

DEFORMATION MECHANISM OF POLYETHYLENE/CALCIUM CARBONATE NANOCOMPOSITES

M. Mohezenzadeh, S. M. Zebarjad*, M. Mazinani

Dept. of Materials Science and Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

* Corresponding author (Zebarjad@um.ac.ir)

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1. Introduction

Several studies have demonstrated an increase in toughness of polymer matrix using rigid particles. Bartczak *et al.* [1] used calcium carbonate (CaCO₃) filler particles for toughening of HDPE. They found that the Izod impact toughness of HDPE could be improved, depending on the size and loading of CaCO₃ utilized. The jump in HDPE toughness was explained on the basis of Wu's criterion [2]. Combination of particle size and volume fraction of the filler allowed the condition of interparticle ligament thickness below a value of 0.6 μ m. Under these conditions transcrystalline layers around the particles come into contact. These layers exhibit low plastic resistance. When the material percolates through the system, large plastic deformation of interparticle ligaments under impact loading result in a sharp brittle-to-tough transition. Thio *et al.* [3] used CaCO₃ with different particle size. It was found that CaCO₃ particles with an average size of 0.7 μ m improved Izod impact energy of polypropylene. No information was provided regarding the interparticle ligament thickness, neither indication was given for the existence or not of a transcrystallized PP layer around the CaCO₃ particles. The claimed toughening mechanism was plastic deformation of interparticle ligaments, following particle-matrix debonding with additional contribution resulting from crack deflection toughening. The smallest particles agglomerated and the largest particles were irregular in shape and size that led to earlier fracture. Zuiderduin *et al.* [4] investigated the toughening of CaCO₃ filled

polypropylene using a combination of different filler particle size and loading. The maximum improvement of impact strength achieved with stearic acid-treated filler having 0.7 μ m size which agree closely with the results of Thio *et al.* [3] but particle sizes less than 0.7 μ m tended to aggregate and showed very poor dispersion, which had a detrimental effect on impact strength.

In the present study, deformation mechanism of medium density polyethylene/Calcium Carbonate (MDPE/CaCO₃) nanocomposites in the form of films have been investigated. For this purpose, a number of mechanics and microscopy techniques, such as the Essential work of fracture (EWF) technique, transmission optical microscopy (TOM) were employed.

2 Experimental Procedure

Medium density polyethylene HP3840UA with MFI (measured at 190C and 2.16kg) of 4.2 g/10min and a density of 0.937 g/cm³ used as the matrix. Precipitated calcium carbonate nanoparticles were obtained from solvay company, France, under a trade name of social312. The particle sizes were about 70 nm. Fig. 1 shows the transmission electron micrograph of the CaCO₃ nanoparticles used in this study. As it can be seen in this TEM micrograph, particles have an irregular morphology. In order to avoid agglomeration and better dispersion of CaCO₃ nanoparticles in the matrix, the MDPE and CaCO₃ powder were mixed in a mixer mill (Retsch MM400) at pre-selected mass ratio. The mixing was performed

at a frequency of 20 Hz for 10 min. Then, the mixtures were compression molded into films of 0.3 mm thickness at 170 °C and 30 kPa. Deeply double edge notched tension (DDENT) specimens with a total length of $H=110$ mm, with a length between the grips of $h=60$ mm and a width of $W=40$ mm were cut from compression molded films. The notches were made using sharp scissors followed by sharpening with a fresh razor blade. Tensile test on DDENT specimens were performed using a Zwick (Z 250) universal testing machine at room temperature under a constant crosshead speed of 5 mm/min.

In order to investigate the deformation micro-mechanisms, DDENT specimens were tensile loaded, at a constant crosshead speed of 5mm/min, until plastic zones form in front of the crack tips (Fig. 2). After formation of plastic zones, the specimens were unloaded, and the surface of plastic zones evaluated by a transmission optical microscope (TOM), under cross-polarization conditions.

