Polym. Bull. (2010) 65:815–824
DOI 10.1007/s00289-010-0329-3

ORIGINAL PAPER

Impact fracture toughness and morphology of polypropylene nanocomposites

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Received: 28 April 2010 / Revised: 7 June 2010 / Accepted: 15 June 2010 /
Published online: 25 June 2010

Abstract The nanometer calcium carbonate (nano-$CaCO_3$)-filled polypropylene (PP) composites were prepared using a twin-screw extruder, and the filler particle surface was pretreated, respectively, with fat acid (SI) and titanate coupling agent (SII) in this article. The notched and unnotched impact fracture properties were measured at room temperature by means of a Charpy impact instrument to identify the effects of the surface treatment and the filler concentration on the impact fracture properties. The results showed that the V-notched and U-notched impact strength slightly increased with an addition of the nano-particle volume fraction (ϕ_f) for both two nanocomposites. When ϕ_f was more than 10%, the V-notched impact strength of the system SII was obviously greater than that of the system SI, and the effect of surface treatment of the nanometer particles on the U-notched impact strength is insignificant. Furthermore, the impact fracture surface was observed by means of scanning electron microscopy to understand the relationship between the interfacial morphological structure and the impact fracture toughness of the PP nanocomposites.

Keywords Polypropylene · Nano-$CaCO_3$ · Composite · Impact toughness

Introduction

Polypropylene (PP) is extensively used in automobile and electronic appliance applications due to its good performance and processing properties as well as low cost. However, its application is somewhat limited due to its high shrinkage rate and relatively poor impact resistance at room or low temperatures. Therefore, how to

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improve the impact toughness of PP resin has been extensively paid attention [1–4]. In general, the stiffness and dimensional stability of PP may be improved significantly by filling with rigid inorganic particles, such as calcium carbonate, mica, talcum powder, and so on. This method or way is widely used in industry, but the tensile strength and impact toughness might be reduced in some extent, especially in the case of hight concentration of the fillers. Hence, how to promote further the mechanical properties of the inorganic particulate-filled PP composites has been extensively paid attention during the past decade. Liang et al. [5] studied the impact fracture behavior of PP/EPDM/glass bead ternary composites and found that the impact fracture toughness was improved obviously when the glass beads were capsulated with the elastomer. In this case, there was a thin elastic interlayer on the surface of the glass beads.

Recently, the preparation and properties of polymer filled with nanometer inorganic rigid particles have been become as one of research hot points in this field [2]. In general, the mechanical and physical properties of polymeric composites are related closely with the dispersion state of the filler particles in the matrix, especially for nanometer particles. Several researchers attempted to modify polymeric materials by filling with nanometer inorganic rigid particles and discussed the dispersion property and its toughening mechanisms, such as nano-calcium carbonate (nano-$CaCO_3$) [2], nano-$Mg(OH)_2$ [3], nano-SiO_2 [6], nano-Rectorite [7], nano-organoclay [8, 9], carbon nanotube [10], and nano-bentonite [11].

In general, the applications of nano-$CaCO_3$ particles are relatively extensive in polymer composite industry because of its low cost. The objective of this article is to prepare the PP filled with nano-$CaCO_3$ particles and investigate the effects of the surface treatment and content of the nano-$CaCO_3$ particles on the impact properties of the PP nanocomposites.

Experimental

Raw materials

The PP used in this work was an injection grade granular resin with trade mark of CJS-700, supplied by Guangzhou Petrochemical Co. Ltd. in China. The resin density in solid state was 0.910 g/cm^3, and the melt flow index was 10 g/10 min (ASTM D1238). The filler was a nanometer calcium carbonate (nano-$CaCO_3$), manufactured by Guangping Chemical Plant in China, and the mean diameter and density of the particles were 40 nm and 2.55 g/cm^3, respectively.

Preparation

After the surface of the nano-$CaCO_3$ particles was pretreated, the filler was simply mixed with the PP resin in a high speed compounding machine, and then they were put into a twin-screw extruder for molten blending, the extrudate was granulated to produce the composites. In these experiments, the surface activation the nano-$CaCO_3$ particles was made with fat acid (surface activation) and was named SI, while the surface of the nano-$CaCO_3$ particles pretreated with a titanate coupler was called as SII. The volume fractions of the nanometer particles were 0.5, 1.0, 1.5, and 3.0%, respectively. Finally, the impact test specimens were prepared by using an injection-molding machine after the composites were dried at 80 °C for 5 h. The geometry of these specimens was according to the ASTM standard.

