FATIGUE CRACK PROPAGATION OF INORGANIC NANOPARTICLE FILLED POLYAMIDE 6,6

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ABSTRACT

Polymeric nanocomposites are very promising materials for various applications. Major specific feature of polymeric nanocomposites is their huge interfacial surface area. Low strain rate (long duration) tests, e.g. creep and fatigue, are very sensitive to changes in the interphase and bulk properties, which have been concentrated recently by the authors' group. In the present study, fatigue crack propagation of TiO_2 nanoparticles filled polyamide 6,6 (PA6,6) were conducted under cyclic tension-tension tests at a given stress amplitude. The fatigue crack growth rate at the same stress intensity amplitude was significantly reduced by the incorporation of only 1vol.% 21nm TiO_2 particles. It is assumed that nanoparticle-induced molecular and morphological immobilisation may contribute positively to the resistance of fatigue crack propagation.

1 INTRODUCTION

Polymeric nanocomposites are very promising materials for various applications [1-5]. Major specific feature of polymeric nanocomposites is their huge interfacial surface area. As a consequence the interface/interphase properties may become the dominant parameters of the macroscopic response of polymer nanocomposites. The structure of polymer nanocomposites is very complex as it covers the aspects in different scales, including dispersion state of nanoparticles, changes in molecular and macro-molecular level in the matrix, interphase formation between surfaces of nanoparticles and bulk materials. Most characteristics are interrelated. It is considered that aspects of polymer physics may dominate in low frequency mechanical tests (creep and fatigue), whereas in case of high frequency loading (dynamic and impact) the use of continuum mechanics seems to be straightforward [5].

In general, few literatures can be found on the low strain rate yield, creep and fatigue behavior of polymer nanocomposites, as reviewed recently by Karger-Kocsis and Zhang [5]. However, these long duration tests are very sensitive to changes in the interphase and bulk properties. Studying the temperature and strain rate sensitivity of organoclay modified PA6 and PP nanocomposites, Mallick and Zhou [6] found that the Eyring equation works well also for these composites. Bellemare et al [7] concluded that the fatigue life of organic clay/PA6 composites depended on whether the cyclic tension-tension tests were performed at a given stress or strain amplitude. Unexpectedly, the resistance to fatigue crack propagation decreased in the presence of organoclay. This is at odds with the effect of short fibre reinforcement in thermoplastics, to which clays are often compared. The increase in the fatigue crack growth rate at the same stress intensity amplitude was attributed to enhanced micro-void formation ahead of the crack tip. Recently, Zhang et al [8] carried out one of the unique improvements, an enhanced creep resistance in polyamide with a very low volume fraction of inorganic nanoparticles. It was found out that the TiO_2 nanoparticles contributed to a remarkable reduction of the creep rate under various constant loads. It is assumed that the nanoparticles restrict the slippage, reorientation and motion of polymer chains. In this way, they influence the stress transfer on a nanoscale, which finally results in these improvements.

In the present study, fatigue crack propagation (FCP) of TiO_2 nanoparticles filled polyamide 6,6 (PA6,6) were conducted under cyclic tension-tension tests at a given stress amplitude.

Nanoparticle-induced molecular and morphological immobilisation may contribute positively to the resistance of crack propagation. Further studies are still on the way, by considering various nanoparticles, e.g. SiO_2, Al_2O_3, nanoclay, filled PA6,6 at different fatigue conditions. These results are expected to be reported on the ICF XI in 2005.

2 EXPERIMENTAL

A commercial Polyamide 6,6 (DuPont, Zytel 101) was considered as a matrix material. TiO_2 particles (a white, dry powder of Degussa P25) were applied as fillers with a density of 4 g/cm^3 and a diameter of 21 nm. The volume content was in the range of 1 to 3 %.

Nanocomposites were compounded using a Berstorff twin-screw-extruder (screw diameter=25 mm, screw aspect ratio L/D=44). Compounding was carried out at a barrel temperature of 292°C, a screw speed of 150 rpm, and a finial extrusion rate of 9 kg/hour. PA6,6 was dried in a vacuum oven at 70°C for a minimum of 24 hours before extrusion. Other processing parameters were also optimised in order to achieve a fine nanoparticle distribution in the matrix. In order to precisely control the filler content of nanoparticles, commercial K-Tron weight-controlled feeders were applied. After cooling by water bath, the extruder blanks were cut as granules with a length in a range of 3 to 5 mm for further injection moulding. The composites were finally manufactured using an Arburg All-rounder injection moulding machine for various specimen sharps, according to different moulds, e.g. plate specimens (80×80×4 mm^3) from which the compact tension (CT) specimens can be cut out. The barrel temperature of the injection-moulding machine was selected to be 295°C. The injection pressure was kept constant at 500 bars, the mould temperature was fixed at 70°C, and a constant injection speed of 80 ccm/s was applied for all specimens. Transmission electron microscopy (TEM) observation displays a satisfactory dispersion of TiO_2 nanoparticles in a melt compounded PA6,6/nano-TiO_2 system as shown in Figure 1 [8].