3. RESULTS AND DISCUSSION

The photographs of the fractured MDPE specimen and different nanocomposites are shown in Fig. 3. As can be seen in these photographs, all the specimens have fractured in a fully ductile manner. Furthermore, the well-defined yielding of the regions neighboring the initial ligaments of the specimens can be observed in this series of photographs. The development of macroscopic plastic deformation zones in the nanocomposite samples was different from that of the MDPE. A double plastic zone was observed in the nanocomposite samples. The double plastic zone is schematically illustrated in Fig. 4. The whole plastic zone in this figure consists of an intense outer plastic zone (IOPZ) near the fracture process zone and a diffuse outer plastic zone (DOPZ) slightly away from it, depending upon the intensity of stress whitening in the sample. The contrast in intensity observed in the

plastic zone indicates that different stages of deformation have taken place during fracture experiment [7]. Fig. 5a to 5d show the transmission optical micrographs (TOM) of the plastic zones formed in DDENT samples. The TOM micrographs clearly indicate that extensive plastic deformation have occurred in front of the crack tip. In nanocomposites samples, two distinct regions are visible in front of the crack tip, a dark zone and a diffuse zone that extends out around the dark zone and its area increases with increasing amount of CaCO_3 . The contrast in intensity is due to the differences in the deformation mechanisms within the two zones. The dark zone is called intense outer plastic zone (IOPZ) and the diffuse zone is named diffuse outer plastic zone (DOPZ). The phenomenon of double plastic zone has already been reported by other authors [4-6]. In the case of ethylene-propylene block copolymer [6], the spherical micro-voids produced in the DOPZ because of the presence of ethylene phase. However they elongated and coalesced with neighboring voids in the IOPZ that resulted in different extent of stress whitening between IOPZ and DOPZ.

The concentration of localized stress near the fracture process zone is higher than that in the region away from this region. Beyond the fracture process zone, DOPZ was observed where the stress concentration is comparatively lower. This is probably the reason for the formation of double plastic zone in these nanocomposite samples. As can be clearly seen in Fig. 5, the size of DOPZ depends on the CaCO_3 content in the composite samples. The higher CaCO_3 content has resulted in a larger DOPZ since the number of stress concentration sites increases considerably within the matrix with increasing filler content. At approximately the end of the linear elastic region, the DOPZ has been formed without having consumed a noticeable amount of plastic work. On the other hand, the formation of the IOPZ has taken place during the whole fracture experiment during

which it has expanded into the previously formed DOPZ [7]. The formation of double plastic zone has been previously reported for the case of Ethylene-Propylene block copolymer [7,8], Polypropylene-EPDM rubber blends [9], and PP/CaCO₃/PP-g-MAH composites [10]. The occurrence of this phenomenon has been attributed to the elongation and coalescence of microvoids which increase the intensity of stress-whitening in the IOPZ [8].

4. CONCLUSION

The EWF approach was successfully used to characterize the fracture behavior of the medium density Polyethylene (MDPE) as well as that of the composite samples when 1, 2.5 and 5wt.% CaCO₃ nanoparticles are added to MDPE. It was shown the CaCO₃ nanoparticles added into the MDPE matrix in all quantities to decrease the specific essential work of fracture. This detrimental effect of CaCO₃ nanoparticles was attributed to the introduction of a certain number of stress concentration sites within the matrix and the fact that the situation becomes much more severe when greater amounts of nanoparticles are added to the composite giving rise also to increase the chance of particles agglomeration during the manufacture of test specimens.

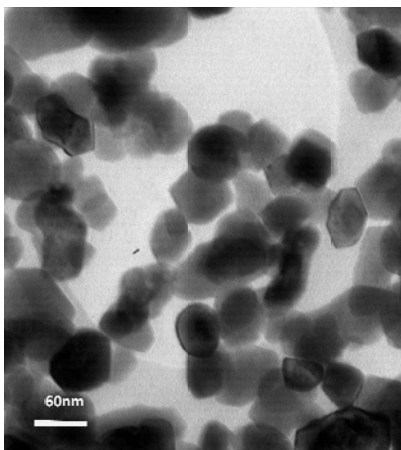


Figure 1: Transmission electron micrograph showing the nano sized CaCO₃ particles

