MECHANICAL PROPERTIES AND FRACTURE MECHANISMS OF Al_2O_3/POLYPROPYLENE NANOCOMPOSITES

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ABSTRACT

The key objectives of this investigation are to study the fracture characteristics and identify the fracture mechanisms of spherical alumina (Al_2O_3) nanoparticle filled polypropylene (PP) composites. Nanocomposites containing 1.5, 3.0 and 5.0 wt% of Al_2O_3 particles (average diameter ~ 47 nm) were prepared for investigation. The Al_2O_3 nanoparticles were pre-treated with silane coupling agent before melt blending with PP matrix. Tensile test shows that both Young's modulus and tensile yield strength increase with the particle content. This suggests that the interaction between the nanoparticles and the PP matrix is strong enough so as to restrict inter-molecular sliding and subsequent yielding in the localized scale. Under quasi-static loading rate, the fracture toughness (G_C) was found to be insensitive to filler content. Using the SEDN-4PB specimens, numerous microcracks were observed to form around the sub-critical crack tip. Under impact loading rate, fracture toughness of the nanocomposites were evaluated by the Izod impact test and the impact G_C value. Both techniques indicate the impact fracture toughness increased initially with the addition of 1.5 wt% of Al_2O_3 nanofillers into the PP matrix. However, with the further addition of up to 3.0 and 5.0 wt% nano-Al_2O_3, both Izod impact strength and impact G_C decreased slightly. Considering the small size of Al_2O_3 nanoparticles, their roles in the fracture mechanisms need to be studied by means of transmission electron microscopy (TEM). This part of work is currently in progress and will be presented in due course.

1 INTRODUCTION

With the addition of nano-size rigid fillers into polymer matrices, it is possible to achieve dramatic properties improvements that cannot be achieved with micron-size fillers. In general, as only relatively low levels of nano-fillers are needed, conventional melt processing methods can be conveniently adopted to process the nanocomposites. For the successful application of nanocomposites, an acceptable level of fracture resistance is needed. Some research studies showed the toughening offered by nano-particle additions [1], while other studies showed that the addition of nano-fillers de-toughened the polymer matrices [2]. The toughness of composite

materials are generally determined by a number of factors, such as the intrinsic features of fillers and polymers, the interfacial characteristics between filler and matrix, and the degree of filler dispersion.

In this research study, the focus is to study the fracture characteristics of spherical alumina (Al_2O_3) nanoparticles filled polypropylene. The reason of using spherical filler particles is to simplify the effect due to filler orientation which exist in fibre (carbon nanotube) [3] or plate-like filler (nanoclay) [2] filled composites. As the filler/matrix interfacial bonding and filler dispersion are crucial for the final composite performance, different surface treatments will be applied to the alumina nanofillers. In this paper, some preliminary results on using silane surface treatment will be reported.

2 EXPERIMENTAL

2.1 Sample preparation

Spherical alumina (Al_2O_3) nanoparticles with average diameter of 47 nm (NanoTek®, Nanophase Co.) were used in this study. The particles were supplied in the non-treated state, and were therefore surface treated with silane coupling agent (A-187, Cromton Co.). The silane treated alumina nanoparticles were melt blended with a commercial grade of polypropylene (Pro-fax 6331) using a Brabender twin screw extruder. The extrudates were pelletized and injection moulded into ASTM type-I tensile bars. Al_2O_3/PP nanocomposites containing 1.5, 3.0 and 5.0 wt% of fillers respectively were prepared for investigation.

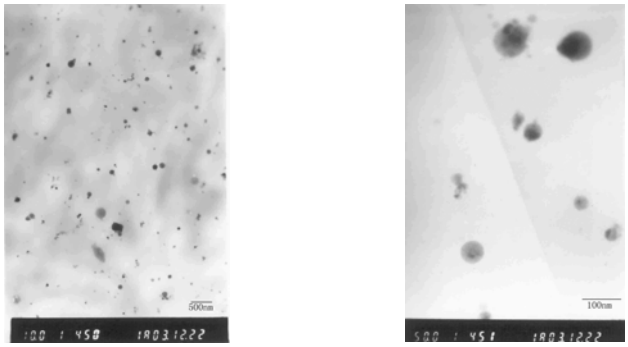
2.2 Characterization and measurements

The melting behaviour of the nanocomposites was studied by differential scanning calorimetry (DSC 2910, TA Instruments), from which the crystallinities were calculated. The *heat distortion temperatures* (HDT) of the nanocomposites were determined from storage modulus *versus* temperature plots as explained in reference [4]. The storage moduli were measured by a dynamic mechanical analyzer (DMA 2980, TA Instruments) in the temperature range of -60 to 120 ^{0}C. Tensile tests and fracture toughness measurements were carried out using a universal tensile tester (Model 4206, Instron) at a cross head speed of 10 mm/min (quasi-static rate). Fracture toughness measurements were carried out using the single-edge-notched three point bending (SEN-3PB) geometry. As the load-displacement curves indicated the samples failed in linear elastic manner, the critical strain energy release rate (G_C) for the nanocomposites were determined according to LEFM approach [5]. For the study of deformation mechanisms at the crack tip region before catastrophic crack growth, the single-edge-double-notched four point bending (SEDN-4PB) specimens were used [6]. Due to the unstable nature of the propagated crack, damages ahead of the non-propagated crack can be preserved. The impact resistance was characterized by the Izod impact test and the impact G_C. A pendulum impact tester (Ceast Code 6545/000) was used for the measurement.