Instruments and methodology

The V-notched, U-notched, and unnotched impact strength of the composites were measured at room temperature by using a Charpy impact machine (model XJJ-5) supplied by Jinjian Instrument Co. Ltd. (Chengde, China). The Charpy impact tests were carried out according to ASTM D256 standard, and five tests were conducted and the average was reported for each composition.

The impact fracture surfaces of the specimens were examined by means of the scanning electronic microscope (SEM, model LEO1530VP) supplied by Carl-Cest Instrument Company in Germany to observe the interfacial morphology and the dispersion of the particles in the PP matrix. All specimens were gold coated before SEM examination.

Results and discussion

Relationship between V-notched impact strength and filler content

Figure 1 shows the relationship between the V-notched impact strength (σ_I) and the volume fraction (ϕ_f) of the nano-$CaCO_3$ particles for these two composite systems. It can be seen that with an addition of ϕ_f the σ_I decreases slightly as ϕ_f is less than

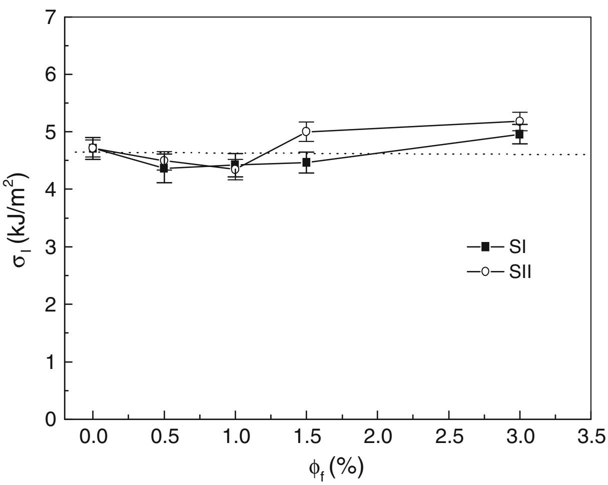

Fig. 1 Influence of ϕ_f on V-notched impact strength

1.0%, while increases when ϕ_f is more than 1.0%. Under the same experimental conditions, the values of the σ_I for the SII system are greater than those for the SI system. In addition, the maximum value of the σ_I for the SII system is 1.1 times of that for the unfilled PP resin (about 10% increase). This indicates that the surface treatment of nano-$CaCO_3$ particles is beneficial to improve the impact fracture toughness of the filled PP composites, especially for the system with the surface pretreated by using a titanate coupling agent.

Relationship between unnotched impact strength and filler content

Figure 2 displays the correlation between the unnotched impact strength and the volume fraction of the nano-$CaCO_3$ particles for these two composite systems. It may be observed that the unnotched impact strength of the SII system is somewhat higher than that of the unfilled PP resin, except for individual measured data point, and the variation of the σ_I is slightly with an increase of the volume fraction of the particles. When ϕ_f is less than 1.5%, the unnotched impact strength of the SII system is slightly greater than that of the SI system. Furthermore, the unnotched impact strength of the SI system is evidently smaller than that of the SII system when ϕ_f is more than 1.5%. This indicates that toughening effect of the composite which the particle surface treated with a titanate coupler is better than that of the composite which the particle surface treated with surface activation agent (fat acid).

Relationship between U-notched impact strength and filler content

Figure 3 illustrates the relationship between the U-notched impact strength and the volume fraction of nano-$CaCO_3$ particles for these two composite systems. With an increase of the volume fraction of the nano-$CaCO_3$ particles, the U-notched impact strength of the two composite systems increases and the difference in the σ_I values between these two systems is not obvious. However, the variation of the σ_I with ϕ_f

