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Effect of morphology on the brittle ductile transition of polymer blends: 6. Influence of rubber particle spatial distribution on the toughening and stiffening efficiency of poly(vinyl chloride)/nitrile rubber blends

Z. H. Liu[a], X. D. Zhang†, X. G. Zhu[c], Z. N. Qi[a,*], F. S. Wang[a], R. K. Y. Li[b] and C. L. Choy[c]
[a] *State Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*
[b] *Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, People's Republic of China*
[c] *Department of Applied Physics, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, People's Republic of China*
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The influence of rubber particle spatial distribution on the toughening and stiffening efficiency of poly(vinyl chloride) (PVC)/nitrile rubber (NBR) blends is quantitatively studied. Blends with the pseudonetwork morphology or the morphology of well-dispersed rubber particles are used to elucidate the influence. The spatial distribution and matrix ligament thickness considerably affect the impact strengths of PVC/NBR blends. On the other hand, the tensile modulus of the blends is a function of rubber content but not of particle spatial distribution. Quantitative analysis shows that the modulus for the blend with the pseudonetwork morphology is much higher than that for the blend with the morphology of well-dispersed rubber particles for the same values of rubber particle size, size distribution and high impact strength. The dependence of toughening and stiffening efficiency on the spatial distribution is stronger than on the matrix ligament thickness. The pseudonetwork morphology is thus demonstrated to be very efficient in generating PVC/NBR blends simultaneously with high toughness and high stiffness. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Toughness and stiffness are two important mechanical properties for the applications of engineering plastics. However, the majority of neat polymers do not possess high toughness and high stiffness simultaneously. Many routes have been separately tried to toughen or stiffen polymer matrices. On the one hand, incorporation of a compatible rubbery material with a polymer matrix has been a major method for toughening used in industry, but this approach usually causes a great sacrifice of stiffness. On the other hand, rigid inorganic fillers and fibres have been widely used to effectively stiffen polymers without efficient toughening. It is well known that it is very difficult to toughen and stiffen a polymer matrix at the same time through chemical modification of the polymer chain structure and through physical blending.

Kurauchi and Ohta[1] raised a new concept of toughening a ductile matrix by inclusion of plastic particles through the studies on polycarbonate (PC)/poly(styrene-co-acrylonitrile) (SAN) and PC/ABS blends. Other ductile matrix/plastic particle systems, e.g. PC/poly(methyl methacrylate) (PMMA)[2,3], PC/polystyrene (PS)[2,3], poly(butylene terephtalate) (PBT)/SAN[2], PBT/PMMA[2], nylon/SAN[4], nylon/polyethylene (PE)[5–7] and nylon/polypropylene (PP)[8], were also investigated. The toughening effects for these blends at the low rate of deformation may be marked depending on the systems. However, the toughnesses of most of the above blends measured at the high speed impact exceed those of ductile matrices by less than 100%, indicating that the toughening efficiencies for these systems are not high. Only the nylon-6,6/maleic anhydride (MA) grafted low density PE blends[5] were supertoughened.

Li and Qi[9,10] proposed another new concept of toughening a polymer matrix by inclusion of rigid inorganic fillers through the *J*-integral study on the fracture toughness of PP/$CaCO_3$ composites. Supertoughened composites, i.e. PE/$CaCO_3$[11–13] and PP/kaolin[14], have been obtained by means of the employment of ductile matrix, interfacial modification, addition of very fine fillers and control of filler content higher than a critical value. The high speed impact toughnesses of these composites are four to five times higher than those of ductile matrices. The notched Izod impact strengths of the above PE and PP are 175 J/m and 150 J/m, respectively. So far there has been no report on the

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

supertoughened PE or PP composites for matrices having notched Izod impact strengths of less than about 100 J/m. The ductility of the matrix is thus one of the key factors in the toughening of polymer composites.

