Toughening behaviour of rubber-modified thermoplastic polymers involving very small rubber particles: 3. Impact mechanical behaviour of poly(vinyl chloride)/methyl methacrylate–butadiene–styrene graft copolymer blends

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The resistance of methyl methacrylate–butadiene–styrene graft copolymer (MBS) particles against cavitation increases with decreasing particle size, and there exists a critical particle size below which the MBS particles are unable to cavitate. The inability of small particles to cavitate is the reason for the decrease of the impact properties of poly(vinyl chloride) (PVC)/MBS blends with very small MBS particles ($d_0 < 150$ nm). A toughening mechanism is proposed for the PVC/MBS blends in which the particle size of the rubber particles and the interparticle distance play equally crucial roles.

(Keywords: rubber toughening; particle size; Izod impact strength)

INTRODUCTION

Substantial enhancement of the toughness of brittle or notch-sensitive polymers can be achieved by dispersing rubber particles in the polymer matrix. In pseudoductile thermoplastic matrices which deform preferentially by shear yielding, the major toughening mechanisms are thought to be cavitation of the rubbery particles and shear yielding of the matrix[1–3]. Rubber cavitation occurs first if the Poisson ratio of the rubber is close to 0.5[4,5]. This relieves the hydrostatic tension in the material and thereby promotes ductile matrix shear yielding.

The transition from brittle to ductile behaviour in rubber-modified pseudoductile thermoplastics occurs at a critical value of the interparticles distance (*IPD*) which is given by the following[1,6]:

$$IPD = d_0\left[\left(\frac{\pi}{6\Phi_r}\right)^{1/3} - 1\right] \qquad (1)$$

where d_0 is the particle diameter and Φ_r is the rubber volume fraction. The onset of the brittle–tough transition at the critical interparticle distance is matrix polymer dependent[1]. A least squares regression of the relationship between the critical interparticle distance (IPD_c) and the intrinsic ductility of the matrix polymer[1] has given the following:

$$\log[IPD_c(\mu\mathrm{m})] = 0.74 - 0.22C_\infty \qquad (2)$$

where C_∞ is the characteristic chain ratio of the matrix polymer, and is a measure of the intrinsic ductility.

According to the interparticle distance concept, the toughness improves with improved dispersion, i.e. with decreasing rubber particle size. However, experiments have shown that if the rubber particle size is decreased below a critical value of ~200 nm, the impact toughness of the blend substantially decreases and approaches the value of the unmodified matrix[7–10]. There appears to be a critical particle size, below which the toughening efficiency of the rubber is practically zero. In the preceding paper[11], it was established that the cavitation strain of MBS particles in a PVC matrix under uniaxial tension increases with decreasing rubber particle size and that there also exists a critical particle size, below which the particles are unable to cavitate. If very small particles do not cavitate during an Izod impact test, then the hydrostatic tension in front of the notch tip of the Izod

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impact bar is not relieved. Consequently, shear yielding cannot initiate in the matrix and the blend will not be ductile. The inability of small particles to cavitate is therefore the reason for the decrease in toughening efficiency below a critical particle size[7–9,12,13].

The results in this present paper confirm the existence of a critical rubber particle size for the toughening of PVC/MBS blends and also illustrate the relationship between the critical particle size and the inability of small particles to cavitate. A toughening mechanism is proposed in which the rubber particle size and the interparticle distance play equally crucial roles.

EXPERIMENTAL

Materials

The chemical composition of the MBS core–shell rubber particles is dictated by the requirement to obtain transparent blends with PVC. For this reason, the SBR rubber core in this study has a butadiene (Bd)/styrene (St) weight ratio of 77/23; and is synthesized by radical emulsion copolymerization. To this composition, a small amount (a few percent) of crosslinking agent is added so that the crosslink density of the SBR equals 4.3×10^{25} crosslinks per cubic metre. The St–methyl methacrylate (MMA) shell is grafted on to the SBR core by a radical graft emulsion copolymerization and has a MMA/St weight ratio of 50/50. The core/shell weight ratio of the MBS particles used in this study is 60/40. The MBS particle size is controlled by the processes of agglomeration (AGGL), aggregation (AGGR) or 'grow-out' (GO) of the particles, as described in the preceding paper[11].