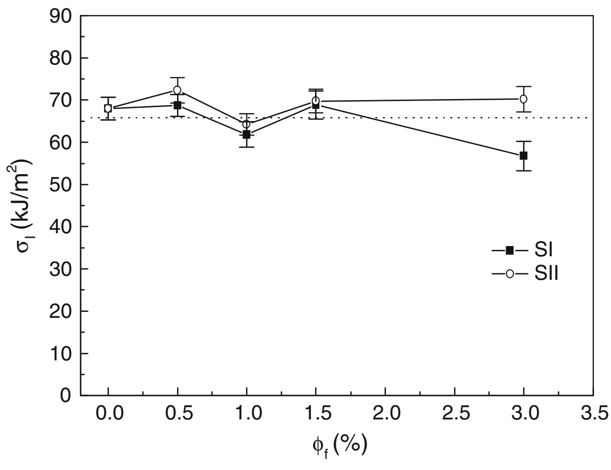

Fig. 2 Dependence of unnotched impact strength on ϕ_f

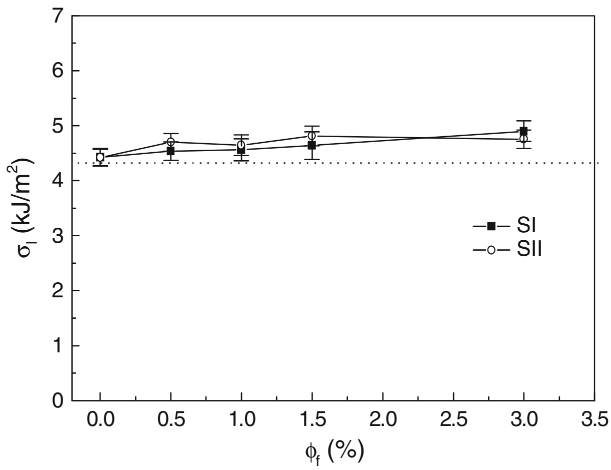

Fig. 3 Relationship between U-notched impact strength and ϕ_f

for the SI system is different from that for the SII system. For the SI system, the σ_I is approximately as a linear function of ϕ_f, which is given by

$$\sigma_I = \alpha + \beta\phi_f, \quad (1)$$

where α and β are the constants related to the impact fracture toughness. The values of α and β may be determined by means of linear regression analysis method from experimental data. From Fig. 3, the values of α and β of the SI system are, respectively, 4.431 and 0.154, and the linear correlation coefficients are more than 0.992.

For the SII system, the σ_I increases nonlinearly with increasing ϕ_f. In addition, the σ_I of the two composite systems is 1.108 times of the unfilled PP resin at ϕ_f of 3.0% (about 10.8% increase). This means that the effects of the two surface treatment methods on the U-notched impact fracture toughness of the specimens for these two composites are insignificant under these test conditions.

Morphology of impact fracture surface

Figure 4 shows the SEM photograph of impact fracture surface for the unfilled PP. It may be observed that the fracture surface looks like waves. It means that the unfilled PP specimen break relatively fast due to quick development of micro-crack under impact load, leading to low impact strength. In the previous work, the authors [12] observed some small platforms on the fracture surface in addition to the waves.

Figure 5 is the SEM picture of V-notched impact fracture surface morphology of the SI system when the volume fraction of the nano-$CaCO_3$ particles is 0.5%. It can be seen that the distribution of the nano-$CaCO_3$ particles are approximately uniform. Furthermore, there are some small platforms on the fracture surface, which is different from the impact fracture surface morphology in the unfilled PP resin. This presents that the toughening effect of the nano-$CaCO_3$ particles on the filled PP

