

# Toughening and Reinforcing in Rigid Inorganic Particulate Filled Poly(propylene): A Review

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**ABSTRACT:** The recent advances in the toughening and reinforcing methods and theories in rigid inorganic particulate (RIP)-filled poly(propylene) (PP) composites have been reviewed. Studies have shown that under given conditions, in addition to the obvious increase of modulus, an obvious brittle–ductile transition also appears in these composites. The key to toughening a polymer is the role that inclusions can play as agents that (1) induce extensive plastic deformation following the interfacial debonding between the inclusion itself and the matrix, (2) induce shear yielding of the matrix, and (3) terminate the propagation of cracks. The main factors with regard to reinforcing mechanisms are how to enhance the interfacial bonding between the particles and the matrix and how to improve the dispersion of inclusions in the matrix. The major theories interpreting the toughening mechanisms of polymer–RIP composites include micro-voiding theory, damage competition theory, shear yielding theory, etc. It is necessary to form a soft shell/hard core structure to simultaneously toughen and reinforce polymers. Therefore, RIPs should be encapsulated with an elastic thin layer.  
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**Key words:** reinforcing; toughening; particulate; poly(propylene); composite

## INTRODUCTION

Poly(propylene) (PP) is a thermoplastic widely used in automobile, electrical equipment, furniture, and packing industries because of its good and comprehensive use properties, processability, and relatively low cost. Every year, PP is one of the most highly consumed resins in the world. However, the applications of PP are limited by drawbacks such as obvious molding shrinkage and poor impact resistance at room temperature or lower temperature. To improve its toughness and widen its application range, extensive and thorough studies on toughening PP with rubber

particles have been done over the past 20 years.<sup>1</sup> Filling-compounding is an effective, simple and economic way for modifying polymers and developing new functional polymeric materials. Currently, the methods of toughening and reinforced PP are mainly divided into four types: rigid organic particle (ROP)-filled PP, rigid inorganic particle (RIP)-filled PP, blending PP with rubber, and ROP- or RIP-filled PP–rubber blends. Of increasing interest among these types are the RIP- and ROP-filled brittle or quasi-ductile polymers, which are called non-elastic toughening polymers, are being which is paid attention increasingly. In general, the toughening effect for PP–rubber blends is much better than that for PP–ROP and PP–RIP composites, but the stiffness for the former will be obviously decreased. It is quite necessary, therefore, to understand the toughen-

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ing and reinforcing mechanisms of rigid particulate-filled thermoplastic (e.g., PP) composites so that one can design and develop advanced materials with good use properties and processability.

In this paper, the focus will be put on reviewing advances in the studies of the toughening and reinforcing methods and their mechanisms in PP-RIP composites in the past 20 years.

## BACKGROUND

Since the 1970s, a number of researchers have investigated the relationship between the morphological structure and properties of RIP-filled PP composites.<sup>2-14</sup> Busigin et al.<sup>3</sup> reported the properties of a mica-filled PP composite and pointed out that the fracture energies (notched Izod) and the heat-distortion temperatures were not appreciably influenced by the size or aspect ratios of the mica within the range. These authors believed that increased fracture toughness could be achieved by reducing the mica concentration or employing a PP copolymer. But the results of the mechanical properties of particulate-filled polymers measured by Bigg<sup>5</sup> show that the relative impact strength (i.e., the impact strength ratio of the composite to the matrix) of the PP filled with irregular-shaped silicon carbide was higher than that of the PP filled with aluminum flakes (aspect ratio of 56:1) and the PP filled with steel fibers under the same conditions. In addition, the values were quite low, even at the lowest filler concentrations. Bigg believed the reason for these results was that the long dimension of these fillers (6 mm for the steel fibers and 1.4 mm for the aluminum flake) was of the same order of magnitude as the cross-section of the test samples (i.e., 3 mm). Therefore, a particle lying perpendicular to the plane on the sample could rapidly propagate an impact-induced crack along the particle-polymer interface. The impact failure of such materials is due to rapid propagation of cracks through the specimen.