The sizes of the MBS particles on the emulsion latexes were characterized by dynamic light scattering (d.l.s.) using a Nicomp apparatus. Both the particle size and the particle size distribution were obtained. Particle sizes were also characterized independently from the light transmission intensity of the latex and by transmission electron microscopy (TEM) on the PVC/MBS blends. The same average particle size was essentially obtained by the three different methods. The different particle types, their average size (from TEM) and their size distribution widths (from d.l.s.) are summarized in *Table 1*. For obtaining the particle sizes by TEM, OsO_4 was used to stain the PVC/MBS blends. Since OsO_4 only stains the double bonds of the butadiene, the particle sizes that are obtained by this method represent the sizes of the SBR rubber cores (as indicated in *Table 1*).

This table also demonstrates that in the AGGL procedure, a bimodal particle size distribution is realized with a low level of agglomeration agent. When the amount of agglomeration agent added to the emulsion polymerization is increased to produce larger particles, a broad but monomodal particle size distribution results.

Blend preparation

Powder blends of the PVC compound with 10 phr MBS were prepared at room temperature. The PVC compound was composed of 100 phr PVC (*K* value = 57), 2 phr octyltin mercaptide (heat stabilizer), 0.8 phr glycerine rincinolate and 0.2 phr ester of montanic acid (lubricant). The mixtures were processed by roll milling at 170°C for 5 min. The films from the roll mill were then pressed into sheets by compression moulding at 190°C for 15 min; the sheet thickness was 5 mm. The blend composition of the materials (103 phr PVC compound with 10 phr MBS) corresponds to a MBS concentration of 8.85 wt%, and 12.0 vol%. Likewise, the total concentration of the SBR cores in the PVC/MBS blends equals 7.8 vol%.

Morphology

From the particle sizes of the SBR rubber cores and from the rubber core volume fraction ($\Phi_r = 0.078$), the interparticle distance can be computed by using equation (1); the values obtained are also given in *Table 1*. For the blends with a bimodal particle size distribution, the interparticle distance can be calculated from the following equation:

$$6\Phi_r/\pi = x_1 d_1^3/(d_1 + IPD)^3 + x_2 d_2^3/(d_2 + IPD)^3 \qquad (3)$$

where x_1 and x_2 are the fractions (by number) of the two particle populations with sizes d_1 and d_2, respectively. In

Table 1 Characteristics of the MBS particles employed in this study[a]

Particle	Polymerization technology	SBR core diameter (mm)	Size distribution, σ[b] (nm)	Interparticle distance (nm)
M1	AGGR	130	63	115
M2	AGGR	165	76	146
M3	AGGR	205	90	182
M4	AGGR	255	103	226
M5	AGGL	82 (0.76), 270 (0.24)[c]	Bimodal	75
M6	AGGL	81 (0.62), 230 (0.38)[c]	Bimodal	78
M7	AGGL	85 (0.06), 270 (0.94)[c]	Bimodal	150
M8	AGGL	260	94	230
M9	AGGL	300	78	266
M10	GO	92	21	82
M11	GO	178	32	158
M12	GO	195	37	173
M13	GO	255	29	226

[a] The core/shell ratio in all cases is 60/40: the rubber volume fraction $\Phi_r = 0.078$

[b] σ is the standard deviation from a Gaussian approximation of the distribution curve; this value is obtained from dynamic light scattering and is a measure of the breadth of the distribution

[c] Bimodal particle size distributions; the volume fractions of the two populations with different average particle sizes are given in parentheses

the case of monomodal particle size distributions ($x_1 = 1$, $x_2 = 0$), this relationship converts into the well known equation (1). *Table 1* demonstrates that even a small fraction of small particles drastically influences the average interparticle distance in the blend.