However, the brittle matrices, which can be effectively toughened with the rubbery phases, have not been efficiently toughened with the rigid fillers, such as plastic particles and inorganic fillers. Therefore, it would be interesting to find a route to the toughening and stiffening of brittle matrices. We believe that the rubber particles have much higher toughening effect than the plastic and inorganic ones. Consequently the rubber toughening of brittle polymer matrices is promising.

Several brittle matrix/rubber particle systems have shown that the rubber particle spatial distribution (spatial packing or dispersion state) considerably affects the toughening effect. Breuer *et al.*[15,16] studied the morphology–toughness relationship of poly(vinyl chloride) (PVC)/ABS blends, where ABS has the structure of butadiene-co-styrene rubber core/acrylonitrile (AN) plastic shell. Increasing the AN level as well as the blending temperatures markedly improved the dispersion of ABS in the PVC matrix, but lowered the impact strength owing to the fusion of the PVC primary particles. Recently, we[17,18] named the state of uniform dispersion of rubber particles as the morphology of well-dispersed particles having high toughening efficiency, the intermediate level of dispersion as the pseudonetwork morphology having much higher toughening efficiency and the poor dispersion as the morphology of agglomerated particles lowering toughness. We[17–21] have found that the PVC/nitrile rubber (NBR) blend with the pseudonetwork morphology, where the NBR particles are dispersed between the PVC primary particles, is much tougher than that which has the morphology of well-dispersed particles, where the PVC primary particles are completely broken down and the NBR particles are randomly dispersed in the PVC matrix. The importance of the PVC primary particles in the toughness–morphology relationship of PVC/rubber blends was also well addressed in other literature[22,23].

It should be pointed out that the phenomenon that the toughening efficiency of pseudonetwork morphology is higher than that of the morphology of well-dispersed particles was also observed in other blend systems. Keskkula *et al.*[24,25] reported that the highest impact strengths for the SAN/rubber blends were obtained with the pseudonetwork morphology compared with the morphology of agglomerated particles and the morphology of well-dispersed particles. They also showed the same phenomenon in nylon-6/ABS[26–28], PBT/core–shell impact modifier[29] and PC/core–shell impact modifier[30] blends. The very high toughening and stiffening effect in ABS-g-MA/nylon-6 blends reported by Aoki and Watanabe[31] may be a result of pseudonetwork morphology.

The effect of particle spatial distribution on the toughening effect in the above blends suggests that a blend with the pseudonetwork morphology has the rubber content for generating toughened blend lower than that with the morphology of well-dispersed particles. In general, the lower the rubber content the higher the stiffness of a blend. So toughening through the pseudonetwork morphology is a possible way to retaining the stiffness.

It is essential to quantitatively analyze the toughening and stiffening effect to optimize morphology on which the mechanical properties, especially toughness, of polymer blends rely. Nishi and coworkers[32–34] proposed a simple model for analyzing particle spatial distribution by digital image analysis. However, an equation for correlating key morphological parameters was not given. This model has been used to analyze the particle spatial distribution–mechanical property relationships of nylon/rubber[35], poly (phenylene oxide) (PPO)/rubber[36] and PC/core–shell impact modifier[30] blends. Recently, we[21,37] derived another new equation for correlating morphological parameters of binary or ternary polymer blends with the pseudonetwork morphology and with the rubber particles conforming to log-normal distribution. However, a quantitative method for the better understanding of toughening and stiffening effect originating from the change in rubber particle spatial distribution has not been established.

In this work, we present the toughening and stiffening effect in PVC/NBR blends. The blends with two types of morphologies, i.e. the pseudonetwork morphology and the morphology of well-dispersed rubber particles, are investigated. The toughness and modulus are quantitatively examined in the case of the same toughness, rubber particle size and size distribution.