Chen et al.<sup>7</sup> selected two types of calcium carbonate (CaCO<sub>3</sub>) Omyacarb 2T and Winnofil S [a standard (~2.7 μm) and a submicron (~75 nm), respectively] to fill two types of PP, a homopolymer (GXM43) and an ethylene-propylene copolymer (GWM 101), respectively, and found that these fillers did not have any appreciable effect on the impact fracture energy ( $G_c$ ) of the copolymer-based composites. However, the Omyacarb fillers improved the  $G_c$  of the homopolymer at low tem-

peratures ( $\leq 20$  °C) due to enhanced microplastic flow. Jancar and Kucera<sup>9</sup> investigated the influence of interfacial adhesion on the yield stress ( $\sigma_{yc}$ ) of PP-CaCO<sub>3</sub> and PP-Mg(OH)<sub>2</sub> composites and noted that poor interfacial adhesion between PP and CaCO<sub>3</sub> accounted for a decrease of  $\sigma_{yc}$  with increasing the filler volume fraction ( $V_f$ ), but for poor interfacial adhesion between PP and Mg(OH)<sub>2</sub>; that  $\sigma_{yc}$  either slowly decreased with increasing  $V_f$  or remained constant up to  $V_f = 0.25$ ; that surface treatment of the fillers facilitated better dispersion in PP; that addition of the maleated PP enhanced the interfacial adhesion; and that  $\sigma_{yc}$  can also increase with enhanced adhesion. Jilken et al.<sup>10</sup> observed the effects of the shape, content, and surface treatment of mineral fillers on impact and tensile properties of PP-RIP composites. The results showed that higher modulus and strength were obtained for high aspect ratio fillers, like mica and wollastonite compared with dolomite, but very high impact strength at high filler content could be obtained for low aspect ratio fillers, like dolomite and calcium carbonate. This high impact strength was obtained only with sufficiently fine fractions and if the filler particles were well dispersed by suitable surface treatment. This result suggests that the effects of filler size and filler shape on the strength and toughness of composites are different.

Recently, Sjogren et al.<sup>12,13</sup> studied the tensile and impact failure initiation and mechanism in PP with glass beads by fractography, *in situ* scanning electron microscopy, and finite element analysis. These authors noted that the impact properties correlated with the ability of the composites to reach high strain to failure and that debonding was the initial failure mechanism.

## TOUGHENING AND REINFORCING THEORIES

### Toughening Theories

There have been a number of toughening theories for polymer-rubber blends since Merz et al.<sup>15</sup> proposed the microcrack theory in 1956; for examples, shear yielding theory, multiple-crazing theory, shear band-craze interaction theory, etc. However, most of the toughening theories proposed before 1980s were based on the amorphous polymer modified with rubber and were qualitative. In fact, both brittle and ductile polymers can be divided into amorphous and crystalline poly-

mers. The toughening mechanisms for the latter would be more complicated; therefore, there have been relatively few toughening theories for the crystalline polymer modified with rubber systems, especially for RIP-filled crystalline polymer composites. Generally, for polymer–RIP composites, the toughening effects resulting from shear yielding and multiple-crazing are much lower than those for polymer–rubber blends because of the very high modulus of the RIPs. Therefore, there would be some inherent toughening mechanisms for polymer–RIP composites.

In the past 10 years, some important advances in this field have been made and some new toughening theories and brittle–ductile criteria have been presented. The criteria include critical ligament thickness and critical plastic area, and the theories include the micro-void theory and the damage competition theory.

#### Micro-Voiding Theory

For PP–RIP binary composites, because the Young's modulus of the filler is much greater than that of the matrix, the fillers will basically not deform when the specimen is subjected to external loading and the PP is a semi-brittle thermoplastic. Thus the plane strain state cannot be released, making matrix deformation difficult. Therefore, the main toughening mechanisms would be as follows:<sup>16</sup> When the stress applied exceeds the interfacial adhesion strength between the RIP and polymer matrix, debonding at the interface will occur first, leading to the formation of micro-voids. In this case, the deformation restraint of the matrix around the filler is released, resulting in the production of extensive elastic deformation and absorbing strain energy and the promotion of the brittle–ductile transition (BDT). Moreover, the tip of crack is blunted and the stress concentration is alleviated, resulting in slowing down the propagation of crack.

At the same time, multiple-crazing and shear yielding in the polymer matrix also exist. For strong interfacial adhesion, crazing is favored, whereas for poor interfacial bonding, shear yielding is favored. In the case of some interfacial adhesion, there is a competition between them. As already stated, of course, this kind of toughening effect is relatively minor compared with polymer–rubber blends.