Izod impact tests

The notched Izod impact strength was determined according to ASTM D-256. The impact speed was 3.46 m s^{-1}, and the energy of the hammer was 10.8 J; the loss energy was corrected in all cases. Specimens (63.5 x 12.7 x 5 mm) were cut from the mid-sections of the compression moulded sheets (250 x 160 x 5 mm). A notch of 0.25 mm was machined on all specimens and checked for notch defects. The Izod impact tests were carried out in an air-conditioned room, at a constant relative humidity of 50% and at temperatures ranging from 23 to 60°C. Prior to the test, the samples were conditioned overnight.

RESULTS AND DISCUSSION

In the two preceding articles in this series[11,13], it was demonstrated that the resistance against cavitation of the rubber particles increases with decreasing particle size. A theoretical relationship was derived which explains the experimental observations. This relationship is based on the assumption that rubber caviation can be considered as a competition between the strain energy associated with the deformation and the surface energy associated with cavitation. The strain energy is the elastic energy that is relieved when cavitation occurs and is proportional to the volume of the particle, and consequently to the third power of the particle radius. The surface energy, on the other hand, is the energy associated with the creation of a new surface, and is proportional to the second power of the particle size. Consequently, the total energy associated with cavitation goes through an optimum as a function of the rubber particle size and may be written as follows[13]:

$$U_{\mathrm{total}} = U_{\mathrm{strain}} + U_{\mathrm{surface}}$$
$$= -\pi/12 K_r \Delta^2 d_0^3 + (\gamma_r + \Gamma_{\mathrm{sc}})\pi\Delta^{2/3} d_0^2 < 0 \qquad (4)$$

where K_r is the rubber bulk modulus, γ_r is the van der Waals surface tension, Γ_{sc} is the chain scission energy per unit surface, d_0 is the rubber particle diameter and Δ is the relative volume strain of the particle. The first term is negative and corresponds to the hydrostatic strain energy in the particle that will be relieved by cavitation; the second term in the equation is positive and corresponds to the surface energy that is needed to create the new surface. The relationship between the volume strain at which cavitation occurs and the particle diameter can be found by rearranging equation (4) into the following:

$$d_0 = \frac{12(\gamma_r + \Gamma_{\mathrm{sc}})}{K_r \Delta^{4/3}} \qquad (5)$$

This relationship[13] predicts that the cavitation strain (Δ or ε, since $\Delta = (1 - 2\nu_m)\varepsilon$ in uniaxial tension) increases with decreasing particle diameter (d_0). Experimentally, cavitation strains were determined by using a real-time stress-whitening analysis on initially transparent PVC/MBS blends with different MBS particle sizes[11]. Experiment and theory were found to be in good agreement. The experiments confirmed that the resistance against cavitation increases with decreasing particle size. In addition, if it was assumed that cavitation must occur during the elastic deformation, i.e. at a longitudinal strain below 8%, then a critical particle size for cavitation of 150 nm was predicted[11]. The inability of small particles to cavitate and the inverse relationship between cavitation resistance and rubber particle size were independently confirmed by the use of transmission electron micrographs and volume strain measurements of the blends, respectively.

It is therefore clearly established that small particles require a much higher volume strain or hydrostatic stress to cavitate. The question now arises as to how this will influence the impact mechanical properties of the blend. In Izod impact experiments with a pronounced triaxiality at the notch tip, relief of the hydrostatic tension by rubber cavitation is essential for the initiation of matrix shear yielding. It is therefore expected that very small particles will be inefficient for toughening of the matrix. The inability of small particles to cavitate has been used in the past to explain the decrease in the Izod impact strength of rubber-modified nylon-6 systems with decreasing particle size, below a critical particle size of ~200 nm[7,8]. Other blend systems also show this behaviour[10,14]. For comparison with these systems and to relate the cavitation behaviour of the MBS rubber particles[11] to the PVC/MBS blend toughness, Izod impact experiments were carried out on the blend systems.

