

Microcharacterization of Creep Behavior of Carbon Nanofiber Reinforced HDPE Nanocomposites using a Depth Sensing Method

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ABSTRACT

Depth-sensing indentation at micro- and nano-scale levels is a useful tool for material characterization due to the simplicity of the experimental procedure. Most Polymer or polymeric composites usually exhibit a time-dependent behavior even at room temperature. This work reports an investigation on creep behavior of UHMWPE, HDPE and its nanocomposite (HDPE/CNF) with functionalized carbon nanofibers by the simple and non-destructive micro-indentation technique instead of traditional uniaxial tensile creep test. The comparison of creep compliance derived from the indentation deformation were made between the HDPE/CNF nanocomposites, neat HDPE and UHMWPE specimens. The influences of the addition of CNFs and the surface modification of CNFs on the creep behavior of HDPE nanocomposites were discussed.

Keywords: Creep, Indentation, Carbon Nanofiber, Nanocomposites.

1 INTRODUCTION

Micro-characterization of local mechanical properties of materials at surface or sub-surface using depth-sensing indentation technique has been developed and widely used during the last decade. Compared with other approaches of mechanical testing, indentation method is non-destructive, easy to operate and simple to prepare the test specimen. There are many well-established methods for determining local mechanical properties including elastic modulus, yielding stress, hardness and fracture toughness of small volumes of solids by indentation [1, 2]. In recent years, indentation testing has been explored as a promising technique to determine the creep (time-dependent) behavior of viscoelastic materials [3-5].

Most Polymer or polymeric composites usually exhibit time-dependent mechanical behavior even at room temperature which reduces their applicability as load-bearing components. Creep would not be desirable, particularly when the polymer material, such as ultra-high molecular weight polyethylene (UHMWPE) or high density polyethylene (HDPE), is applied in artificial joints as the bearing material. Creep has been found to be the dominant cause in dimensional changes of polyethylene component in

vivo [6]. The creep of UHMWPE thus has to be reduced or eliminated in order to improve the long-term performance of the total hip replacement, especially for more active patients [7, 8]. Recently, CNFs were added into HDPE to improve the wear resistance of the HDPE/CNF nanocomposites [9-11], which had the promise to work as bearing materials in industrial and medical applications. The creep behavior of HDPE/CNF nanocomposites has been rarely reported in the literature. The knowledge of creep behavior of polyethylene is essential for predicting its performance in material selection.

In this paper, the indentation creep behaviors of a few PE materials are studied, including UHMWPE, HDPE and its nanocomposite (HDPE /CNF) with functionalized CNFs. The Kelvin Chain Model was used to derive a creep formula to fit the experimental creep data. The creep compliances of polymeric materials were derived and the influences of CNFs and the functionalization of CNFs on the creep behavior of the nanocomposites were discussed.

2 EXPERIMENT

2.1 Materials

The HDPE (HP54-60 Flake) used in this research was supplied by Bamberger Polymers, Inc. with a density of 0.954 g.cm⁻³. The UHMWPE used was from Intersate Plastic, Inc.. The pristine CNFs (PR-24-HHT) and pretreated oxidized CNFs (PR-24-HHT-OX) as the fillers were obtained from Applied Sciences Inc., which were approximately 60 to 150 nm in diameter and 30 to 100 nm in length. Octadecyltrimethoxy-silane (ODMS) (90% technical grade) was manufactured by Sigma-Aldrich. The pretreated oxidized CNFs were modified with ODMS and ethanol solution, and then a silane coating was formed to cover the fiber surface. By changing the ratio of ODMS to ox-CNF added and the percentage of ethanol and water in this reaction, it was possible to control the degree of hydrolysis and the thickness of silane coating. In a previous work, the average silane coating thickness (46 nm) was determined using TGA data and TEM [10,12]. Two levels of fiber concentrations of 0.5 wt.% and 3 wt.% for both pristine CNFs and silanized CNFs were mixed with HDPE by a Haake Torque Rheometer to achieve good dispersion. A neat HDPE reference was prepared under the same

conditions. The detailed descriptions of the silane coating synthesis and nanocomposite manufacturing procedures were given in [10, 12]. The descriptions of the samples are shown in Table 1.

Sample	Matrix	CNF	CNF concentration
P-05	HDPE	Pristine	0.5 wt. %
P-3			3 wt. %
T-05		silane treated	0.5 wt. %
T-3			3 wt. %
HDPE	HDPE	-	-
UHMWPE	UHMWPE	-	-

Table 1: Descriptions of the HDPE/CNF nanocomposite samples.