#### Damage Competition Theory

It is known from the damage mechanism during the BDT for thermoplastics that the damage is

caused mainly by crazes or micro-cracks and micro-voids in the brittle region and by shear yielding in the tough region. When the yield deformation process is dominated by shear flow, the material will be damaged in the tough region; if the process is dominated by craze and the craze is not blocked by rubber particles, then the material will become damaged in the brittle region. In summary, the appearance of shear yield is the BDT point. Therefore, the BDT is the result of the competition between the brittle fracture mechanism and the shear yield mechanism. From this analysis, the damage competition dimensionless number, a criterion of BDT, is defined as:

$$N_d = \sigma_{bc}^2 / \sigma_{yc}^2 \quad (1)$$

where  $\sigma_{bc}$  and  $\sigma_{yc}$  are the fracture strength and yield strength of composites, respectively.

By comparison with the Ludwik–Davidenkov–Orowan theory,<sup>17</sup> the BDT damage competition criterion can be determined as follows: when  $N_d$  is  $<1$ , the polymer blend would fail in a brittle fashion; if  $N_d$  is  $>1$ , the blend would be tough; and when  $N_d = 1$ , the brittle–ductile transition would occur.

Recently, Based on the Ludwik–Davidenkov–Orowan theory, Lyu et al.<sup>18</sup> proposed a new criterion of BDT for polymer–rubber blends as follows:

$$N_d = F_g L_{ym} / L_D \quad (2)$$

and

$$L_{ym} = G_{cm} E_m / \sigma_{ym}^2 \quad (3)$$

$$F_g = 4\delta / \pi \quad (4)$$

$$L_D = d \frac{(1 + 1.27V_f^{2/3})(1 - 1.21V_f^{2/3})^2}{1 + \alpha V_f} \quad (5)$$

where  $\delta$  is a factor related to the plane–stress state and  $\alpha$  the constant related to the interfacial adhesion. The footnote “m” stands for the matrix.

For polymer–RIP composites, the key to toughening polymers is to induce large elastic deformation or shear yielding of the matrix by the fillers to absorb strain energy without blocking the propagation of cracks. In other words, this is a question of how to achieve BDT. It can be seen from the results already presented that the factors af-

**Table I Crystallinity of iPP/CaCO<sub>3</sub> Composites (DSC Method)<sup>19</sup>**

$V_f$ (%)	Crystallinity (%) (Treated)	Relative Izod Impact Strength	
		Untreated	Treated
0	62.2	1.01	1.01
1.89	78.1	1.20	1.24
3.90	71.6	1.48	1.53
8.37	66.2	1.41	1.50
16.45	54.2	1.24	1.45
26.78	44.8	1.16	1.31
35.42	40.4	0.90	1.02

fecting the toughening effect in RIP-filled PP are relatively complicated as is the crystallinity of PP. For large-sized RIP-filled thermoplastics composites, the defect will be easily formed in the matrix to harm the strength and toughness of materials, especially for the RIPs with irregular shape, even thought the hardness and rigidity of the system can be improved. For thermoplastics with a small-sized RIP, the interfacial adhesion between the matrix and the inclusion is better because small-sized RIPs have less surface defect and more nonpair atoms, and the possibility of physical or chemical combination with the polymer is high. In addition, these characteristics are helpful to improve the dispersion of the inclusions in the matrix. Thus, the toughness of the system may be enhanced.

#### Other Toughening Mechanisms

As already stated, there are still other toughening mechanisms for PP–RIP composites, such as shear yielding theory, as well as the effect of crystalline structure of the matrix, resulting from the addition of RIPs, on the toughening effect. Inorganic particles may play a role of nucleation agent in filled i-PP composites. However, the impact strength of CaCO<sub>3</sub> filled i-PP doesn't depend on the crystallinity of i-PP directly. Maiti et al.<sup>19</sup> investigated the relationship between crystallinity and impact strength of i-PP/CaCO<sub>3</sub> composites, and the results are shown in Table I. It can be seen that the value of crystallinity reaches a maximum when surface-treated CaCO<sub>3</sub> is at  $V_f = 1.89$  vol %, whereas the highest Izod impact strength appears at  $V_f = 3.9$  vol % either for the i-PP composite filled with surface-treated CaCO<sub>3</sub> or for the untreated system.