Fatigue crack propagation (FCP) resistance was carried out by a Schenck Servohydraulic Tester using CT specimen equipped with a crack opening displacement (COD). CT specimens were cut into a dimension of 40×40×4 mm^3, and sharp pre-notches were prepared by razors according to ASTM E647. The cyclic tension-tension fatigue test was performed based on a protocol of ESIS TC4. A maximum load of 160N was applied, and the minimum/maximum load ratio used was 0.2. A sine waveform load was applied with a frequency of 5 Hz. The average incremental crack length (Δa) from a known pre-notch (a) was adopted by the COD monitored during the whole testing duration. The crack growth rate is represented by the derivative, da/dN, of the crack length, a, to the number of fatigue cycles, N. Each test was repeated at least three specimens, and the average results were reported.

3 RESULTS AND DISCUSSIONS

The FCP rate, da/dN, could be related to the stress intensity factor range, ΔK, through the Paris-Erdogan relationship:

$$\frac{da}{dN} = A \cdot \Delta K^m \tag{1}$$

where A and m are material dependent constants. This equation suggests that the FCP rate is a logarithmically linear function of ΔK. At a particular value of ΔK, the higher is the da/dN, the lower the FCP resistance is. Alternatively, the higher is the ΔK for a particular da/dN, the more resistant the material is supposed to be.

Figure 2 presents the FCP rate versus applied stress intensity factor range curve measured at room temperature for both neat PA6,6 and nanocomposite with 1 vol.% nano-TiO_2. It is clear that the FCP rate at the same stre

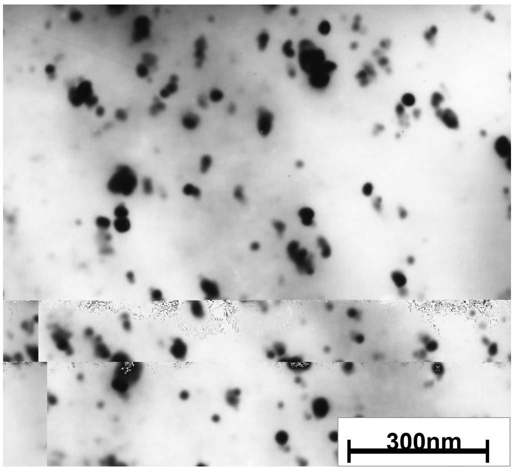

Figure 1 TEM picture taken of a PA6,6/TiO_2 (21 nm, 2 vol.%) nanocomposite produced by melt compounding in a twin-screw extruder.

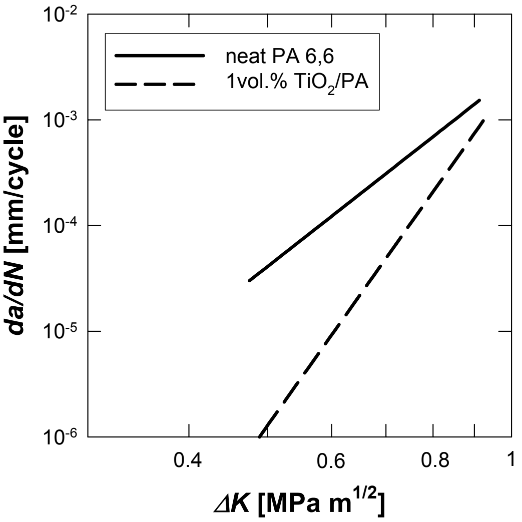

Figure 2 Fatigue crack growth speed versus applied stress intensity factor range curve of neat PA6,6 and nanocomposite with 1 vol.% TiO_2 (21nm). Maximum load=160N, R=0.2, and frequency=5 Hz.

Fitting by the equation 1, *A* and *m* can be obtained for various materials, respectively. For neat PA 6,6, *A* is 1.7×10^{-3} and *m* is 6, whereas for nanocomposite, the curve is much steeper and the *m* increases to 11, and *A* is 2.7×10^{-3}. The fatigue life of notched specimens were enhanced more than 5 times, i.e. from 5×10^4 cycles of neat polymer to 2.8×10^5 of nanocomposite.

