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# Effect of morphology on the brittle ductile transition of polymer blends: 4. Influence of the rubber particle spatial distribution in poly(vinyl chloride)/nitrile rubber blends

**Z. H. Liu[a], X. D. Zhang†,[a], X. G. Zhu[c], R. K. Y. Li[b], Z. N. Qi[a,*], F. S. Wang[a] and C. L. Choy[c]**
[a]*State Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China*
[b]*Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong*
[c]*Department of Applied Physics, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*
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We have derived a new equation for correlating the average matrix ligament thickness with other morphological parameters of a polymer blend with the pseudonetwork morphology in order to evaluate the effect of rubber particle spatial distribution on the brittle ductile transition of poly(vinyl chloride) (PVC)/nitrile rubber (NBR) blends. Two types of rubber particle spatial distributions, i.e. well-dispersed particles and pseudonetwork, are investigated. The formation of PVC primary particles favours the toughening of PVC. An approximate master curve of brittle ductile transition for the blends with the pseudonetwork morphology is obtained by plotting the impact strength *versus* the average matrix ligament thickness. The critical matrix ligament thickness for the blends with the pseudonetwork morphology is 0.11 $\mu$m, which is much larger than that (0.059 $\mu$m) for the blends with the morphology of well-dispersed rubber particles. Therefore, pseudonetwork morphology is much more effective in toughening PVC than the morphology of well-dispersed rubber particles. Moreover, the critical matrix ligament thickness depends on the rubber particle spatial distribution, and is thus not a characteristic of the PVC matrix. The effects of morphological parameters and PVC molecular weight on the toughness of PVC/NBR blends are discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(**Keywords: rubber particle spatial distribution; brittle ductile transition; rubber toughened ploy(vinyl chloride)**)

## INTRODUCTION

Toughness is often an important factor in materials selection. However, many plastics are brittle, particularly at low temperatures and during high speed impact. It is well known that the impact properties of these materials can be considerably enhanced by the incorporation of a rubbery phase[1,2]. The rubber bulk is broken into discrete rubber particles on mixing, which are usually randomly dispersed in the plastic matrix. The rubber particles act as stress concentrators to promote crazing or shear yielding of the matrix, and whether crazing or shear yielding is the dominant toughening mechanism depends on the intrinsic toughness of the matrix material[3] and the morphology of the polymer blend[4,5].

For binary polymer blends, the important morphological parameters include the average particle size, particle size distribution, particle volume fraction, spatial distribution of particles in the matrix and average matrix ligament thickness (average surface-to-surface interparticle distance). The influences of average particle size, particle volume fraction and average matrix ligament thickness on the impact strength have been documented in a number of papers. Wu and other workers[4–10] have concluded that the average matrix ligament thickness is the single morphological parameter determining the impact toughness of polymer blends, and a blend becomes tough when the average matrix ligament thickness is smaller than a critical value. A small average matrix ligament thickness can be achieved by reducing the average particle size or increasing the particle volume fraction. However, it has been shown for a number of blend systems[1,2,11–19] that there is also a lower particle size limit below which a blend becomes brittle. Therefore, there is an optimum average particle size range for achieving the toughening of polymers. In this series of papers, we have derived a new equation for correlating the average matrix ligament thickness to the average particle size, particle size distribution and particle volume fraction, and have pointed out that the particle size distribution has a strong effect on the impact toughness of polymer blends, and that a wide distribution of particle sizes is unfavourable to the toughening of polymers[20–22].

The toughness of a blend increases with increasing rubber particle volume fraction. However, many properties, e.g., stiffness, heat distortion temperature and processability,

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[*] To whom correspondence should be addressed.
[†] Present address: P.O. Box 13, Taiyuan 030051, Shanxi, P. R. China.

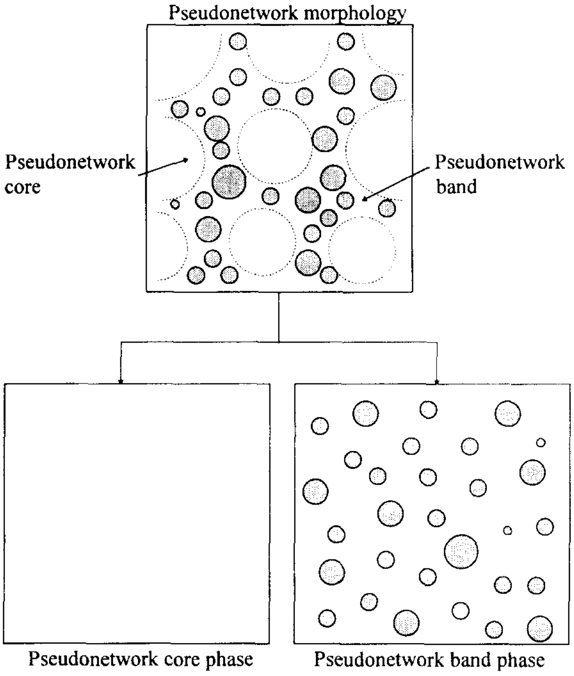

**Figure 1** Schematic illustration of the pseudonetwork morphology. The filled circles represent the rubber particles. The dashed circles denote the pseudonetwork cores

become worse when the rubber particle volume fraction increases. Therefore, it is desirable to achieve high toughening efficiency with less rubber. It is known that reducing the width of particle size distribution and optimizing the average particle size are effective ways to increase the toughening efficiency. Is there any other way? The toughness of a blend depends also on the spatial distribution of the dispersed rubber particles. It is known that a blend with uniformly dispersed particles, i.e. having the morphology of well-dispersed particles, is much tougher than a blend with agglomerated particles[5].

Breuer and co-workers[12,23] reported that there is a particular spatial distribution of rubber particles that is much more effective than the morphology of well-dispersed rubber particles in the toughening of poly(vinyl chloride) (PVC) by blending with acrylonitrile–butadiene–styrene copolymer (ABS). When the ABS particles are dispersed between the PVC primary particles, the PVC/ABS blend is tough. On the other hand, if the PVC primary particles are broken down and the ABS particles are well dispersed in the PVC matrix, the toughness of the blend is greatly reduced. Other examples are PVC/rubber-g-poly(methyl methacrylate) (PMMA)[24] and PVC/methyl methacrylate–butadiene–styrene core-shell modifier (MBS)[23,25–27] blends. This phenomenon cannot be understood in terms of current models[2,21] because these models have not taken the effect of the particle spatial distribution into account.

Tanaka and co-workers[28–32] proposed a simple model for analyzing the effects of two morphological parameters, namely particle spatial distribution and average particle or cluster size, on the impact toughness. However, their model does not consider the effects of particle size distribution, particle volume fraction and average matrix ligament thickness. It is known that all the above morphological parameters affect the impact toughness. Therefore, it is inadequate to attribute the observed change in impact strength completely to changes in particle spatial distribution and average particle or cluster size.

