

PERFORMANCE IMPROVEMENT OF POLYMERS BY THE ADDITION OF GRAFTED NANO-INORGANIC PARTICLES*

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Abstract An irradiation grafting method was applied for the modification of nanoparticles so that the latter can be added to polymeric materials for improving their mechanical performance using existing compounding techniques. The following items are discussed in this paper: (a) chemical interaction between the grafting monomers and the nanoparticles during irradiation, (b) properties including modulus, yield strength, impact strength and fracture toughness of the resultant composites, and (c) possible morphological changes induced by the addition of nanoparticles. Through irradiation grafting polymerization, nanoparticle agglomerates turn into a nano-composite microstructure (comprised of the nanoparticles and the grafted, homopolymerized secondary polymer), which in turn builds up a strong interfacial interaction with the surrounding, primary polymeric matrix during the subsequent mixing procedure. Due to the fact that different grafting polymers brought about different nanoparticle/matrix interfacial features, microstructures and properties of the ultimate composites could thus be tailored. It was found that the reinforcing and toughening effects of the nanoparticles on the polymer matrix can be fully brought into play at a rather low filler loading in comparison to conventional particulate filled composites.

Keywords Nanoparticles, Polymer composites, Graft polymerization, Reinforcement

INTRODUCTION

Incorporation of mineral fillers into polymers in commercial production is done primarily for reasons of cost reduction and stiffness improvement^[1, 2]. Although most studies dealing with the modification of semi-crystalline polymers with inorganic particulates reported embrittling effects by comparing ultimate elongation and impact strength of composite materials with those of unfilled resins^[3–5], some researchers showed the enhancement of toughness in rigid particle-filled polypropylene^[6, 7] and polyethylene^[8, 9].

It is worth noting that in the case of micrometer-sized particulates, high filler content (typically higher than 20% by volume) is generally required to bring the above-stated positive effects of the fillers into play. This would detrimentally affect some important properties of the matrix polymers such as processability, appearance, density and ageing performance. Therefore, a composite with improved performance and low particle concentration is highly desired. With regard to this, the newly developed nanocomposites would be competitive candidates.

The extremely high surface area is one of the most attractive characteristics of nanoparticles because it facilitates creating a great amount of interphase in a composite. Introduction of nanoparticles into a polymer changes the intermolecular interaction of the matrix^[10]. As estimated by Reynaud *et al.*^[11], an interphase 1 nm

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thick represents roughly 0.3% of the total volume of polymer in the case of microparticle-filled composites, whereas it can reach 30% of the total volume in the case of nanocomposites. That is, the non-negligible contribution made by the interphase provides diverse possibilities of performance tailoring, and is able to influence the properties of matrices to a much greater extent at a rather low nano-filler loading. The crux of the matter lies in the questions of how to well distribute nanoparticles over a polymer matrix and how to improve nanoparticles/matrix interaction.

From a practical point of view, dispersive mixing in preparing polymer based particulate composites has an important technical meaning. However, a homogeneous dispersion of nanoparticles in a polymer is very difficult to achieve by using the existing compounding techniques due to the strong tendency of the fine particles to agglomerate and the high melt viscosity of the matrix. In many cases, the so-called nanoparticle-filled polymers contain a number of loosened clusters of nanoparticles, as demonstrated by the work of Jana and Jain^[12] dealing with untreated nanosilica/polyethersulphone composites. When the composites are subjected to force, the nanoparticle agglomerates can be split easily and a premature failure of the materials would thus take place^[12-15].

To overcome this dilemma and to give full play to nanoparticles, we used irradiation grafting polymerization to modify nanoparticles first, and then the treated particles were mechanically mixed with a polymer as usual^[16]. Owing to their low molecular weight, the grafting monomers can penetrate into the agglomerated nanoparticles easily and react with the activated sites of the nanoparticles inside as well as outside the agglomerates^[17]. As a result, the following effects would be obtained^[18]: (1) Hydrophobicity of the nanoparticles is increased, facilitating the filler/matrix miscibility; (2) Filler/matrix interaction is enhanced through the entanglement between the grafting polymer and the polymer matrix; (3) The nanoparticle agglomerates become stronger because they turn into a nanocomposite microstructure comprising the nanoparticles and the grafted, homopolymerized polymer; (4) The interfacial characteristics between the treated nanoparticles and the matrix polymer can be tailored by changing the species of the grafting monomers and the grafting conditions. In this context, a uniform dispersion of nanoparticles in the matrix might no longer be critical.

The present paper is going to show how efficiently the mechanical performance of the composites can be improved by the above approach. Polypropylene and nano-silica are chosen as the matrix and the filler, respectively, partly because of the special practical importance of these materials and the extensive information available on the fracture mechanism of normal particle-filled composites. The chemical interaction between monomers and nanoparticles during the irradiation procedure, the fracture mechanism of these composites, as well as the morphological changes induced by the addition of nanoparticles are discussed in detail.

EXPERIMENTAL

Materials

General-purpose isotactic PP homopolymer (F401, $MI = 8.5$ g/10 min and 6.7 g/10 min, 230°C, 2.16 kg) provided by Guangzhou Petroleum Chemical Co. was used as matrix in this test. Pyrogenic colloidal silica (SiO_2) used was Degussa 'Aerosol' 1380 with an average primary particle size of 7 nm and a specific gravity of 2.2 g/cm³. Various commercial monomers: styrene, methyl methacrylate, butyl acrylate, ethyl acrylate, methyl acrylic acid, and vinyl acetate were used as grafting monomers without further purification.

Pregrafting of Nanoparticles by Irradiation

The typical pregrafting procedure of SiO_2 is as follows. The nanoparticles was preheated at 120°C for 5 h before being mixed with monomers to eliminate possible absorbed water on the surface of particles. Then the mixture of particles/monomer (100/20) and a certain amount of solvent was irradiated by ⁶⁰Co γ -rays under atmospheric pressure at a dose rate of 10⁶ rad/h at room temperature. After being exposed to a dose of 10 Mrad, the solvent was recovered and the dried residual powder could be compounded with thermoplastics directly.

Meanwhile, some structure changes of irradiation products under different irradiation conditions (irradiation dose of 2, 4, 8 Mrad, 500°C pretreatment, with or without solvent system) were discussed in detail to find the suitable grafting conditions. The structure of irradiation products will be changed with the irradiation condition,

which may bring about great effects on structure and properties of composites. Therefore, different irradiation doses, pretreatment temperatures, and different contents of monomer were also used to study their influence on the mechanical properties of composites.

