Effect of Calcium Carbonate Nanoparticle on the Toughening Mechanisms of Polypropylene Nanocomposite

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Introduction

Inorganic particle-filled polymer composites show an increase in modulus but a decrease in toughness and ductility, mainly because of the induced stress concentration, agglomeration, and confinement of matrix molecular mobility around the rigid filler phase. However, a few exceptions have also been reported in the literature [1,2]. In toughening polyethylene, CaCO₃ and chalk particles have been shown to be able to improve toughness of PE effectively [1]. For PP, Thio and Argon [2] found that the CaCO₃-toughened PP composites could exhibit greatly improved impact strengths up to 40-50 kJ/m², as compared to 2-8 kJ/m² for that of neat PP.

In this study, particular attention is given to understanding the underlying toughening mechanisms responsible for the impressive toughening effect found in PP/CaCO₃ nanocomposite.

Experimental

Materials. PP homopolymer, PD403 (density = 1.04 g/cc) from Basell USA, was used in this study. CaCO₃ nanoparticles (ca. 44 nm) were obtained from Guang Ping Nano Technology Group Ltd. Compounding was carried out at 180 °C with a rotor speed of 60 rpm in a batch mixer (Haeke 40 System). The content of CaCO₃ nanoparticles in PP matrix was 9.2 vol%.

Microscopy and Toughening Mechanism. Optical microscopy (OM) and transmission electron microscopy (TEM) were employed to observe the morphology and to determine the toughening mechanisms of the nanocomposite after the impact tests. The impact damage zones were cut along the crack propagation direction but perpendicular to the plane of fracture surface using a diamond saw. The plane-strain core regions of the damage zone were prepared for OM and TEM observations.

Results and Discussion

The DN-4PB technique is one of the most effective ways of generating a subcritical crack tip damage zone [3]. The key toughening mechanism(s) and the sequence of toughening events can be unambiguously identified in the arrested crack tip damage zone region using a variety of microscopy techniques.

When OM is conducted, massive crazing (Figure 1a) and birefringent plastic deformation (Figure 1b) around the arrested crack tip are observed. The intensive plastic deformation is evidenced by the presence of a birefringent zone encapsulated by a larger light scattering cavitation zone, indicating that shear yielding mechanism occurs along the crack wake. TEM study is further employed to confirm the above conjecture.

Figure 1. OM of DN-4PB Charpy impact damage zone of PP/CaCO₃ nanocomposite: (a) bright field and (b) cross-polarized field. The crack propagates from left to right.

To learn about the early stages of the toughening process, it is necessary to investigate the damage feature far away from the crack tip, but inside the damage zone. TEM observation at about 120 µm above the crack tip region has been made and found the presence of small, but widespread crazes (Figure 2a). Interestingly, these crazes appear to be initiated by the CaCO₃ nanoparticles. This indicates that the CaCO₃ nanoparticles act as effective stress concentrators, which help trigger craze formation and growth.

In the region at the transition between the light-scattering craze zone and the birefringent shear banding zone, the crazes appear to be more diffuse and slightly distorted (Figure 2b). However, no sign of CaCO₃ nanoparticles debonding is observed in this region.

To check whether or not possible debonding of CaCO₃ nanoparticles from the PP matrix has taken place, TEM micrographs were taken immediately below the fracture surface near the crack tip (Figure 2c). The crazes were further smeared by the shear banding process, making the crazes even more defused and less well-defined. Careful observation reveals that some of the CaCO₃ nanoparticles have debonded from the PP matrix (See arrows in Figure 2c). For reference, the morphology of the intact, undeformed PP/CaCO₃ is shown in Figure 2d.

Figure 2. TEM of DN-4PB charpy impact-tested PP/CaCO₃ specimen taken from (a) 120 µm above the crack surface, (b) 60 µm above the crack surface, (c) immediately above the crack surface and (d) undamaged region. The arrow indicates the crack propagation direction.

It should be noted that judging from the fact that the crazes are initiated near the equatorial region of the CaCO₃ nanoparticles and/or their small aggregates, particle-matrix debonding and/or splitting of aggregated nanoparticles should have taken place before the formation of crazes. This is simply because the maximum stress concentration site around an inclusion is located at the equatorial region if the inclusion phase is softer than the matrix phase. Since the CaCO₃ nanoparticles are much harder than the PP matrix, the CaCO₃ nanoparticles should have been debonded and/or split between the aggregated particles before the crazes were initiated.

The present study shows that debonding and splitting of the aggregated CaCO₃ nanoparticles, which lead to massive crazing in PP, have helped trigger crack tip shear banding of PP matrix. The impact strength of PP is thus significantly improved. In addition, it is possible to use nanometer-sized rigid filler to toughen PP matrix and in the meantime increase the modulus of PP.

Conclusions

The effect of CaCO₃ nanoparticle on the morphology and toughening mechanisms of PP nanocomposite were investigated using OM and TEM techniques. It is clearly observed that the incorporation of CaCO₃ nanoparticles positively altered the toughenability in PP matrix. In this study, the main toughening mechanisms of the PP/CaCO₃ nanocomposites, massive crazing, followed by shear banding of the matrix.

Reference