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Effect of grafted polymeric foaming agent on the structure and properties of nano-silica/polypropylene composites

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Abstract

To promote dispersion of nano-silica in polypropylene (PP), a polymerizable foaming agent *p*-vinylphenylsulfonylhydrazide was synthesized and grafted onto the nanoparticles via free-radical polymerization. It was found that the grafted poly(*p*-vinylphenylsulfonylhydrazide) played dual role when being melt mixed with PP. The side sulfonylhydrazide groups were gasified to form polymer bubbles, leading to rapid inflation of the surrounding matrix that pulled apart the agglomerated nanoparticles, while the remaining backbone of the grafted polymer helped to improve the filler/matrix interaction through chain entanglement and interdiffusion at the interface. Mechanical tests indicated that the grafted nano-SiO_2/PP composites prepared according to the above strategy were simultaneously toughened, strengthened and stiffened. Compared with conventional graft polymerization treatment where no blowing function is associated, the technique proposed in this work could significantly enhance notch impact strength of PP.

Keywords: Nanoparticles; Surface treatment; Composites

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1. Introduction

In recent years, organic–inorganic nanocomposites have received great interests due to their unusual combination of the individual characteristics that might lead to dramatic improvement of polymers' properties [1–4]. Because of the high surface energy, however, these particles have a great inclination for agglomeration, especially during melt compounding with polymers that are usually characterized by high viscosity. In the case of poor dispersion, the so-called nanoparticles filled polymer composites have to contain a number of loosened clusters of nanoparticles and exhibit properties even worse than conventional micrometer-sized particle/polymer systems. To break up the agglomerates, efforts have been made to pre-treat the nanoparticles in terms of physical and chemical methods [5]. Comparatively, graft polymerization onto nanoparticles seems to be rather effective [6]. Taking the advantage of low molecular weight, grafting monomers can easily penetrate into the agglomerated nanoparticles and react with the activated sites of the nanoparticles. Accordingly, the interstitial volume inside the nanoparticle agglomerates would be partly filled with grafted macromolecular chains, resulting in separation of the nanoparticles from each other. Besides, when the grafted nanoparticles are mixed with a polymer, interfacial interaction can be greatly enhanced by chain interdiffusion/entanglement between the grafted polymer and the matrix.

Nevertheless, our previous studies indicate that the graft pre-treatment has to inevitably generate some compact agglomerates (consisting of nanoparticles, grafted polymer and ungrafted homopolymer) that are hard to be split by the limited shear forces offered by conventional mixers [7]. As

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a result, the nanocomposites are notch sensitive, exhibiting the improvement on notch impact strength is far less significant than that on the unnotched one.

In consideration of the fact that stretching is superior to shearing in separating aggregated granules, Wu and co-workers recently proposed an in situ bubble-stretching (ISBS) model [8,9]. It was believed that the rapid inflation of polymer bubble could result in the polymer melt surrounding the bubble being subjected to high stretching rates that may lead to effective stretching dispersion of the dispersed phase in the polymer melt. Theoretically, when the bubble expands, the order of magnitude of stretching rate of the surrounding polymer can reach $10^5-10^6\ s^{-1}$ [8,10], which is about 2 orders of magnitude higher than the shearing rate ($10^3-10^4\ s^{-1}$) obtained with screw extrusion. The minimum grain size of the dispersed granules with this method should be therefore 2 orders of magnitude less than that observed when the particles are dispersed by screw extrusion.

With the enlightenment of Wu's work, the authors of the current paper plan to combine graft polymerization and in situ bubble stretching into a new approach for pre-treating nanoparticles. By graft polymerization of monomers containing specific side groups that can be decomposed to gas under certain temperature onto nanoparticles, the nanoparticles are thus connected with macromolecular foaming agent. When the nanoparticles of this kind are incorporated into a polymer melt, the foaming agent would be triggered producing the aforesaid in situ bubble-stretching effect to remarkably separate the agglomerated nanoparticles. In addition, the remainder backbones of the grafted polymers might still help to increase interfacial compatibility, which would also contribute to the improvement of stretching-induced extensionality and hence dispersion of the nanoparticle agglomerates [11]. Compared to the case of Wu et al. [8], in which nano-$CaCO_3$ and foaming agent were individually mixed with high-density polyethylene, the method suggested by the authors ensures that the foaming agent is intimately attached to the nanoparticles. Consequently, the efficiency of bubble stretching might be much higher, or in other words, much less foaming agent would be enough to achieve the same goal. This is particularly important when mechanical properties of the ultimate composites are considered. Because the amount of the side groups on the grafted polymer chains serving as foaming agents is so few that not many small-scale bubbles can be generated, defoaming would be no longer required in the subsequent injection molding for manufacturing bulk composites using these micro-foamed compounds.