Characterization of Irradiation Products and Interaction Between Nanoparticles and Grafted Polymers

To measure the molecular weight of grafted and homopolymerized polymer as well as to characterize the interaction feature on the surface of the particles, a certain amount of product was extracted with an appropriate solvent (benzene for polystyrene, acetone for PMMA, PEA, PBA and PVA, methanol for PMA respectively) for over 37 h using a Soxhlet apparatus and dried under vacuum for 5 h at about 80°C. After being extracted, the product was called polymer-grafted silica. The weight increase of silica due to grafting was obtained by two methods, weighing and thermogravimetric analysis (TGA). The amounts of unextractable polymer determined by the two methods were consistent with each other within experimental error. The unextractable polymer in one of the grafted silica samples was obtained after dissolving SiO₂ by treatment with 10%–20% HF solution for 1–2 days. The molecular weights of both grafted and homopolymerized polymers were measured by GPC with chloroform as solvent at room temperature. An Escalab ZZOI-XL for electron spectroscopy for chemical analysis (ESCA) and a Nicolet SDX Fourier transform infrared spectrometer (FTIR) were also utilized to characterize the changes of the nanoparticle surface and the molecular structure of grafted polymers.

As a reference, SiO₂ particles coated with polymers (PS-coated SiO₂) were prepared by solution blending in certain solvent, then precipitated by centrifugation and dried in vacuum. A Shimadzu TA-50 thermogravimeter and a Hitachi H-800 transmission electron microscope were used to compare the thermal stability and dispersion stability in solvents of polymer-grafted and polymer-coated SiO₂. The TEM samples were prepared from benzene dispersion of the modified particles, which were deposited on a copper grid with a carbon film in advance.

Preparation of Composites and Testing Procedure

Composites were prepared first by tumble mixing preweighed quantities of polypropylene and grafted fillers, followed by compounding in a single screw extruder. The melt temperature was kept at 200°C and screw speed was 25 r/min. The specimens for mechanical tests were machined from the compression molded plaques (65 × 45 × 3 mm³) of extrudates. The volume fraction of the filler, V_f was calculated from the known weights of the polymer matrix, fillers and polymers introduced by irradiation. The reinforcement effects were examined with particular attention to parameters like elastic modulus, yield stress, impact strength, and fracture toughness. Tensile tests were carried out on dumbbell shaped specimens with an LWK-5 testing machine at room temperature and at a crosshead speed of 10 mm/min. An XJJ-5 tester was used for measuring the unnotched Charpy impact strength. The fracture-toughness testing of samples was performed by using single edge notched bending specimens (SENB) and a crosshead speed of 5 mm/min according to ASTM 5045-93. The fractured surfaces were observed by using a Hitachi S-520 scanning electron microscope (SEM). TEM was performed on ultrathin sections of specimens using a Hitachi H-800 transmission electron microscope.

The influence of untreated SiO₂ and polymer-grafted SiO₂ on the flow behavior of PP was measured using a computer controlled Haake Rheocord 90 torque rheometer and an electrically heated Rheomix600 laboratory mixer (mixer temperature 190°C, rotor speed 50 rpm, sample weight 50 g).

RESULTS AND DISCUSSION

Effect of Irradiation Conditions and Characterization of Interactions Between Nanoparticles and Grafting Polymers

Nanoparticles possess properties which are quite different from those estimated for particles of conventional size; these differences are due to size effects, interfacial effects, and structural defects. Since there is not much information available about the irradiation grafting reaction of polymers on nanoparticles, some important irradiation parameters, such as irradiation dose, effect of solvent and preheating temperature, should be identified at the very beginning.

Table 1 lists the experimental data of a styrene/SiO₂ system as an example. It can be seen that the

conversion and percentage of grafting of styrene increase as the irradiation dose increases, while the grafting efficiency decreases. This phenomenon indicates that a higher irradiation dose can produce more activated sites for homopolymerization than for grafting reactions, in spite of the fact that an increase in either of the reactions contributes to an increase in monomer conversion.

Table 1. Percent grafting and grafting efficiency of styrene/SiO₂ system as a function of irradiation conditions

Weight ratio of styrene/SiO ₂	Preheating temperature (°C)	Irradiation dose (Mrad)	Monomer conversion ^a (%)	Percent Grafting ^b (%)	Grafting efficiency ^c (%)
20/1	120	2	0.84	0.84	33.9
20/1	120	4	1.20	1.20	24.7
20/1	120	8	5.02	5.02	9.4
10/1	500	10	39.1	17.3	3.7
3/1 (at the presence of heptane)	500	10	43.0	10.5	7.2

^a Monomer conversion = weight of polymer/weight of monomer

^b Percent grafting = weight of grafting polymer/weight of SiO₂

^c Grafting efficiency = weight of grafting polymer/weights of grafting polymer and homopolymer

As nanoparticles have higher surface activity, strict irradiation grafting conditions, such as high vacuum and purification of monomers which are usually required in the case of conventional particles, are no longer necessary. To iron out the differences caused by monomer diffusion and to ensure sufficient wetting of each of the nanoparticles, a larger amount of monomer (styrene/SiO₂ = 20/1) was used in the absence of solvent. However, styrene conversion remains at a rather low level in the irradiation dose range of 2 to 8 Mrad (Table 1). Considering that a higher irradiation dose and less monomer at the presence of a specific solvent (for a good contact with the particles) may facilitate a higher conversion rate, the irradiation dose was increased to 10 Mrad, and the weight ratio of styrene/SiO₂ was reduced to 10/1–3/1. The data in Table 1 suggest that the method works, especially when heptane is present. A further decrease in the monomer fraction can even result in almost 100% conversion as shown in Table 2 (e.g. in the case of the styrene/SiO₂ system, the relative percentage of the grafting plus homopolymer fraction equals approximately 20/100, i.e. the weight ratio of styrene/SiO₂ prior to the irradiation treatment). In addition, the rise in grafting efficiency in the presence of heptane, as shown in Table 1, implies that the solvent impeded the formation of the homopolymer probably due to the effect of chain transfer. Therefore, in the present work a reaction system with an appropriate solvent is chosen as a typical condition.

Table 2. Grafting details of SiO₂ grafted with different polymers^a

Grafting polymers	PS ^b	PBA ^c	PVA ^d	PEA ^e	PMMA ^f	PMA ^g
Percent grafting (%)	3.64	3.32	2.82	1.73	1.85	2.16
Homopolymer fraction ^h (%)	16.3	15.4	13.7	12.3	15.5	15.4

^a Irradiation dose = 10 Mrad; weight ratio of monomer/SiO₂ = 20/100; all the systems used acetone as solvent when they were irradiated, except for methyl acrylic acid/SiO₂ system with ethanol as solvent.

^b PS = polystyrene

^c PBA = polybutyl acrylate

^d PVA = polyvinyl acetate

^e PEA = polyethyl acrylate

^f PMMA = polymethyl methacrylate

^g PMA = polymethyl acrylate

^h Homopolymer fraction = weight of homopolymer/weight of SiO₂

As a kind of pyrogenic colloidal silica, the surface of SiO₂ generally contains 5 wt%–10 wt% absorbed water which might interrupt the contact of monomers with SiO₂. However, in the case of conventional micron-scale particles, the absorbed water can be almost completely removed by heat treatment at 120–130°C^[19]. On heating above 120°C, the dehydration of silanol groups on the SiO₂ surface takes place gradually, leading to a decline in reaction activity of the particles. When the treatment temperature exceeds 500°C, the structure of SiO₂

starts to change from amorphous to a crystalline one and its specific surface area diminishes stepwise. As a result, the percentage of grafting would decrease with increasing preheating temperature, with monomer conversion being equal. In contrast to this tendency, the current nano-SiO₂/system exhibits a higher percentage of grafting when the SiO₂ was heated at 500 °C (Table 1), which must be related to a higher surface activity of the nanoparticles in this case. Even at a temperature as high as 500 °C, dehydration of silanol groups was not significant due to the high absorption feature of the nanoparticles surface. The phenomenon of the relatively wide preheating temperature window can also be perceived from the impact tests of the composites (see section 3.3). That is, no differences in impact strength were detected within a preheating temperature range between 120 and 500 °C. Therefore, a low temperature treatment at 120 °C was applied to the nano-SiO₂ in this work for energy saving.

