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Effect of morphology on the brittle ductile transition of polymer blends: 2. Analysis on poly(vinyl chloride)/nitrile rubber blends

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The effects of morphological parameters, especially rubber particle size distribution, on the brittle ductile transition of poly(vinyl chloride) (PVC)/nitrile rubber (NBR) blends with the morphology of well-dispersed NBR particles have been studied. PVC has been supertoughened with well-dispersed NBR particles. A master curve of the brittle ductile transition of PVC/NBR blends is obtained by plotting impact strength *versus* average matrix ligament thickness. The relationships of critical particle size and critical rubber volume fraction to rubber particle size distribution are discussed. It is argued that rubber particle size distribution is one of the morphological parameters dominating the toughness and the toughening mechanisms of PVC/NBR blends, in addition to the average rubber particle size, rubber particle volume fraction and average matrix ligament thickness. A narrow rubber particle size distribution favours the rubber toughening of PVC. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: rubber toughened poly(vinyl chloride); morphology of well-dispersed rubber particles; brittle ductile transition)

Nomenclature

ABS	Acrylonitrile-butadiene-styrene
HDPE	High density polyethylene
MBS	Methyl methacrylate-butadiene-styrene
NBR	Nitrile rubber or arylonitrile-butadiene copolymer
PVC	Poly(vinyl chloride)

Symbols

d	Average particle size of particles conforming to a log-normal distribution
d_c	Critical particle size for the onset of brittle ductile transition
d_i	An average particle size for a grade of particles
σ	Particle size distribution defined by a log-normal distribution
ϕ	Particle volume fraction
ϕ_c	Critical particle volume fraction for the onset of brittle ductile transition
T	Average matrix ligament thickness
T_c	Critical matrix ligament thickness for the onset of brittle ductile transition
$f(d_i)$	Frequency of a particle size d_i

INTRODUCTION

The brittle ductile transition of polymer blends stemming from the change in morphological parameters has been widely observed. It occurs when the average rubber particle size is smaller than its critical value[1,2], or when the rubber volume fraction if larger than its critical value[3,4]. The critical rubber particle size increases with the rubber volume fraction. On the other hand, the critical rubber volume fraction increases with the reduction of average rubber particle size. So, the brittle ductile transition depends not only on the rubber volume fraction, but also on the average rubber particle size. Wu[1,2] suggested the criterion of critical matrix ligament thickness for rubber toughening, where the effects of average rubber particle size and rubber volume fraction have been formulated as the effect of average matrix ligament thickness. The brittle ductile transition occurs when the average matrix ligament thickness equals its critical value; a blend is tough when the average matrix ligament thickness is thinner than its critical value; a blend is brittle when average matrix ligament thickness is thicker than its critical value. The average matrix ligament thickness has been suggested to be the single parameter determining the critical behaviour. The critical matrix ligament thicknesses have been found in rubber toughened matrices, such as nylon[1,2], polypropylene[4,5], polyoxymethylene[6] and polyethylene terephthalate[7], and in high density polyethylene (HDPE)/$CaCO_3$ composites[3].

In addition to the average particle size, particle volume fraction and average matrix ligament thickness, the morphological parameters of binary polymer blends include the particle size distribution and the particle spatial distribution, which should influence the brittle ductile transition of polymer blends. However, there has been no paper deeply investigating the influences of particle size distribution and particle spatial distribution.

Poly(vinyl chloride) (PVC)/nitrile rubber (NBR) blends can be a quite useful model system. It is possible to study the

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effects of particle size distribution and particle spatial distribution on the impact toughness and the toughening and stiffening efficiency of PVC/NBR blends. It is also possible to study the effect of interfacial adhesion on the impact toughness of PVC/NBR blends. That is why we select the blends in two series of our investigations on the relationships among morphology, interfacial adhesion and mechanical properties. However, there has been no paper reporting the validity of critical matrix ligament thicknesses criterion for the brittle ductile transition of PVC/rubber blends.