In *Figures 1–3*, the notched Izod impact strength of the blends is plotted as a function of temperature for PVC containing 10 phr MBS (7.8 vol% SBR), for the three different types of modifiers shown in *Table 1*.

In *Figure 1*, the notched Izod impact strength as a function of temperature is shown for blends of PVC with MBS particles polymerized according to the grow-out (GO) procedure. Using equation (2) and with $C_\infty = 7.6$ for PVC[1], the critical interparticle distance for ductile behaviour at room temperature is estimated to be 117 nm. At a blend composition of 7.8 vol%, this corresponds to a SBR particle size of 132 nm. In contrast it is observed that the PVC/MBS blend with a particle size of 92 nm behaves as a brittle material up to 60°C. A very small particle size does not apparently improve the toughness

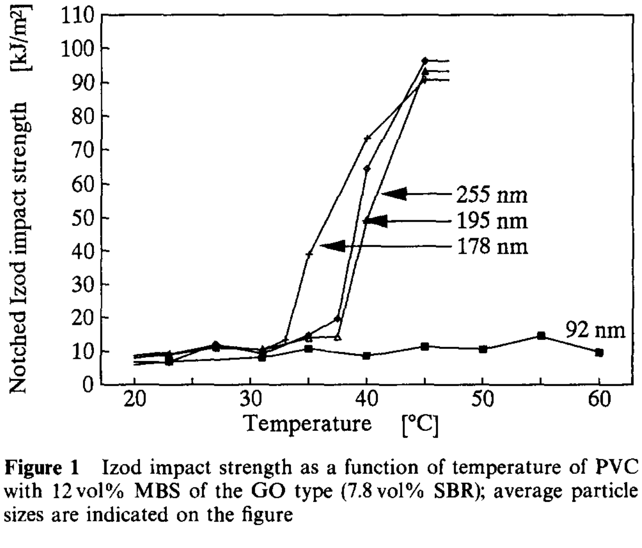

Figure 1 Izod impact strength as a function of temperature of PVC with 12 vol% MBS of the GO type (7.8 vol% SBR); average particle sizes are indicated on the figure

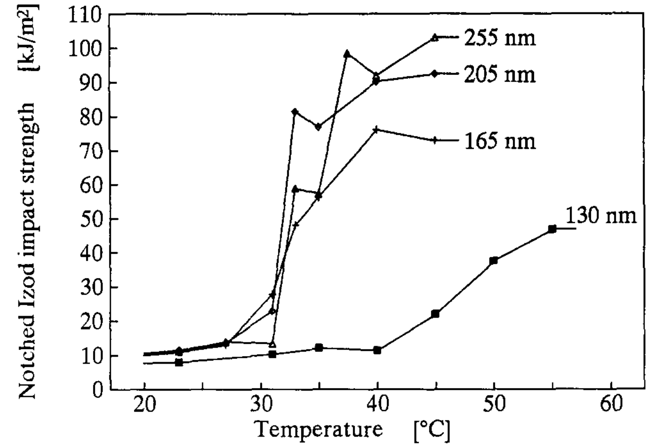

Figure 2 Izod impact strength as a function of temperature for PVC with 12 vol% MBS of the AGGR type (7.8 vol% SBR); average particle sizes are indicated on the figure

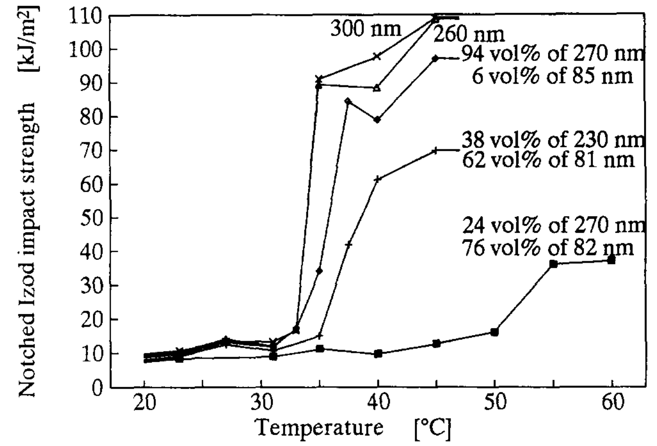

Figure 3 Izod impact strength as a function of temperature for PVC with 12 vol% MBS of the AGGL type (7.8 vol% SBR); volume fractions and particle sizes of the two size populations are indicated on the figure