Wu[4,5] suggested that the critical matrix ligament thickness for achieving toughening is an intrinsic property of the matrix. The quantitative relationship between the critical matrix ligament thickness and the molecular parameters of the matrix has been obtained based on this assumption[33]. We have found that the critical matrix ligament thickness of PVC/NBR blends depends strongly on the interfacial adhesion[34,35]. Whether or not it is affected by the rubber particle spatial distribution would also be interesting.

In this work, a new model is proposed in order to evaluate the effect of rubber particle spatial distribution on the impact toughness of polymer blends. PVC/nitrile rubber (NBR) blend is used as the model system to investigate this effect. The effects of rubber particle spatial distribution, other morphological parameters and PVC molecular weight on the toughness of the blends are discussed.

## MODEL

### *Pseudonetwork morphology*

The main role of the discrete rubber particles in a matrix is to act as stress concentrators to promote shear yielding or crazing, thereby resulting in a toughened blend. The brittle ductile transition of polymer blends is a critical phenomenon, which has been interpreted by using percolation models[36–39]. These percolation models simplified the stress field (generated at the moment of impact) around a rubber particle into a spherical stress volume, which encapsulates the rubber particle. A rubber particle and its spherical stress volume have a common sphere center. Therefore, both of them have the same spatial distribution according to our model established in this section. The percolation threshold has been defined as the critical volume fraction of the spherical stress volume. The percolation phenomenon begins to take place as an infinite percolation cluster starts to form at the percolation threshold. The percolation theory[40] points out that the percolation threshold is determined by the particle spatial distribution. As a result, the change in the dispersion of rubber particles would result in different critical phenomena.

The average matrix ligament thickness has been shown to be the single morphological parameter controlling the toughness of polymer blends with the morphology of well-dispersed particles[4–10,21,22]. In fact, the rubber particles act as stress concentrators in both the blend with the morphology of well-dispersed particles and that with the pseudonetwork morphology. So, we expect that the average matrix ligament thickness is also an important morphological parameter determining the toughness of polymer blends with the pseudonetwork morphology.

PVC primary particles (0.1–2 $\mu$m) play an important role in rubber toughened PVC[23–27,43]. If the PVC grains (*ca.* 100 $\mu$m) are broken into PVC primary particles on mixing, the PVC primary particles will force the rubber particles to be dispersed between them. This dispersion is favourable to the toughening of the blends. If they are broken further into smaller domains (0.01–0.1 $\mu$m), the rubber particles will be dispersed uniformly in the matrix, and the toughness of the blends will become lower. Therefore, the morphological parameters associated with the primary particles should be included in the equation for evaluating the average matrix ligament thickness.

It has been shown that the toughening efficiency of the PVC/rubber blends with the morphology of well-dispersed rubber particles is lower than that with the morphology in which the rubber particles are dispersed between neighboring PVC primary particles[12,23–27]. We term the latter the pseudonetwork morphology. The pseudonetwork morphology, shown in *Figure 1*, is assumed to be composed of two parts: (1) the pseudonetwork band phase containing rubber particles uniformly dispersed in the band and the fused PVC, and (2) the pseudonetwork core phase consisting of PVC primary particles. Is it necessary to distinguish the matrix of the pseudonetwork band from the pseudonetwork core material? The answer to this question should be based on the probability of finding a rubber particle. The probability of finding a rubber particle in the pseudonetwork core material is zero, but the probability of finding a rubber particle in the unoccupied matrix of the pseudonetwork band is greater than zero. Therefore, the pseudonetwork core material cannot be considered as identical to the unoccupied matrix of the pseudonetwork band.

In general, the pseudonetwork morphology differs from the rubber network morphology (where the rubbery phase is continuous) in the role of the rubbery phase. The rubber particles in the blends with the pseudonetwork morphology act as stress concentrators to promote matrix shear yielding or crazing, and only absorbs a very small amount of impact energy. However, the continuous rubbery phase in the blends with the network morphology directly absorb a large amount of impact energy. So, the toughening mechanisms for the two morphologies are different. That is why we propose a new morphological term, the pseudonetwork morphology.

In PVC/rubber blends with the rubber network morphology, the rubber bands can directly absorbs impact energy[3,41–48]. While in PVC/rubber blends with the pseudonetwork morphology, the rubber particles act as stress concentrators to promote the matrix shear yielding[49]. The role of the rubber particles in these PVC/rubber blends is the same as that of rubber particles in the blends with the morphology of well-dispersed rubber particles[1–10,29,50,51]. Deformation studies of PVC/NBR blends indicate that the particle spatial distribution affect the yield behaviour of the blends[49]. In blends with well-dispersed rubber particles, the PVC matrix deforms uniformly. In blends with the pseudonetwork morphology, the pseudonetwork cores are stiffer than the pseudonetwork bands, so the PVC material in the band phase yields more easily.

### *Definitions of average particle size and particle size distribution*

The sizes of the rubber particles in binary polymer blends usually obey the log-normal distribution[4,5,7,20,21]. We shall show in the following section that the sizes of PVC primary particles also obey this distribution. For a log-normal distribution, the frequency $f(d_i)$ of a particle size $d_i$ is defined as[52]

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

where the average particle size $d$ and the particle size distribution parameter $\sigma$ are given by equation (2) and equation (3), respectively[52]

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

and

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

In the case of monodispersity, $\sigma = 1$; and $\sigma > 1$ when the particle sizes are polydisperse.

### *Average matrix ligament thickness*

In a previous study[20], we have pointed out that the particle size distribution has a great influence on the average matrix ligament thickness of polymer blends with the morphology of well-dispersed particles, and have derived a new equation for calculating the average matrix ligament thickness $T(d,\sigma,\phi)$, which is given by

$$T(d,\sigma,\phi) = d\left[\left(\frac{\pi}{6\phi}\right)^{1/3}\exp(1.5\ln^2\sigma) - \exp(0.5\ln^2\sigma)\right] \tag{4}$$

where $\phi$ is the particle volume fraction.

Equation (4) cannot be used to estimate the average matrix ligament thickness of polymer blends with the pseudonetwork morphology. The reason is that equation (4) does not include the effects of the morphological parameters of PVC primary particles, which results in the deviation of rubber particle spatial distribution significantly from the cubic lattice. In other words, the average matrix ligament thickness should be a function of the morphological parameters of both the rubber particles and the PVC primary particles.