Wu[7] classified polymers into two main types: brittle matrices (deform by crazing) and pseudoductile matrices (deform by shearing). His main purpose for this classification is to correlate brittle ductile behaviour with microstructural and molecular parameters, i.e. correlating the critical matrix ligament thickness with the chain entanglement density and the characteristic ratio of a chain. The intermediate matrices compared with the brittle and pseudoductile matrices deform by both crazing and shearing. It has been proposed that the intermediate matrices require certain special rubber phase morphologies, such as the pseudo-network and network morphologies, to attain supertoughness (notched Izod impact strength > *ca.* 500 J m^{-1}). It seems that the intermediate matrices cannot be supertoughened with the morphology of well-dispersed rubber particles. Is this hypothesis applicable to PVC (an intermediate matrix)?

In the first paper of this series, we derived a new equation for correlating the average particle size, particle volume fraction and average matrix ligament thickness, which is much more accurate in predicting the relations among morphological parameters than others[8]. In the present work, PVC/NBR blends with the morphology of well-dispersed rubber particles is prepared to find out whether PVC can be supertoughened with this morphology, and the new equation is applied to examine the validity of the critical matrix ligament thicknesses criterion proposed by Wu[1,2]. The effect of particle size distribution on the critical particle size and the critical particle volume fraction is also quantitatively analysed. This work thus provides some basis for our two series investigations.

EQUATION FOR CORRELATING MORPHOLOGICAL PARAMETERS

The definition of particle size distribution

For a log-normal distribution, the frequency $f(d_i)$ of a particle size d_i is defined as[9]

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

where the average values of particle size d and its distribution σ are given by[9]

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

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

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

The equation for correlating morphological parameters

Wu[1,2] proposed an idealized equation for estimating the average matrix ligament thickness (T) given by

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

where ϕ is the particle volume fraction.

In fact, the particle size in equation (4) is assumed to be uniform-sized. In a previous paper[8], we pointed out that the particle size distribution has a great influence on the average matrix ligament thickness, and derived a new equation for calculating the average matrix ligament thickness given by

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

where σ is the particle size distribution.

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 spatial distribution of well-dispersed particles[8].

EXPERIMENTAL

Materials

The polymers used in this work were a commercial grade of PVC (S-1000, from Qilu Petrochem Company, People's Republic of China) with the number-average molecular weight $M_n = 62\,500$, and a commercial NBR reported by the manufacturer (Lanzhou Chemical Company, People's Republic of China) to be 18% by weight acrylonitrile.

Blend preparation

The NBRa was the commercial product. The NBRa was milled, respectively, on a laboratory two roller mill at room temperature for 15 min and 30 min to give NBRb and NBRc. They were mixed at 160°C for 6 min, respectively, with suspension PVC (containing 0.4 phr lubricator, 3 phr stabilizer, and 5 phr plasticizer). These milled sheets were stacked together and compressed-moulded at 160°C for 10 min, then cooled slowly down to the room temperature to give 4 mm thick plates. The samples for impact tests and morphological observatons were cut from these plates.

Impact tests

Izod impact tests were performed at 16°C according to ASTM-D256 Standards.

Morphological observations

The samples were cryo-fractured. The fracture surfaces were etched in the oxidizer composed of 100 ml H_2SO_4, 30 ml H_3PO_4, 30 ml H_2O, and 3 g $K_2Cr_2O_7$ at 30°C for 5 min to remove rubber phase. Then, they were coated with Au. The morphologies were observed in a Hitachi S-530 scanning electron microscope (SEM).

Analysis of morphological parameters

The SEM photographs were used to analyse the particle size and particle size distribution using a computerized image analyser. The number of rubber particles for each sample was between 300-400.

RESULTS AND DISCUSSION

The morphology

The particulate nature of PVC is responsible for the morphologies of PVC/rubber blends. The three particulate structures, domain, primary particle and resin grain, can be identified[10]. The sizes of a domain, a primary particle and a resin grain are about 100 Å, 0.1–2 μm and 100 μm, respectively.

At least, two different morphologies of PVC/rubber blends which are effective in the rubber toughening of PVC have been observed. One is the pseudo-network morphology, where the rubber particles are randomly dispersed in between the PVC primary particles, as shown in *Figure 1a.* Typical examples are PVC/ABS[11] and PVC/MBS[12] blends. Another is the network morphology, where two phases continue and the PVC primary particles are the major form of particulate structure, as shown in *Figure 1b.* Typical example is PVC/NBR blends[13]. The morphology of well-dispersed particles, as shown in *Figure 1c*, is very common in polymer blends, and has been shown to be effective in obtaining supertoughened polymer blends.