GENERALIZED EQUATION FOR CORRELATING MORPHOLOGICAL PARAMETERS

For the hard spherical particles conforming to log-normal distribution and occupying any lattice, the generalized equation for correlating morphological parameters is

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

where T is the matrix ligament thickness (surface to surface interparticle distance), d is particle size, ϕ is the particle volume fraction, σ is the particle size distribution and ξ is the particle spatial distribution parameter.

ξ can be evaluated by

$$\xi = \xi^{*}\xi^{**} \qquad (2)$$

where ξ^{*} is the particle spatial distribution parameter of reference lattice. We have calculated the ξ^{*} values, ranging from 1 to 1.12, for eight different regular lattices and the arrangement of random close packing system with equal-sized spheres. The relevant work will be published elsewhere. ξ^{**} can be exactly evaluated by[21,37]

$$\xi^{**} = \sqrt[3]{1-\phi_P} \qquad (3)$$

where ϕ_P is the excluded volume fraction of material in which the spherical particles are absent.

T is a useful geometrical parameter, which can be related to some mechanical and physical properties of multiphase materials, for instance, impact strength, toughening and stiffening effect and electric conductivity of polymer blends and composites which the spherical rubbery or electrically conductive particles are incorporated with.

TOUGHENING AND STIFFENING EFFECT IN PVC/NBR BLENDS

The brittle ductile transition

The toughening and stiffening effect arising from the change in the rubber particle spatial distribution can be reasonably compared under the conditions of the same impact strength, rubber particle size and rubber particle size distribution. Under these preconditions, one should attain the rubber contents for blends with different rubber particle spatial distributions. Then it is possible to assess the stiffnesses of these blends. To attain the rubber contents, the brittle ductile transition master curve for the blends with the morphology of well-dispersed rubber particles is at least required.

The pseudonetwork morphology, the morphology of well-dispersed particles and the morphology of agglomerated particles are schematically presented in *Figure 1a–c*, where the filled dark circles represent the rubber particles. *Figure 1a* shows the pseudonetwork morphology. The rubber particles are dispersed in a plastic matrix between the pseudonetwork cores (dashed circles). It must be pointed out that there is no limit to the shape of pseudonetwork cores. For the purpose of simple drawing, we give an example of spherical pseudonetwork cores shown in *Figure 1a. Figure 1b* displays the morphology of well-dispersed particles. The rubber particles are randomly dispersed in a plastic matrix. *Figure 1c* exhibits the morphology of agglomerated particles.

We assume $\xi = \xi^* = 1$ for the morphology of well-dispersed particles[17–21]. For the pseudonetwork morphology, ϕ_P is the volume fraction of PVC primary particles in this work, ξ and ξ^{**} is estimated by[20,21]

$$\xi = \xi^{**} = \left\{ \frac{\left[\frac{d}{d_P} + \exp(0.5\ln^2\sigma_P)\right]^3 - \frac{\pi}{6}[\exp(1.5\ln^2\sigma_P)]^3}{\left[\frac{d}{d_P} + \exp(0.5\ln^2\sigma_P)\right]^3} \right\}^{1/3} \tag{4}$$

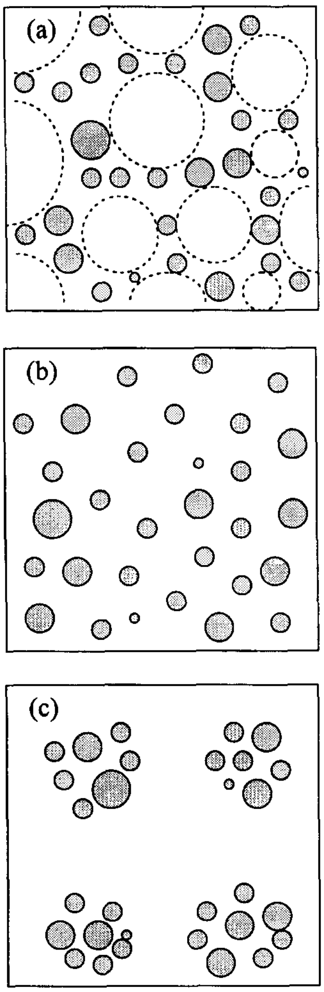

Figure 1 Schematics of particle spatial distributions: (a) pseudonetwork, (b) well-dispersed and (c) agglomerated. After ref 18