Suetsugu<sup>20</sup> reported that the impact strength of PP can be increased largely by filling small particles of surface treated with CaCO<sub>3</sub>, which have average diameters of  $<1 \mu\text{m}$ . He proposed cavitation formation and a ligament polymer deformation mechanism for the toughening of that type of filled PP composite.

#### BDT Criterion and Percolation Model

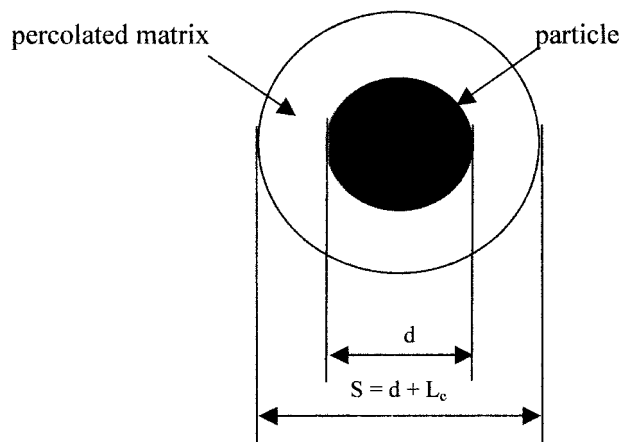
##### BDT Criterion

*Critical Matrix Ligament Thickness.* Wu<sup>21</sup> studied the relationship between the impact strength and rubber content of nylon-6–EPDM blends, created a BDT master curve, and proposed a concept of the matrix ligament thickness,  $L$ , which is defined as the nearest distance of the matrix between two neighboring rubber particles (see Figure 1). When the average ligament thickness is smaller than the critical ligament thickness,  $L_c$ , the blend will be tough; conversely, when  $L > L_c$ , the blend will be brittle. In other words, the BDT will occur at  $L_c$ . The  $L_c$  is independent of particle volume fraction and particle size, and is characteristic of the matrix alone at a given mode, temperature, and rate of deformation. For blends with dispersed spherical particles,  $L_c$  is given by:

$$L_c = d_c \left[ k \left( \frac{\pi}{6V_f} \right)^{1/3} - 1 \right] \quad (6)$$

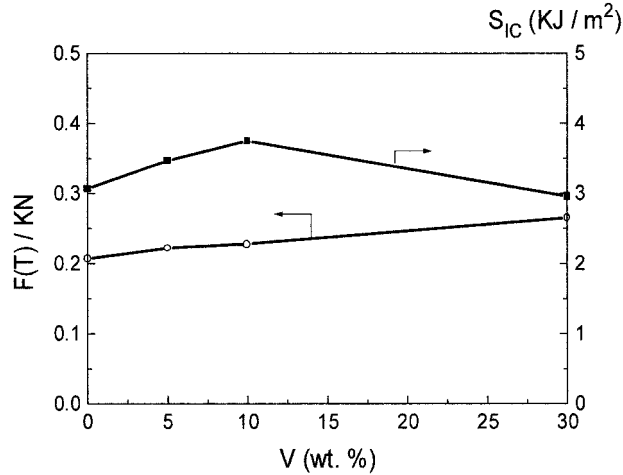
where  $d_c$  is the critical particle diameter and  $k$  is the geometric constant; for example,  $k = 1$  for a cubic lattice.

The critical ligament thickness concept and master curves provide a simple and useful crite-



**Figure 1** Diagram of stress sphere.





**Figure 2** Plot of  $F(T)$  and  $S_{IC}$  versus  $V$  for PP-CaCO<sub>3</sub> composite.<sup>14</sup>

tion to identify the BDT phenomenon of polymer alloys. Although the concept and the proposed eq. 6 are based on the studies of polymer-rubber blends, for RIP-filled thermoplastics such as PP-CaCO<sub>3</sub>, HDPE-CaCO<sub>3</sub>, and PP-glass bead, the BDT phenomenon and similar BDT master curves have also been observed<sup>19-24</sup> (see Figure 2). For given RIPs (i.e., the diameter is constant), there should be a critical volume fraction of the particles,  $V_{fc}$ , for which the toughening effect is the best. Bajaj et al.<sup>8</sup> investigated the effect of titanate coupling agents on mechanical properties of mica-filled PP and found that the values of Izod impact strength were the highest at a weight fraction of 30%. Jancar, et al.<sup>11</sup> examined the fracture toughness of PP-CaCO<sub>3</sub> composites and also observed a similar phenomenon: the values of Charpy notched impact strength reached the maximum values when the volume fraction was 10%. These phenomena may be explained from the previous discussion.

