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Improvement of tensile properties of nano-SiO_2/PP composites in relation to percolation mechanism

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Abstract

Low nano-silica loaded polypropylene composites are produced by conventional compounding technique in which the nanoparticles are grafted by polystyrene using irradiation beforehand. A high interfacial stress transfer efficiency is demonstrated by both strengthening and toughening effects perceived in tensile tests. The role of the modified nanoparticles in improvement of tensile properties of the nanocomposites is discussed in terms of percolation concept. A double percolation of yielded zones is presented to explain the specific influence generated by the nano-SiO_2 particles at low-filler loading regime. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocomposites; Polypropylene; Percolation

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1. Introduction

Mechanical properties of polymers can be improved by incorporating nanoparticles. In order to reach this improvement, it is generally believed that a homogeneous dispersion of the particles in the polymer matrix is a prerequisite, otherwise the loosely agglomerated nanoparticles would easily result in failure of the composites when they are subjected to force. Therefore, specific techniques (e.g. intercalation polymerization and solution blending) are nowadays used for the preparation of polymer-based nanocomposites [1,2]. In this way, however, the nanoparticles cannot be compounded with polymers like conventional particulate fillers, which have been employed in plastics industry on a large scale since many years.

To overcome this difficulty, in the work presented here nanoparticles are treated through irradiation grafting so that macromolecular grafting chains are formed onto their surfaces both inside and outside the nanoparticle agglomerates. Then these modified nanoparticles are mechanically mixed with polymers as usual [3]. The significantly increased hydrophobility of the nanoparticles due to the presence of the grafting polymers is beneficial for a good interfacial bonding between the nanoparticles and the matrix, even though a completely uniform distribution of the particles cannot be achieved during this compounding process. Nevertheless, it was found that the deformation habit of the matrix polymer can be improved remarkably already at rather low-filler loading [4,5]. In this context, it can be of interest to discuss the role of the treated nanoparticles in strengthening and toughening as a result of percolation mechanisms. This will be done in the present work, which reports about the tensile behavior of a polypropylene (PP)-based nanocomposites filled with polystyrene-grafted nano-SiO_2 (denoted by SiO_2-*g*-PS).

2. Experimental

An isotactic PP homopolymer (melting flow index: 6.7 g/10 min) and nanoparticles of SiO_2 (diameter: 7 nm) were selected as the matrix polymer and the fillers, respectively. Styrene was used as grafting monomers. Mixture of particles/monomer (100/20) and solvent were irradiated by ^{60}Co γ-ray at a dose rate of 1 Mrad/h in air. During this process, the monomer was polymerized into polystyrene (PS) molecules. Having been exposed to a dose of 30 Mrad, the solvent was recovered and the dried residual powder was ready for compounding.

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PP and the PS-grafted fillers were melt mixed in a single screw extruder at 200°C and 25 rpm. After pelletizing and compression molding, dumbbell-shaped specimens were cut from the compression-molded plaques ($65 \times 45 \times 3$ mm^3). Tensile tests were carried on a LWK-5 tester at a crosshead speed of 10 mm/min. In the meantime, tensile stress–strain curves were recorded and the areas under these curves were calculated as a measure of energy consumed during the tests. The mechanical properties reported hereinafter are the average of five successful tests. Besides, a CEAST 6500/00 Vicat tester was used to determine the resistance of the materials to thermal deformation. With a rise in temperature at a rate of 50°C/h, the temperature at which a cylindrical rod with a cross-sectional area of 1 mm^2 made an indentation 1 mm deep into specimens under a constant pressure of 5 kg/cm^2 was taken as Vicat softening temperature.