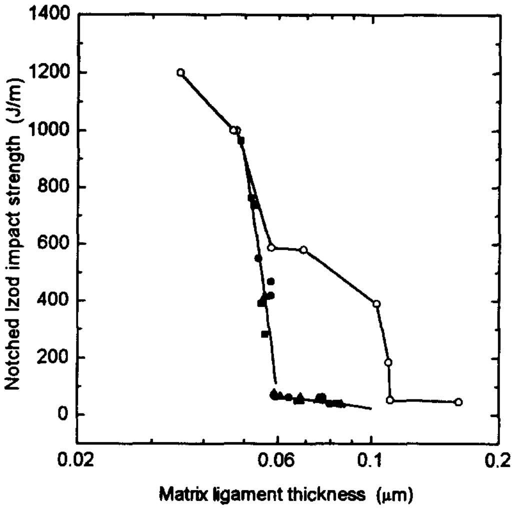

Figure 2 Notched Izod impact strength *versus* matrix ligament thickness for PVC/NBR blends with well-dispersed rubber particles (solid symbols) and the pseudonetwork structure (open circles). After ref 21

where d_P and σ_P are the PVC primary particle size and its distribution, respectively.

Based on the above more specific models, we[17,20,21] have obtained the relationships of impact strength with T for PVC/NBR blends with the pseudonetwork morphology (open symbols) and the morphology of well-dispersed particles (solid symbols), as shown in *Figure 2*. For the blends with the pseudonetwork morphology, the experimental data fall on the curve since the ξ values[20,21] calculated by equation (4) vary from 0.69 to 0.86, indicating that their difference is not great. There is an approximate critical value $T_{c1} = 0.11$ μm for the onset of brittle ductile transition. For the blends with the morphology of well-dispersed particles, the brittle ductile transition occurs at the critical value $T_{c2} = 0.059$ μm, which is much smaller than T_{c1}. In the T range from 0.059 to 0.11 μm, the toughness of the blend with the pseudonetwork morphology is much higher than that with the morphology of well-dispersed particles.

The quantitative relationship between impact strength (*IS*) and T for the blends with the morphology of well-dispersed particles is useful for the evaluation of moduli in the case of $T < T_{c2}$. Therefore, it is established here. By the least-square regression, we get

$$IS = 3021 - 9353T + 664475T^2 \text{ (J/m)} \tag{5}$$

The correlation coefficient of equation (5) is 0.92.

From equation (1) and for the constant d and σ, we have

$$\frac{\phi_{c1}}{\phi_{c2}} = \left[\frac{T_{c2} + d\exp(0.5\ln^2\sigma)}{T_{c1} + d\exp(0.5\ln^2\sigma)}\right]^3 \xi^3 \tag{6}$$

where ϕ_{c1} and ϕ_{c2} are the critical rubber volume fractions for blends with the pseudonetwork morphology and the morphology of well-dispersed particles, respectively.

Equation (6) predicts that ϕ_{c1} must be smaller than ϕ_{c2} due to $\xi < 1$ and $T_{c2} < T_{c1}$. To more clearly see the variation of ϕ_{c1}/ϕ_{c2} with ξ for the PVC/NBR blends, we assume $T_{c1} = 0.11$ μm, $T_{c2} = 0.059$ μm, $d = 0.1$ μm and $\sigma = 1.5$. These assumptions are feasible for the PVC/NBR blends in this work. Then plot ϕ_{c1}/ϕ_{c2} *versus* ξ, as shown in *Figure 3*, where ξ is fixed in the range 0.7–0.9 since T_{c1} is a function of ξ. In the ξ range ϕ_{c1}/ϕ_{c2} increases with ξ from 0.155 to 0.328. Therefore, ϕ_{c1} is much smaller than ϕ_{c2}. Based on