**Critical Plastic Area.** Sjoerdsma<sup>25</sup> queried whether the model as shown in Figure 1 was suitable when the particle size was too small to induce plastic deformation. He derived a new criterion for BDT in rubber-modified polymers by assuming that the connectivity of volume elements that did not yield determined the toughness. The critical condition for tough behavior of blends or composites is

$$[1 - F(c)V_f^2]^{D/d} \leq P_c \quad (7)$$

where  $F(c)V_f^2$  is the yielded area fraction,  $D$  is the height of the plastic region, and  $P_c$  is the critical probability.

### Percolation Model

Percolation is a random process. It has been found from experiments that the BDT process of particulate-filled polymers is a percolation process in which the matrix yields first in the local region, and then the yielding propagates and percolates in the entire matrix under the action of an outside force. Therefore, the BDT is considered a percolation phenomenon.

From the viewpoint of percolation theory, Margolina and Wu<sup>26</sup> proposed a concept of stress volume sphere (see Figure 1): the BDT of a PP-rubber blend system can be described by a percolation process of a stress volume sphere; when  $L < L_c$ , two neighboring spheres overlap and, at the percolation threshold, the spheres come in contact with each other, resulting in the onset of a BDT. In this case, the critical diameter of the stress sphere is expressed as

$$S_c = d_c + L_c \quad (8)$$

When the volume fraction of the stress volume sphere,  $V_s$ , reaches the critical value,  $V_{sc}$ , the spheres yield and the continuum percolation, which corresponds to the BDT, will occur. Because  $V_f \approx d^3$ , and  $V_s \approx S^3$ , the critical condition of BDT can be written as

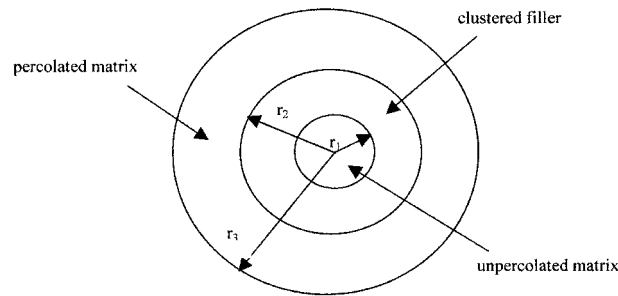
$$V_{sc} = V_c(S_c/d_c)^3 \quad (9)$$

According to the scaling law of the percolation, a relationship among the toughness of materials,  $G$ ,  $V_s$ , and  $V_{sc}$  can be expressed:

$$G \sim (V_s - V_{sc})^g \quad (10)$$

where  $g$ , which is  $\sim 0.45$ , is the critical exponent.

The BDT phenomenon was also found in PP-glass bead hybrid composites.<sup>24</sup> During preparation of polymer blends or composites (e.g., extrusion or injection molding), it is easy for aggregation of the fillers to take place in the matrix. In this case, the matrix encircled by the fillers may be unpercolated. Considering the aggregation phenomenon of inclusions in the matrix and on the basis of the concept of stress sphere proposed by Margolina and Wu<sup>25</sup> (see Figure 1), Liang and Li<sup>24</sup> proposed a modified model for stress sphere volume, as shown in Figure 3, and the following equation describing the relationship between the stress sphere volume fraction ( $\varphi_s$ ) and  $V_f$ :



**Figure 3** Sketch of a model of stress sphere volume.

$$\phi_s = V_f \left[ \frac{\pi}{6V_{fc}} + V_f - \frac{6V_{fc}}{\pi} \right] \quad (11)$$

where  $V_{fc}$  is the critical volume fraction of the particles.

### Reinforcing Mechanisms

The strength of particulate-filled polymer composites depends, to a great extent, on the interfacial adhesion between the matrix and the inclusions, the properties of the matrix material, and the filler shape, size, and content. For semicrystalline polymers such as PP, the addition of particles may cause variation in crystallization and the crystalline grain size to affect the mechanical properties of the composites. Among the properties, the interfacial adhesion is the main factor affecting the strength on the composites. Usually, the interfacial adhesion is divided into three types: poor adhesion, some adhesion, and strong adhesion. Generally, the modulus of the filled composites increases obviously with increasing the content of RIPs. Among the mechanical properties, yield stress of the composites has primary importance, giving information on the maximum allowable load without considerable plastic deformation.