If the pseudonetwork band phase is regarded as a 'blend' with the morphology of well-dispersed rubber particles, we have

$$T_r = d_r\left[\left(\frac{\pi}{6\Phi_r}\right)^{1/3}\exp(1.5\ln^2\sigma_r) - \exp(0.5\ln^2\sigma_r)\right] \tag{5}$$

where the subscript 'r' denotes the rubber particle, and $\Phi_r$ is the rubber volume fraction in the 'pseudonetwork band blend'. It is given by

$$\Phi_r = \frac{V_r}{V_r + V_M} \tag{6}$$

where $V$ denotes the volume, and the subscript 'M' denotes the fused PVC matrix. Therefore, $V_r$ is the rubber particle volume, and $V_M$ is the volume of fused PVC. Since $V_M$ is unknown, the rubber volume fraction in the 'pseudonetwork band blend' must be calculated from other morphological parameters of the PVC/NBR blend with the pseudonetwork morphology.

The rubber particle volume fraction that can be experimentally measured is

$$\phi_r = \frac{V_r}{V_r + V_M + V_P} \tag{7}$$

where the subscript 'P' denotes the PVC primary particle or the pseudonetwork core; $V_P$ is thus the PVC primary particle volume or pseudonetwork core volume. Therefore, the total volume of the blend is $V_r + V_M + V_P$.

The PVC primary particle volume fraction is

$$\phi_P = \frac{V_P}{V_r + V_M + V_P} \tag{8}$$

Thus the relation between $\Phi_r$, $\phi_r$ and $\phi_P$ is

$$\Phi_r = \frac{\phi_r}{1 - \phi_P} \tag{9}$$

For the PVC/NBR blends studied here, the PVC primary particle volume fraction $\phi_P$ in equation (9) is unknown. However, the relation given by equation (9) is very important because a new morphological parameter will be calculated based on the equation as follows.

Let $\xi$ be

$$\xi = \sqrt[3]{1 - \phi_P} \tag{10}$$

then

$$\Phi_r = \frac{\phi_r}{\xi^3} \tag{11}$$

Combining equations (5) and (11) yields

$$T_r(d_r, \sigma_r, \phi_r, \xi) = d_r\left[\xi\left(\frac{\pi}{6\phi_r}\right)^{1/3}\exp(1.5\ \ln^2\sigma_r) - \exp(0.5\ \ln^2\sigma_r)\right] \tag{12}$$

Equation (12) is the generalised equation for evaluating the average matrix ligament thickness. The geometrical significance of the new parameter $\xi$ will be discussed in the next part of this section.

Now we find the volume fraction $\phi_P$ of pseudonetwork cores according to the definition in equation (8) which will then lead to $\xi$ according to equation (10). We divide the PVC/rubber blends with the pseudonetwork morphology into two parts (see the upper part of *Figure 1*): the PVC primary particles (the dispersed phase) and the pseudonetwork bands (the continuous phase) consisting of rubber particles and fused PVC. Because our experimental results show that the sizes of the PVC primary particles fit the log-normal distribution, the average surface-to-surface interparticle distance $T_P(d_P,\sigma_P,\phi_P)$ between PVC primary particles is given by

$$T_P(d_P, \sigma_P, \phi_P) = d_P\left[\left(\frac{\pi}{6\phi_P}\right)^{1/3}\exp(1.5\ \ln^2\sigma_P) - \exp(0.5\ \ln^2\sigma_P)\right] \tag{13}$$

So, $\phi_P$ is given by

$$\phi_P = \frac{\pi}{6}\left[\frac{\exp(1.5\ \ln^2\sigma_P)}{\frac{T_P}{d_P} + \exp(0.5\ \ln^2\sigma_P)}\right]^3 \tag{14}$$

Insertion of equation (14) into equation (10) gives

$$\xi = \left\{\frac{\left[\frac{T_P}{d_P} + \exp(0.5\ \ln^2\sigma_P)\right]^3 - \frac{\pi}{6}\left[\exp(1.5\ \ln^2\sigma_P)\right]^3}{\left[\frac{T_P}{d_P} + \exp(0.5\ \ln^2\sigma_P)\right]^3}\right\}^{1/3} \tag{15}$$

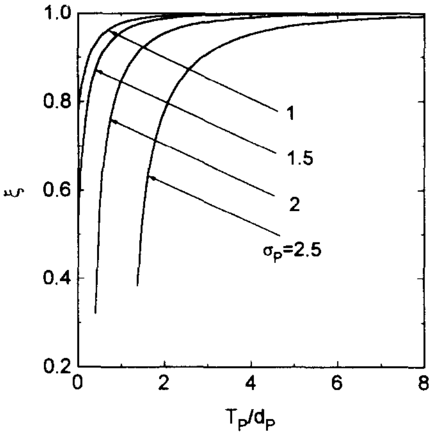

**Figure 2** Calculated variations of the rubber particle spatial distribution parameter $\xi$ with the morphological parameters of pseudonetwork cores

Equation (15) is applied only for PVC/NBR blends with the pseudonetwork morphology.

*Rubber particle spatial distribution*

The geometrical significance of the new morphological parameter $\xi$, defined by equation (10), can be seen as follows. For particles conforming to the log-normal distribution and occupying any lattice, the average center-to-center interparticle distance $L$ can be exactly calculated from[53,54]

$$L = T + d\exp(0.5\ \ln^2\sigma) \tag{16}$$

Applying equations (4) and (16) to the morphology of well-dispersed particles, we have

$$L_{r,1} = d_r\left(\frac{\pi}{6\phi_r}\right)^{1/3}\exp(1.5\ \ln^2\sigma_r) \tag{17}$$

Applying equation (12) and equation (16) to the pseudonetwork morphology, we have

$$L_{r,2} = d_r\xi\left(\frac{\pi}{6\phi_r}\right)^{1/3}\exp(1.5\ \ln^2\sigma_r) \tag{18}$$

For the case of constant average rubber particle size, rubber particle size distribution and rubber particle volume fraction, combining equation (17) and equation (18) gives

$$\xi = \frac{L_{r,2}}{L_{r,1}} \tag{19}$$

It is clear that $\xi$ is the ratio of average center-to-center interparticle distance of the particles occupying the lattice of the pseudonetwork morphology to that of the particles occupying the lattice of the morphology of well-dispersed particles when the average rubber particle size, rubber particle size distribution and rubber particle volume fraction are identical. It is characteristic of the rubber particle dispersion state and is thus called the rubber particle spatial distribution parameter. By comparing equation (4) with equation (12), one obtains $\xi = 1$ for polymer blends with the morphology of well-dispersed particles. It is clear from equation (10) that the rubber particle spatial distribution parameter $\xi$ for the pseudonetwork morphology is smaller than 1.