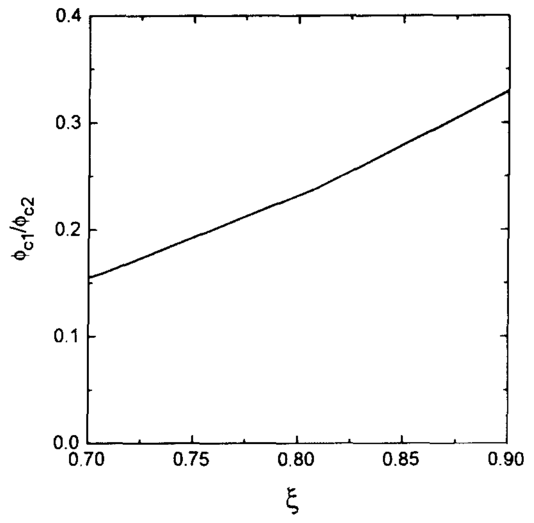

Figure 3 Calculated variation of ϕ_{c1}/ϕ_{c2} with ξ for the PVC/NBR blends with the pseudonetwork morphology

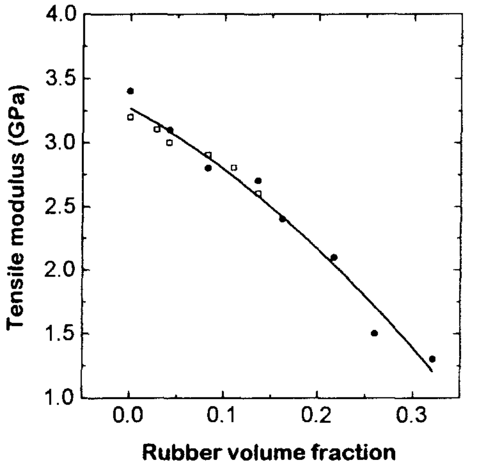

Figure 4 Tensile modulus *versus* rubber volume fraction for PVC/NBR blends with the pseudonetwork morphology (open symbols) and the morphology of well-dispersed particles (solid symbols)

this fact, it is possible to obtain a PVC blend with the pseudonetwork morphology that has the same high toughness as but much higher stiffness than that with the morphology of well-dispersed rubber particles.

The toughening and stiffening effect

The tensile moduli of the blend systems with the two types of morphologies were measured at the crosshead speed of 5 mm/min and 16°C on an Instron universal materials testing machine (model 8500) according to ASTM-D638. The strain was monitored with strain gauge so that the modulus can be more accurately calculated. The tangent modulus was computed in this work.

Figure 4 gives the tensile modulus–rubber volume fraction relationship of PVC/NBR blends with the two types of morphologies. It is seen from this figure that the tensile modulus is insensitive to the change in the rubber particle spatial distribution and that it decreases with increasing rubber volume fraction. The data in *Figure 4* can be fitted by

$$E = 3.27 - 4.068\phi - 7.338\sigma^2 \text{ (GPa)} \tag{7}$$

where E is the tensile modulus of a blend. The correlation coefficient of equation (7) is 0.99.

Kim *et al.*[25] reported the tensile modulus–acrylonitrile (AN) content relation of SAN/rubber blends. The tensile modulus is independent of AN level. In fact, the rubber particle dispersion was improved with the addition of AN[24,25]. As a result, the dispersion does not affect the tensile modulus. Moreover, they found that the improved rubber particle dispersion (from the morphology of agglomerated particles to the pseudonetwork morphology) in toughened PBT[29] leads to slightly higher modulus. Similar results were also observed in toughened PC[30]. Interestingly, the variations of brittle ductile transition temperature and modulus of nylon-6/ABS blends with compatibilizer concentration go through a minimum and a maximum, respectively[27,28]. The morphological observations indicated that the rubber particle dispersion became better with the addition of compatibilizer[27,28]. In other words, we may think that the pseudonetwork morphology has the lowest brittle ductile transition temperature and highest modulus for the blends among the three types of particle dispersions illustrated in *Figure 1a–c*. The experimental evidence given here proves that the pseudonetwork morphology does not impair modulus.