In this work, *p*-vinylphenylsulfonylhydrazide was synthesized and grafted onto silane coupling agent pre-treated nano-silica via aqueous radical polymerization. Then, the grafted nanoparticles were melt compounded with polypropylene (PP) as usual. The monomer was selected because it possesses (i) double bond that can be used to react with the functional groups on the nanoparticles and to grow into macromolecules, and (ii) chemical structure similar to the foaming agents with sulfonyl hydrazide groups that can be decomposed to gas at around 120–160 °C (matching the processing temperature of PP) [12]. In accordance with the above idea, melt blending of poly(*p*-vinylphenylsulfonylhydrazide) grafted nano-silica with PP should arouse bubble-stretching effect to improve nanoparticles' dispersion in the PP matrix (Fig. 1). The present paper characterized the grafted nanoparticles and preliminarily evaluated effect of the grafted nano-silica on the structure and properties of the PP-based composites.

2. Experimental

2.1. Materials

Silica (Aerosil 200) was supplied by Degussa Co., Germany with an average diameter of 12 nm and a specific surface area of 200 m^2/g. The particles were dried at 120 °C under vacuum for 24 h to eliminate the physically absorbed and weakly chemically absorbed species. Isotactic PP homopolymer (trade name: HZ730L) with melt flow index (MI) of 5.52 g/10 min (ASTM D569-90), provided by Samsung ATOFINA Co. Ltd., Korea, was used as matrix polymer of the nano-silica filled composites in this work.

Silane coupling agent (γ-methacryloxypropyl trimethoxy silane, trade name: KH570) was provided by Liao Ning Gaizhou Chemical Industry Co. Ltd., China. 4-Styrenesulfonic acid sodium salt hydrate was obtained from Aldrich Chemical Company, Inc., USA. *N*,*N*-Dimethylformamide (DMF) was purified to obtain anhydrous solvent. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol before use.

2.2. Introduction of double bonds onto nano-silica

Pre-treatment of silica nanoparticles with silane coupling agent was carried out as follows to introduce double bonds onto nano-silica. An excess of the coupling agent was added to a suspension of nano-silica in toluene solution. Having experienced ultrasonic agitation for 30 min, the suspension was refluxed for 10 h under protection of dry nitrogen flow. Afterwards, the nano-silica was filtrated and extracted with ethanol for 24 h to remove the excess silane absorbed on the particles, and then the silane treated nano-silica was dried in vacuum at 50 °C for 24 h. The content of the coupling agent introduced onto the nanoparticles was subsequently characterized by thermogravimetric analysis (TGA) measurement.

2.3. Graft polymerization of *p*-vinylphenylsulfonylhydrazide onto nano-silica

Firstly, *p*-vinylphenylsulfonylhydrazide and poly(*p*-vinylphenylsulfonylhydrazide) were synthesized according to the method proposed by Kamogawa et al. [13]. The polymer was produced for purposes of assessing the blowing possibility of the grafted poly(*p*-vinylphenylsulfonylhydrazide) to be made in the subsequent works. In brief, hydrazide hydrate was dropped with stirring into a solution of *p*-styrenesulfonyl chloride in tetrahydrofuran, and then cooled in an ice bath. The mixture was poured into water with vigorous stirring to