We now analyze the relationship between the morphology of well-dispersed particles and the pseudonetwork morphology in PVC/NBR blends. *Figure 2* shows the rubber particle spatial distribution parameter $\xi$ as a function of the ratio $T_P/d_P$ calculated according to equation (15). $\xi$ increases with $T_P/d_P$ for a given PVC primary particle size distribution. In the range of PVC primary particle size distribution parameter $\sigma_P$ of 1 to 2.5, $\xi$ increases rapidly to above 0.9 as $T_P/d_P$ increases from 0 to 4. It gradually approaches unity with further increase of $T_P/d_P$. The wider the PVC primary particle size distribution the smaller the value of $\xi$ at a fixed $T_P/d_P$. So, the difference in the average matrix ligament thicknesses predicted by equation (4) and equation (12) becomes less significant for blends with a larger average surface-to-surface interparticle distance of PVC primary particles $T_P$ and a smaller average PVC primary particle size $d_P$. Then the morphology of well-dispersed particles will be similar to the pseudonetwork morphology.

## EXPERIMENTAL

### *Materials*

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

### *Blend preparation*

Scheme 1 for preparing PVC/NBR blends with the well-dispersed rubber particles: NBRa was milled on a laboratory two-roller mill at room temperature for 15 and 30 min, respectively, to give NBRb and NBRc. Each of NBRa, NBRb and NBRc was mixed at 160°C for 6 min with a PVC suspension (containing 0.4 parts per hundred parts of resin (abbreviated to phr) lubricator, 3 phr stabiliser, and 5 phr plasticiser).

Scheme 2 for preparing PVC/NBR blends with the pseudonetwork morphology: NBRa was mixed with a PVC suspension (containing 0.4 phr lubricator and 3 phr stabiliser) on a laboratory two-roller mill at a temperature of 150°C for 3–6 min.

The milled sheets were compression-molded for 10 min at 160°C. They were then cooled slowly to room temperature to give 4 mm thick plates. The samples for impact tests and morphology observations were cut from these plates.

### *Impact tests*

Izod impact tests were carried out according to ASTM-D256 at 16°C.

### *Morphological observations*

The samples were cryo-fractured. The fracture surfaces were etched in an oxidiser consisting 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 the 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 determine the sizes of the rubber particles and PVC primary particles and the particle size distributions using a computerised image analyzer. At least 300 particles were studied for each sample.

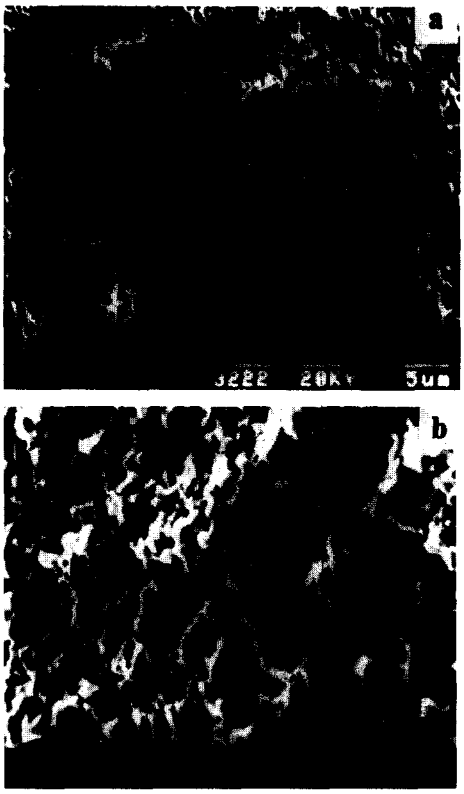

**Figure 3** SEM microphotographs of PVC/NBR blends, showing (a) the morphology of well-dispersed rubber particles and (b) the pseudonetwork morphology

## RESULTS AND DISCUSSION

### *Morphology*

In binary polymer blends, two types of particle spatial distributions are usually observed. One is the morphology of well-dispersed particles, and the other is the morphology of agglomerated particles. Owing to the presence of PVC primary particles, PVC/rubber blends can exhibit the pseudonetwork morphology. The three-particle spatial distributions in PVC/NBR blends can be controlled by varying the processing conditions, i.e. processing temperature, shear rate, milling time, PVC molecular weight, and processing additives. In this work, these factors are well considered. In general, higher processing temperature, longer milling time, stronger shear, lower PVC molecular weight, and higher plasticiser content favour the formation of the morphology of well-dispersed particles. By carefully controlling these conditions, the pseudonetwork morphology can be obtained. The morphological features of PVC/NBR blends with the two morphologies are described below.

*Figure 3a* and *Figure 3b* show the SEM photomicrographs of the morphology of well-dispersed particles and the pseudonetwork morphology, respectively. In *Figure 3a* the PVC primary particles are completely broken down, and the NBR rubber particles are well dispersed in the PVC matrix. The PVC primary particles can be clearly seen in *Figure 3b*, and the NBR rubber particles are dispersed between the PVC primary particles embedded in the fused PVC material.

For all PVC/NBR blends reported here, the sizes of the NBR rubber particles fit the log-normal distribution. *Figure 4* shows the typical NBR rubber particle size distributions for the morphology of well-dispersed particles (solid symbols) and the pseudonetwork morphology (open circles).

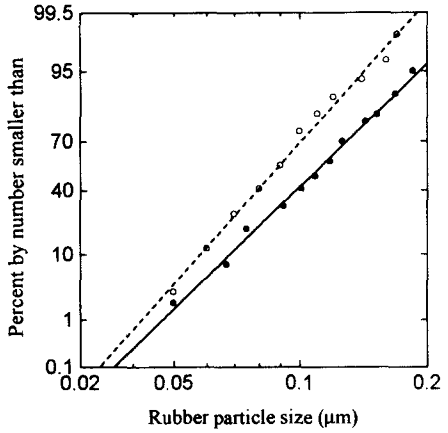

**Figure 4** Log-normal distributions of rubber particles in a PVC/NBR blend with well-dispersed particles (filled symbols) and a PVC/NBR blend with the pseudonetwork structure (open circles)

