Creep Resistance of Novel Polyethylene/Carbon Black Nanocomposites

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***Abstract*—The effects of processing method and carbon black (CB) nanofiller content on the creep resistance of the ultra-high molecular weight polyethylene (UHMWPE)/high density polyethylene (HDPE) blend were investigated. Two processing methods (M1 and M2) were used to prepare the materials, with CB content (up to 3wt.%). The results showed that the creep resistance of UHMWPE can be improved 32 and 10% with the addition of HDPE using M1 and M2, respectively. However, a reduction in the creep resistance was observed with the addition of CB nanoparticles using M1. Further enhancement (35%) was observed with the incorporation of the nanoparticles using M2. This was attributed to the improvement of the dispersion of the nanoparticle and the interaction between the nanoparticle and the blend matrix using M2. The Burger's model was employed to understand the effect of the processing method and the nanoparticle on the creep mechanism.**

***Index Terms*—creep, nanocomposite, polyethylene, carbon black**

I. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) is a high performance thermoplastic with outstanding mechanical properties, such as high wear strength, chemical resistance and high toughness, which provide not only practical benefits but also scientific interest [1]-[3]. However, its extremely high molecular weight, and subsequent high viscosity, raises difficulties in processing using standard techniques, such as twin screw extrusion and compression moulding. Reducing the viscosity of UHMWPE is an effective method of avoiding these processing difficulties. Blending UHMWPE with other polymers that have lower viscosity, such as high density polyethylene (HDPE), can therefore be used to improve processability. HDPE has a similar structure to UHMWPE but with lower molecular chain length, however, it exhibits lower wear resistance, yield strength and toughness than UHMWPE [1]. This reduction in performance on adding HDPE to UHMWPE can potentially be mitigated, whilst retaining the improved processability, by the addition of nano-reinforcement, which has been shown to improve the mechanical performance of polyethylene [4]-[13]. To date, no work has been reported on the improvement of creep resistance of the UHMWPE/HDPE by the incorporation of nanoparticles. In this work, two in-house processing methods were used to incorporate the CB nanoparticles into the UHMWPE/HDPE matrix. The correlation between the morphology, the volume fraction of the CB and the creep resistance were investigated. The creep response was analysed using the Burger's model.

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II. Experimental Methods

A. Materials

The materials tested in this study were UHMWPE/HDPE blended polymers with carbon black nanofiller. Nascent UHMWPE powders (Sabic®UHMWPE3548) were purchased from SABIC which had an average molecular weight of 3×10^6g/mol. HDPE powders (ExxonMobil ™ HDPE HMA 014) were purchased from ICO Ltd. Carbon black powder with the commercial product name, black pearls ® 4040 (BP4040) with 28nm average diameter were provided by the Cabot Corporation. 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 CB into the UHMWPE and HDPE powders. A twin-screw extruder was used to blend the 75wt.% UHMWPE and 25wt.% HDPE powders pre-mixed with CB, to form nano-filled UHMWPE/HDPE blends with various CB nanoparticle contents, (0.5, 1 and 3wt.%). Two processing methods (M1 and M2) were used and the mixing temperature was controlled using five zones from feeding port to die, the processing parameters are shown in Table I. A blend of 75wt.% UHMWPE and 25wt.% HDPE, abbreviated to U75H25, was used as the hybrid PE matrix to accommodate the nanofillers. Compression moulding was used to mould

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the nanocomposite materials. The raw material was placed into a square mould (100×100×1.65mm), and then heated to 190℃, which is higher than the melting point of the composite (approximately 135℃). Various mould pressures (154, 232, 309, and 386MPa) were investigated to optimise the properties of the material such as hardness and crystallinity. Various holding times at maximum pressure (10, 15 and 30 minutes) were also used to identify the most appropriate moulding parameters. The optimal moulding pressure and holding time were found to be 309MPa and 15 minutes respectively, which resulted in the highest measured values of hardness and crystallinity. After compression moulding, the mould was cooled to room temperature using water. Then, the specimens were cut from the plaques. All dumbbell dimensions and creep testing methods were according to ASTM D2990-09.

