Creep Resistance of Polyethylene-based Nanocomposites

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***Abstract*—The purpose of this work is to investigate the effects of carbon black (CB), carbon nanotubes (CNTs) and nanoclay sheets addition on the creep behavior of polyethylene-based nanocomposites synthesized with an in-house processing method. A blend of 75 wt.% UHMWPE and 25 wt.% HDPE, abbreviated to U75H25, was used as the hybrid PE matrix to accommodate the nanofillers. A 0.5 wt.% of CB, CNTs or nanosheets clay was embedded separately into the blend matrix in order to improve the creep resistance. The scanning electron microscope (SEM) and transmission electron microscope showed that the nanofillers were homogeneously dispersed in the U75H25. The addition of just 0.5 wt.% nanoclay resulted in a significant increase in the creep resistance of the polyethylene blend. Conversely, the addition of CB or CNTs caused a reduction in the creep resistance. The embedding of CNTs into the matrix resulted in creep behavior almost close to the creep behavior of pure UHMWPE. The Burger's model was employed to understand the effect of the nanoparticle addition on the creep mechanism.**

Keywords-UHMWPE; HDPE; polymer; creep; nanocomposite; polyethylene

I. INTRODUCTION

Polyethylene (PE) is the most widely used thermoplastic because of its outstanding mechanical properties, such as moisture absorption, chemical resistance, high toughness and ease of processing [1]. It was found that the incorporation of various nanofillers can lead to a significant improvement in the polyethylene composite properties which can be used in many applications such as packaging, electrical and thermal energy storage, automotive, and biomedical [1-6]. Recently, new polyethylene nanocomposites have been developed with the use of various processing methods, different types, and amounts of reinforcements [7-16]. These nanocomposites can be a cost-effective alternative to the high cost advanced composites and can be widely used in various industrial applications [1]. However, achieving uniform dispersion of the nanoparticles is still an important scientific and technological challenge in nanocomposite fabrication. Poor dispersion of the nanofillers, weak interaction between the filler and the matrix, and agglomeration can lead to the reduction of the mechanical properties [9]. In [10], it was found that the embedding of MWCNT and nanoclay into the polyethylene matrix increased significantly hardness, elastic modulus and indentation resistance of polyethylene-based nanocomposites. In this work, different types of nanofillers with different geometric shapes were used in order to improve the creep resistance of the UHMWPE/HDPE. The volume of fractions was kept at low percentage to minimize the effect of agglomeration, especially for CB and CNT. The creep response was analyzed using the Burger's model.

II. EXPERIMENTAL WORK

A. Materials

The materials tested in this study were UHMWPE/HDPE blended polymers with various nanofillers. Nascent UHMWPE powders (Sabic®UHMWPE3548) were purchased from SABIC, having an average molecular weight of 3×106mol/g. HDPE powders (ExxonMobil TM HDPE HMA014) were purchased from ICO Ltd. Carbon black (CB) powder with the commercial product name, black pearls ® 4040 (BP4040) and average particle diameter of 28nm was provided by Cabot Corporation. Natural hectorite nanoclay was supplied by Elementis specialties. Multi-wall Nanotubes (MWNT) with diameters in the range of 5nm to 50nm, were provided by Nanocyl. Butylated hydroxytoluene and Tris (nonylphenyl) phosphate, supplied by Sigma-Aldrich, were used as primary and secondary antioxidants, to maintain the long term thermal stability and melt processing stability, respectively.

B. Processing

An in-house pre-mix technology was used to incorporate the nanofillers into the UHMWPE and HDPE powders. A twin-screw extruder was then used to blend the UHMWPE and HDPE powders pre-mixed with 0.5wt.% of CB, carbon nanotubes (CNT) or nanoclay to form nano-filled UHMWPE/HDPE composites. A blend of 75wt.% UHMWPE and 25wt.% HDPE, abbreviated to U75H25, was used as the hybrid PE matrix to accommodate the nanofillers. During processing, the mixing temperature was controlled using five zones from feeding port to die, the processing parameters are shown in Table I. Compression moulding was used to mould the nanocomposite materials. The raw material was placed into a mould (100mm×100mm×1.65mm), and then heated to 190ºC, which is higher than the melting point of the composite (approximately 135ºC). Various mould pressures (154, 232,

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309, and 386MPa) were studied in order to optimize material properties such as hardness and crystallinity. Various holding times at maximum pressure (10, 15 and 30min) were also used to identify the most appropriate moulding parameters. The optimal moulding pressure and holding time were 309MPa and 15min respectively, which resulted in the highest values of hardness and crystallinity. After compression moulding, the mould was cooled to room temperature with the use of water. Then, the specimens were cut from the plaques into a dumbbell shape using a die punch cutter with the following dimensions: 75mm overall length, 25mm length of narrow parallel-sided portion, 12.5mm width at the ends, 4mm width of narrow portion and 1.65mm thickness.