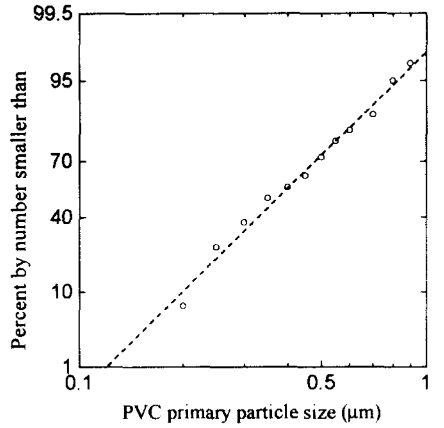

**Figure 5** Log-normal distribution of PVC primary particles in a PVC/NBR blend

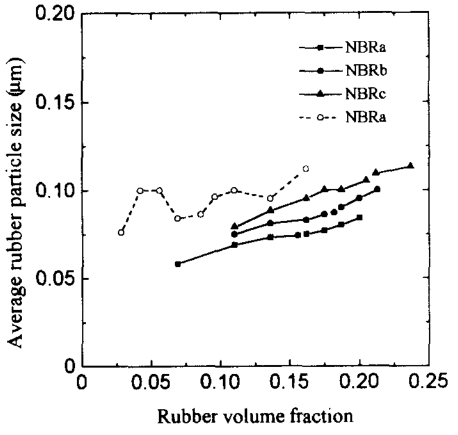

**Figure 6** Average rubber particle size *versus* rubber volume fraction for PVC/NBR blends with the morphology of well-dispersed rubber particles (filled symbols) and the pseudonetwork morphology (open circles)

*Figure 5* displays the log-normal distribution of the PVC primary particles. This distribution is applicable to all PVC/NBR blends with the pseudonetwork structure.

*Figure 6* shows the rubber particle size *versus* rubber volume fraction for blends with the two particle spatial distributions. For a given rubber volume fraction, the rubber particle size of the blend with the pseudonetwork structure (open circles) is larger than those of the blends with well-dispersed particles (solid symbols). The processing conditions for preparing the blends with the pseudonetwork structure were not kept identical. So, it is not adequate to attribute the change in the rubber particle size solely to the rubber volume fraction. For the blends with well-dispersed, the rubber particle size increases with the rubber volume fraction and the time for milling the rubber.

### *Brittle ductile transition*

*Figure 7* shows the notched Izod impact strength *versus* rubber volume fraction for PVC/NBR blends with the two particle spatial distributions. For the blends with well-dispersed particles (solid symbols) and a given rubber, a sharp brittle ductile transition is found to occur at a critical rubber volume fraction. The critical rubber volume fraction increases with the time for milling the rubber. For the blends with the pseudonetwork structure (open circles), a sharp brittle ductile transition occurs at a critical rubber volume fraction ($\approx 0.05$) much lower than those for the blends with the well-dispersed particles. the critical rubber volume fraction observed here for the blends with the pseudonetwork structure is close to those reported in other PVC/rubber blends[24,26].

In order to establish the relationship between the impact strength, average matrix ligament thickness and rubber particle spatial distribution, the rubber particle spatial distribution parameter is first calculated using equation (15). All the morphological parameters on the right hand side of equation (15) except the average surface-to-surface interparticle distance of PVC primary particles $T_P$ can be measured. We have shown that the average surface-to-surface interparticle distance of PVC primary particles obtained experimentally from SEM or TEM micrographs is greater than the actual value. The relevant work will be published elsewhere. So, we use the following approach to estimate the $T_P$ value. Morphological observations indicate that only one layer of rubber particles is located between the nearest points of two adjacent PVC primary particles for the blends studied here. One example is shown in *Figure 3b*. If we assume that $T_P = d_r$, equation (15) becomes

$$\xi = \left\{ \frac{\left[\frac{d_r}{d_P} + \exp(0.5 \ln^2\sigma_P)\right]^3 - \frac{\pi}{6}\left[\exp(1.5 \ln^2\sigma_P)\right]^3}{\left[\frac{d_r}{d_P} + \exp(0.5 \ln^2\sigma_P)\right]^3} \right\}^{1/3} \tag{20}$$

As shown in *Table 1*, the values of rubber particle spatial distribution parameter $\xi$ for the PVC/NBR blends with the pseudonetwork morphology, calculated using equation (20), are smaller than unity. This will lead to a smaller average matrix ligament thickness for the pseudonetwork morphology than that for the morphology of well-dispersed particles when the average rubber particle size, rubber particle size distribution and rubber particle volume fraction are identical.

Equation (12) is now used to calculate the average matrix ligament thickness. For the PVC/NBR blends with well-dispersed rubber particles, the rubber particle spatial distribution parameter $\xi$ is assumed to be one. For the PVC/NBR blends with the pseudonetwork morphology, the values of rubber particle spatial distribution parameters listed in *Table 1* are used to calculate the average matrix ligament thickness $T_r$. After evaluating $T_r$, the notched Izod

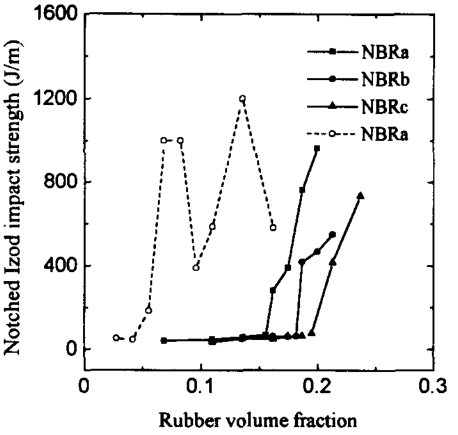

Figure 7 Notched Izod impact strength *versus* rubber volume fraction for PVC/NBR blends with the morphology of well-dispersed rubber particles (solid symbols) and the pseudonetwork morphology (open circles)

Table 1 The rubber particle spatial distribution parameter $\xi$ for PVC/NBR blends with the pseudonetwork morphology

| $\phi_r$ | $d_r$ ($\mu$m) | $d_P$ ($\mu$m) | $d_r/d_P$ | $\sigma_P$ | $\xi$ |
|---|---|---|---|---|---|
| 0.028 | 0.076 | 0.45 | 0.169 | 1.36 | 0.839 |
| 0.042 | 0.100 | 0.39 | 0.256 | 1.54 | 0.800 |
| 0.056 | 0.100 | 0.41 | 0.244 | 1.46 | 0.826 |
| 0.069 | 0.084 | 0.40 | 0.210 | 1.65 | 0.693 |
| 0.086 | 0.086 | 0.38 | 0.226 | 1.61 | 0.740 |
| 0.096 | 0.096 | 0.31 | 0.310 | 1.48 | 0.848 |
| 0.110 | 0.100 | 0.35 | 0.286 | 1.52 | 0.824 |
| 0.136 | 0.095 | 0.41 | 0.232 | 1.59 | 0.757 |
| 0.162 | 0.112 | 0.33 | 0.339 | 1.55 | 0.836 |