TABLE I. PROCESSING METHOD PARAMETERS

Processing Method	Extruder Speed (rpm)	Processing Temperature (℃)					
		Zone 1	Zone 2	Zone 3	Zone 4	Die	Cooling
M1	400	180	190	200	210	220	water
M2	190	220	250	260	270	280	water

C. Material Testing and Characterisation

In order to characterise the CB dispersion, the microstructure and the viscoelastic behaviour of the nanocomposites, several experimental techniques were used. These included Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and creep test.

Differential Scanning Calorimetry (DSC), (TA instruments, Shimadzu DSC60) was used to analyse the effect of different compression moulding parameters and CB content 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 20 to 180℃ at a rate of 10℃ 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) [14]. The surface morphology was investigated using a Philips XL30 Environmental Scanning Electron Microscope-Field Emission Gun (ESEM-FEG) from FEI Company (Eindhoven, The Netherlands). A Japan Electron Optics Laboratory (JEOL) 2000FX Transmission Electron Microscopy (TEM) from JEOL Ltd. (Welwyn Garden, UK) was used to analyse the dispersion of CB into the blend matrix.

Creep tests were carried out using an Instron 3366 tensile testing machine from Instron Corporation (Norwood, MA, USA) at room temperature (22±2℃). The samples were subjected to constant stress (9.2MPa) for specific period of time (600s) and each test was repeated at least 5 times.

III. RESULTS AND DISCUSSION

A. Dispersion

The dispersion of nanofillers into the polymer matrix is a key challenge to achieve the desired properties. It is extremely difficult to disperse the nanoparticle uniformly in the polymer matrix due to the Van der Waal forces between particles and the high surface energy. The agglomeration of the nanoparticles tends to be as defects inside the matrix, which affects the mechanical properties of a nanocomposite. In this work, two processing method were used in attempt to improve the dispersion of CB into the polyethylene matrix. It is known that the separation of the CB nanoparticles is difficult; however, minimizing the agglomeration size can be used to increase the surface to volume ratio, and consequently enhance the material properties. It can be seen from the TEM and SEM images in Fig. 1a and Fig. 2a that large agglomerations for CB nanoparticles are occurred for materials processed using M1. However, Fig. 1b and Fig. 2b show that a uniform distribution of the CB nanoparticles with small agglomerations can be obtained using processing method M2. More information and discussions about the nanoparticle dispersion can be found in our published work [15], [16].

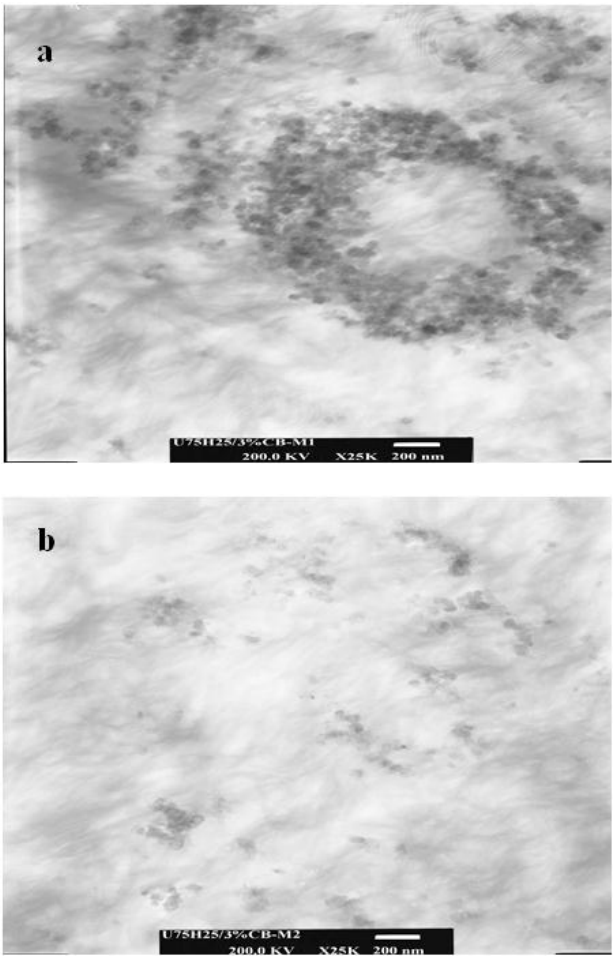

Figure 1. TEM images for 3 wt.% CB dispersion in the U75H25 matrix a) processing method M1 and b) processing method M2.