SEM image shows a typical fatigue fracture surface at the crack tip of a pre-notched PA6,6 specimen (cf. Figure 3a). It can be imaged that after cyclic load application showing crack advance into several crazes. The crack surface is quite smooth as shown in Figure 3b. On the other hand, dimple type fracture surface (cf. Figure 3c) was observed for the nanocomposite studied. The fracture surface was very rough (Figure 3d), which reflects higher energy dispersion under fatigue loading in comparison with neat polymer. In this case, nanoparticle-induced molecular and morphological immobilisation may be responsible for the enhanced FCP rate.

4 CONCLUSIONS

Fatigue crack propagation data showed that 1vol.% TiO_2 nanoparticles affect positively to the resistance of stable crack growth, resulting in reduced fatigue crack propagation rate. It is assumed that nanoparticle-induced molecular and morphological immobilisation may contribute positively to the resistance of fatigue crack propagation. Further studies are on the way, by considering various nanoparticles, e.g. SiO_2, Al_2O_3, nanoclay, filled PA6,6 at different fatigue conditions. The results are expected to be reported on the ICF XI in 2005.

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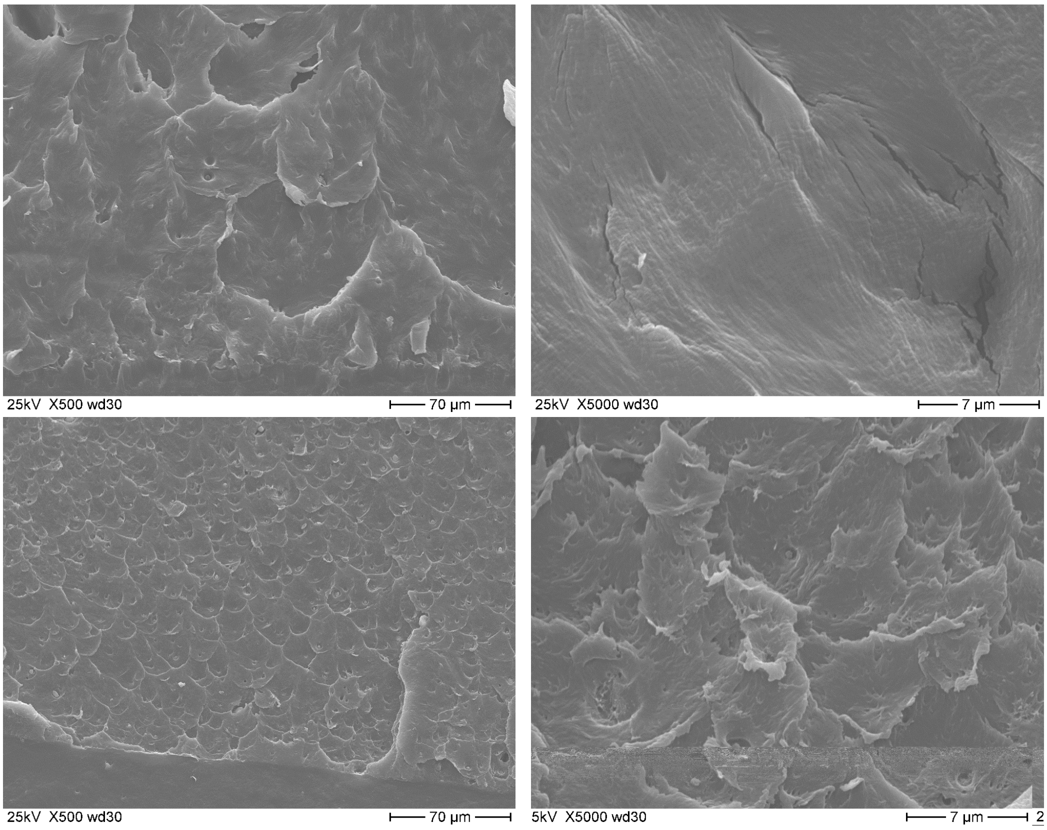

a	b
c	d

Figure 3 SEM fractography of fatigue crack propagation specimens at pre-crack tip region with lower (a,c) and higher (b,d) magnifications, for neat PA6,6 (a,b) and 1vol.% 21nm TiO_2/PA6,6 (c,d).

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