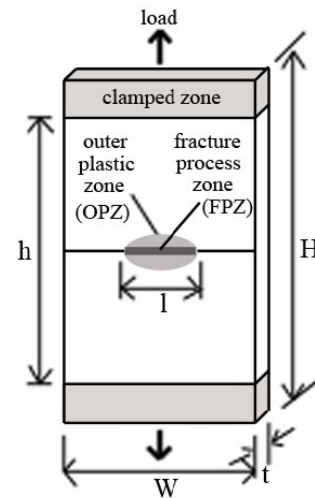


Figure 2: DDENT sample used for EWF tests

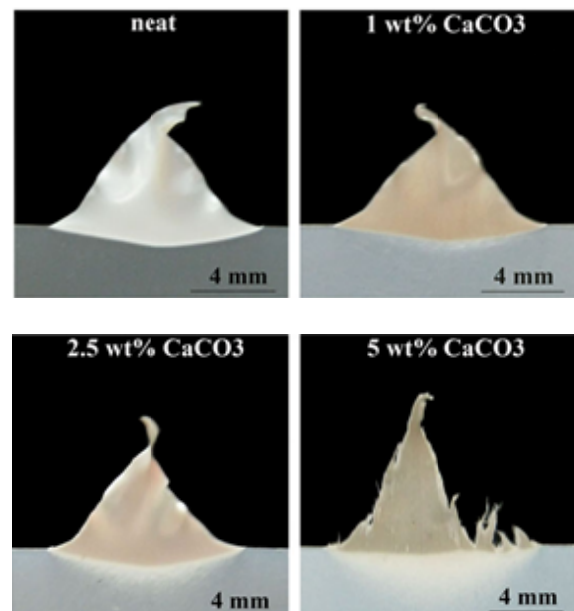


Figure 3: Fractured specimens during EWF fracture experiments; MDPE, and composites with 1, 2.5 and 5 wt.% CaCO₃

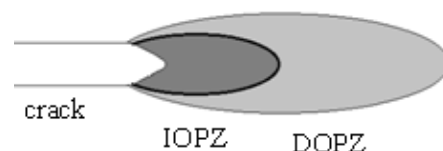


Figure 4: Schematic illustration of a double plastic zone (DPZ) consisting IOPZ and DOPZ

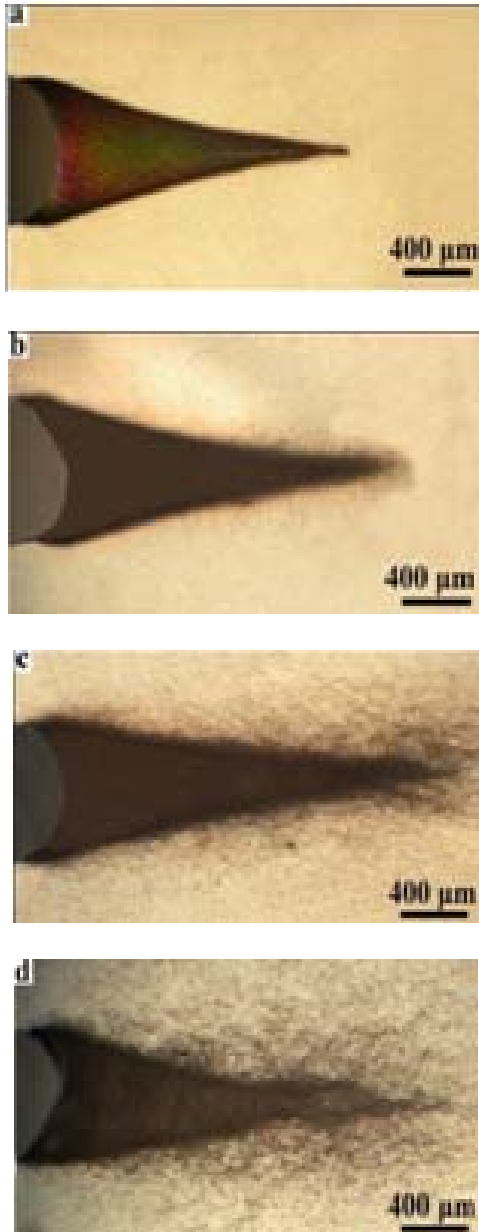


Figure 5: TOM micrographs of the plastic deformation zones in front of the crack a)MDPE, b)MDPE-1, c)MDPE-2.5 d)MDPE-5.

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