Breuer *et al.*[11] have studied the effect of ABS particle spatial distribution on the impact toughness of PVC/ABS blends. Two types of morphologies, the pseudo-network morphology and the morphology of well-dispersed particles, were obtained. The conclusion is that the pseudo-network morphology is more effective in toughening than the morphology of dispersed particles. So, the toughness of the blends depends strongly on the rubber phase morphologies.

In this work, the morphology of well-dispersed rubber particles is desired. The particular structure plays a key role in the toughening of PVC. Adding a plasticizer[14], blending at the elevated processing temperature[12,14], and selecting PVC with lower molecular weight[15], favour the breakdown of PVC primary particles and the dispersion of the rubber phase. These strategies have been employed in preparing PVC/NBR blends. *Figure 2a* shows that the NBR particles are well dispersed in the PVC matrix, and that the PVC primary particles have been broken down. For the purpose of comparison, *Figure 2b* shows the pseudo-network morphology in a PVC/NBR blend prepared using other processing methods described elsewhere, where the PVC primary particles are evident.

It has been shown that the average particle size is a function of the viscosity ratio of dispersed phase to matrix in addition to the interfacial tension, viscosity of blend,

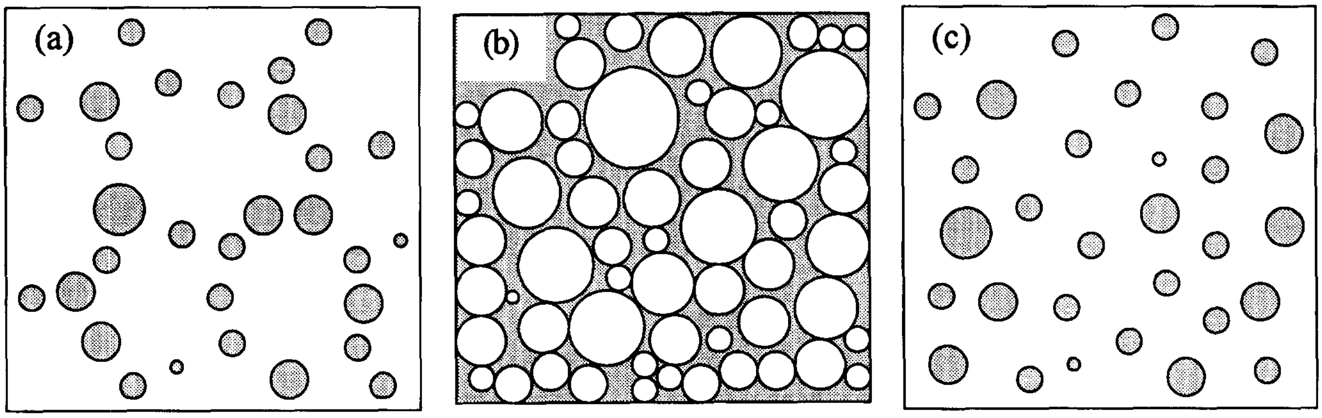

Figure 1 Schematics of rubber dispersion in PVC/rubber blends: (a) pseudo-network; (b) network; and (c) well-dispersed. The filled regions represent the rubber phase