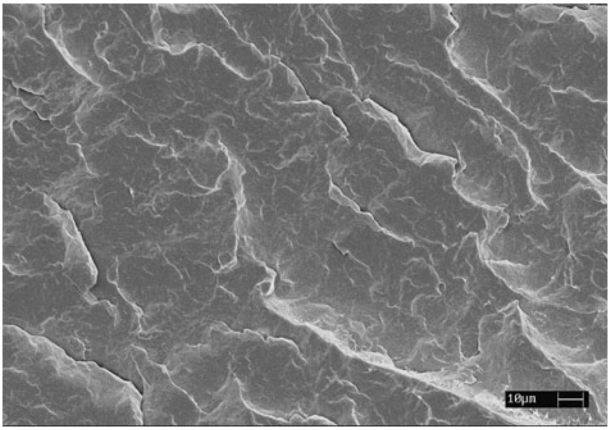

Fig. 4 SEM photograph of impact fracture surface of unfilled PP

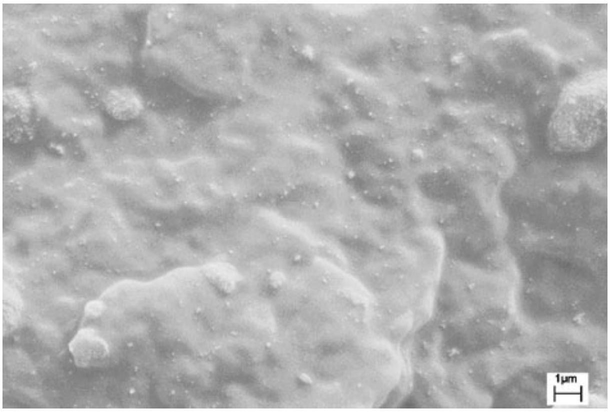

Fig. 5 SEM photograph of impact fracture surface of SI system ($\phi_f = 0.5\%$)

composites is insignificant in the case of low concentration of the nanometer particles. The interfacial effect between the filler and the matrix might be also insignificant due to there being less number of the nano-$CaCO_3$ particles in the matrix resin, resulting in that there is too small stress concentration generated in the matrix around the nanometer particles to form some crazes under impact loading. On the other hand, these nanometer particles in the matrix resin produce some kind of effects of cutting apart the matrix, and these cutting apart effects might form some defects like as micro-cracks. These micro-cracks will develop as soon as the specimen is subjected to impact loading, leading to slight reduction of impact strength (see Fig. 1).

Figure 6 is the SEM picture of the V-notched impact fracture surface morphology of the SI system when the volume fraction of the nano-$CaCO_3$ particles is 1.5%. Although the number of the nano-$CaCO_3$ particles in the matrix increases obviously comparing with the composite system with ϕ_f of 0.5%, the

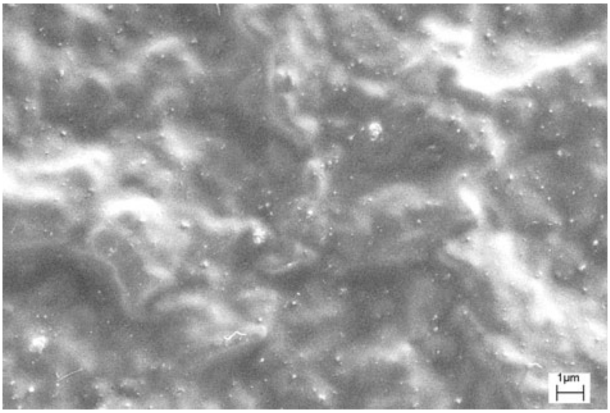

Fig. 6 SEM photograph of impact fracture surface of SI system ($\phi_f = 1.5\%$)

Fig. 7 SEM photograph of impact fracture surface of SI system ($\phi_f = 3\%$)

dispersion and distribution of the nano-$CaCO_3$ particles in the matrix are still relatively uniform, while obvious agglomerate phenomenon is not observed. It can be also seen that there are some morphologies that look like small hills on the fracture surface, and it is different from the platforms as shown in Fig. 5. This because that stress concentration generated in the matrix around the nanometer particles increases to form some crazes with increasing further the filler content and the matrix around the inclusion will yield first to form plastic deformation under impact loading. In this case, relevant impact deformation energy will be absorbed, leading to improving the impact fracture toughness of the composites (see Fig. 1).

Figure 7 is the SEM picture of the V-notched impact fracture surface morphology of the SI system when the volume fraction of the nano-$CaCO_3$ particles is 3.0%. Similarly, although the number of the nano-$CaCO_3$ particles in the matrix increases further, the dispersion and distribution of the nano-$CaCO_3$ particles in the matrix are still relatively uniform and even though there is small agglomerate.

It can be also seen that there are some morphologies that look like small hills on the fracture surface, instead of the platforms as shown in Fig. 5. Generally, the number of fillers is inversely proportional to the cube of the particle diameter when the inclusion concentration is constant. That is

$$N_{\mathrm{d}} = f\left(d^3, \phi_{\mathrm{f}}\right), \quad (2)$$

where N_{d} and d are the number and diameter of the filler particles, respectively.