of the PVC matrix, since the toughness of the blend corresponds to that of the unmodified matrix. This behaviour can certainly not be explained on the basis of the critical interparticle distance concept since the brittle–tough transition temperature in this case should decrease with decreasing interparticle distance, and thus with decreasing particle size[2,15].

The inability of small particles to cavitate must also hold in Izod impact tests, although the absolute value of the critical particle size may differ considerably from the value of 150 nm found in the uniaxial tensile test[11]. However, due to the high deformation speeds and the complexity of the stress state at the notch tip of an Izod impact bar, it is not possible to determine cavitation strains in this test. As a first approach, it will therefore be assumed that the critical particle size for tough behaviour in Izod impact tests is also 150 nm.

Using this concept, the brittleness of PVC/MBS blends with an SBR particle size of 92 nm (see *Figure 1*) can be explained. If the particle size is below the critical value then the particles will not cavitate, and the hydrostatic tension will not be relieved, which is a necessary condition for initiation of the ductile shear yielding mechanism. If the volume strain required to cavitate the rubber particles is higher than the volume strain required for the initiation of crazing in the matrix, then crazing will be initiated and the blend will exhibit brittle behaviour. This supports the concept of a critical particle size for the toughening of matrices that deform primarily by shear yielding. On the other hand, in the ductile region for the blends with particle sizes above the critical value of 150 nm, stress-whitening and lateral contraction of the Izod bar are observed, indicating that rubber cavitation and associated yielding occurs in these systems.

In *Figure 2*, the notched Izod impact strength of PVC/MBS blends is shown as a function of temperature for MBS particles prepared by the aggregation (AGGR) process. The brittle–tough transition temperature for blends with a SBR particle size above 150 nm is located at 34°C. When changing from a rubber particle size of 165 nm to one of 130 nm, the brittle–tough transition temperature suddenly rises to ~47°C. Again, such an abrupt change must be explained from the critical particle size concept for cavitation. Particles below the critical value of 150 nm do not cavitate. Consequently, the triaxial tensile stress state is not relieved, and thus yielding cannot be induced.

In *Figure 3*, the notched Izod impact strength of PVC/MBS blends is shown for MBS particles manufactured by the agglomeration (AGGL) procedure. By using the appropriate agglomeration agent, bimodal particle size distributions can be obtained by this method at low levels of the agent. However, if the amount of agglomeration agent is increased in order to produce larger particles, a broad but monomodal particle size distribution results. The small particles (80–85 nm) in the bimodal size distribution are unable to cavitate. The large particles, on the other hand, were found to deform by a debonding mechanism from the matrix. Although debonding is mechanistically different from cavitation, debonding also results in a relief of the triaxial tension, thereby promoting matrix yielding. In a separate paper, it was shown that the position of the brittle–tough transition in Izod impact measurements is not influenced by the type of microvoiding mechanism in the blend[16].

The brittle–tough transition temperature of the two blends with monomodal particle size distributions (particle sizes 260 (M8) and 300 nm (M9); see *Table 1*) is 34°C, which is equal to that of the PVC/MBS blends where the MBS particles were prepared by the aggregation process. As the volume fraction of small particles increases, the brittle–tough transition temperature shifts to higher values. The transition temperature increases from 34°C when the volume fraction of the large particles is 1, to 37°C at a volume fraction of 0.38, and finally to 53°C at a volume fraction for the large particles of 0.24. These experimental observations confirm the fact that very small rubber particles do not contribute to the toughening of PVC.