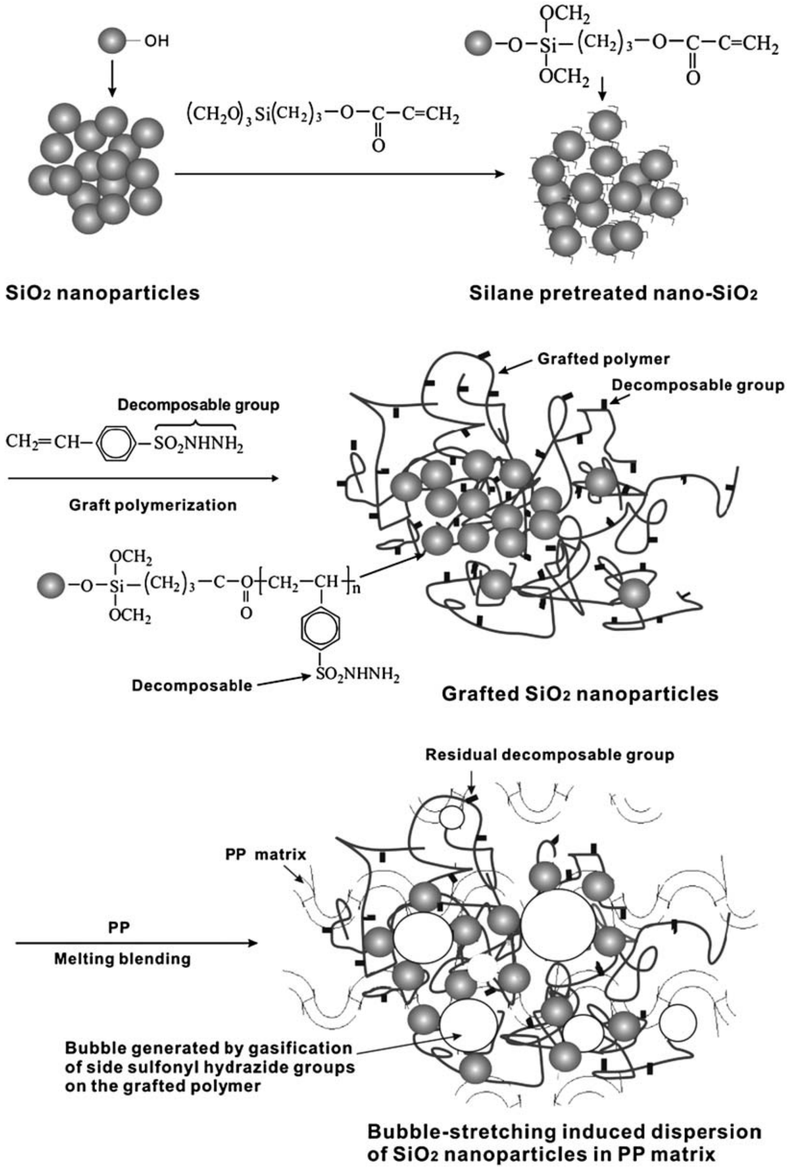


Fig. 1. Schematic drawing of the proposed bubble-stretching effect realized via graft macromolecular foaming agent onto silica nanoparticles.

get *p*-vinylphenylsulfonylhydrazide. The polymerization was carried out at 50 °C using AIBN as an initiator.

Secondly, the silane pre-treated nano-silica (the amount of silane coupling agent attached to nano-silica was 6.13 wt%) was added into a three-neck flask fitted with a stirrer containing 25 ml anhydrous DMF and ultrasonically agitated for 30 min. The mixture was placed into oil bath equipped with a condenser under flowing of dry nitrogen. AIBN was added to the system when the reactant reached 60 °C. After 30 min, *p*-vinylphenylsulfonylhydrazide was charged in one batch, allowing the reaction to proceed for a period of time, which was eventually stopped by ice cooling. In the meantime, monomer concentration, initiator concentration and reaction time were changed to study their influences on the reaction.

After the graft polymerization, the product was collected by suction filtration to get sample 1, and the filtrate was precipitated by adding excess methanol and filtered to get sample 2. Subsequently, both samples 1 and 2 were extracted with ethanol for 12 h to isolate the remaining monomer. Meanwhile, DMF absorbed on the samples surfaces was replaced with volatilizable methanol. Then, the two samples were dried at 40 °C under vacuum for 48 h to get samples 1′ and 2′. Sample 1′ was extracted with DMF for 48 h to isolate the polymer-grafted silica from the absorbed polymers, and the grafted nanoparticles were replaced with volatilizable methanol again, followed by drying at 40 °C under vacuum for 48 h to get sample 3. Some of them were transferred to TGA instrument to determine the total percentage of grafting. Accordingly, the poly(*p*-vinylphenylsulfonylhydrazide) grafted nano-silica with a percent grafting of 13.28% (monomer conversion = 55.36%, grafting efficiency = 9.20%) was used for the subsequent characterization and composites preparation. The reaction for producing these grafted nanoparticles was conducted on the silica of 0.95 g at 60 °C for 48 h at a monomer concentration and initiator concentration of 0.5 mol/L and 0.01 mol/L, respectively.

For separating the grafted poly(*p*-vinylphenylsulfonylhydrazide) from the surface of nano-silica, hydrofluoric acid (HF) solvent ($HF/H_2O = 20\%$ v/v) was applied. The modified nanoparticles that had been thoroughly extracted by DMF in advance were etched in HF solvent with stirring for 48 h, and then the suspended polymer was isolated and washed with distilled water for several times to remove the residual solvent, followed by drying at 40 °C under vacuum for 48 h.

2.4. Composites preparation

To prepare PP composites, ungrafted or grafted nano-silica was compounded with PP in the mixer of a Haake Rheocord 300p torque rheometer at 180 °C for 10 min. Rotation speed of the mixing rotors was set at 60 rpm. Then, the mixture was injection molded into ultimate nanocomposites standard bars for mechanical tests with a Y-350 vertical injection molding machine. The dimensions of deformable region of tensile dumbbell specimens are $25.0 \times 3.2 \times 2.0\ mm^3$, while those of the rectangular bars for testing impact strength are $80 \times 10 \times 4\ mm^3$. The bars were further notched in the middle using a CSI cutter to produce "V" type notches with a depth of 2 mm.

2.5. Characterization

Fourier-transform infrared (FTIR) spectroscopy was employed to investigate the variation in surface chemical structure of the nanoparticles. The spectra were recorded in KBr pellets on a Nicolet 5DX FTIR spectrometer. Blank scanning was performed before measurements to eliminate the influence of water vapor and CO_2 in air. An electron probe micro-analyzer, JXA-8800R, was used to determine surface elements of the grafted silica.

TGA measurements were performed on a NETZSCH TG 209C thermogravimetric analyzer from 30 to 800 °C at a heating rate of 10 °C/min under the flow of anhydrous air.

To assess nanoparticles dispersion in the composites matrix, ultrathin sections of the compounds obtained from the melt mixing were examined by a FEI TECNAI 12 transmission electron microscope (TEM) at an accelerating voltage of 100 kV.

Tensile properties of the nanocomposites were determined with a Hounsfield 10K-S universal tester at a crosshead speed of 50 mm/min according to ASTM D638-98. Notched Charpy impact strength was measured by an Atlas advanced pendulum impact device in accordance with ISO 179-2. All the specimens were conditioned at 30 °C and a relative humidity of 50% for 48 h prior to the measurements, which were then tested under the same conditions.