3 RESULTS AND DISCUSSION

3.1 Microstructure and crytallinity

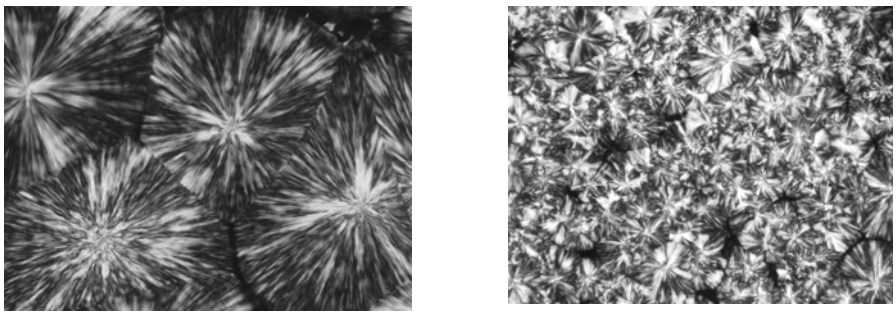
Fig.1 shows the TEM micrographs of an Al_2O_3/PP nanocomposite containing 1.5 wt% of Al_2O_3. From the high magnification micrograph (Fig. 1b), it can be seen that the Al_2O_3 particles are close to spherical particles, but their sizes are not monodisperse. The low magnification micrograph (Fig. 1a) shows that the nanoparticles are well dispersed in the PP matrix.



(a) (b)

Fig. 1 TEM micrographs for Al_2O_3/PP nanocomposite containing 1.5 wt% nanofillers. (a) Low magnification (×10,000); (b) High magnification (×50,000)

From DSC measurements, the crystallinity for the PP homopolymer and the different nanocomposites were about 50%. The incorporation of the nanofillers does not seem to have any effect on the PP crystallinity. Chan et al. [1] also observed that with the addition of up to 13 vol% of nano-$CaCO_3$, the crystallinity of the PP matrix has not been changed significantly. On the other hand, the nano-Al_2O_3 particles provide numerous nucleation sites upon cooling from the melt. This gives dramatic reduction in the spherulite sizes found in the nanocomposites (see Fig. 2).



(a) (b)

Fig. 2 Polarizied TOM photos for (a) PP homopolymer and (b) nanocomposite with 3.0 wt% Al_2O_3 nanoparticles

3.2 Mechanical properties and fracture characteristics

The tensile modulus and tensile yield strength of the nanocomposites are shown in Fig. 3. It can be seen that both tensile modulus and the tensile yield strength increase to some extents with the particle content. It is well known that for particulate microcomposites with poor interfacial bonding, the tensile yield strength will be reduced compared to the unreinforced matrix [7]. Therefore, the observed tensile yield strength improvement indicates that the silane surface treatment provides an acceptable level of interfacial bonding between the Al_2O_3 nanoparticles and the PP matrix.

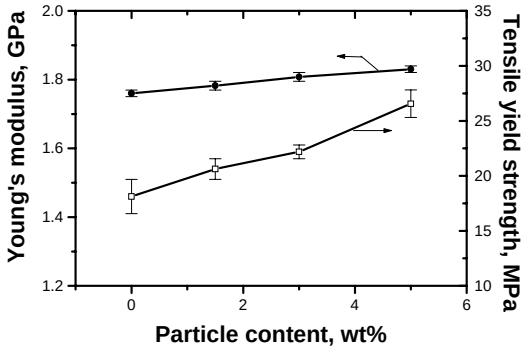


Fig. 3 Effect of nanofiller content on the tensile properties of Al_2O_3/PP nanocomposites

The HDT values for the nanocomposites are shown in Fig. 4. It can be seen that increasing the nanoparticle concentration bring about a gradual increase in HDT.