#### Poor Adhesion

In the case of a poor bond (or no adhesion) between the matrix and the filler, the interfacial layer cannot transfer stress. Therefore, one can assume the strength of a particulate-filled polymer composite is determined by the effective available area of load born by the matrix due to the absence of the filler.<sup>27–33</sup> Thus, the yield strength depends on the effective load bearing cross-section area fraction ( $1 - \Psi$ ). If one assumes

that  $\Psi$  is a power law function of the volume of the filler,  $V_f$ , then

$$\sigma_{yc} = \sigma_{ym}(1 - aV_f^b) \quad (12)$$

where  $\sigma_{yc}$  and  $\sigma_{ym}$  are the yield strengths of the composite and the matrix, respectively and  $a$  and  $b$  are the constants related to stress concentration, adhesion, and the geometry of the particle.

For spherical particles with no adhesion to the polymer matrix, which fail by random fracture, eq. 12 becomes<sup>27,28</sup>

$$\sigma_{yc} = \sigma_{ym}(1 - 1.21V_f^{2/3}) \quad (13)$$

Jancar et al.<sup>30</sup> believed that the stress concentration depends on the content of the particles, with reduction of effective matrix cross section being the principal factor, and presented the following modified form of eq. 13:

$$\sigma_{yc} = \sigma_{ym}(1 - 1.21V_f^{2/3})S \quad (14)$$

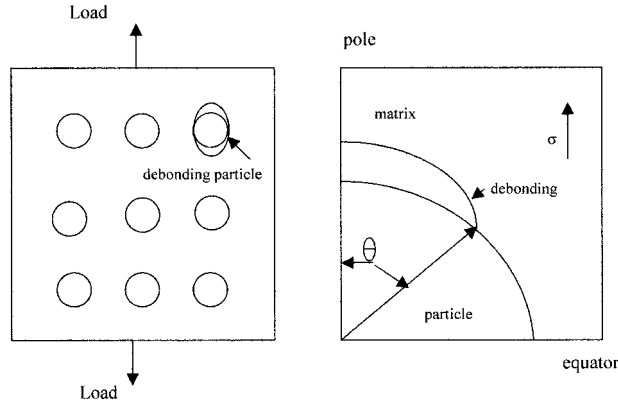
The strength reduction factor  $S$  can be determined by finite element analysis and in general varies between 1.0 and 0.2, respectively, for low and high filler volume fraction.

Considering the packing characteristic of particles, Turcsanyi, et al.<sup>31</sup> proposed a simple hyperbolic function to express  $(1 - \Psi)$ , and then presented a formula of  $\sigma_{yc}$  as follows:

$$\sigma_{yc} = \sigma_{ym} \frac{1 - V_f}{1 + 2.5V_f} \quad (15)$$

#### Some Adhesion

In the case of some interfacial adhesion between the matrix and inclusions (i.e., the interfacial adhesion is between poor and good), the interfacial layer can transfer a small section of the stress when the deformation of the matrix is very small, and then the debonding between the matrix and particle will be produced with increasing the deformation (or stress). In other words, the yield strength should be the contribution of both of them. Therefore, the value of  $a$  in eq. 12 becomes  $<1.21$ , whereas  $b = 1$  when the sample fails by planar fracture. Recently, Liang and Li<sup>32</sup> proposed a debonding model (see Figure 4) and a concept of bonding angle ( $\theta$ ). On the basis of the assumption of cubic array of spherical particles they derived a modified equation as follows:



**Figure 4** Interfacial debonding model.

$$\sigma_{yc} = \sigma_{ym}(1 - 1.21 \sin^2 \theta V_f^{2/3}) \quad (16)$$

### Strong Adhesion

In the case of well-bonded particles, the stress is transferred through a shear mechanism. Therefore, eq. 12 can be rewritten as<sup>34</sup>

$$\sigma_{yc} = (\sigma_a + 0.83\tau_m) + K\sigma_a(1 - V_f) \quad (17)$$

where  $\sigma_a$  is the strength of the interfacial bond and  $\tau_m$  is the shear strength of the matrix.