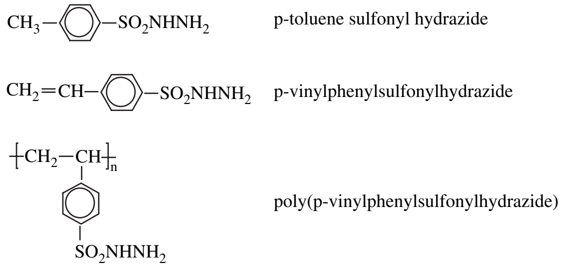
Densities of the materials were measured using pycnometer at 30 °C.

3. Results and discussion

3.1. Characterization of poly(*p*-vinylphenylsulfonylhydrazide)

To the authors' knowledge, neither *p*-vinylphenylsulfonylhydrazide nor poly(*p*-vinylphenylsulfonylhydrazide) has been used as blowing agent for polymers, although their derivative *p*-toluene sulfonyl hydrazide is well known in this aspect (Scheme 1) [14]. At the beginning of discussion, therefore, it should be studied whether the polymer of *p*-vinylphenylsulfonylhydrazide is capable of acting the role of blowing agent, since it is planned to be grafted onto nano-silica and to bring about bubble-stretching effect during the subsequent melt mixing with PP.

Fig. 2 gives the FTIR spectra of *p*-vinylphenylsulfonylhydrazide and poly(*p*-vinylphenylsulfonylhydrazide). The spectrum of the former chemical exhibits adsorptions at 3260 and 1595 cm^{-1} that are characteristic of N–H and phenyl, respectively. Besides, the peaks at 1328 and 1162 cm^{-1} result from the characteristic responses of SO_2, and those at 1629, 1002 and 941 cm^{-1} represent the appearance of vinyl. For the spectrum of poly(*p*-vinylphenylsulfonylhydrazide), the bands at about 954 and 1012 cm^{-1} are attributed to the in-plane bending vibration of phenyl groups, while that at around 1600 cm^{-1} might be due to stretching of phenyl framework. By comparing the two spectra in Fig. 2, it is known that



Scheme 1.

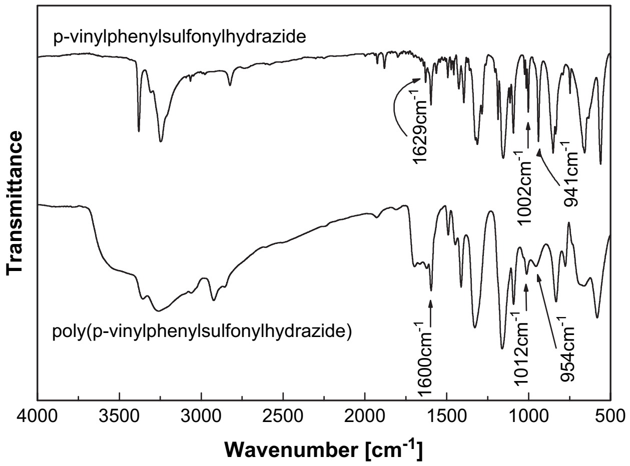


Fig. 2. FTIR spectra of *p*-vinylphenylsulfonylhydrazide and poly(*p*-vinylphenylsulfonylhydrazide).

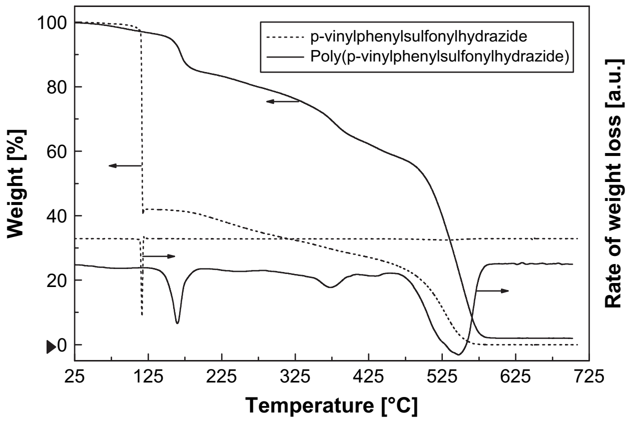


Fig. 3. TGA thermogram of *p*-vinylphenylsulfonylhydrazide and poly(*p*-vinylphenylsulfonylhydrazide).

poly(*p*-vinylphenylsulfonylhydrazide) has the same basic structure as its monomer.