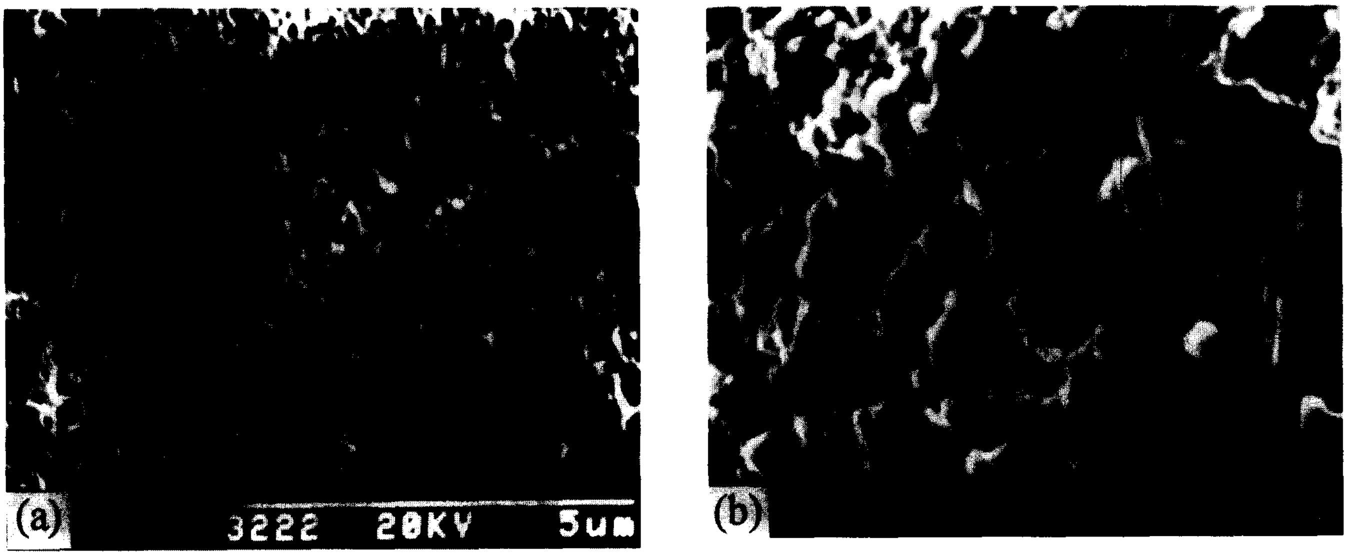

Figure 2 SEM photographs of the typical spatial distribution of rubber particles in PVC/NBR blends: (a) well-dispersed, $\phi = 0.213$, impact strength = 413 J m^{-1}; and (b) pseudo-network, $\phi = 0.083$, impact strength = 1000 J m^{-1}

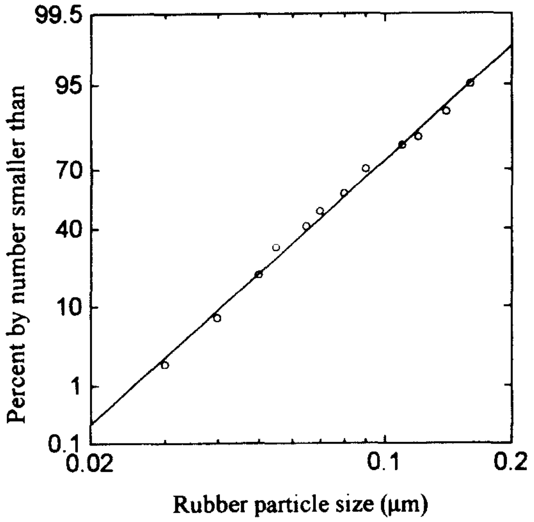

Figure 3 Log-normal distribution of rubber particles in a PVC/NBR blend with $\phi = 0.136$.

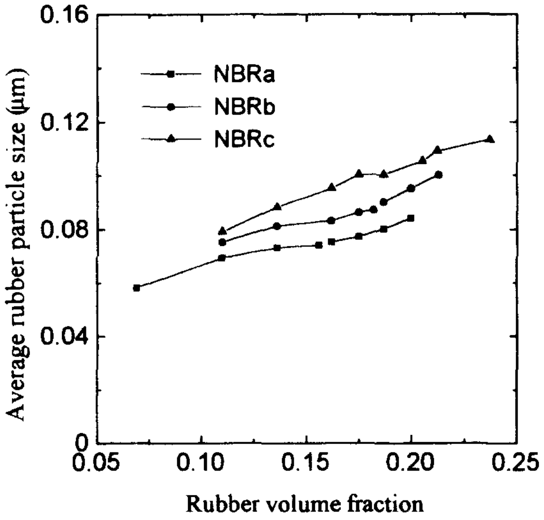

Figure 4 Relationship between average rubber particle size and rubber volume fraction in the PVC/NBR blends with the morphology of well-dispersed particles

volume fraction of dispersed phase and shear rate[16,17]. In order to control the NBR particle size in the PVC/NBR blends, three different types of NBRs, namely NBRa, NBRb and NBRc, were prepared by varying the time for milling the rubber. In fact, this method is a process of the mechanical degradation of NBR rubbers, which reduces the molecular weight and its distribution of NBR. So, the milling process reduces the viscosity of NBR.