To illustrate the critical particle size concept, the brittle–tough transition temperature of all the blends with a *monomodal* particle size distribution is represented as a function of particle size in *Figure 4*. Clearly, below a critical particle size of 150 nm, the effect of the particle size is very pronounced and the increase in the brittle–tough transition temperature is attributed to the inability of small particles to cavitate. Above 150 nm, this transition temperature is nearly particle-size independent in the range of particle sizes between 165 and 300 nm. The different ways of preparing the MBS particles have only a minor effect on the brittle–tough transition

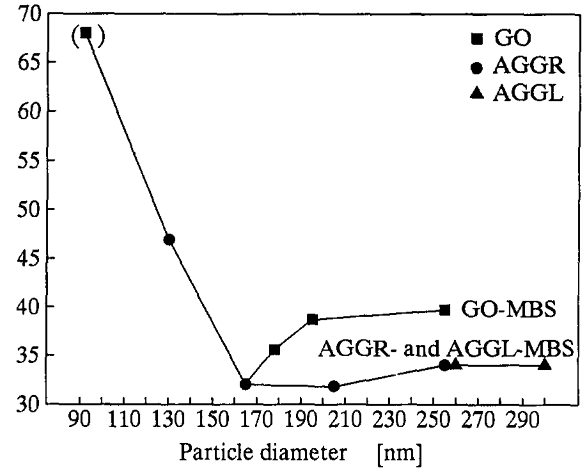

Figure 4 Brittle–tough transition temperature as a function of particle diameter for PVC/MBS blends where the MBS particles have a monomodal particle size distribution; the three types of modifiers are indicated on the figure

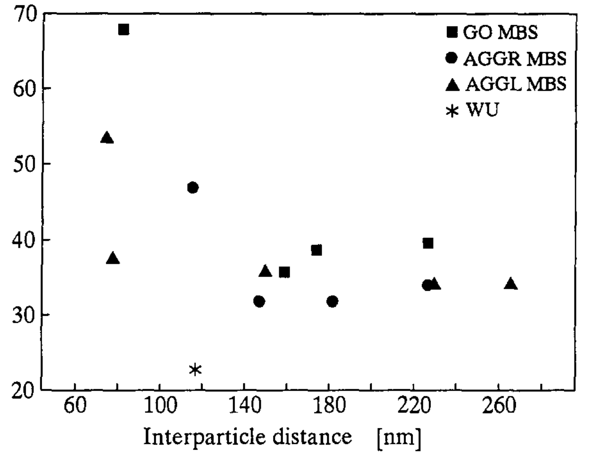

Figure 5 Brittle–tough transition temperature of the three types of MBS as a function of the interparticle distance; the theoretical estimation obtained from the Wu equation (equation (2)) is also indicated on the figure

temperature. For the PVC/MBS samples prepared by the aggregation or agglomeration technique, no distinction can be made, although the first type deforms by internal cavitation, while the latter deforms by debonding[16]. MBS produced by the grow-out technology gives rise to slightly inferior blends. At the present time, it is difficult to explain this small difference, since very many factors are affected by the MBS technology that is used, such as the particle size distribution, the grafting density, the particle shape, etc. However, the principal morphological factor controlling the toughness of the PVC/MBS blends is certainly the particle size. Other morphological factors result in only a small difference in the blend toughness.

Using the Izod impact data of *Figures 1–3*, it is tempting to correlate the brittle–tough transition temperature to the interparticle distance of the blend. One expects that an increase in temperature facilitates yielding in the polymers, and that therefore the critical interparticle distance for tough behaviour increases with temperature[2,15].