TABLE I. PROCESSING METHOD PARAMETERS

Extruder Speed (rpm)	Processing Temperature (ºC)					
	Zone 1	Zone 2	Zone 3	Zone 4	Die	Cooling
190	220	250	260	270	280	water

C. Mechanical Testing and Characterization.

In order to characterize the nanofiller dispersion and the microstructure of the U75H25 nanocomposites, several experimental techniques were used. These included differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). DSC, (TA instruments, Shimadzu DSC60) was used to analyze the effect of different compression moulding parameters and nanofiller types on the crystallinity of the blend and nanocomposites. The specimens, with average mass of 5±0.2mg, were sealed in aluminium pans and heated from 20ºC to 180ºC at a rate of 10ºC per minute. The mass fraction degree of crystallinity was then determined by comparing the heat of fusion with that for fully crystalline polyethylene at the equilibrium melting point (290kJ/kg) [17]. The surface morphology was investigated using a LEO 440 SEM from Leo Electron Microscopy Ltd and Philips XL30 ESEM-FEG from FEI Company. The dispersion of the nanofillers was studied after fracturing the samples in liquid nitrogen, and then coating them using platinum. A JEOL 2000FX TEM from JEOL Ltd. was used to analyze the dispersion of nanofillers into the blend matrix. Tensile creep tests were carried out using an Instron 3366 tensile testing machine from Instron Corporation) at room temperature (22±2ºC).

D. Burger's Model.

Creep modeling and analysis is important to determine time response, which leads to understanding chain dynamics. The Burger's model, which is a combination of Kelvin-Voigt and Maxwell elements, is the most used model to describe the linear viscoelastic behavior of composites. The total strain as a function of time can be obtained from (1) [18]:

$$\varepsilon_B = \frac{\sigma}{E_M} + \frac{\sigma}{E_K}\left(1 - e^{-t/\tau}\right) + \frac{\sigma}{\eta_M} t \quad (1)$$

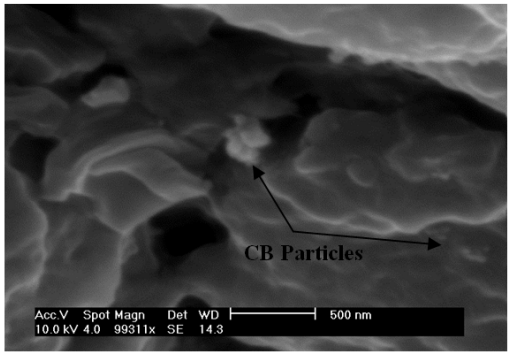
where E_M and η_M are the elastic and viscous components of Maxwell model, $\tau=\eta_K/E_K$ is the retardation time taken to produce 63.2% of the total deformation in the Kelvin unit, η_K and E_K are elastic and viscous components of Kelvin model.

III. RESULTS AND DISCUSSION

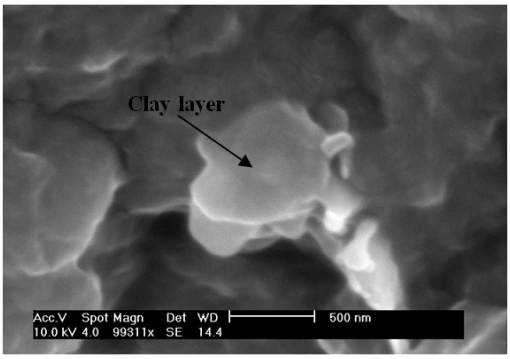
A. Nanofillers Dispersion

Figure 1 shows the SEM images for the microstructure of U75H25/nanofillers. It can be seen that CB, nanoclay and CNTs are dispersed homogenously in the U75H25 matrix. However, small agglomeration of the CB nanofillers can be observed, which can lead to a reduction of load carrying capacity between CB and the polymer matrix. Similarly, these CB nanofillers agglomerations have been observed in the TEM image, as seen in Figure 2(a). Moreover, Figure 1(c) shows good dispersion of CNTs into the polyethylene matrix. Single clay nanosheet and CNT can be seen in Figures 2(b) and 2(c), respectively. This indicates a uniform distribution of both clay nanosheets and CNTs into the blend matrix.