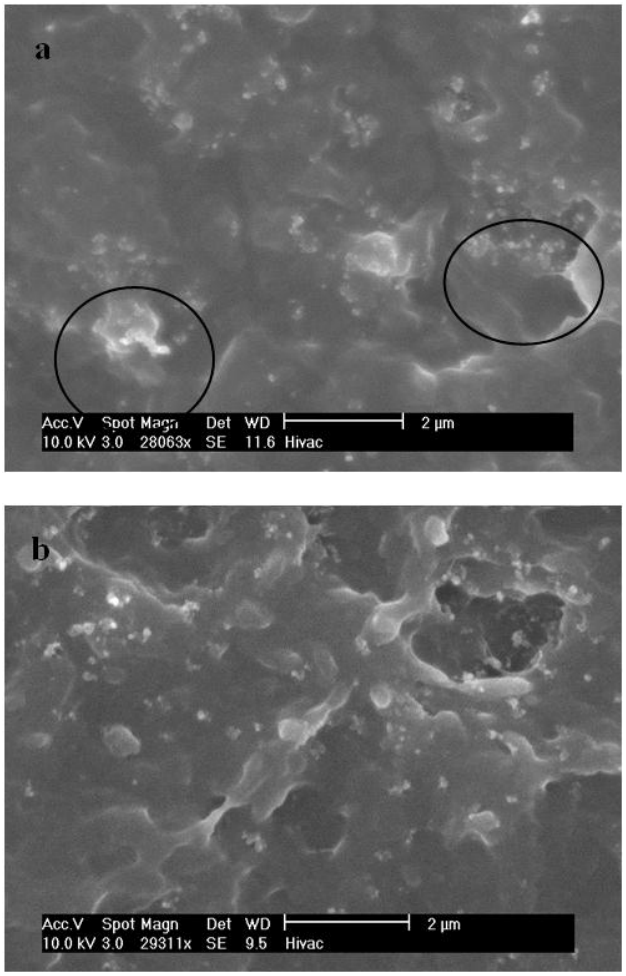

Figure 2. SEM images for 3 wt.% CB dispersion in the U75H25 matrix a) processing method M1 and b) processing method M2 (large agglomeration is highlighted).

B. Creep Results

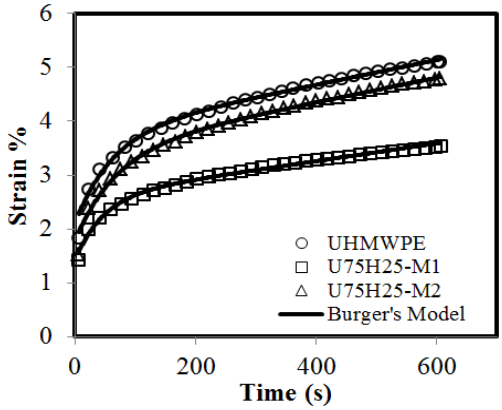

Figure 3. Comparison between the creep resistance of UHMWPE and the blends processed using M1and M2.

In this study, the effect of the degree of crystallinity is negligible for the blends and the nanocomposites, as no significant change was observed from the DSC tests (crystallinity values ~54±1.2). Fig. 3 shows the effect of the addition of the HDPE on the creep resistance of UHMWPE using two different processing method parameters. It can be seen that blending the HDPE with the UHMWPE using processing method M1 increases the creep resistance by 32% compared to 10% after 600s using M2. This can be proposed to the improvement in the miscibility of the blend using processing method M2, where high temperature was applied resulting in a homogenous structure. In processing method M1, the temperature was not sufficient to melt the UHMWPE, which resulted in two different phases with different spherulites properties. The viscoelastic behaviour 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.