Table 3. Molecular weights of grafting PS and homopolymerized PS in SiO₂-g-PS^a

Materials	$M_w \times 10^4$	$M_n \times 10^4$	M_w/M_n
Grafting PS ^b	3.5	1.7	2.1
Homopolymerized PS ^b	7.3	4.3	1.7
Grafting PS ^c	5.3	2.2	2.4
Homopolymerized PS ^c	2.1	6.3	3.3

^a SiO₂-g-PS means SiO₂ grafted with PS; preheating temperature = 500 °C; irradiation dose = 10 Mrad.

^b Solvent was absent during the irradiation treatment; weight ratio of monomer/SiO₂ = 10/1.

^c Heptane was present during the irradiation treatment; weight ratio of monomer/SiO₂ = 3/1.

Number average molecular weight, M_n , and weight average molecular weight, M_w , of both grafting and homopolymerized polystyrene obtained by irradiation are shown in Table 3. The larger M_n of the homopolymer than that of the grafting polymer could be ascribed to the higher mobility of the nanoparticles compared with conventional particles, which made chain termination between radicals easier. Besides, a wider distribution of the molecular weight of PS in the system with heptane should be a result of chain transfer from the radicals to the solvent.

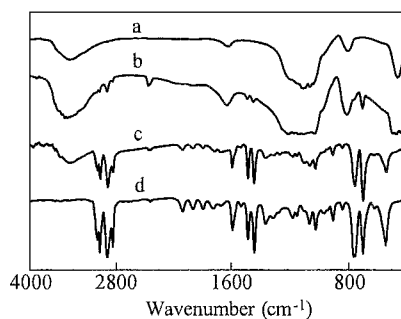


Fig. 1 FTIR spectra of (a) SiO₂ as-received, (b) SiO₂-g-PS, (c) grafting PS, and (d) homopolymerized PS

Figure 1 shows the infrared spectra of SiO₂ as-received, SiO₂-g-PS, grafting PS and homopolymerized PS. The latter two polymers were isolated from the irradiation product of styrene/SiO₂. In the spectrum of SiO₂-g-PS, there are absorption peaks at 700 and 1400–1600 cm⁻¹, which are characteristic for PS. The most interesting finding is the appearance of a hydrogen bond peak in the spectrum of grafting PS (at a wavenumber of 3500 cm⁻¹), which is absent in the spectrum of PS homopolymer, indicating the existence of Si—O—C bonds. In other words, styrene had reacted with silanol groups of SiO₂ under the conditions of irradiation. Figure 2(a) shows the C_{1s} spectrum of PS-coated SiO₂, which consists of two components at 285.1 eV and 282.3 eV representing C—C or C—H and an aromatic ring, respectively. In the case of SiO₂-g-PS (Fig. 2b), two additional peaks appear, reflecting the chemical interaction between SiO₂ and the grafting polymers. The

appearance of the high binding energy (BE) peak reveals that some carbon atoms become electron-poorer after PS has been grafted on the surface of SiO_2 . If bonds of $\text{Si}-\text{O}-\text{C}$ were present, the ether oxygen atom would have a strong electron-withdrawing effect on the carbon atoms of PS, resulting in a decrease in the electron density of the PS chains. On the other hand, the appearance of a low BE peak can be attributed to the formation of $\text{Si}-\text{C}$ bonds which caused the attached carbon atoms to be electron-rich. The corresponding variation in the electron structure of Si is shown in Fig. 3, where the electron-poor Si in SiO_2 -g-PS results in a shift of the Si_{2p} peak towards a high BE regime as compared with that of SiO_2 as-received. In addition, the peak position increases with a rise in the irradiation dose, indicating more silicon atoms can be activated by a higher irradiation dose. In conclusion it can be ruled out here that PS is chemically connected with SiO_2 through $\text{Si}-\text{O}-\text{C}$ and $\text{Si}-\text{C}$ bonds due to the effect of irradiation grafting.

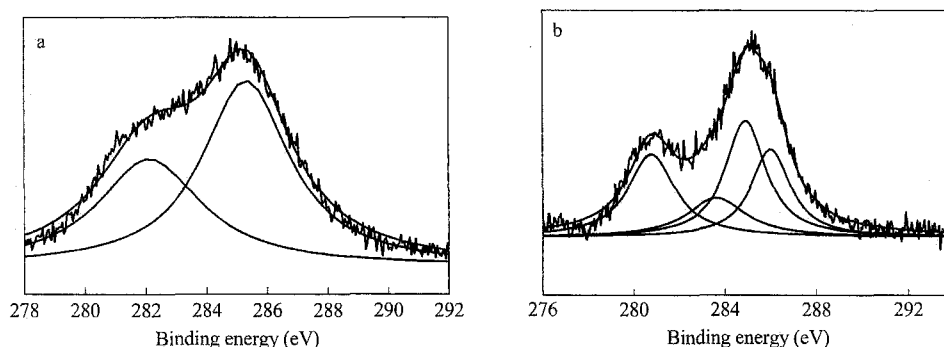


Fig. 2 C_{1s} spectra of (a) PS coated SiO_2 and (b) SiO_2 -g-PS

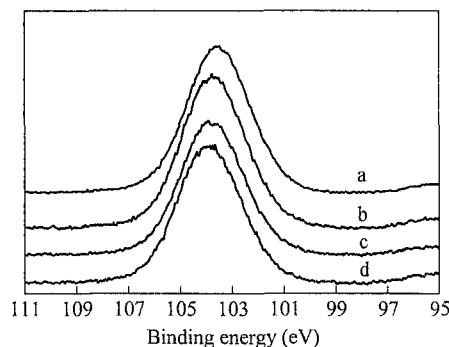


Fig. 3 Si 2p spectra of (a) SiO_2 as-received, (b) SiO_2 -g-PS (irradiation dose = 2 Mrad), (c) SiO_2 -g-PS (irradiation dose = 4 Mrad), and (d) SiO_2 -g-PS (irradiation dose = 8 Mrad)

The structural difference between SiO_2 /PS systems with and without chemical bonding between nanosilica and PS actually results in different thermal stabilities, as demonstrated by TGA tests (Fig. 4). It can be roughly estimated from the curves that the temperature corresponding to the maximum weight loss rate of SiO_2 -g-PS is over 30°C higher than that of PS coated SiO_2 .