3. Results and discussion

The tensile strengths of SiO_2-*g*-PS/PP nanocomposites are plotted against their SiO_2 volume fraction in Fig. 1. With a rise in filler content, the strength of the nanocomposites increases first and then keeps nearly unchanged. As interfacial interaction in a composite material governs stress transfer efficiency and extent of induced matrix deformation and eventually determines the mechanical performance of the composite, the above filler loading dependence of strength should be analyzed at this angle. In general, particulate composites exhibit a reduced tensile strength and elongation to break due to weak interfacial adhesion [6]. However, when bonding between fillers and matrix is strong enough, as suggested by Jancar and co-workers [7], the tensile yield strength of a composite σ_{yc} can be 1.33 times as high as that of the unfilled matrix polymer, σ^*_{ym} :

$$\sigma_{yc}/\sigma^*_{ym} = 1 + 0.33F(c)V_f^2 \qquad (0 < F(c)V_f^2 \le 1) \tag{1}$$

$$\sigma_{yc}/\sigma^*_{ym} = 1.33 \qquad (1 < F(c)V_f^2) \tag{2}$$

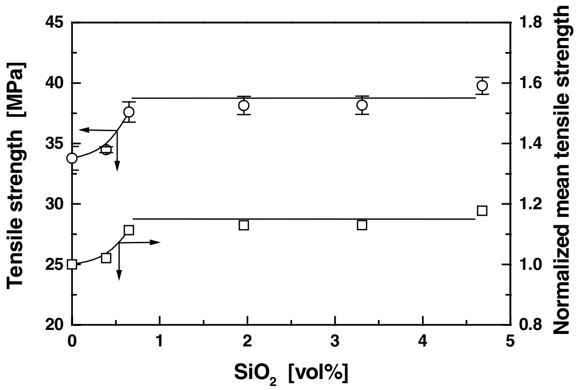

Fig. 1. Tensile strength of SiO_2-*g*-PS/PP nanocomposites as a function of SiO_2 content (The lines represent the results of curve fitting in terms of Eqs. (1) and (2)).

where V_f denotes the particle volume fraction and $F(c)$ is proportional to the average yielded area per particle. In this case, overlapping of stress concentration field around particulate fillers is responsible for shear yielding of the matrix; the latter can be considered as the dominant energy dissipation mechanism. As shown in Fig. 1, the good regression results in terms of the above equations demonstrate that a "perfect" adhesion is associated with the current PP-based nanocomposites when $V_f > 0.65$ vol%. It should be noted that the equilibrium relative strength is about 1.15 but not 1.33, which can be attributed to the low ductility of the matrix polymer employed.

When the filler content exceeds the critical value of 0.65 vol%, i.e. $F(c)V_f^2 = 1$, the corresponding $F(c)$ can be estimated to be around 2.4×10^4. In consideration of the fact that $F(c)$ characterizes the rate of increase in connectivity of yielded microzones around individual particles, one might conclude that the reinforcing effect generated by the nano-SiO_2 particles here is far superior to that by conventional particles. For example, the $F(c)$ values for $CaCO_3$ (10 μm in diameter) filled PP composites range only from 3 to 5 [7]. In addition, the greater value of $F(c)$ is factually indicative of a strong interfacial interaction. This is also confirmed indirectly by an enhanced resistance to thermal deformation resulting from the restriction effect of the nanoparticles (Fig. 2).

In another approach, Wu predicted that a connection of shear yielded zones throughout the whole polymer matrix would result in a brittle–tough transition [8,9]. A critical matrix ligament thickness τ_c, at which the matrix ductility is improved remarkably, was found to represent a key parameter for the toughening effect. That is, only when the inter-particle distance $\tau(\tau = d[(\pi/6V_f)^{1/3} - 1]$, where d symbolizes the particle diameter), is smaller than τ_c, a drastic increase in toughness of a composite is perceivable. Based on this criterion, the smaller the particles, the less fillers are needed to realize a brittle–tough transition in the case of sufficient interfacial adhesion (Fig. 3). As both strengthening and toughening effects have been observed with a rise in filler loading in the current nanocomposites

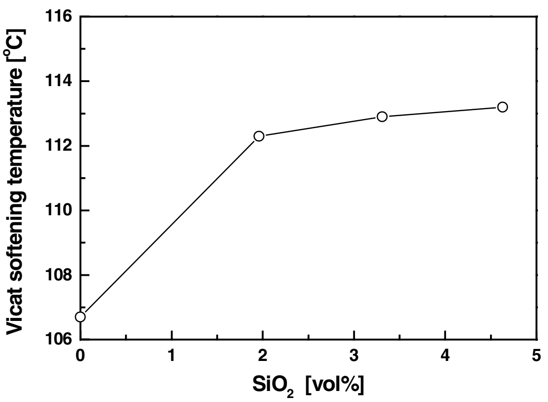

Fig. 2. Vicat softening temperature of SiO_2-*g*-PS/PP nanocomposites as a function of SiO_2 content.