The three NBRs were mixed, respectively, with PVC on a laboratory two roller mill to give blends with different morphological parameters and impact toughness. *Figure 3* displays that the NBR particle size obeys a log-normal distribution. The average particle size is the particle size at the accumulative probability of 50%, and its distribution is the ratio of the particle size at 84% to that at 50%. The average particle size of the blends is plotted against the NBR volume fraction, as shown in *Figure 4*. For a given rubber volume fraction, the longer the milling time, the larger the average particle size. Moreover, the average particle size increases with the rubber volume fraction. The values of rubber particle size distribution for the blends range from 1.3 to 1.6.

The brittle ductile transition

Figure 5 shows the relation between the notched Izod impact strength of the blends and the rubber volume fraction: Sharp brittle ductile transitions occur at different critical values of rubber volume fraction. Since the NBR particles are well dispersed in the PVC matrix and the PVC primary particles are broken down, the difference in the critical behaviour should result mainly from the changes in the average particle size, particle volume fraction and average matrix ligament thickness.

By plotting impact strength against average matrix ligament thickness calculated by equation (5), a master curve is observed, as shown in *Figure 6*. The brittle ductile transition is found to occur at the critical matrix ligament thickness 0.059 μm. So, the average matrix ligament thickness is a single parameter dominating the toughening behaviour of the PVC/NBR blends with the morphology of well-dispersed particles, and the critical matrix ligament thickness criterion is applicable to the brittle ductile transition of the PVC/NBR blends.

Neglecting the effect of rubber particle size distribution, we have reported that the critical matrix ligament thickness was 0.036 μm[18] for the same blends studied here, which is

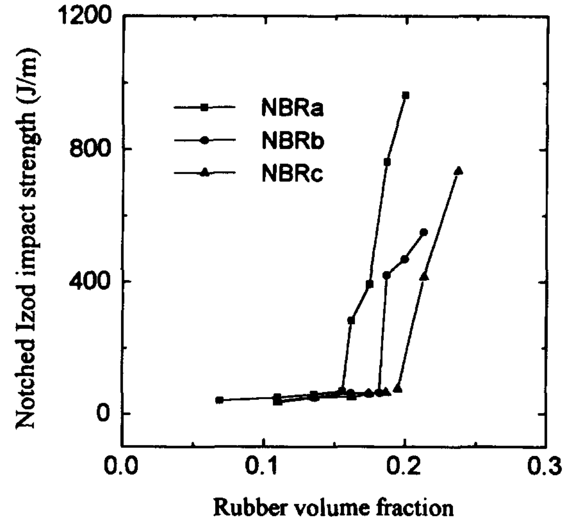

Figure 5 Notched Izod impact strength *versus* rubber volume fraction for the PVC/NBR blends with the morphology of well-dispersed particles

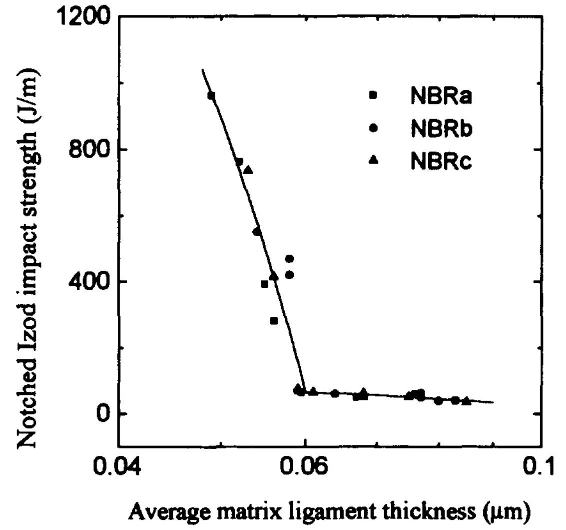

Figure 6 Notched Izod impact strength *versus* average matrix ligament thickness for the PVC/NBR blends with the morphology of well-dispersed particles

much smaller than the value obtained from *Figure 6*. So, if the effect of rubber particle size distribution on the average matrix ligament thickness were neglected, the critical matrix ligament thickness calculated from equation (4) would be unreliable for further analysis based on it.

