
- C_∞ Characteristic ratio for a coiled polymer chain (equation (9))
- d Particle size, defined by equation (2)
- d_c Critical particle size at brittle ductile transition
- d_i Uniform particle size (equation (1))
- $f(d_i)$ Frequency of a particle size, d_i , defined by log-normal distribution (equation (1))
- IS Impact strength (equation (6))
- N Number of particle grading (equations (2) and (3))
- n_i Number of particles with a size, d_i (equations (2) and (3))
- T Matrix ligament thickness or surface-to-surface interparticle distance
- T_c Critical matrix ligament thickness or critical surface-to-surface interparticle distance at brittle ductile transition
- σ Particle size distribution, defined by equation (3)
- σ_{\max} Maximum value of particle size distribution for the onset of brittle ductile transition. The brittle ductile transition cannot take place when $\sigma \geq \sigma_{\max}$
- ϕ Particle volume fraction
- ϕ_c Critical particle volume fraction at brittle ductile transition

2. List of acronyms

EPDM	Ethylene propylene diene monomer
HDPE	High density polyethylene
NBR	Nitrile rubber
PA	Polyamide
PE	Polyethylene
PET	Polyethylene terephthalate
POM	Polyoxymethylene
PP	Polypropylene
PVC	Polyvinyl chloride

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