In previous papers[38,39], we demonstrated that the brittle ductile transition of the blends with the morphology of well-dispersed particles is a function not only of T but also of the interfacial adhesion, and the interfacial adhesion was enhanced through an increase of AN level in NBR. In this work, the interfacial adhesion is kept constant because the AN content is fixed at 18 wt%. So, the impact strength of the blends with the morphology of well-dispersed particle is a function of T. However, the brittle ductile transition for the blends with the pseudonetwork morphology involves more morphological parameters (T and ξ) and is thus more complicated than that for the blends with the morphology of well-dispersed particles. Thereafter, we select the relevant data for the blends with the pseudonetwork morphology and calculate the corresponding data for the blends with the morphology of well-dispersed particles to rationally compare the toughening and stiffening effect. In the case of the same impact strength 1000 J/m, d and σ, we compare the modulus of the blend having the pseudonetwork morphology with that of the blend having the morphology of well-dispersed particles (see *Table 1*). For instance, the morphological parameters for Blend E with the pseudonetwork morphology are $d = 0.084$ μm, $\sigma = 1.41$, $\xi_E = 0.693$ and $T_E = 0.047$ μm. Its modulus is 2.95 GPa estimated by equation (7) where $\phi_E = 0.069$. We now calculate the modulus of Blend F with the morphology of well-dispersed particles. T_F for Blend F is 0.049 μm obtained from equation (5). The appropriate ϕ_F is 0.32 evaluated by equation (1) in the case of $\xi_F = 1$. The resultant modulus of the blend is 1.22 GPa calculated by equation (7). Compared with pure PVC (with impact strength 30 J/m and modulus 3.27 GPa), the toughnesses of Blend E and Blend F are increased by 33 times, and the modulus of Blend E is reduced by only 9.8%. However, the modulus of Blend F is decreased by as much as 62.7%, which is much greater than that of Blend E. The calculations suggest that it is possible to generate PVC/rubber blends simultaneously with both high toughness and high stiffness (characterized here by the tensile modulus). Compared with Blend F, Blend E is indeed stiffened owing to the decrease of ξ from 1 to 0.693.

The dependences of toughening and stiffening effect upon T and ξ cannot be distinguished by the above examples since $T_E \approx T_F$. The importance of ξ is magnified by the following examples. In the case of the same impact strength

Table 1 Comparison of toughness and modulus of PVC/NBR blends having the pseudonetwork morphology or the morphology of well-dispersed particles

Parameter	Blend				
	E	F	G	H	PVC
ϕ	0.069	0.32	0.162	0.352	
d (μm)	0.084	0.084	0.112	0.112	
σ	1.41	1.41	1.61	1.61	
d_P (μm)	0.4		0.33		
σ_P	1.65		1.55		
ξ	0.693	1	0.836	1	
T (μm)	0.047	0.049	0.069	0.054	
Impact strength (J/m)	1000	1000	580	580	30
Tensile modulus (GPa)	2.95	1.22	2.42	0.92	3.27