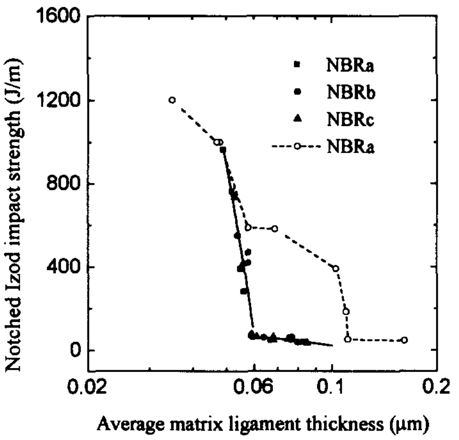

Figure 8 Notched Izod impact strength *versus* average matrix ligament thickness for PVC/NBR blends with the morphology of well-dispersed rubber particles (solid symbols) and the pseudonetwork morphology (open circles)

impact strength is plotted against the average matrix ligament thickness for PVC/NBR blends with the two particle spatial distributions (*Figure 8*). For the blends with the morphology of well-dispersed particles, all the data for the three different types of rubber fall on a master curve of brittle ductile transition. It is also interesting to note that for the blends with the pseudonetwork morphology, the oscillating data in the plot of impact strength *versus* rubber volume fraction (see *Figure 7*) turn into a rather smooth curve when the impact strength is plotted against the average matrix ligament thickness (see *Figure 8*). In the range of $T_r$ = 0.06–0.1 $\mu$m, the impact strengths of the blends with the pseudonetwork morphology are much higher than those of the blends with the morphology of well-dispersed particles, indicating that impact strength is a function not only of the average matrix ligament thickness but also of the rubber particle spatial distribution. The average matrix ligament thickness has been proposed to be the single morphological parameter controlling the brittle ductile transition of the polymer blends with the well-dispersed rubber particles[3–10,21,22]. *Figure 8* suggests that this conclusion is not valid for blends with the pseudonetwork morphology. From *Figure 8* two critical matrix ligament thickness values are obtained. The critical matrix ligament thickness for the blends with well-dispersed rubber particles is 0.059 $\mu$m, which is much smaller than that (0.11 $\mu$m) for the blends with the pseudonetwork morphology. A larger critical matrix ligament thickness implies that toughening can be achieved for larger rubber particle size and lower rubber particle volume fraction. Therefore, the pseudonetwork morphology is much more effective in toughening than the morphology of well-dispersed particles.

The fact that for $T_r$ = 0.06–0.1 $\mu$m the impact strength of the blends with the pseudonetwork morphology is much higher than that of the blends with the morphology of well-dispersed rubber particles implies that the impact strength is determined not only by the average matrix ligament thickness but also by the rubber particle spatial distribution. However, the data for blends with the two different spatial distributions tend to fall on one curve as the average matrix ligament thickness is smaller than *ca.* 0.059 $\mu$m, indicating that the rubber particle spatial distribution has a weaker effect on the impact strength when the matrix ligament thickness is small.

Wu[4,5] has suggested that the critical matrix ligament thickness is characteristic of the matrix at a given temperature and for a given mode and rate of deformation. However, the present study clearly shows that it is also a function of the rubber particle spatial distribution. It has also been shown that the critical matrix ligament thickness decreases with increasing interfacial adhesion[34,35].

### *Effects of the morphological parameters of pseudonetwork cores and rubber particles on average matrix ligament thickness*

It has been shown that the average matrix ligament thickness is an important morphological parameter controlling the brittle ductile transition of polymer blends not only for the blends with the well-dispersed rubber particles but also for the blends with the pseudonetwork morphology. Clearly a small average rubber particle size yields a small average matrix ligament thickness since equation (12) shows that the average matrix ligament thickness is proportional to the average rubber particle size when other factors are identical. It has been shown that there is a lower critical rubber particle size below which the rubber particles are not able to induce toughening of the matrix[1,2,11–19]. We have shown that the lower critical rubber particle size is a function of the rubber particle size distribution, rubber volume fraction and critical matrix ligament thickness, and that it is also influenced by interfacial adhesion[55]. We may also define an upper critical rubber particle size above which the rubber particles are not able to induce toughening. The upper critical rubber particle size has the similar dependences on those factors influencing the lower critical rubber particle size. We expect that there are corresponding upper and lower critical matrix ligament thicknesses. Therefore, the average rubber particle size should be reduced such that

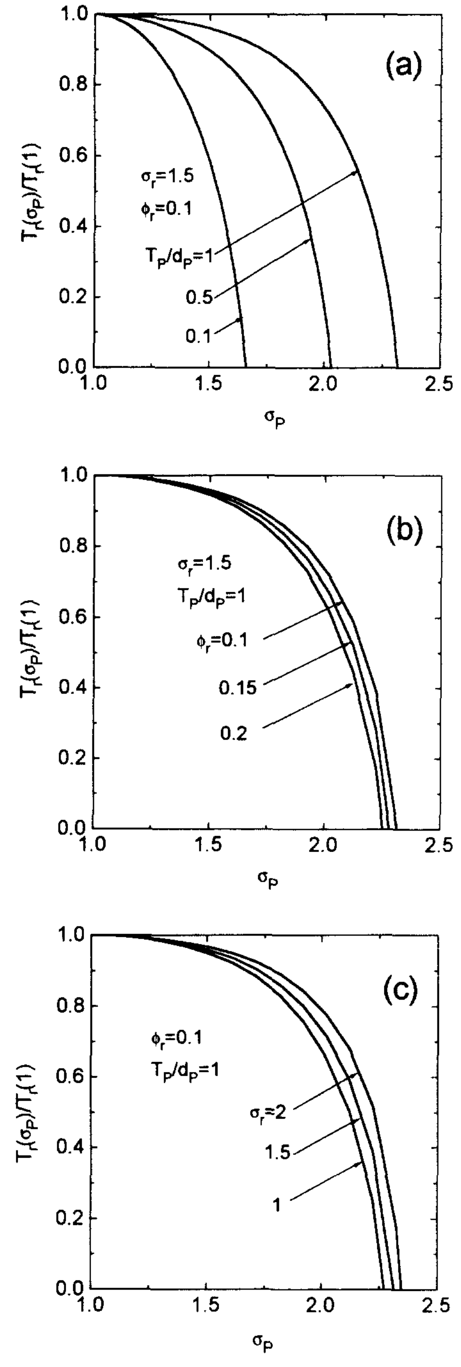

**Figure 9** Calculated variations of $T_r(\sigma_P)/T_r(1)$, the ratio of the average matrix ligament thickness for the case of polydispersity ($\sigma_P > 1$) to the average matrix ligament thickness for the case of monodispersity ($\sigma_P = 1$), with the PVC primary particle size distribution parameter $\sigma_P$ for blends with the pseudonetwork morphology. The values of the other parameters are given in the figures

the matrix ligament thickness would lie between the upper and lower critical matrix ligament thickness.