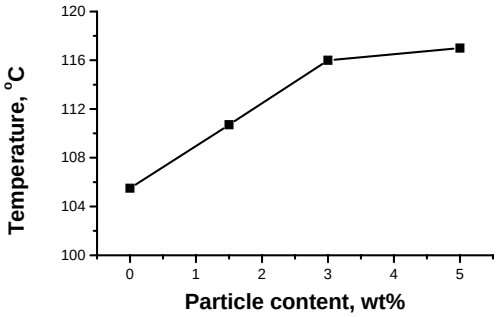


Fig. 4 Effect of nanofiller content on HDT of Al_2O_3/PP nanocomposites

Under quasi-static SEN-3PB loading, the load-displacement curves for virgin PP and the nanocomposites are linear elastic up to unstable crack growth. The quasi-static G_C values (which will be called simply as G_C in following discussions) are shown in Fig. 5. Basically, G_C is not

sensitive to the incorporation of the nano-Al_2O_3 particles. Transmission optical microscopy (TOM) technique was used to study the sub-critical crack tip deformation of the SEDN-4PB specimens. The TOM image for a 1.5wt% Al_2O_3/PP nanocomposite is shown in Fig. 6. It is found that numerous crazes and microcracks were formed adjacent to the sub-critical crack. The fine details of these crazes and microcracks are currently under investigation by using TEM technique. Other than these dilatational features of deformation, one would also like to determine if deformation by shear banding has taken place. Although shear bands have birefringence features under cross polarized OM [8], the presence of the spherulitic structure in PP matrix obscured the birefringence feature of the shear bands.

The Izod impact strength and the impact G_C values are also shown in Fig. 5. In contrary to the quasi-static G_C measurement, well defined "*impact toughening*" was introduced by the Al_2O_3 nanoparticles, irrespective of the impact testing methodology. The Izod impact strength is higher than the impact G_C values for the corresponding nanocomposites. This may be attributed to the use of sharp cracks and blunt cracks in the impact G_C and Izod impact specimens respectively.

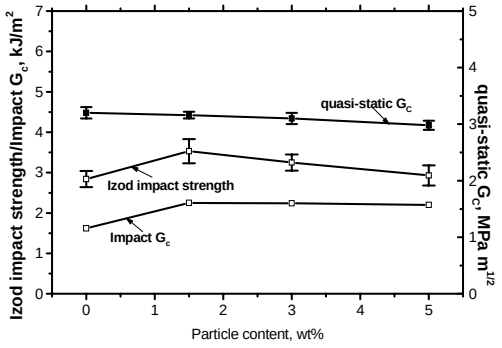


Fig. 5 Effect of nanofiller content on quasi-static *Gc*, impact *Gc* and Izod impact strength of Al_2O_3/PP nanocomposites

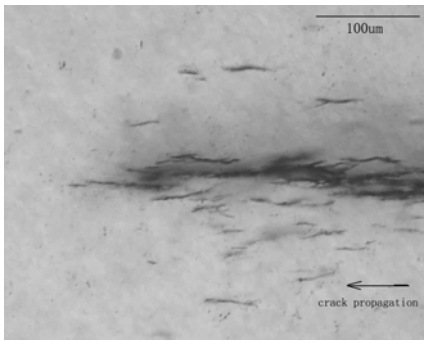


Fig. 6 TOM micrograph showing damages at the arrested crack tip of a SEDN-4PB specimen. The nanocomposite contains 1.5 wt% of Al_2O_3 particles.

4 CONCLUSIONS

The Al_2O_3 nanoparticles were well dispersed in the PP matrix by melt compounding method after particle surface treatment with silane coupling agent. Both Young's modulus and tensile yield strength values are improved, indicating the interaction between the two components is strong enough to restrict the macromolecular shear yielding. By SEDN-4PB technique, some craze like damages and microcracks can be observed adjacent to the crack tip damage zone where only stable crack propagation takes place. Further work on fracture mechanisms of Al_2O_3/PP nanocomposites is now under investigation.

5 ACKNOWLEDGEMENT

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6 REFERENCE

1. Chan CM, Wu JS, Li JX, Cheung YK, Polypropylene/calcium carbonate nanocomposites, Polymer, 43, 2981-2992, 2002
2. M. Alexandre and P. Dubois, Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials, Mater. Sci. Engng. R, 28, 1-63, 2000.
3. G.M. Odegard, T.S. Gates, K.E. Wise, C. Park and E.J. Siochi, Constitutive modeling of nanotube-reinforced polymer composites, Compos. Sci. Tech., 63, 1671-1687, 2003.
4. J.J. Scobbo, Jr., Thermomechanical performance of polymer blends, in Polymer Blends, Volume 2: Performance, D.R. Paul and C.B. Bucknall, eds., John Wiley & Sons (2000).
5. Tam WY, Cheung T, Li RKY, An investigation on the impact fracture characteristics of EPR toughened polypropylene, Polymer Testing, 15, 363-379, 1996.
6. H.-J.Sue, A.F.Yee, Study of fracture mechanisms of multiphase polymers using the double-notch four-point-bending method, J.Mater.Sci, 28, 2975-2980, 1993
7. Zuiderduin WCJ, Westzaan C, Huétink J, Gaymans RJ, Toughening of polypropylene with calcium carbonate particles, Polymer, 44, 261-275, 2003
8. J.Lee, A.F.Yee, Role of inherent matrix toughness on fracture of glass bead filled epoxies, Polymer, 41, 8375-8385, 2000

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