It was reported that PVC was supertoughened, respectively, with the pseudo-network[11] and network[13] morphologies. The toughening efficiency is lowered as long as the morphology of well-dispersed particles is obtained[11]. On the other hand, the present work clearly shows that PVC can be supertoughened with the well-dispersed NBR particles. For example, the impact strength is higher than 800 J m^{-1} as the average matrix ligament thickness is thinner than 0.5 μm (see *Figure 6*). So, it is inadequate to say that PVC requires the pseudo-network morphology or network morphology to attain supertoughness.

The effect of particle size distribution

The mechanism of brittle ductile transition should be the ligament yielding and propagation through connectivity of thin ligaments[2]. The average matrix ligament thickness must be thinner than its critical value for the ligament to yield. Moreover, we have shown that the particle size distribution has a great influence on the average matrix ligament thickness[8]. So, it should influence the connectivity of thin ligaments and their yielding. The wider the particle size distribution, the less easily the ligament yielding takes place.

The effects of average particle size and particle volume fraction on the toughness of nylon/rubber blends have been roughly analysed by plotting impact strength against average particle size for a given particle volume fraction[1,2]. By plotting impact strength against particle volume fraction for a given average particle size, these effects on the impact toughness of HDPE/$CaCO_3$ composites were also estimated[3]. Thus, the effects of average particle size and particle volume fraction on the toughness of polymer blends were claimed to be separated. However, the effects of particle size distribution cannot be seen by above procedures.

Rearranging equation (5), we have

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

where the subscript "c" denotes the critical behaviour. So, d_c is the critical particle size, T_c is the critical matrix ligament thickness.

Clearly equation (6) predicts that the critical particle size is not a constant, even for a given particle volume fraction. The effect of rubber particle size distribution on the critical rubber particle size in the PVC/NBR blends can be seen by plotting critical rubber particle size *versus* rubber particle size distribution for a given particle volume fraction. *Figure 7* shows that the critical rubber particle size is not a constant for a given particle volume fraction, and that it decreases with increasing the rubber particle size distribution. For example, in the case of $\phi = 0.16$, the critical rubber particle size decreases from 0.123 to 0.07 μm as the rubber particle size distribution increases from 1 to 1.5. It can be seen from equation (6) and *Figure 7* that the higher the rubber volume fraction, the more quickly the critical rubber particle size reduces with increasing the rubber particle size distribution.

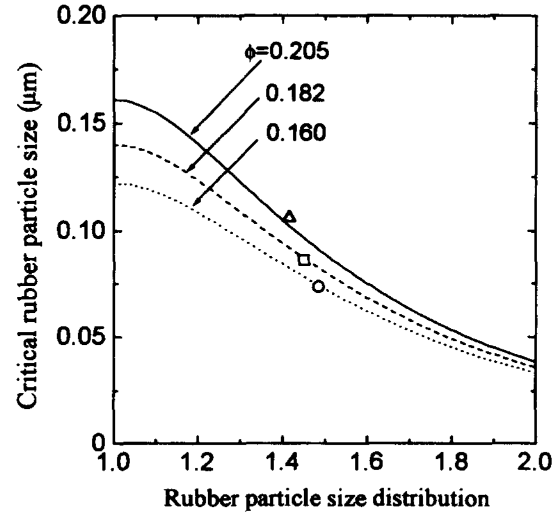

Figure 7 Effect of rubber particle size distribution on critical rubber particle size in the PVC/NBR blends with the morphology of well-dispersed particles

It has been reported that for nylon/rubber blends[1,2], a sharp brittle ductile transition occurs at a critical rubber particle size for a given rubber volume fraction, and that there is no significant deviation of experimental data near a critical rubber particle size from the corresponding brittle ductile transition curve. If a smaller average rubber particle size does not result in a larger particle size distribution for the blends with the same rubber volume fraction, it is possible to observe that the impact strength increases with decreasing the average rubber particle size, since the average matrix ligament thickness is thinner than its critical value. In contrast, if the average rubber particle size is slightly smaller than its critical value, and if the smaller average rubber particle size has a much larger particle size distribution, we expect that the blend with the smaller average rubber particle size to be brittle because the average matrix ligament thickness is thicker than its critical value.

Equation (5) can be rewritten as

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

where ϕ_c is the critical volume fraction.