To look at the structural characteristics of the pre-grafted nanoparticles from another angle, the stability of dispersion of SiO_2 -g-PS in benzene (a good solvent for PS) was compared with that of PS coated SiO_2 in benzene and SiO_2 as-received in water, respectively. The untreated SiO_2 completely precipitated within 1 day, while the SiO_2 -g-PS/benzene solution kept transparent for several days. TEM observations (Fig. 5) reveal that the PS physically absorbed on the silica scarcely contributes to the improvement of particles' dispersiveness, but SiO_2 -g-PS gives a stable colloidal dispersion in benzene. It manifests that the grafting polystyrene chains on the surface of the nanoparticles interfere with the agglomeration of the particles as shown in Fig. 5(c).

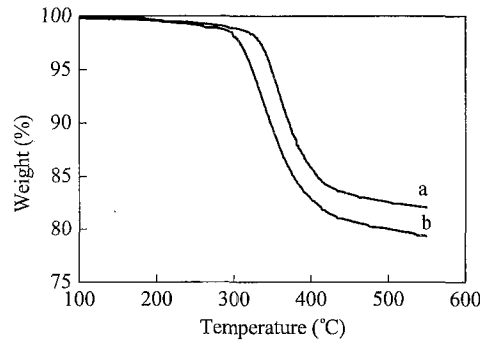


Fig. 4 Thermogravimetric analysis of (1) SiO_2 -g-PS in comparison with (2) PS coated SiO_2

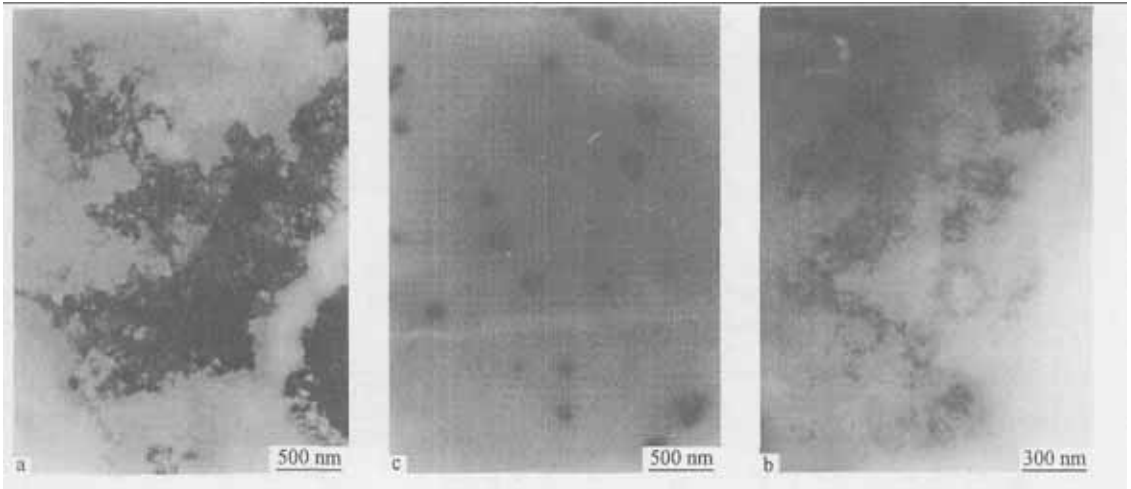


Fig. 5 TEM micrographs of (a) SiO_2 as-received, (b) PS coated SiO_2 , and (c) SiO_2 -g-PS

It can be expected that the above specific features of polymer grafted nano- SiO_2 will also be beneficial for the interfacial interactions between the modified particles and the matrix polymer during the subsequent composite manufacturing procedure.

Tensile Properties of the Composites

Typical tensile stress-strain curves of neat PP and its filled version are shown in Fig. 6, indicating that both a reinforcing and a toughening effect of the nanoparticles on the polymeric matrix were fully brought into play, as expected from the introductory part of this paper. That is, a structural weakness, that would have resulted from the agglomerating behavior of the nanoparticles, has been fully eliminated by the grafting macromolecular chains.

By examining the composition-dependent tensile properties of the materials (Fig. 7), it can be seen that the incorporation of untreated nano- SiO_2 lowers the tensile strength of PP in the lower loading region, but then leads to a slight increase in strength when the particle fraction reaches 4.68 vol% (Fig. 7a). When the composites are filled with PS or PMMA grafted SiO_2 , however, the situation is quite different. There is a considerable rise in the strength of SiO_2 -g-PS/PP composites at a SiO_2 content as low as 0.65 vol%, then the strength keeps almost unchanged with further addition of the filler. A similar behavior can be observed in the case of SiO_2 -g-PMMA/PP, except that a slight drop in strength occurs when the filler content exceeds 1.96 vol%. Nevertheless, compared to the untreated case, it can be stated here that mechanical loading seems to be more effectively transferred from the matrix to the filler particles owing to the interfacial bonding effect of the grafting polymers,

which might stem from an interdiffusion and entanglement between the molecules of the grafting polymers and the matrix. The decrease in tensile strength of SiO₂-g-PMMA/PP above 1.96 vol% can be interpreted by a change in the dispersion status of the fillers. It is believed that a higher filler loading is detrimental to its uniform dispersion in the polymer matrix. In fact, TEM observation showed that the size of the dispersed phases increases with increasing filler content in the composites (Fig. 8). It should be noted here that the dispersed phases in the composites illustrated in Fig. 8 (b)–(e) are clearly smaller than the untreated SiO₂ (Fig. 8a), but they are still much larger than the size of the primary nano-SiO₂ particles (7 nm). Therefore, these dispersed phases are actually microcomposite agglomerates consisting of primary particles, grafting polymer, homopolymer, and a certain amount of matrix.

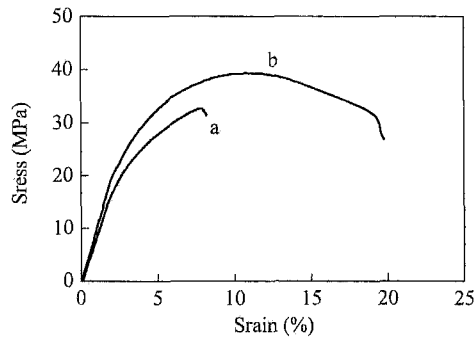


Fig. 6 Typical tensile stress-strain curves of (1) the neat PP matrix resin (*MI* = 6.7 g/10 min), and (2) the one filled with SiO₂-g-PS (content of SiO₂ = 1.96 vol%)