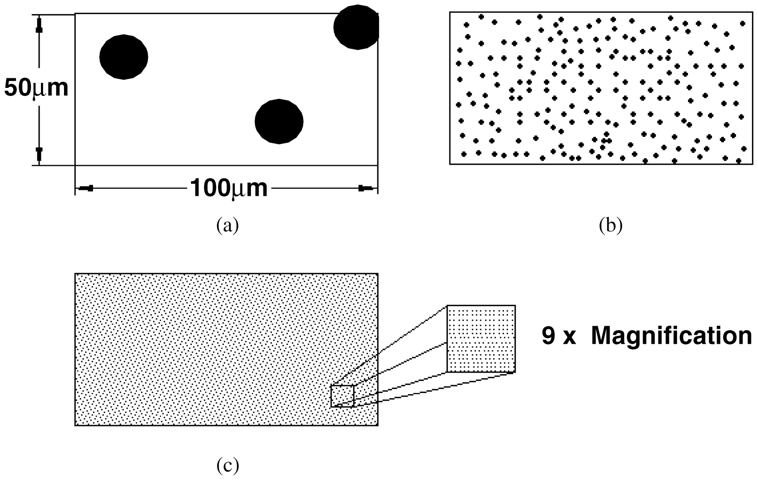

Fig. 3. Schematic drawings of microstructural appearance of typical-particulate vs. fine-particulate vs. nano-particulate composites based on electronic microscopic observations: (a) 3 vol% of particles with 10 μm diameter (2.86 particles within a volume of 50 000 μm^3); (b) 3 vol% of particles with 1 μm diameter (2860 particles within a volume of 50 000 μm^3); and (c) 3 vol% of particles with 0.1 μm = 100 nm diameter (2.86 million particles within a volume of 50 000 μm^3).

[4,5], it is believed that the above percolation mechanism might play the leading role here also.

Fig. 4 illustrates the variation in the toughness of the nanocomposites characterized by the area under the stress–strain curves [10] as a function of SiO_2-*g*-PS content. The critical filler volume content for a brittle–tough transition V_{fc} of SiO_2-*g*-PS was determined to be around 1.03 vol%. But this volume fraction cannot be considered directly for further calculation of critical SiO_2 particle distances etc. because the particles exist only in the form of agglomerates of SiO_2-*g*-PS as can be seen under the inspection of transmission electron microscopy (TEM) [11]. As the TEM size of SiO_2-*g*-PS agglomerates at this filler loading is approximately 100 nm (according to the result of interpolation), this yields to a critical distance of $\tau_c = 270$ nm. Supposing that the shear force concentration induced by each SiO_2-*g*-PS agglomerate is described by the stress volume around the agglomerate, a superposition of neighboring stress volumes would result in a shear deformation of the matrix ligament between these agglomerates. Based on the filler content dependence of the fraction of stress volume ϕ_s [12]

$$\phi_s = [(d + \tau_c)/d]^3 V_f, \quad (3)$$

Table 1
Microstructural parameters of SiO_2-*g*-PS/PP nanocomposites

Volume fraction of SiO_2 (vol%)	0.39	0.65	1.96	3.31	4.68
Volume fraction of SiO_2-*g*-PS (vol%)	0.44	0.73	2.21	3.73	5.27
TEM diameter of SiO_2-*g*-PS agglomerates (nm)	80	90	125	150	175
ϕ_s (vol%)	37	47	70	82	87

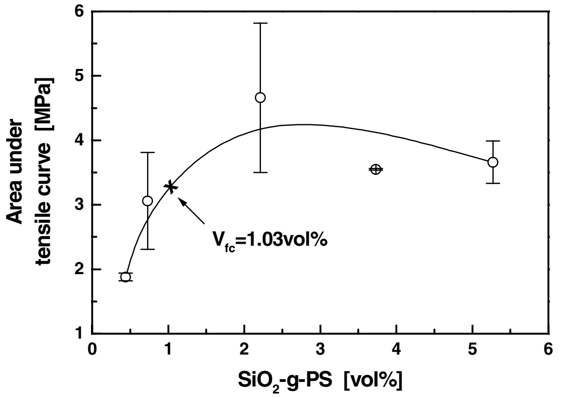

Fig. 4. Area under the tensile stress–strain curve of SiO_2-*g*-PS/PP nanocomposites as a function of SiO_2-*g*-PS content. The critical filler volume content at brittle–tough transition V_{fc} is defined as the peak position of the first derivation of the area under tensile stress–strain curve with respect to the filler content.