Fig. 3 shows the pyrolytic behaviors of *p*-vinylphenylsulfonylhydrazide and poly(*p*-vinylphenylsulfonylhydrazide) in air. The former undergoes an obvious weight loss at about 120 °C, which is the same as the case of *p*-toluene sulfonyl hydrazide due to gasification of sulfonyl hydrazide groups driven by internal oxidation–reduction reaction [12]. It means that the replacement of methyl in *p*-toluene sulfonyl hydrazide with vinyl does not influence its foaming ability. Similarly, Fig. 3 indicates that the polymerized *p*-vinylphenylsulfonylhydrazide retains the pyrolytic habit of its monomer besides raising the decomposition temperature to 169 °C. In fact, this might favor to increase foaming efficiency as it approaches the melting point of PP. By comparing the degradation curves of the two substances shown in Fig. 3, it is seen that with a rise in temperature poly(*p*-vinylphenylsulfonylhydrazide) keeps on gradual weight loss after the obvious decomposition at 169 °C. It means that some of the sulfonyl hydrazide groups on the polymer remain undecomposed at the same temperature. Therefore, the weight loss of poly(*p*-vinylphenylsulfonylhydrazide) at 169 °C is lower than that of *p*-vinylphenylsulfonylhydrazide at 120 °C.

In short, the above results manifest that the approach proposed in the introductory part, i.e. anchoring a macromolecular foaming agent to nano-silica can be carried out by grafting poly(*p*-vinylphenylsulfonylhydrazide) onto the nanoparticles.

3.2. Characterization of the grafted nanoparticles

In general, a certain amount of homopolymer has to be generated during graft polymerization. For separating the ungrafted poly(*p*-vinylphenylsulfonylhydrazide), the grafted nanoparticles were extracted by DMF for 48 h. The remains were then examined by an element analyzer (Fig. 4). The appearance of N and S elements in addition to Si suggests that poly(*p*-vinylphenylsulfonylhydrazide) has been covalently bonded to the nano-silica.

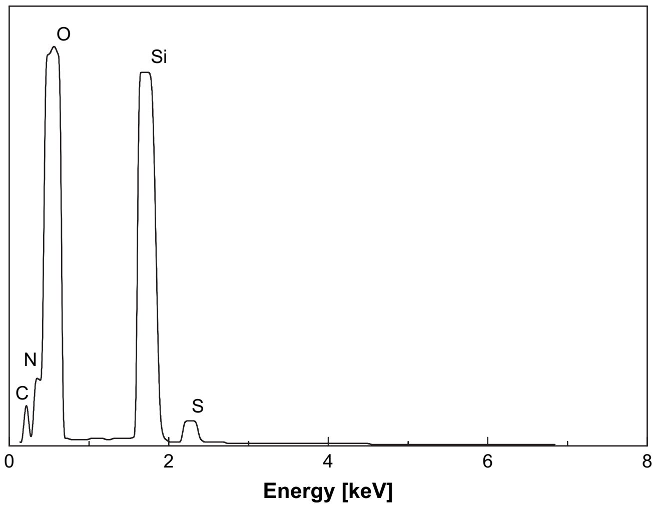


Fig. 4. Element analysis of poly(*p*-vinylphenylsulfonylhydrazide) grafted nano-silica. The ungrafted polymer had been extracted prior to the measurement.

Since the modified nanoparticles are going to bring the macromolecular foaming agent into PP, pyrolytic behaviors of the related substances were measured (Fig. 5). The visible differences among the grafted nano-silica, untreated nano-silica and silane treated silica should be indicative of the role of the grafted polymer. There is an obvious weight loss at around 140 °C on the thermogram of the grafted nanoparticles, which ranks between the gasification temperatures of *p*-vinylphenylsulfonylhydrazide (120 °C) and poly(*p*-vinylphenylsulfonylhydrazide) (169 °C) as shown in Fig. 3. It means that the grafted nanoparticles have maintained the blowing ability. By defining the first peak pyrolytic temperature recorded by the TGA test as T_d (i.e. the gasification temperature of the polymer), influence of percent grafting of the grafted poly(*p*-vinylphenylsulfonylhydrazide) on the decomposition feature of the treated nano-silica is illustrated in Fig. 6. Clearly, the amount of the grafted poly(*p*-vinylphenylsulfonylhydrazide) has little influence on T_d. In this context, when the grafted nanoparticles with different percent grafting are melt compounded with PP, it is unnecessary to appropriately change the processing temperature to meet the foaming temperature.

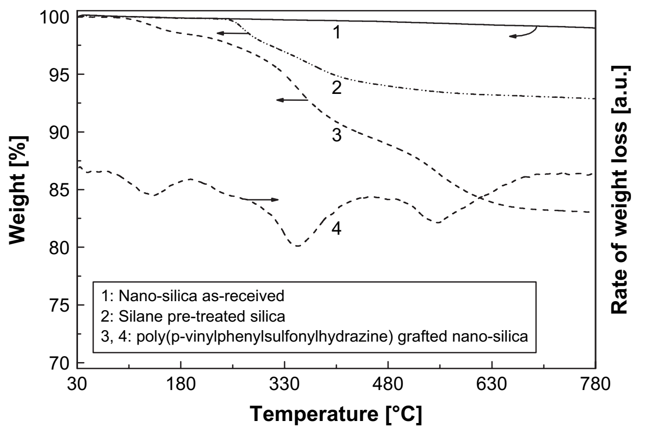


Fig. 5. TGA thermogram of nano-silica, silane pre-treated nano-silica and poly(*p*-vinylphenylsulfonylhydrazide) grafted nano-silica.