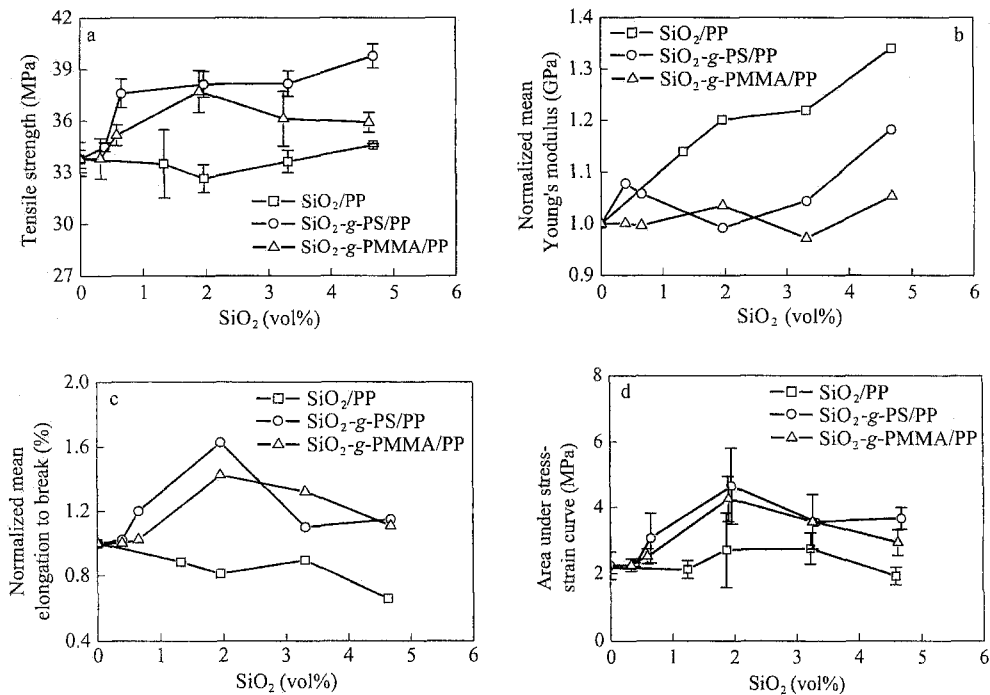


Fig. 7 Tensile properties of PP (*MI* = 6.7 g/10 min) based nanocomposites as a function of SiO₂ content: (a) tensile strength, (b) Young's modulus, (c) elongation at break, and (d) area under stress-strain curve

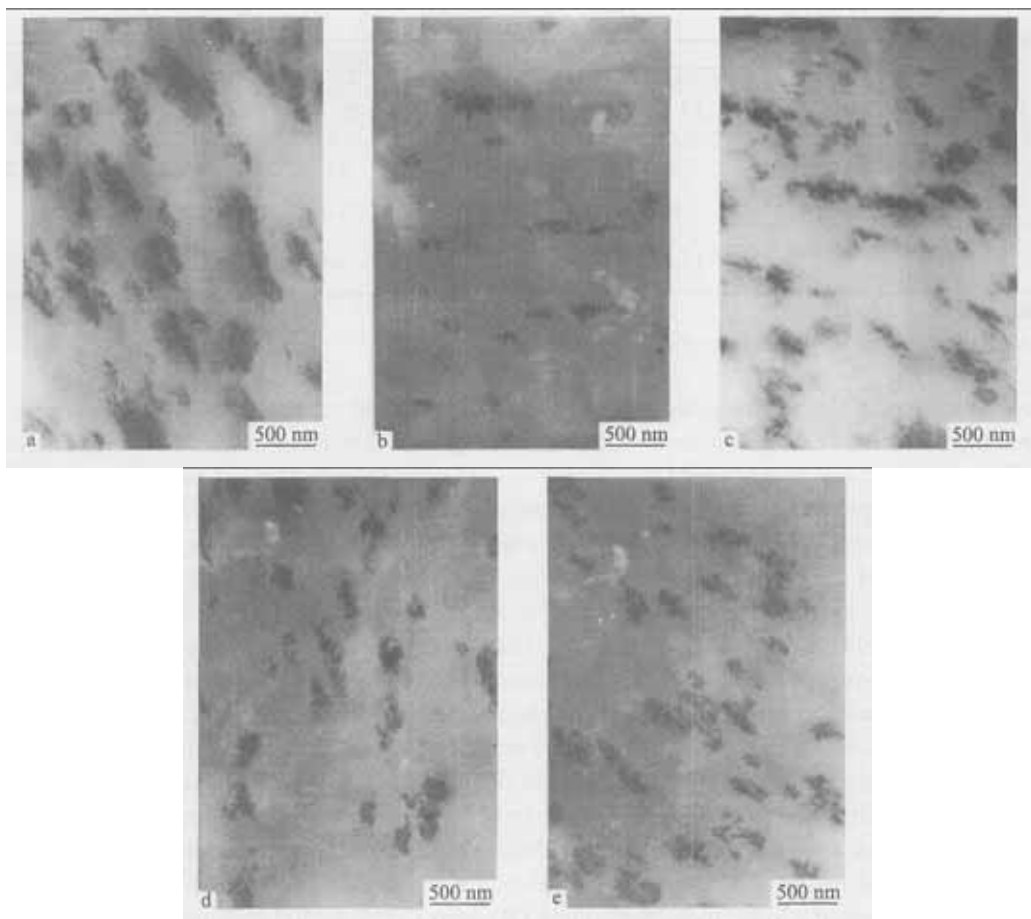


Fig. 8 TEM micrographs of PP ($M_I = 6.7\text{g}/10\text{ min}$) based nanocomposites filled with (a) SiO_2 as-received (content of $\text{SiO}_2 = 1.96\text{ vol\%}$), (b) $\text{SiO}_2\text{-g-PS}$ (content of $\text{SiO}_2 = 1.96\text{ vol\%}$), (c) $\text{SiO}_2\text{-g-PS}$ (content of $\text{SiO}_2 = 6.38\text{ vol\%}$), (d) $\text{SiO}_2\text{-g-PMMA}$ (content of $\text{SiO}_2 = 1.96\text{ vol\%}$), and (e) $\text{SiO}_2\text{-g-PMMA}$ (content of $\text{SiO}_2 = 6.38\text{ vol\%}$)

It is well-known that the interface adhesion markedly influences the mechanical behavior of particulate filled polymer composites^[20–25]. The present irradiation grafting pretreatment provides possibilities for interfacial design, *i.e.*, both surface characteristics of the nanoparticles and the particle agglomerates/matrix interface can be changed by using different grafting monomers. As a result, mechanical properties of the composites can be tailored accordingly. Table 4 gives the mechanical properties of composites filled with SiO_2 particles, grafted with various polymers, at a fixed SiO_2 fraction. Although the monomers of the grafting polymers should have different miscibilities with PP, all the grafting polymers except PEA exhibit a reinforcement effect on the tensile strength of the composites. These results contribute to a further understanding of the modified nanoparticles and their role in the composites. That is, interdiffusion and entanglement of the grafting polymer segments with the polypropylene molecules, instead of a miscibility between the grafting polymer and the matrix, dominate the interfacial interaction in the composites. This leads to the conclusion that a PP matrix with a higher molecular weight should entangle even more effectively with the nanoparticle agglomerates, thus leading to a higher tensile strength increment (comparing Fig. 6 with Table 4). In fact, Kendall and Sherliker^[26] studied the effect of the polymer molecular weight on colloidal silica filled thermoplastics and observed a similar phenomenon.