(a)



(b)



(c)

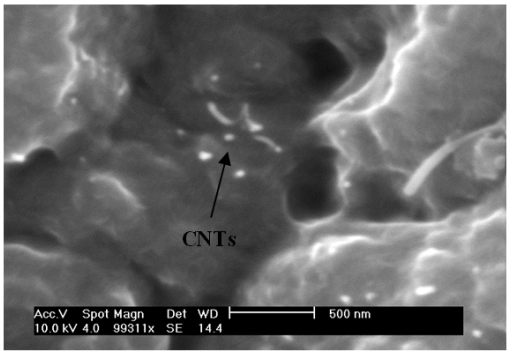


Fig. 1. SEM images for the microstructure of (a) U75H25-0.5wt.%, (b) U75H25-0.5wt.% clay, and (c) U75H25-0.5wt.% CNTs

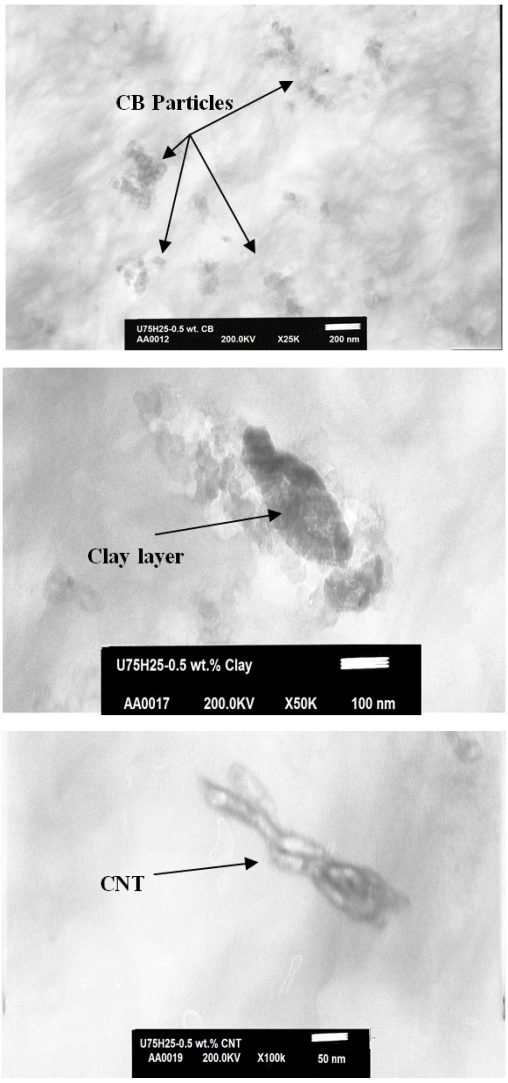


Fig. 2. TEM images for the microstructure of (a) U75H25-0.5wt.%, (b) U75H25-0.5wt.% Clay, and (c) U75H25-0.5wt.% CNTs

B. Thermal Analysis

Table II presents the DSC results for U75H25 and its nanocomposites. It can be seen that the addition of 0.5wt.% CB nanoparticles has no effect on crystallinity, however crystallinity is increased significantly with the addition of 0.5wt.% clay nanosheets. The incorporation of 0.5wt.% CNTs resulted in a slight reduction in the crystallinity value. These changes in the crystallinity values can be attributed to the effect of nanofiller shapes and the interaction between the nanofillers and the polyethylene matrix.