In *Figure 5* the brittle–tough transition temperature is plotted as a function of the interparticle distance, using data taken from *Table 1*. Although different blend types are considered, this figure suggests that there is no relationship between the brittle–tough transition temperature and the critical interparticle distance. However, we have shown that very small particles, i.e. those below 150 nm, do not play a role in the toughness enhancement of PVC/MBS blends. Therefore, the interparticle distance should be the average distance between particles of a size larger than 150 nm. On the basis of the average and the standard deviation of the particle sizes given in *Table 1*, the fraction of the total particle population with a particle size greater than 150 nm (f_{150}) can be estimated. For the bimodal particle size distributions, f_{150} corresponds to the population of large particles. The values of f_{150} that have been obtained are given in *Table 2*. Likewise, a modified average particle size (d_{150}) can be defined as the average size of the population of particles corresponding to f_{150}. Both the volume fraction (f_{150}) and the modified average particle size (d_{150}) can then be combined to determine the modified interparticle distance between particles with a size greater than 150 nm (IPD_{150}), by using the following:

$$IPD_{150}=d_{150}\{[\pi/(6f_{150}\Phi_r)]^{1/3}-1\} \tag{6}$$

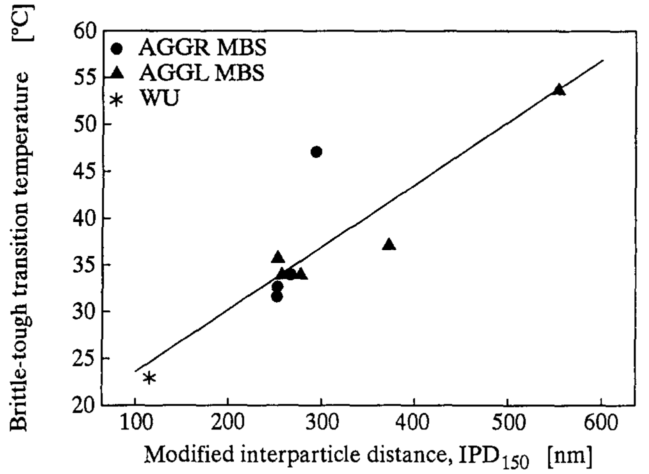

Figure 6 Brittle–tough transition temperature of two types (AGGR and AGGL) of MBS as a function of the modified interparticle distance (IPD_{150}); the theoretical estimation obtained from the Wu equation (equation (2)) is also indicated on the figure

Table 2 Volume fraction (f_{150}), average particle size (d_{150}) and modified interparticle distance (IPD_{150}) for the fraction of MBS particles with a minimum particle size of 150 nm[a]

Particle	SBR core diameter (nm)	f_{150}	d_{150} (nm)	IPD_{150} (nm)
M1	130	0.38	192	303
M2	165	0.58	215	268
M3	205	0.73	244	265
M4	255	0.85	276	274
M5	82 (0.76), 270 (0.24)[b]	0.24	270	553
M6	81 (0.62), 230 (0.38)[b]	0.38	230	372
M7	85 (0.06), 270 (0.94)[b]	0.94	270	252
M8	260	0.88	276	267
M9	300	0.98	300	271
M10	92	0.00	154	∞
M11	178	0.81	188	190
M12	195	8.90	202	193
M13	255	1.00	255	226

[a] Rubber volume fraction $\Phi_r = 0.078$

[b] Bimodal particle size distributions; the volume fractions of the two populations with different average particle sizes are given in parentheses

where Φ_r is the total rubber volume fraction ($\Phi_r = 0.078$ at a core/shell ratio of 60/40). Values for the modified interparticle distance, IPD_{150}, are also given in *Table 2*.

Figure 6 illustrates the relationship between the brittle–tough transition temperature and the modified interparticle distance (IPD_{150}). In agreement with other observations[2,15], this transition temperature increases with increasing modified interparticle distance. The theoretical estimation which is obtained from the Wu equation (equation (2)) agrees well with the experimental observations. Therefore, the concept of the critical interparticle distance can be applied to these PVC/MBS blends, but with the condition that only particles above the critical particle size (150 nm) are considered.

CONCLUSIONS

The critical particle size for cavitation in PVC/MBS blends during Izod impact experiments is 150 nm. The inability of small particles to cavitate is the reason for the decrease in toughening efficiency below this critical particle size. In addition to the rubber particle size, the interparticle distance is equally important. It has been demonstrated that the brittle–tough transition temperature increases with increasing modified interparticle distance, where the latter is defined as the distance between particles with a size greater than 150 nm.

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