The effects of the morphological parameters of pseudonetwork cores and rubber particles are analyzed using two normalised average matrix ligament thicknesses, namely the ratio $T_r(\sigma_P)/T_r(1)$ of the average matrix ligament thickness for polydisperse pseudonetwork cores ($\sigma_P > 1$) to that for monodisperse pseudonetwork cores ($\sigma_P = 1$), and the ratio $T_r(\sigma_r)/T_r(1)$ of the average matrix ligament thickness for polydisperse rubber particles ($\sigma_r > 1$) to that for monodisperse rubber particles ($\sigma_r = 1$).

For a constant average rubber particle size, the influences of the morphological parameters of pseudonetwork cores on the average matrix ligament thickness can be expressed as

$$\frac{T_r(\sigma_P)}{T_r(1)} = \frac{\xi(\sigma_P)\left(\frac{\pi}{6\phi_r}\right)^{1/3}\exp(1.5\ln^2\sigma_r) - \exp(0.5\ln^2\sigma_r)}{\xi(1)\left(\frac{\pi}{6\phi_r}\right)^{1/3}\exp(1.5\ln^2\sigma_r) - \exp(0.5\ln^2\sigma_r)} \tag{21}$$

*Figure 9a–c* illustrates the calculated effects of the morphological parameters of pseudonetwork cores on the average matrix ligament thickness. The left hand side of equation (21) is plotted against the pseudonetwork core size distribution parameter $\sigma_P$ at the different conditions indicated in these figures. When the rubber particle size distribution parameter $\sigma_r$ is 1.5 and the rubber particle volume fraction $\phi_r$ is 0.1, $T_r(\sigma_P)/T_r(1)$ decreases with an increase in the pseudonetwork core size distribution parameter for a given $T_P/d_P$, and the decrease is more rapid with the reduction of $T_P/d_P$ (*Figure 9a*). Consequently, the average matrix ligament thickness $T_r$ decreases with an increase in the average pseudonetwork core size $d_P$ and the pseudonetwork core size distribution parameter and a decrease in the average surface-to-surface interparticle distance $T_P$ of pseudonetwork cores. For a constant $T_P/d_P$ value of 1 and rubber particle size distribution parameter of 1.5, an increase in the rubber volume fraction also leads to a reduction in $T_r(\sigma_P)/T_r(1)$, especially when there is a wider pseudonetwork core size distribution (*Figure 9b*). However, for $T_P/d_P = 1$ and rubber volume fraction $\phi_r = 0.1$, an increase in the width of the rubber particle size distribution results in an increase of $T_r(\sigma_P)/T_r(1)$, especially when the pseudonetwork core size distribution is wider (*Figure 9c*). It is interesting to notice that $T_P/d_P$ has a more significant influence than the rubber particle size distribution parameter $\sigma_r$ and the rubber volume fraction $\phi_r$ on the relationship between $T_r(\sigma_P)/T_r(1)$ and the pseudonetwork core size distribution parameter $\sigma_P$.

For a constant average rubber particle size, the influences of other morphological parameters of rubber particles on the average matrix ligament thickness can be expressed as

$$\frac{T_r(\sigma_r)}{T_r(1)} = \frac{\xi\left(\frac{\pi}{6\phi_r}\right)^{1/3}\exp(1.5\ln^2\sigma_r) - \exp(0.5\ln^2\sigma_r)}{\xi\left(\frac{\pi}{6\phi_r}\right)^{1/3} - 1} \tag{22}$$

*Figure 10* shows $T_r(\sigma_r)/T_r(1)$ *versus* the rubber particle size distribution parameter $\sigma_r$ for various values of rubber particle spatial distribution parameter $\xi$ and rubber particle volume fraction $\phi_r$. When blend contains well-dispersed rubber particles, the rubber particle spatial distribution parameter equals one (solid line). In this case, $T_r(\sigma_r)/T_r(1)$ is always larger than unity and increases with the rubber particle size distribution parameter. The higher the rubber particle volume fraction, the more significant the influence of the rubber particle size distribution on $T_r(\sigma_r)/T_r(1)$. When the blend has a pseudonetwork structure, the rubber particle spatial distribution parameter is smaller than one (dotted and dashed lines). For constant $\xi$ and $\phi_r$, $T_r(\sigma_r)/T_r(1)$ increases with the rubber particle size distribution parameter. Furthermore, the dependence of $T_r(\sigma_r)/T_r(1)$ on the rubber particle size distribution is stronger when the rubber particle volume fraction is higher (dotted lines). For a given rubber particle volume fraction, e.g., 0.2, $T_r(\sigma_r)/T_r(1)$

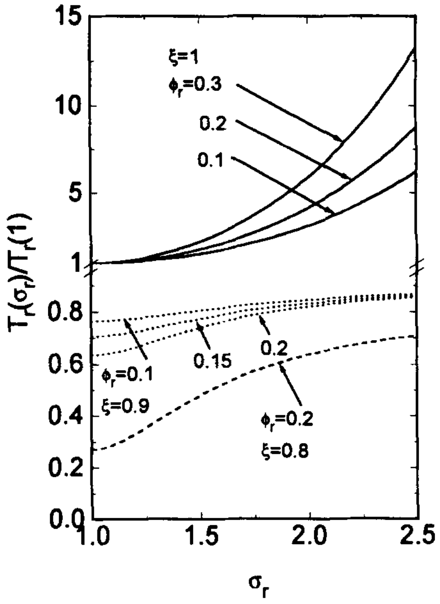

**Figure 10** Calculated variations of $T_r(\sigma_r)/T_r(1)$, the ratio of the average matrix ligament thickness for the case of polydispersity ($\sigma_r > 1$) to the average matrix ligament thickness for the case of monodispersity ($\sigma_r = 1$), with the rubber particle size distribution parameter $\sigma_r$ for the blends with the pseudonetwork morphology. The values of the other parameters are given in the figure

increases with the increase in the width of the rubber particle spatial distribution. So, a narrower rubber particle size distribution and a higher rubber particle volume fraction result in a smaller average matrix ligament thickness.

It is seen from *Figure 10* that for $\xi < 1$ $T_r(\sigma_r)/T_r(1)$ is smaller than 1. However, this does not mean that $T_r(\sigma_r)/T_r(1)$ is always smaller than 1 when $\xi < 1$. Equation (22) shows that $T_r(\sigma_r)/T_r(1) < 1$ when

$$\xi < \left(\frac{6\phi_r}{\pi}\right)^{1/3} \frac{\exp(0.5 \ln^2\sigma_r) - 1}{\exp(1.5 \ln^2\sigma_r) - 1} \qquad (23)$$

### *Effect of PVC molecular weight on toughness*

The impact strength of PVC/rubber blends has been found to depend strongly on the PVC molecular weight. The critical modifier content increases with the reduction of PVC molecular weight, as observed in MBS[26,56], ABS[25,56] and chlorinated polyethylene (CPE)[26] toughened PVC, respectively. This observation could be understood in terms of the present model.