Piggott and Leidner<sup>35</sup> argued that the uniform filler arrangement assumed in most models was unlikely in practice and proposed an empirical relationship by introducing a coefficient of the particle–matrix adhesion,  $\alpha$ , as follows

$$\sigma_{yc} = K\sigma_{ym} - \alpha V_f \quad (18)$$

Some results show that  $\sigma_{yc}$  is an increasing function of  $V_f$  for the filled composites with very strong interfacial bonding. In view of these results, Turcsany et al.<sup>31</sup> proposed an empirical equation by modifying eq. 14

$$\sigma_{yc} = \sigma_{ym} \frac{1 - V_f}{1 + 2.5V_f} \exp(BV_f) \quad (19)$$

The calculated results indicate strong interfacial adhesion when  $B > 3$ ; that is,  $\sigma_{yc}$  increases with increasing  $V_f$ .

## DISCUSSION

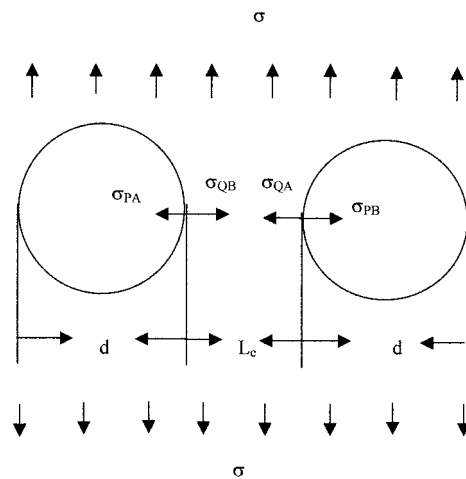
### The Main Factors Affecting Toughening and Reinforcing Effect

It is generally believed that the main factors affecting toughening and reinforcing effects on

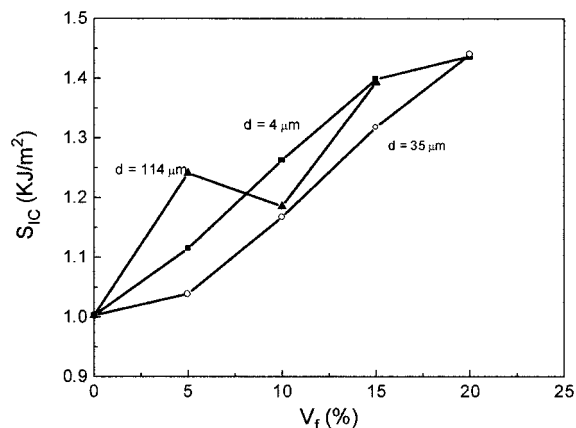
thermoplastic–RIP blends are: (i) particle geometry, such as shape, size, and content; (ii) dispersive state of the fillers in the matrix; (iii) the interfacial structure and adhesion; and (iv) processing conditions, etc.<sup>36,37</sup>

For given particles, the stress is determined mainly by the matrix if the concentration of the particles is too low; that is, the toughening effect is insignificant because  $L$  is much higher than  $L_c$ . But when the concentration increases up to a certain extent (e.g.,  $V_f > V_{fc}$ ), the toughening effect decreases because the interaction between particles cannot be neglected because the adjacent particles are closer to each other. As shown in Figure 5, when  $L$  is sufficient large, the compressive stresses undergone by particles A and B are  $\sigma_{PA}$  and  $\sigma_{PB}$ , respectively, under the action of uniform outside stress field; but particles A and B will be close to each other with increasing  $V_f$ . In this case, the compressive stresses of A and B, in fact, should be  $(\sigma_{PA} - \sigma_{QB})$  and  $(\sigma_{PB} - \sigma_{QA})$  respectively, leading to the decrease of the compressive stress undergone by the matrix around the particles and poor BDT. Thus, for given particles (the particle size is constant), there should be a filler concentration that the matrix ligament achieves,  $L_c$ , which results in the best toughening effect. This relationship provides an explanation for why the notched Izod impact fracture strength ( $S_{IC}$ ) has a maximum value at some concentration of the particles (see Figure 2).