Table 4. Mechanical properties of PP (*M*_w = 8.5 g/10 min) based nanocomposites^a filled with different polymers grafted SiO₂^b

Grafting polymers	Nanocomposites						Neat PP
	PS	PBA	PVA	PEA	PMMA	PMA	
Tensile strength (MPa)	34.1	33.3	33.0	26.8	35.2	33.9	32.0
Young's modulus (GPa)	0.92	0.86	0.81	0.88	0.89	0.85	11.7
Elongation to break (%)	9.3	12.6	10.0	4.6	12.0	11.9	2.2
Area under tensile stress-strain curve (MPa)	2.4	3.3	2.3	0.8	3.2	2.9	
Unnotched Charpy impact strength (kJ/m ²)	19.8	19.4	22.9	14.6	20.5	4.7	8.0

^a Content of SiO₂ = 3.31 vol%

^b The grafting conditions are the same as those used in Table 2.

For the moment, it can be concluded that the reinforcing effect of nanoparticles on the polymeric matrices can be realized as long as the particles are grafted and a proper dispersion of the modified particles can be formed. Besides, the tensile properties of the composites can be purposely adjusted according to the interfacial viscoelastic properties provided by different grafting monomers.

As a parameter closely related to the static stress transfer at the interface, Young's moduli of the composites show another aspect of the role played by the grafting polymers, or rather by the interphase related to them (Table 4). The increase in stiffness of the composites is obviously a result of the high modulus of the particulate fillers (modulus_{silica} = 70 GPa). However, considering that the tensile modulus was determined within only a small strain range (where Hooke's law is still valid), the formation of a relatively compliant layer at the interface (PBA, PVA and PEA, for example) tends to hinder a complete stress transfer under such a low stress level and thus masks the stiffness of the filler particles. Figure 7(b) provides evidence for this masking effect of the grafting polymers, showing that the modulus of the composites filled with untreated SiO₂ increases almost linearly with the addition of SiO₂, while grafting PS and PMMA greatly decrease the stiffening effect of SiO₂. Walter and co-workers obtained similar results in differently treated kaolin/high density polyethylene systems^[27].

The elongation at break of the composites exhibits a more complicated relationship to the interfacial characteristics in the case of a lower molecular weight PP matrix (Table 4). Relative to the neat matrix, the values of the grafting polymer treated particle reinforced composites remain on the same level, except for the PEA treated system. For the matrix with the higher molecular weight (Fig. 7c), however, the filler content dependence of the elongation at break seems to be clearly evident. The reduction in elongation at break of the composite by the addition of untreated SiO₂ implies that the fillers cause a reduction in matrix deformation due to an introduction of mechanical restraints. When the nanoparticles are grafted with PS and PMMA, on the other hand, an increase in elongation at break can be found because both interfacial viscoelastic deformation and matrix yielding can contribute to this value. The further tendency of a decrease in elongation at break above a filler content of about 1.96 vol% suggests that matrix deformation is not only related to the interface feature but also to the dispersion state of the fillers.

Compared with elongation at break, the area under the tensile stress-strain curve is able to characterize more reasonably the toughness potential of the composites under static tensile loading circumstances. From the data in Table 4, it can be seen that the addition of modified nano-SiO₂ helps to improve the ductility of the PP, except in the case of SiO₂-g-PEA. It is believed that localized plastic deformation or drawing of the matrix polymer, being the main energy absorption process in particulate filled polymer systems, can be induced more efficiently by SiO₂-g-PS and SiO₂-g-PMMA than by untreated SiO₂ (Fig. 7d). The deteriorating effect of grafting PEA on the tensile behavior of the composites can not be explained by the present results, *i.e.* further detailed studies have to be carried out.

The above discussion is focused mainly on the effects of modified SiO₂ due to the presence of grafting polymers. In fact, the internal structure of the grafted nanoparticles also plays an important role in determining the mechanical properties of the composites. It can be assumed that the molecular weight, the branching degree

and the content of both the grafting polymer and the homopolymer around the modified nanoparticles are closely related to the stress distribution of the dispersed phases in the composites. As shown in Table 5, both tensile strength and elongation to break of the composites decrease with a rise in irradiation dose from 2 to 20 Mrad, due to a possible crosslinked structure of PS as a result of over-irradiation. A uniform dispersion of the grafted nanoparticles in the polymer matrix would thus be obstructed during the compounding process. Table 6 demonstrates that the area under the tensile stress-strain curve of the composites decreases with increasing amount of styrene; this can be considered as an indication of the importance of the arrangement of primary SiO₂ particles inside the grafted agglomerates.

Table 5. Dependence of mechanical properties of PP (*MI* = 8.5 g/10 min) based nanocomposites^a filled with SiO₂-g-PS^b on irradiation dose during pregrafting

Irradiation dose (Mrad)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Area under tensile stress-strain curve (MPa)	Unnotched Charpy impact strength (kJ/m ²)
2	36.5	0.89	11.8	3.3	37.5
10	34.1	0.92	9.3	2.4	19.8
20	33.2	0.82	8.0	2.0	3.7
Neat PP	32.0	0.75	11.7	2.2	8.0

^a Content of SiO₂ = 3.31 vol%
^b Weight ratio of styrene/SiO₂ = 20/100

Table 6. Dependence of mechanical properties of PP (*MI* = 8.5 g/10 min) based nanocomposites^a filled with SiO₂-g-PS on the content of styrene during pregrafting^b

Weight ratio of styrene/SiO ₂	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Area under tensile stress-strain curve (MPa)	Unnotched Charpy impact strength (kJ/m ²)
10/100	32.9	0.83	9.9	2.8	29.5
20/100	34.1	0.92	9.3	2.4	19.8
30/100	32.7	0.84	8.7	2.1	13.6
Neat PP	32.0	0.75	11.7	2.2	8.0

^a Content of SiO₂ = 3.31 vol%
^b Irradiation dose = 10 Mrad

In short, the distribution of nanoparticles in the dispersed phases and that of the dispersed phases in the composites greatly affect the mechanical properties of composites, which should be fully considered when designing novel composites.

Impact Resistance and Fracture Toughness of the Composites

Figure 9 illustrates the effects of untreated SiO₂ and polymer-grafted SiO₂ particles on the unnotched Izod impact strength of polypropylene. Both PS and PMMA grafted SiO₂ increase the impact strength more effectively than untreated SiO₂. In contrast to the general brittle-tough transition behavior in particulate filled polymeric composites, a decrease in impact strength is only observed here when the filler loading exceeds the value corresponding to the maximum impact strength. The unnotched Charpy impact tests show a similar trend (Fig. 10a), but an even more impressive increase in the impact strength by a factor of around 4 at a rather low filler loading (0.65 vol% for SiO₂-g-PS). Considering that Izod and Charpy impact tests are actually industrial testing methods that are to some degree influenced by the specimen geometry, the SENB test, which has a more stringent theoretical basis, is better suited to characterize the toughness properties of the composites. It is seen from Fig. 10(b) that with a rise in filler content, the fracture energy, *G*_{IC}, increases first, and then decreases. Evidently, a higher content of grafted nanoparticles is detrimental to the impact properties and the fracture energy of the composites. The toughness improvement with the addition of modified silica should also be a result of the improved interfacial interaction in the composites owing to the interdiffusion and entanglement between the grafting polymer chains and the matrix molecules at the interfacial region. With respect to the decreasing

tendency of the fracture toughness at higher filler loadings, this might be attributed to the nanoparticle clusters originating in this range (refer to Fig. 8); they may inhibit plastic deformation of the matrix by constraining effects or simply by splitting. It is reasonable to assume that a filler content dependent competition exists between the inducing and the restricting effects of fillers on the matrix deformation, and that the trends in toughness of the composites is a function of the predominating mechanisms.