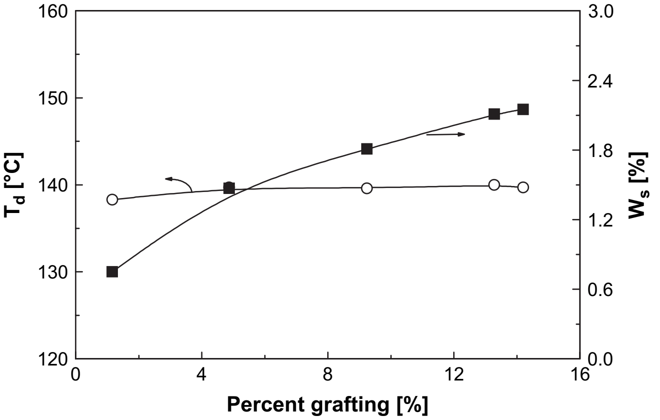


Fig. 6. Influence of percent grafting on gasification temperature of poly(p-vinylphenylsulfonylhydrazide) grafted nano-silica (the first peak pyrolytic temperature on the thermal degradation curve of the modified nanoparticles, refer to Fig. 5), T_d, and weight loss of poly(p-vinylphenylsulfonylhydrazide) grafted nano-silica during the simulative heating process (i.e. 180 °C for 10 min in TGA cell), W_s.

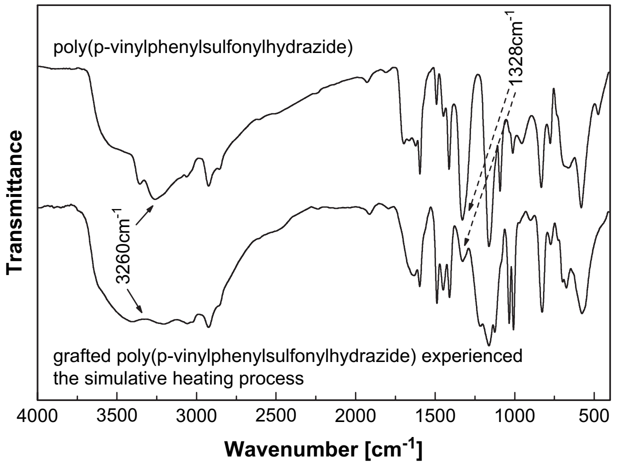


Fig. 7. FTIR spectra of grafted poly(p-vinylphenylsulfonylhydrazide) (that had been isolated from the modified nano-silica through etching) before and after the simulative heating process (i.e. 180 °C for 10 min in TGA cell).

On the other hand, because no method is available to determine the decomposition habits of the grafted nano-silica in the course of melt blending, the investigation has to be performed indirectly under simulative conditions using TGA as follows. The grafted poly(p-vinylphenylsulfonylhydrazide), which was isolated from the grafted nano-silica by removing the nanoparticles via etching, was quickly heated from room temperature to 180 °C and kept at this temperature for 10 min. Afterwards, the residue was checked by FTIR spectroscopy (Fig. 7). It is seen that the intensities of the typical adsorptions of N–H (3260 cm^{-1}) and SO_2 (1328 cm^{-1}) greatly decrease after the heat treatment, coinciding with the result of decomposition of sulfonyl hydrazide groups. Correlating Fig. 5 with Fig. 7, it is confirmed that the poly(p-vinylphenylsulfonylhydrazide) grafted on nano-silica can be used as a foaming agent.

Similarly, the grafted nanoparticles also experienced the same heating procedures in TGA cell as described above, while the weight loss was measured (marked as W_s) to show the quantity of the gas released by decomposition of the side groups on the grafted polymer chains. For the convenience of comparison, the measured W_s is also plotted as a function of percent grafting of the grafted nanoparticles in Fig. 6. The data reveal that W_s significantly increases with a rise in percent grafting. This is understandable as the amount of the released gas must be proportional to the amount of the grafted polymer. Using the dependence of W_s on percent grafting, the degree of bubble-stretching effect can thus be tailored.

3.3. Dispersion of grafted nano-silica in PP and mechanical properties of the composites

Dispersion status of the grafted nanoparticles in PP matrix was examined by TEM in comparison with the untreated ones (Fig. 8). The size of the nano-silica agglomerates is reduced from over 200 nm for the composite containing untreated particles (Fig. 8(a)) to about 20–30 nm for that containing the grafted versions (Fig. 8(b)). Besides, the particles' intervals