When the diameter of particles is smaller, the required filler concentration that achieves the same interfacial ligament thickness should be relatively less. But, this is not to say that the smaller



**Figure 5** Diagram of the stress interaction between adjacent particles.



**Figure 6** Plot of  $S_{IC}$  versus  $V_f$  for PP-glass bead composites.<sup>32</sup>

the particle, the better the toughening effect because the propagation of the crack depends on the fracture ligament at the end of crack. If the dimension of the particles in the matrix is smaller than the size of the fracture ligament, then the existence of the particle around the front of the crack only changes the rheological properties of the matrix and does not influence the propagation of the crack. On the contrary, if the size of the particle is big enough to block the propagation of the crack, then the toughness of the composite will be improved. On the other hand, big and surface smooth particles (e.g., glass beads) easily cause the aggregation phenomenon in the matrix because of the relatively poor interfacial adhesion between the filler and matrix; that is, the inclusions disperse as a form of cluster in the matrix. In this case, the mechanical properties of the composites will fluctuate (see Figure 6).

For polymer blends or polymer composites, the influence of the morphological structure parameters, such as the size distribution of fillers on BDT, should not be neglected, in addition to particle size and particle content, because the particle size distribution affects the stress distribution in materials. Wu<sup>36</sup> believed the matrix ligament thickness should be a function of the size, size distribution  $\sigma$ , and content  $V_f$  of rubber particle, and proposed a relevant expression:

$$L(d, \sigma, V) = d[\pi/6V_f]^{1/3} - 1 \exp(\ln^2 \sigma) \quad (20)$$

### The Way to Improve Toughness and Strength

Wu and Dong<sup>38</sup> made three-dimensional finite element analysis of the composites filled with

coated spherical inclusions to determine the internal stress. The calculations showed that stress distribution in the matrix and the mechanical properties were sensitive to the interfacial property in the three-phase composites; however, the change in aspect ratios of the inclusions and interface can also affect the internal stress concentrations and the mechanical properties of the material. With increasing the interfacial layer thickness, the values of  $\sigma_e$  decrease, and the distribution of  $\sigma_e$  around the particle is obviously varied with decreasing the Young's modulus of the interfacial layer. Therefore, a key way to improve toughness and strength of RIP-filled polymers is to enhance the interfacial adhesion or to form a soft interfacial layer around the particle. Recently, Liang and co-workers<sup>16,37</sup> investigated the relationship between the morphology and tensile and impact properties of PP-EPDM-glass bead ternary composites and found that the mechanical properties of the composites were significantly improved when glass beads were encapsulated by a thin layer of EPDM elastomer.

Apart from the interfacial adhesion between the matrix and fillers, the interfacial phase structure also is an important factor affecting the effects of toughening and reinforcing polymers. For PP-RIP composites, the interfacial phase structure depends, to much extent, on processing conditions, including the type of compounder (e.g., single screw or twin screw extruder), shear rate, temperature, mixing time, cooling down rate, injection speed, etc. It was found from experimental results that the clustering phenomenon of particles would occur if the dispersion of the fillers in the matrix is not uniform.<sup>24,39-41</sup> In this case, the mechanical strength decreases correspondingly because a discontinuity or defect of the matrix is produced where the clustering phenomenon occurs. Therefore, the mechanical properties of composites are hurt. For crystalline or semicrystalline thermoplastic matrixes (e.g., PP), the mechanical performance of the composites is related to the crystalline structure and crystalline size, which in turn depends on the inclusion property and the cooling down rate in processing (i.e., temperature gradient).

### CONCLUSIONS

PP is a thermoplastic widely used in industry because of its good comprehensive use properties, processability, and low production cost. It is



therefore important and of practical meaning to improve the toughness and strength of PP. Filling, with both rigid inorganic and organic particles, is an effective, simple, and economical way to toughen and reinforce polymers. For RIP-filled PP composites, the key to toughening polymers is that the inclusions can play a role of an agent inducing large plastic deformation due to interfacial debonding between them and the matrix and ending the propagation of cracks. As to reinforcing mechanisms, how to enhance the interfacial bonding between the particles and the matrix is a main factor. All these factors are related to the interfacial structure. To achieve the objective of toughening and reinforcing polymers simultaneously, it is necessary to form a thin soft interfacial layer to encapsulate the inclusions.

Currently, the major theories interpreting the toughening mechanisms of polymer-RIP composites are micro-voiding theory, damage competition theory, and shear yielding theory. These theories are uninterruptedly modified and improved to describe better true toughening and reinforcing mechanisms of polymer-RIP composites. For RIP-filled crystalline polymer (e.g., PP) composites, the exact mechanisms of the influence of the crystalline structure and size on the toughening effect should be studied further.

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