Figure 8 shows the relationship between the critical rubber volume fraction and the rubber particle size distribution for a given ratio T_c/d of the critical matrix ligament thickness to the average rubber particle size in the PVC/NBR blends. For a given average rubber particle size, the critical rubber volume fraction is not a constant either; it increases with the rubber particle size distribution. The difference among the critical values of rubber volume fraction at different average rubber particle size values becomes more evident with increasing the rubber particle size distribution. In other words, the larger the average rubber particle size, the more rapidly the critical rubber volume fraction increases with the rubber particle size distribution.

Fu *et al.*[3,19] have studied the brittle ductile transition of HDPE–$CaCO_3$ composites. They plotted impact strength *versus* $CaCO_3$ volume fraction for a given average particle size. The result is that the critical rubber volume fraction increases with the average particle size. It should be mentioned that there is a coincidence in the relationship between the average particle size and its distribution in so far as the increased average particle size does not cause an increase of particle size distribution[20]. The relationship between the average particle size and its distribution accounts for the observed phenomenon that the critical rubber volume fraction increases with the average particle size.

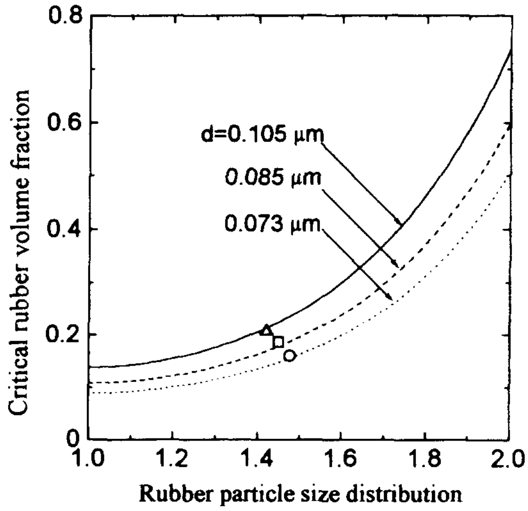

Figure 8 Effect of rubber particle size distribution on critical rubber volume fraction in the PVC/NBR blends with the morphology of well-dispersed particles

Wu *et al.*[1,2] applied equation (4) to calculate the average matrix ligament thickness, and plotted impact strength against average matrix ligament thickness. For nylon/rubber blends and HDPE/$CaCO_3$ composites, the brittle ductile transitions were observed at the corresponding critical matrix ligament thickness values. An interesting phenomenon is that the brittle ductile transition master curves with different rubber volumes fractions for nylon/rubber blends, or with different average particle sizes for HDPE/$CaCO_3$ composites, divorce as the average matrix ligament thickness is smaller than its critical value though the matrix ligament thickness was suggested to be a single parameter determining the critical behaviour. This phenomenon can be mostly attributed to the effect of the particle size distribution on the average matrix ligament thickness[20].

CONCLUSIONS

There is no doubt that morphology imposes a significant influence on the toughening efficiency of PVC/rubber blends. It was concluded that the pseudo-network and network rubber phase morphologies are required to attain supertoughness[7]. In this work, PVC has been successfully supertoughened with the morphology of well-dispersed NBR particles.

Brittle ductile transitions have been observed in PVC/NBR blends by plotting impact strength against rubber volume fraction. A master curve of brittle ductile transition is obtained by plotting impact strength against average matrix ligament thickness. So, the matrix ligament thickness is the single morphological parameter dominating the critical behaviour, and the criterion of critical matrix ligament thickness for rubber toughening is valid for the PVC/NBR blends with the morphology of well-dispersed NBR particles.

The critical rubber particle size is variable for a given rubber volume fraction, and decreases with increasing particle size distribution. The higher the rubber volume fraction, the more quickly the critical rubber particle size reduces with increasing particle size distribution. On the other hand, for a given average rubber particle size, the critical rubber volume fraction is variable too, and increases with the particle size distribution. The larger the average particle size, the more rapidly the critical rubber volume fraction increases with the particle size distribution. Therefore, the particle size distribution is also an important morphological parameter influencing the toughness and the toughening mechanisms of PVC/NBR blends with well-dispersed rubber particles in addition to the average rubber particle size, rubber volume fraction and average matrix ligament thickness. Clearly a narrow particle size distribution is favourable for the rubber toughening of PVC.

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