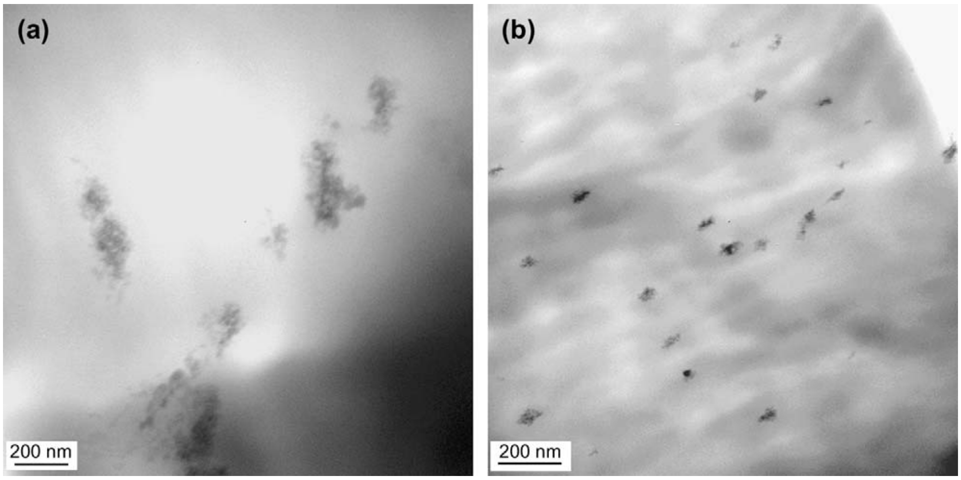


Fig. 8. TEM images of ultrathin sections of (a) untreated nano-silica/PP and (b) poly(p-vinylphenylsulfonylhydrazide) grafted nano-silica/PP composites (nano-silica content = 0.95 vol%).

Table 1
Porosity of poly(*p*-vinylphenylsulfonylhydrazide) grafted nano-silica/PP composites

Content of nano-silica (vol%)	0.47	0.95	1.43	2.41
η_1[a] (%)	3.60	7.53	11.87	15.02
η_2[b] (%)	0.07	0.13	0.08	0.19

[a] η_1: Porosity of the compounds produced by the mixer of the torque rheometer.

[b] η_2: Porosity of the injection molded specimens.

are also significantly increased (Fig. 8(b)). Clearly, the sulfonyl hydrazide groups on the grafted polymer inside the nano-silica agglomerates must have been decomposed to gas like blowing agent forming polymer bubbles during melt blending. Nano-silica agglomerates would thereby be disconnected owing to the in situ stretching of these bubbles. To confirm the estimation in a quantitative way, porosity of the composites, η, was determined using density measurement and is listed in Table 1:

$$\eta = \frac{\rho_0 - \rho_1}{\rho_0} \times 100\% \tag{1}$$

where ρ_0 and ρ_1 denote the theoretical and experimental density of the material, respectively. ρ_0 was calculated from the following equation assuming there were no bubbles in the composites:

$$\rho_0 = \frac{W_{\mathrm{PP}} + W_{\mathrm{silica}} + W_{\mathrm{grafted\text{-}polymer}}}{\dfrac{W_{\mathrm{PP}}}{\rho_{\mathrm{PP}}} + \dfrac{W_{\mathrm{silica}}}{\rho_{\mathrm{silica}}} + \dfrac{W_{\mathrm{grafted\text{-}polymer}}}{\rho_{\mathrm{grafted\text{-}polymer}}}} \tag{2}$$

where W_{PP}, W_{silica} and $W_{\mathrm{grafted\text{-}polymer}}$ denote weights of PP, nano-silica and the grafted polymer used for making the composites, respectively. ρ_{PP} (0.906 g/cm^3), ρ_{silica} (1.926 g/cm^3) and $\rho_{\mathrm{grafted\text{-}polymer}}$ (0.858 g/cm^3) represent densities of PP, nano-silica and the grafted polymer, respectively. The results (refer to η_1 in Table 1) demonstrate that (i) there are detectable voids in the composites, and (ii) the amount of the voids increases with increasing the grafted nanoparticles content, i.e. the content of the blowing agent.

In the last step of this work, the compounds of PP and nano-silica were broken and injection molded to make standard specimens for mechanical testing. Prior to the tests, porosity of the composites filled with the grafted nanoparticles was determined again. As seen in Table 1 (refer to η_2), the internal cavities have been effectively eliminated after injection molding, and this should be favorable for the mechanical properties of the materials.

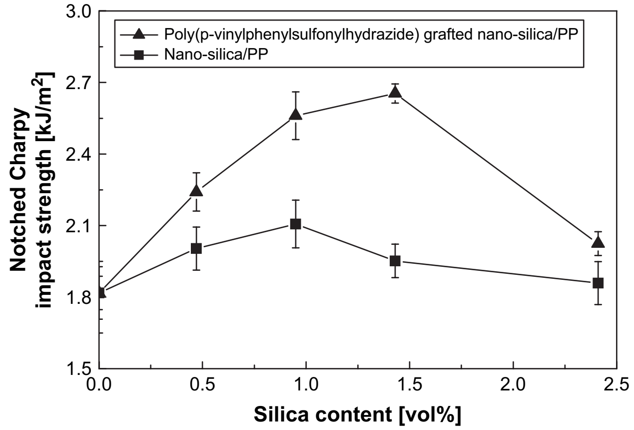


Fig. 9. Notched Charpy impact strength of PP and its composites filled with nano-silica as a function of silica content.