TABLE II. THERMAL PROPERTIS OF HDPE-BASED NANOCOMPOSITES

Materials	Crystallinity %
UHMWPE	53.3
U75H25	55.3
U75H25-0.5wt.% CB	55.2
U75H24-0.5wt.% Clay	69
U75H25-0.5wt.% CNT	50

C. Tensile Creep Results

Figure 3 shows the effect of the blending of HDPE on the creep resistance of UHMWPE and the effects of the addition of nanofillers on the creep resistance of U75H25 blend. It can be seen that blending 25wt.% of HDPE with 75wt.% UHMWPE resulted in an increase in the creep resistance by 32%. This can be proposed to the influence of HDPE chains and spherulite properties on the mobility during creep. The viscoelastic behavior in semi-crystalline polymers such as UHMWPE and HDPE is a combination of crystalline and amorphous phase's mobility and the changes in these microstructures can lead to significant variation in the polymer properties. The addition of CB and CNTs nanofillers resulted in a reduction in the creep resistance of the U75H25 blend. This can be attributed to the agglomerations of the nanofillers, which lead to a reduction in the surface to volume ratio and apply as defects in the microstructure. Polyethylene is a nonpolar polymer; therefore, the interaction between the nanofillers and the polyethylene matrix is almost weak. This can affect the effectiveness of load transfer between the matrix and the nanofiller, which then affects mechanical properties. However, the addition of 2D plate-like nanofillers showed a significant improvement in the creep resistance of the polyethylene blend. The addition of only 0.5wt.% of clay nanosheets resulted in 22% increase in the creep resistance. This can be attributed to the good dispersion, interaction between nanoclay and polyethylene matrix, the increase in crystallinity and the plate-like shape of nanoclay.

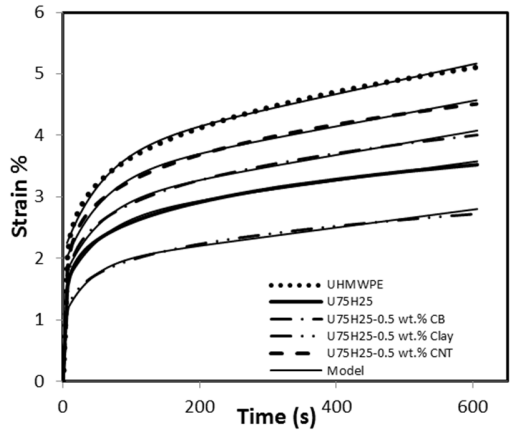


Fig. 3. Effect of GNSs addition on the micro-hardness values.

D. Constitutive Modeling

As shown in Figure 3, curves fitting are in a satisfactory agreement with the experimental data. The data were fitted to the Burger's model, all parameters being obtained by minimizing the sum of the squared differences between the actual and calculated strains, using the solver in Excel. Table II shows the Berger's model parameters that indicate an increasing in the values with blending 25wt.% HDPE with 75wt.% UHMWPE. Further increasing can be observed with the addition of plate-like clay nanosheets. The elasticity E_M and the stiffness of the amorphous phase E_K of the blend have increased by 32% by the addition of nanoclay. The parameter η_M represents the irrecoverable creep strain, which also

increased with the addition of nanoclay. This indicates that a reduction in the dashpot flow can occur, which leads to a reduction in the permanent deformation. However, retardation time, where τ is the delayed response to the applied stress for the U75H25-0.5wt.% clay, is less than the retardation time for the blend and the UHMWPE. Conversely, the addition of CB and CNTs nanofillers to the blend matrix shows a reduction in elasticity, stiffness and in the irrecoverable creep strain.

TABLE III. BURGER'S MODEL PARAMETERS

Material	E_M (MPa)	η_M (x10^3 MPa.s)	E_K (MPa)	τ (s)	η_K (MPa.s)
UHMWPE	445	381	561	56.1	31472.1
U75H25	617	605	789	53.4	42132.6
U75H25-0.5wt.% CB	558.7	480	724	52.3	37865.2
U75H24-0.5wt.% Clay	907	629	1020	37.7	38454
U75H25-0.5wt.% CNT	497	445	626	53.6	33553.6

IV. CONCLUSION

The main findings in this work are summarized as follows:

- Blending 25wt.% of HDPE with 75wt.% UHMWPE resulted in a significant increase in the creep resistance.
- The addition of low weight fraction of plate-like nanoclay leads to further improvement in the creep resistance of the U75H25 blend.
- The embedding of CB and CNTs into the blend matrix resulted in a reduction in the creep resistance, which can be attributed to the weak interaction between the filler and the polyethylene matrix. Moreover, the agglomeration of these types of nanofillers can reduce the surface to volume ratio, which can significantly affect the load transfer between the matrix and the filler.
- Elasticity, stiffness and the irrecoverable creep strain have increased with the addition of plate-like nanoclay.

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