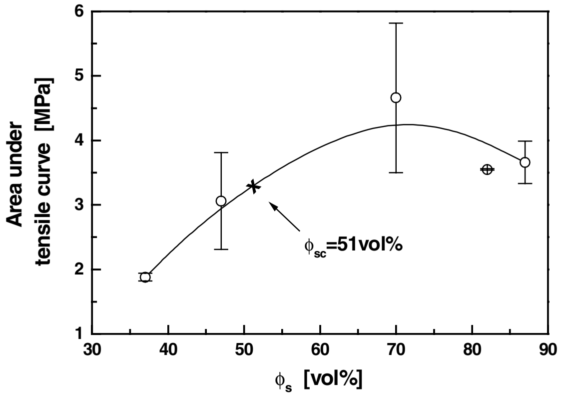

Fig. 5. Area under the tensile stress–strain curve of SiO_2-*g*-PS/PP nanocomposites as a function of the stress volume fraction ϕ_s. The critical stress volume fraction ϕ_{sc} is defined as the peak position of the first derivation of the area under tensile stress–strain curve with respect to the stress volume fraction.

a series of ϕ_s corresponding to different particle loadings can be obtained (Table 1). Accordingly, the critical stress volume fraction ϕ_{sc} is estimated to be 51 vol% (Fig. 5).

Fu et al. studied the brittle–tough transition in $CaCO_3$-filled high-density polyethylene and found $\phi_{sc} = 52$ vol% [13]. The particle sizes of their $CaCO_3$ were 6.66, 7.44 and 15.9 μm and the critical filler concentrations V_{fc} were 9.3, 10.7 and 22.3 vol%, respectively. It means that V_{fc} tends to decrease with a reduction in filler size but ϕ_{sc} remains constant. Returning to the present work, the value of ϕ_{sc} is 51 vol% similar to Fu's result suggesting that the deformation of the nanocomposites also follows the universal percolation phenomenon. However, the extremely low loading of either SiO_2 or SiO_2-*g*-PS required to make PP ductile, as compared with micron-sized particulate composites, indicates that a specific percolation process must be involved, which differs from the conventional one.

By analyzing the microstructure of the nanocomposites, it is assumed that the percolation of the stress volumes is able to occur inside (1) the SiO_2-*g*-PS agglomerates, which have been turned into a nanocomposite microstructure comprised of the nanoparticles and the grafted, homopolymerized PS and (2) the entire nanocomposites. Provided these two percolation processes take place almost simultaneously, the eventual percolation threshold should be equal the product of the individual percolation thresholds, in accordance with the scaling theory [14]. As a result, a rather low filler content is sufficient to bring about the significant improvement of the performance of the nanocomposites. In fact, the concept of a so-called double percolation or multiple percolation has been successfully used in designing very low filler-loaded conductive polymer composites [15]. It should also be applicable to the description of critical transitions in other disordered systems having randomly geometric structure.

Therefore, it is reasonable to assume that a double percolation, characterized by the appearance of connected shear yielded networks throughout the composite, might be responsible for the performance enhancement at low nano-filler loading. This means one is dealing with (1) a percolation of shear-yielded zones inside the dispersed phases (i.e. SiO_2-*g*-PS agglomerates, consisting of nano-SiO_2, the grafting PS on SiO_2 and the homopolymer derived from the grafting styrene monomer) due to the superposition of stress volumes around the nanoparticles and (2) a percolation of shear yielded zones throughout the matrix resin due to the superposition of stress volumes around the dispersed agglomerates. Further studies will be done to verify the above model by changing the microstructural aspects of SiO_2-*g*-PS agglomerates, including the molecular weight, the amount of grafting polymer (i.e. percent grafting) as well as the fraction of the homopolymer because these factors are closely related to the connectivity of the stress volumes.

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