Fig. 9 shows notched Charpy impact strength of PP composites as a function of nano-silica content. It is seen that the contribution of the untreated fillers to the improvement of toughness under high-speed deformation and to the reduction of notch sensitivity is nearly negligible as compared with the grafted ones. The impact strength of untreated nano-silica/PP composites slightly increases with the filler content and reaches maximum at about 0.95 vol% of silica. For poly(*p*-vinylphenylsulfonylhydrazide) grafted nano-silica/PP systems, however, the highest impact strength that appears at 1.43 vol% of silica is about 1.26 times higher than that of the composite with untreated nano-silica. So far, the crack front bowing mechanism has been widely used for explaining the toughening effect in micro-sized particulate filled polymers [15]. Nevertheless, Chan et al. [16] inferred that in the case where the size of rigid particles is of the order of 50 nm or less, the applicability of the bowing mechanism is questionable, because such small size rigid particles may not be able to resist the propagation of the crack. From *J*-integral tests, they suggested that nanoparticles would trigger large-scale plastic deformation of the matrix, which consumes tremendous fracture energy. Since the above morphological investigation reveals that the dispersion scale of the nanoparticles is less than 50 nm in the composites with the grafted nano-silica, it is believed that the mechanism proposed by Chan and co-workers should also be valid in the current study.

Naturally, it is necessary to study the strength properties when the PP composite has been toughened. In comparison with neat PP, all of the composites show higher tensile strength (Fig. 10). At lower silica content, the strength of untreated nano-silica/PP composites increases slightly with silica

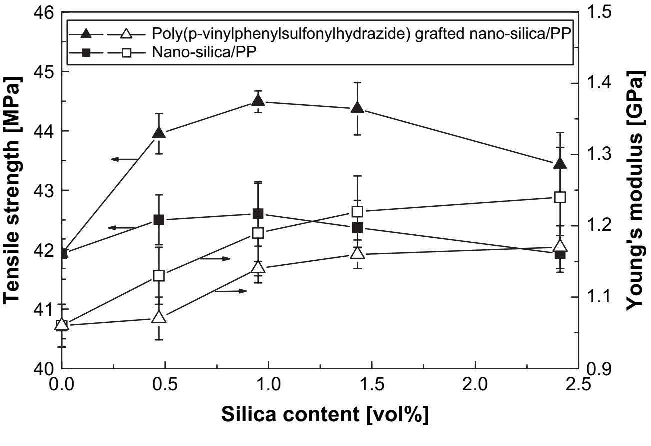


Fig. 10. Tensile strength and Young's modulus of PP and its composites filled with nano-silica as a function of silica content.

content while that of poly(*p*-vinylphenylsulfonylhydrazide) grafted nano-silica/PP shows a much more prominent improvement. The chain entanglement/interdiffusion at the interface between the grafted polymer and PP matrix of the latter composites should also account for the strengthening effect, as the stress transfer efficiency is enhanced accordingly. It is worth noting that, what is more, although the composites' tensile strength starts to decrease with a continuous rise in silica loading due to the gradually deteriorated particles dispersion, the strength of the composites with grafted nanoparticles still remains at a relatively high level. At a silica content of 2.41 vol%, for example, the poly(*p*-vinylphenylsulfonylhydrazide) grafted nano-silica/PP possesses tensile strength obviously higher than the highest value of the untreated silica/PP composites. It manifests that the bubble-stretching effect also works in the case of higher nanoparticles content, which might facilitate manufacturing of highly loaded nanocomposites. On the other hand, the improved tensile strength of the grafted nano-silica/PP composites has ruled out the possible role of the grafted polymers acting as a plasticizer in increasing impact strength of the composites, because a plasticized system usually shows reduced tensile strength.

The filler content dependences of Young's modulus of the composites are also exhibited in Fig. 10. Although addition of the grafted nanoparticles leads to a rise in the stiffness of PP, the flexible grafted polymer with much lower modulus than silica shields the matrix from the particles. Consequently, the untreated nanoparticles can more effectively impart their rigidity to PP as compared to the treated versions at the same silica content. Further works in this aspect will be done to change the stiffness of the grafted polymer by copolymerization and hence the stiffness of the ultimate composites.

4. Conclusions

On the basis of the above discussion, the following conclusions can be drawn.

1. Graft of poly(*p*-vinylphenylsulfonylhydrazide) onto nano-silica can be accomplished in terms of free-radical polymerization via the surface double bonds pre-introduced by silane coupling agent modification. The side groups on the grafted poly(*p*-vinylphenylsulfonylhydrazide) are able to be gasified like foaming agent when the grafted nano-silica is melt compounded with PP. Accordingly, the nearby nanoparticle agglomerates can be disconnected and well dispersed in PP due to the bubble-stretching effect.

2. The amount of the decomposable side groups on the grafted poly(*p*-vinylphenylsulfonylhydrazide) is so small that the porosity of the PP-based compounds is kept at low level. It helps to eliminate the defoaming step when the mixture of the grafted nano-silica and PP is molded into compact material.

3. The PP composites with grafted nano-silica receive simultaneous improvement of toughness and strength. Compared with the case where no blowing function is associated to the grafted polymer and notch impact strength of PP fails to be enhanced [1], the present approach is able to counteract the weakness because the grafted poly(*p*-vinylphenylsulfonylhydrazide) plays dual role to well separate the nanoparticles and to strengthen interfacial interaction in the composites.

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