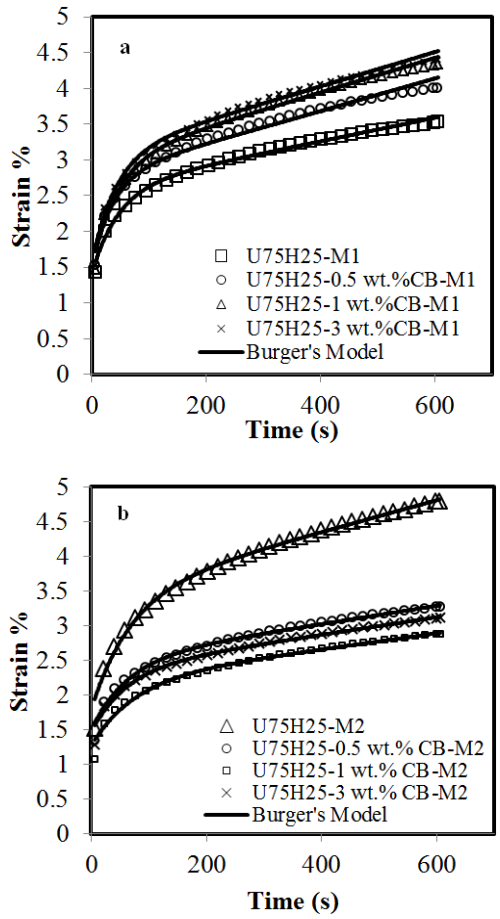

Figure 4. The effects of nanoparticles on the creep resistance the blends processed using M1and M2.

Fig. 4 shows that the addition of CB nanoparticles using processing method M1 causes a reduction in the creep resistance of the blend. This can be attributed to the poor dispersion of the nanoparticle and the large agglomeration, which leads to a reduction in the surface to volume ratio and apply as defects in the microstructure. In processing method M2, the incorporation of the CB nanoparticle shows a significant improvement (35%) in the creep resistance. This can be attributed to the well dispersion and the less agglomeration of the nanoparticles.

Creep modeling and analysis is important to determine the time response, which leads to understanding the 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 behaviour of composites. The total strain as a function of time can be obtained from the following equation (1) [17]:

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

where E_M and η_M are 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. As shown in Fig. 3 and Fig. 4, curves fitting are in a satisfactory agreement with the experimental data. Table II shows the Berger's model parameters that indicate an increasing trend with adding the HDPE for both processing methods. Further increasing can be observed with the addition of CB using processing method M2.

The elasticity E_M and the stiffness of the amorphous phase E_K of the blend can be increased by the addition of the CB. The parameter η_M represents the irrecoverable creep strain, which also increases with the addition of CB. This indicates that a reduction in the dashpot flow can be occurred, which leads to a reduction in the permanent deformation. Retardation time, τ is the delayed response to the applied stress and it can be seen that the retardation time for the blend and the nanocomposites is higher than the retardation time for UHMWPE. Conversely, the addition of CB nanoparticles using processing method M1 shows reduction in all parameters, which indicates a reduction in the elastic modulus and stiffness and increasing in the permanent deformation.

TABLE II. THE SIMULATED PARAMETERS OF BURGER'S MODEL

Materials	CB content (wt.%)	E_M (MPa)	E_K (MPa)	η_M ($\times 10^3$MPa.s)	τ (s)
UHMWPE	---	436	557	402	61.7
U75H25 (M1)	0	645	784	559	46.6
	0.5	604	734	405	37.2
	1	596	642	381	45.1
	3	583	617	365	42.1
U75H25 (M2)	0	513	650	405	67.8
	0.5	610	924	705	63.3
	1	721	990	805	73.8
	3	627	1030	725	63.3

IV. CONCLUSION

The HDPE was blended with UHMWPE and CB nanoparticles were incorporated in the blend matrix using two different processing methods. The effects of the processing method and the incorporation of the nanoparticles on the creep resistance were investigated and modeled. Processing method has significant effect on the creep resistance of the blends and the performance of the nanoparticle. It was found that the creep resistance of the polyethylene blend can be enhanced significantly by the incorporation of CB nanoparticles.

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