Thus, the number of the particles increases quickly with an addition of the volume fraction of the nanometer particles. In this case, the matrix around these nanometer particles generates evidently stress concentration with an increase of the filler content when the specimen is subjected impact loadings, and will yield first and form plastic deformation to absorb relevant impact deformation energy. In addition, this stress concentration might induce crazes in these interfacial layers between the fillers and the PP matrix, and also absorb corresponding impact deformation energy, resulting in the improvement of impact fracture toughness (see Fig. 1).

Figure 8 is the SEM picture of the V-notched impact fracture surface morphology of the SII system when the volume fraction of the nano-$CaCO_3$ particles is 3.0%. It can be seen that the dispersion and distribution of the nano-$CaCO_3$ particles in the matrix are also more uniform than that in the SI system, even though there is a little of agglomerate. Although the fracture morphology is similar to the SI system, by comparing with Fig. 7, the number of these small hills is more and the size is smaller than those of the SI system. In other wards, the fracture surface of the SII system is rougher than that of the SI system. It can be also seen that the interface between the nanometer particles and the PP matrix is more blurred. This suggests that the surface of the particles might be capsulated with single molecular layer after the surface of the nano-$CaCO_3$ particles has been treated with a titanate coupler, the compatibility between the fillers and the resin matrix is improved, and the uniform degree of the dispersion of the particles in the PP resin is further increased.

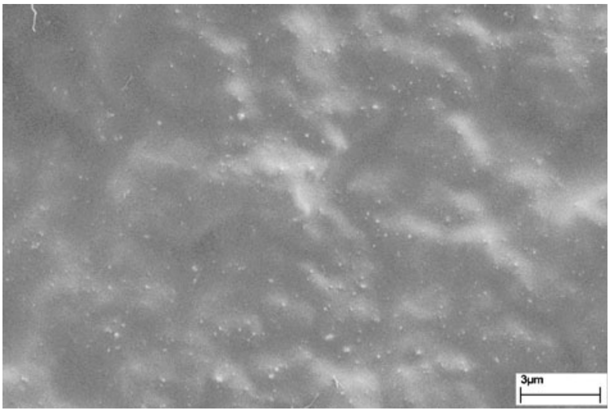

Fig. 8 SEM photograph of impact fracture surface of SII system ($\phi_{\mathrm{f}} = 3\%$)

Generally, the crazes and plastic deformation in the matrix around the inclusions generated due to the stress concentration, and the surface effect of these nanometer particles is beneficial to absorb the impact fracture energy when the PP/nano-$CaCO_3$ composites is under impact loading. In addition, the nanometer inclusions have an effect for blocking or ending the expansion of micro-cracks, leading to improving more effectively for the notched impact fracture toughness of the nanocomposite materials (see Fig. 1).

Conclusions

The U-notched impact strength of both these two PP nanocomposite systems increases with an addition of the volume fraction of the nano-$CaCO_3$ particles in a range of ϕ_f from 0 to 3%, and the σ_I of the SII system is slightly higher than that of the SI system except individual data point, while the influence of the particle surface treatment on the U-notched impact strength is insignificant.

When the volume fraction of the nanometer fillers is more than 1.0%, the V-notched impact fracture strength of both these systems increased somewhat with an addition of the volume fraction of the fillers, and the impact fracture strength of the SII system was obvious greater than that of the SI system.

The surface of the particles might be capsulated with single molecular layer after the surface of the nano-$CaCO_3$ has been treated with a titanate coupler, the compatibility between the fillers and the resin matrix is improved, and the uniform degree of the dispersion of the particles in the PP resin is further increased. The crazes and plastic deformation in the matrix around the inclusions generated due to the stress concentration, and the surface effect of these nanometer particles is beneficial to absorb the impact fracture energy when the PP/nano-$CaCO_3$ composites is under impact loading. Furthermore, the nanometer inclusions have an effect for blocking or ending the expansion of micro-cracks. These might be the major reason for improving more effectively the notched impact fracture toughness of the polymer nanocomposite materials.

Acknowledgment The author would like to thank Ms. L. Wang for her help in this experiment.

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