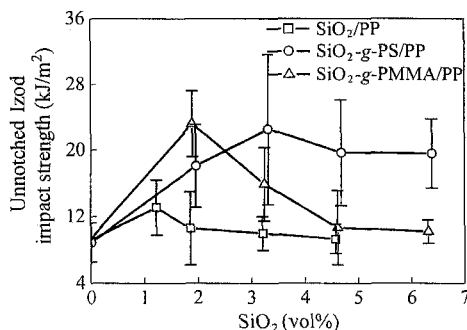


Fig. 9 Unnotched Izod impact strength of PP ($MI = 8.5$ g/10 min) composites filled with various nano-SiO₂ as a function of the filler loading

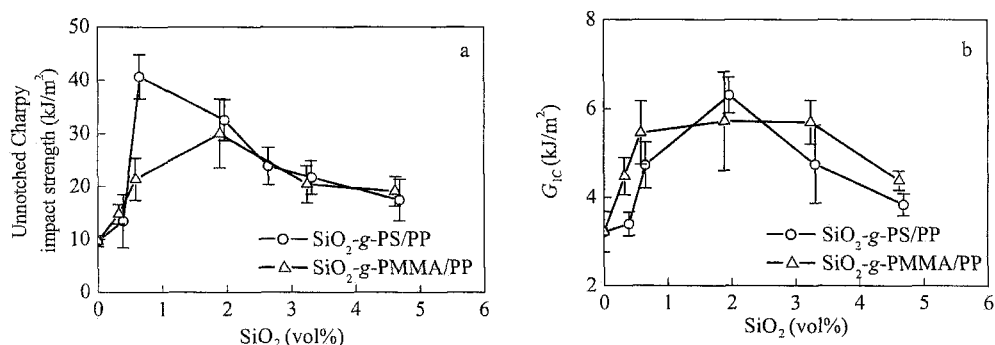


Fig. 10 Filler content dependence of (a) unnotched Charpy impact strength, and (b) fracture toughness, G_{IC} , of PP ($MI = 6.7$ g/10 min) based nanocomposites filled with various nano-SiO₂

As in the tensile tests, the effects of interfacial characteristics on the impact resistance of composites can be seen most clearly by changing the species of the grafting polymers (Table 4). For conventional particulate filled composites, poor interfacial adhesion was shown to be disadvantageous for the materials' impact properties^[28–30]. This is also the case for the present composites. The addition of PMA grafted silica to PP, for instance, results in an impact toughness even lower than that of the neat matrix. This is due to the specific molecular structure of PMA. It contains carboxyl groups and prefers to react with the surface of SiO₂ (possessing hydroxyl groups) rather than entangle with the non-polar matrix. When the composites filled with SiO₂-g-PMA are subjected to impact loading, the weak interfacial regions are not able to resist crack propagation as effectively as the polymer matrix. Nevertheless, there are not many differences between the other grafting polymers, manifesting that a strict miscibility matching between the grafting polymers and the matrix polymer is not required, as long as a certain degree of molecular entanglement takes place.

Returning to the filler loading dependence of the composites' toughness, it should be noted here that the maxima in impact strength and fracture toughness appear already at very low filler loadings (< 1 vol%–3 vol%, Fig. 10). This is opposite to the optimum loading conditions known for conventional particle filled systems. Although the typical size of the modified nanoparticles at the above-mentioned filler content range varies between 100 and 150 nm (as found by TEM observation), the distances between individual particles and

therefore the interparticle ligament thicknesses are still much larger than those found in toughness optimized conventional particle filled systems^[31]. Therefore, the considerable toughening effect perceived at such a low filler loading in the present composites implies that the mechanisms involved should be different from those used as a basis for the single percolation concept of Wu^[32], which has been proved to be well applicable to conventional particulate filled polymer composites. To overcome this problem, a new, hypothetical model of double-percolation is suggested here, in which the appearance of connected shear yielded networks is responsible for the performance enhancement at low filler loading. Its principle is based on (a) a percolation of the shear yielded zones inside the dispersed phases (consisting of the nanoparticles, the grafted and homopolymerized polymer) due to the superposition of stress volumes around the primary particles, and (b) a percolation of the shear yielded zones throughout the matrix resin due to the superposition of stress volumes around the dispersed phases. According to the common law of scaling theory^[33], such a multiple percolation process is beneficial to a low percolation threshold, *i.e.* a low brittle-ductile transition threshold.

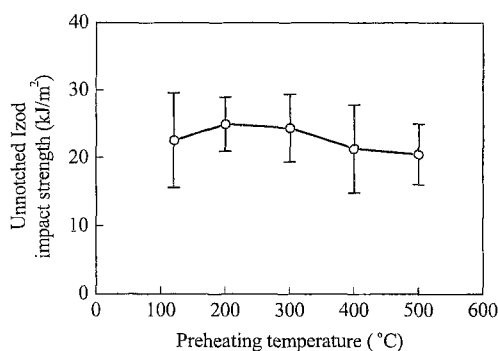


Fig. 11 Preheating temperature dependence of unnotched Izod impact strength of PP ($MI = 8.5$ g/10 min) based nanocomposites filled with SiO_2 -g-PS (content of $SiO_2 = 3.31$ vol%)

Although the above proposed double-percolation model needs quantitative analysis as well as much more evidence, there are already some experimental data supporting it. Regarding the percolation inside the modified nanoparticles, the significant decrease in impact strength with increasing weight ratio of styrene to SiO_2 (Table 6), for example, can be interpreted by the fact that the stress volume fraction is reduced to a value lower than the percolation threshold. Another example is given in Table 5, showing a significant decrease in impact strength with a rise in irradiation dose. As a higher irradiation dose might induce a crosslinking structure of the grafting polymers, shear deformation of the polymers adherent to the nanoparticles becomes more difficult. As a result, a long-range connection of the deformed polymers is hindered. In addition, Fig. 11 indicates that the changes in the percentage of grafting and grafting efficiency, as induced by different preheating temperatures, have almost no influence on the impact strength of the composites; this provides clues for a further investigation of the microstructure dependent toughening mechanisms.