580 J/m, d and σ, we compare the modulus of Blend G having the pseudonetwork morphology with that of Blend H having the morphology of well-dispersed particles (also see *Table 1*). For instance, the morphological parameters of Blend G are $d = 0.112$ μm, $\sigma = 1.61$, $\xi_G = 0.836$ and $T_G = 0.069$ μm. Its modulus is 2.42 GPa estimated by equation (7) where $\phi_G = 0.162$. Compared with pure PVC, the toughnesses of Blend G and Blend H are 19 times greater, and the modulus of Blend G is reduced by 26%. The T_H for Blend H with $\xi_H = 1$ is 0.054 μm. Its modulus is 0.92 GPa calculated by equation (7) where $\phi_H = 0.353$. Compared with the pure PVC, the modulus of the blend is reduced by 72%. Compared with Blend H, Blend G is also stiffened. Clearly, $\xi_G = 0.836 < \xi_H = 1$. However, $T_G = 0.069$ μm $>$ $T_H = 0.054$ μm. The above analysis suggests that the dependence of toughening and stiffening efficiency on ξ is stronger than on T.

The addition of a rubbery material to a plastic will definitely reduce the modulus of the plastic. Compared with the morphology of well-dispersed particles, the pseudonetwork morphology is able to considerably minimize the reduction of stiffness shown in this work. Moreover, it might be possible to generate toughened blends having equivalent stiffness with the plastic matrix by designing the pseudonetwork cores with higher stiffness than the plastic matrix. Aoki and Watanabe[31] reported that the Izod impact strength, flexural modulus and Vicat softening point of ABS-g-MA were substantially improved with the addition of nylon-6. The impact strengths of the blends are greater than those of either pure components as the nylon content is higher than about 30 wt%. The simultaneous enhancements of toughness and stiffness of ABS/nylon blends compatibilized by alloys of nylon and ABS were also reported by Howe and Wolkowicz[40]. Nevertheless, the toughening behaviour in these nylon/ABS blends has not been well understood. Phase separations in these nylon/ABS blends are evident[31,40]. Making a comparison with the toughness–morphology relation of nylon-6/ABS blends revealed by Majumdar and coworkers[27,28], one may believe that the phenomenon observed by Aoki *et al.*[31,40] is a result of pseudonetwork morphology. We postulate that the nylon minor phase acts as the pseudonetwork cores that reject the rubber particles and that the SAN and rubber phases would be the pseudonetwork bands. The modulus of SAN matrix is greater than that of nylon cores[27], whilst the Vicat softening point (190°C) of nylon[31] is higher than that of SAN (about 100°C). The Vicat softening point (about 100°C) of 60/40 ABS-g-SAN/nylon blend is almost the same as that of SAN, and is much higher than that (about 50°C) of ABS-g-MA.

CONCLUSIONS

The toughening and stiffening effect stemming from the variation of ξ in PVC/NBR blends has been quantitatively analyzed. Two types of morphologies, the pseudonetwork morphology ($\xi < 1$) and the morphology of well-dispersed rubber particles ($\xi = 1$), have been obtained through the control of PVC primary particles that govern the rubber particle spatial distribution in the PVC matrix. The presence of PVC primary particles favours the formation of pseudonetwork morphology. On the other hand, the morphology of well-dispersed rubber particles has been achieved due to the breakdown of PVC primary particles.

The experimental results show that the impact strength of PVC/NBR blends varies dramatically with ξ and T. It increases with the decrease of ξ when T is identical. The critical value of T for the occurrence of brittle ductile transition for the blends with the pseudonetwork morphology is much larger than that for the blends with the morphology of well-dispersed particles. In the T range from 0.059 to 0.11 μm, the toughness of the blend with the pseudonetwork morphology is much higher than that with the morphology of well-dispersed particles. The tensile modulus of the blends decreases with the increase of rubber content, and is, however, insensitive to the change in ξ. The modulus for the blend with the pseudonetwork morphology is much higher than that for the blend with the morphology of well-dispersed rubber particles for the same values of rubber particle size, size distribution and high impact strength.

Further analysis demonstrates that ξ considerably affects the toughening and stiffening efficiency of PVC/NBR blends. The dependence of toughening and stiffening efficiency on ξ is calculated to be stronger than that on T. Therefore, the pseudonetwork morphology exhibits a much higher toughening and stiffening efficiency compared with the morphology of well-dispersed particles.

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