The breakdown of the PVC particulate structure has been shown to be affected by the PVC molecular weight in addition to the processing aids and processing conditions. The PVC grains and subgrains start to be broken into primary particles at low temperatures[27,57]. The higher the molecular weight, the higher the PVC fusion temperature[27,58]. As a result, high PVC molecular weight favours the formation of primary particles. This leads to an increase of impact strength of PVC/rubber blends.

## CONCLUSIONS

A new model for predicting the effect of rubber particle spatial distribution on the brittle ductile transition of PVC/NBR blends has been established. Two types of rubber particle spatial distributions, the morphology of well-dispersed particles and the pseudonetwork morphology, have been investigated. The rubber particle spatial distribution parameter $\xi$ is defined by equation (19) and calculated using equation (10). Physically, $\xi$ is the ratio of average center-to-center interparticle distance of particles occupying the lattice of the pseudonetwork morphology to that of particles occupying the lattice of the morphology of well-dispersed particles when the average rubber particle size, rubber particle size distribution and rubber particle volume fraction are identical. For the morphology of well-dispersed rubber particles, $\xi$ is assumed to be equal to 1. For the pseudonetwork morphology, it is smaller than 1.

The rubber particle spatial distribution parameter $\xi$ is also related to the average particle size $d_P$, size distribution parameter $\sigma_P$ and average surface-to-surface interparticle distance $T_P$ of the pseudonetwork cores. A larger average pseudonetwork core size, wider core size distribution and smaller average surface-to-surface interparticle distance of pseudonetwork cores lead to a smaller rubber particle spatial distribution parameter. A larger average surface-to-surface interparticle distance of pseudonetwork cores, narrower pseudonetwork core size distribution and smaller average pseudonetwork core size lead to $\xi = 1$, i.e. the pseudonetwork morphology approaches the morphology of well-dispersed particles.

PVC/NBR blends with the two types of morphologies have been successfully prepared. For the morphology of well-dispersed rubber particles, the PVC primary particles are almost completely broken down, and the rubber particles are randomly dispersed in the PVC matrix. For the pseudonetwork morphology, the PVC primary particles are surrounded by the rubber particles. The PVC primary particles act as the pseudonetwork cores. The brittle ductile transitions of PVC/NBR blends with the two spatial distributions of rubber particles are observed to occur at the different critical rubber volume fractions. The critical rubber volume fraction for the blends with the pseudonetwork morphology is found to be much lower than those for the blends with the morphology of well-dispersed rubber particles.

An approximate master curve of brittle ductile transition for the PVC/NBR blends with the pseudonetwork morphology has been obtained by plotting impact strength against average matrix ligament thickness. The critical matrix ligament thickness is, however, considerably influenced by the rubber particle spatial distribution. The brittle ductile transition of the PVC/NBR blends with the well-dispersed rubber particles is found to occur at a much smaller critical matrix ligament thickness (0.059 $\mu$m) compared to that (0.11 $\mu$m) for the pseudonetwork morphology. This indicates that the pseudonetwork morphology is much more effective in the toughening of PVC than the morphology of well-dispersed rubber particles. Wu[4,5] suggested that the critical matrix ligament thickness is characteristic of the matrix at a given temperature for a given mode and rate of deformation. However, the present study clearly shows that it also depends on the rubber particle spatial distribution.

A smaller rubber particle spatial distribution parameter leads to a smaller average matrix ligament thickness. A larger average pseudonetwork core size, wider core size distribution and higher rubber volume fraction also result in a smaller average matrix ligament thickness. On the other hand, if the average rubber particle size and hence the average matrix ligament thickness is too small, the blend also becomes brittle. Therefore, it is important to choose morphological parameters in the optimum range in order to achieve toughening of PVC.

The dependence of the toughness of PVC/rubber blends on the PVC molecular weight can be explained by the PVC particulate structure. High molecular weight favours the formation of the PVC primary particles, and hence gives rise to enhanced toughness.

## NOMENCLATURE

### *Abbreviations*

| | |
|---|---|
| ABS | Acrylonitrile–butadiene–styrene copolymer |
| CPE | Chlorinated polyethylene |
| MBS | Methyl methacrylate–butadiene–styrene core-shell modifier |
| NBR | Nitrile rubber or acrylonitrile–butadiene copolymer |
| PMMA | Poly(methyl methacrylate) |
| PVC | Poly(vinyl chloride) |

### *Symbols*

| | |
|---|---|
| $d$ | Average particle size defined by log-normal distribution |
| $\sigma$ | Particle size distribution parameter defined by log-normal distribution |
| $\phi$ | Particle volume fraction |
| $T$ | Average matrix ligament thickness (average surface-to-surface interparticle distance) |
| $d_r$ | Average rubber particle size defined by log-normal distribution |
| $\sigma_r$ | Rubber particle size distribution parameter defined by log-normal distribution |
| $\phi_r$ | Rubber particle volume fraction |
| $T_r$ | Average matrix ligament thickness (surface-to-surface interparticle distance between rubber particles) |
| $d_P$ | Average PVC primary particle size defined by log-normal distribution |
| $\sigma_P$ | PVC primary particle size distribution parameter defined by log-normal distribution |
| $\phi_P$ | PVC primary particle volume fraction |
| $T_P$ | Average surface-to-surface interparticle distance between PVC primary particles |
| $\Phi_r$ | Rubber particle volume fraction in the pseudonetwork band phase shown in the lower part of *Figure 1* |
| $\xi$ | Rubber particle spatial distribution parameter |
| $V_M$ | Matrix volume or the fused PVC volume |
| $V_r$ | Rubber particle volume |
| $V_P$ | Pseudonetwork core volume or PVC primary particle volume |
| $L$ | Average center-to-center interparticle distance |
| $L_{r,1}$ | Average center-to-center interparticle distance for particles occupying the lattice of the morphology of well-dispersed particles |
| $L_{r,2}$ | Average center-to-center interparticle distance for particles occupying the lattice of the pseudonetwork morphology |
| $T_P/d_P$ | Ratio of the surface-to-surface interparticle distance between pseudonetwork cores to the average pseudonetwork core size |
| $T_r(\sigma_P)/T_r(1)$ | Ratio of the average matrix ligament thickness for polydisperse pseudonetwork cores ($\sigma_P > 1$) to that for monodisperse pseudonetwork cores ($\sigma_P = 1$) |
| $T_r(\sigma_r)/T_r(1)$ | Ratio of the average matrix ligament thickness for polydisperse rubber particles ($\sigma_r > 1$) to that for monodisperse rubber particles ($\sigma_r = 1$) |

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