Effect of Modified Nanoparticles on the Crystallization Characteristics of PP

The improvement of the mechanical properties of PP by the addition of modified nanoparticles was discussed in the above sections. It is still unclear, however, whether the microstructure of the PP matrix was influenced by these particles, since this might in turn affect the performance of the composites studied here. As PP is a semicrystalline polymer, having properties that are strongly related to its crystalline characteristics, DSC studies of its non-isothermal crystallization and melting behavior are of great interest (Table 7). The experimental data demonstrate that both untreated and PS-grafted SiO_2 particles have some nucleation influence on the crystallinity of the polypropylene even within a small temperature range of less than $1^\circ C$. In fact, the supercooling temperature, ΔT , of the composites decreases with increasing filler content for both untreated and PS-grafted SiO_2 filled systems, indicating that the crystallization becomes easier in the composites due to the nucleation

effect of the fillers. On the other hand, the results show that the crystallinity and melting point of PP are not significantly affected by the addition of the fillers, *e.g.* the difference between the untreated SiO₂ and the PS-grafted SiO₂ filled systems could not be detected during the current non-isothermal crystallization measurements.

Table 7. Non-isothermal crystallization and melting data of PP (*MI* = 8.5 g/10 min) and its nanocomposites

Samples	Content of SiO ₂ (vol%)	<i>T</i> _m ^a (°C)	<i>T</i> _{cn} ^b (°C)	Δ <i>T</i> ^c (°C)	<i>X</i> _c ^d (%)
Neat PP	-	164.7	115.3	49.4	44.6
Nanocomposites filled with untreated SiO ₂	1.96	165.8	117.8	48.0	46.4
	3.31	166.6	118.9	47.7	45.1
	4.68	164.4	118.6	45.8	44.4
	6.38	163.3	118.9	44.4	46.7
Nanocomposites filled with SiO ₂ - <i>g</i> -PS	1.96	164.7	116.5	48.2	45.8
	3.31	166.2	118.9	47.3	43.9
	4.68	164.9	118.7	46.2	46.9
	6.38	165.3	119.1	45.3	44.6

^a *T*_m denotes the peak melting temperature
^b *T*_{cn} denotes the peak crystallization temperature recorded during cooling
^c Δ*T* = *T*_m - *T*_c, denotes the supercooled temperature
^d *X*_c denotes the crystallinity of PP

Table 8. Kinetic parameters of isothermal crystallization of neat PP (*MI* = 8.5 g/10 min) and its nanocomposites

Samples	<i>T</i> _{ci} ^a (°C)	Δ <i>H</i> ^b (J/g)	<i>t</i> _f ^c (min)	<i>t</i> _{max} ^d (min)	<i>t</i> _{1/2} ^e (min)	<i>n</i> ^f	<i>K</i> ^g (min ^{-<i>n</i>)}	<i>T</i> _m (°C)
Neat PP	130	95.6	14.6	5.7	6.1	2.69	5.30 × 10 ⁻³	166.5
	132	97.9	23.8	9.8	10.1	2.75	1.18 × 10 ⁻³	167.1
SiO ₂ as-received/PP ^h	130	92.3	10.2	4.1	4.3	3.10	7.16 × 10 ⁻³	166.8
	132	94.7	17.1	7.5	7.9	2.94	1.64 × 10 ⁻³	167.3
SiO ₂ - <i>g</i> -PS/PP ^h	130	93.4	11.3	4.9	5.0	2.84	7.15 × 10 ⁻³	168.6
	132	95.2	18.7	8.9	8.8	2.99	1.07 × 10 ⁻³	167.2
SiO ₂ - <i>g</i> -PMMA/PP ⁱ	130	94.6	12.4	5.1	5.2	3.02	5.87 × 10 ⁻³	167.0
	132	94.0	18.2	7.7	8.1	2.80	1.98 × 10 ⁻³	168.0

^a *T*_{ci} denotes the present isothermal crystallization temperature
^b Δ*H* denotes the enthalpy of crystallization
^c *t*_f denotes the time at which the crystallization is completed
^d *t*_{max} denotes the time at which the crystallization rate is the maximum
^e *t*_{1/2} denotes the time at which the crystallization is half complete
^f *n* denotes the Avrami index
^g *K* denotes the rate constant of crystallization
^h Content of SiO₂ = 3.31 vol%
ⁱ Content of SiO₂ = 1.96 vol%

Table 8 shows the kinetic parameters of the isothermal crystallization of the neat PP and its composites at 130 and 132 °C, respectively. It is evident that the systems with fillers have shorter crystallization times including *t*_{1/2}, *t*_{max} and *t*_f, and greater crystallization rate constants, *K*, in comparison to the neat PP. This suggests that the crystallization rate of PP is increased by the nucleation effect of the fillers. As the values of *t*_{1/2}, *t*_{max} and *t*_f of untreated SiO₂/PP are the lowest, it becomes obvious that the nucleation effect of the untreated SiO₂ is more profound than that of the other polymer-grafted SiO₂ particles. This is imaginable because in the systems containing modified SiO₂ the contacts between SiO₂ and the matrix are reduced by the grafting polymers. All the kinetic parameters of isothermal crystallization reported here for the modified SiO₂ filled PP are in full agreement

with those of the core-shell structural elastomer/inorganic particles/matrix ternary system^[22]. On the other hand, the data of both the crystallization enthalpy and the melting temperature of the composites, remained almost the same as those measured for the neat PP (Table 8).

On the basis of both the non-isothermal and isothermal DSC measurements, therefore, it can be concluded that the crystalline features of the matrix have not been influenced greatly by the addition of the fillers, even though the fillers exert some nucleation effect on the crystallization of the PP matrix. Due to the fact that the untreated SiO₂, exhibiting a slightly more significant nucleation effect, could not improve the mechanical properties of PP equivalently, it is believed that the reinforcing and toughening effects of the modified nanoparticles are brought into play only through a change of the stress state around the fillers.

CONCLUSIONS

In the current work various polymers were grafted on the surface of nano-scale silica filler particles through a simultaneous irradiation polymerization technique. It was confirmed that the polymer chains were chemically bonded to the fillers. In addition, the modification method was simpler and much easier to carry out because the nanoparticles possessed a higher reactivity in comparison to conventional micron-scale inorganic particles. This means that modified nanoparticles can be more effectively utilized in thermoplastics than conventional particulate fillers, when using the same direct compounding technology.

As a result, reinforcing and toughening effects of the nanoparticles on polymeric materials could be fully brought into play. In fact, the tensile properties, such as strength, modulus and elongation at break of PP were improved simultaneously when the modified nanoparticles were incorporated. This is hard to find in conventional particulate composites. By changing the species of the grafting monomers, the tensile properties of the composites could also be purposely adjusted according to their interfacial viscoelastic properties. It was also found that the internal structure of the modified nanoparticles had an additional influence on the mechanical properties of the composites. The optimum nanoparticle content was related to the optimum distribution of the particles. With respect to the impact resistance and fracture toughness of the composites, a considerable toughening effect could be observed at a rather low loading of the modified fillers.

It is worth noting that the current irradiation grafting modification method has proved to be very effective in improving the strength and toughness of thermoplastics with the addition of only a small amount of modified inorganic nanoparticles (typically less than 3% by volume). Further studies are necessary to obtain information about other advantages of these composites compared to other conventional particulate filled polymeric composites, *e.g.* with regard to a lower processing viscosity, or transparency and lower density of products.

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