2.2 Experimental methods

The creep indentation test was performed on a CETR-UMT-2 tribometer with a spherical indenter connected to the load cell. The UMT-2 tribometer system can provide a displacement resolution of 0.1 μm and an applied force resolution of 1 mN. The indenter ball was made of SS440C stainless steel from Salem Specialty Ball, Inc. with a diameter of 4.762 mm. The indentation sample was fixed on a thick steel compression plate.

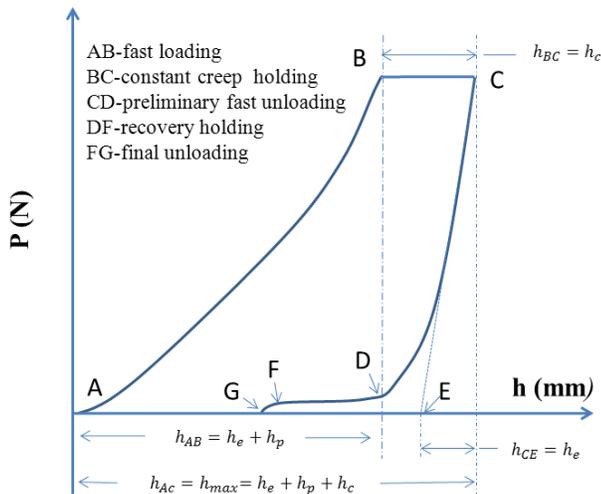


Figure 1: Schematic diagram of the indentation procedure.

In the experiments, the loading rate was set to be 5 N/s to achieve the maximum load of 10 N in 2 seconds. The faster loading rate can minimize the viscoelastic deformation over the loading period of 2 seconds [13]. The maximum load was then held for 1 hour at room temperature. At the end of the holding segment, the unloading rate was still chosen as 5 N/s to prevent any viscoelastic effect. When the force was decreased to 0.3 N, it was held again for 1 hour to recover the viscoelastic displacement before the force was completely unloaded. The indentation procedure is shown in Fig.1, in which each

part of the deformation was recorded, including the elastic deformation $h_e = h_{CE}$, plastic deformation $h_p = h_{AB} - h_{CE}$, and creep deformation $h_c = h_{BC}$. It should be noted that viscoplastic deformation was not considered during the maximum load holding and this study only focused on the creep deformation of viscoelastic polymeric materials and their composites. For each material, 5-10 creep indentation tests were performed and the average creep displacements versus time were plotted to derive the creep behavior of the material. The majority of viscoelastic solutions for the indentation of a rigid axisymmetric indenter into a half-space composed of a homogeneous, linearly elastic and isotropic material were derived by Sneddon [14]. The contact creep compliance for the indentation by a spherical indenter under a constant applied load can be stated as:

$$J_c(t) = \frac{8\sqrt{R}}{3(1-\nu)P_0} [h_c(t)]^{\frac{3}{2}} \quad (1)$$

where R is the radius of spherical indenter, ν is the Poisson ratio of the indented material, P_0 is the constant applied load, and $h_c(t)$ is the creep depth vs. time.

3 RESULTS AND DISCUSSION

3.1 Creep compliance

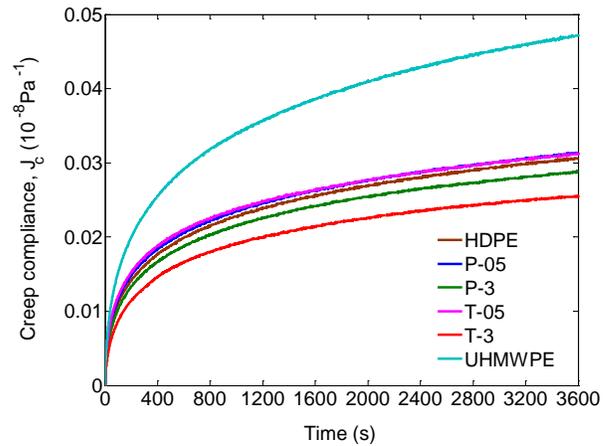


Figure 2: Indentation creep compliance for the six materials.

The indentation creep compliance of each material, calculated using Eq. (1) is shown in Fig. 2. The creep of all samples exhibited two stages, primary creep and steady-state creep. It was noted that compared with traditional uniaxial tensile creep test, the tertiary stage of creep curve was not visible in the indentation creep test, because the steel compression plate at the bottom of the sample limited the material flow and reduced the overall deformation under loading [15].

Compared with UHMWPE, the HDPE and HDPE/CNF nanocomposites all exhibited lower creep compliances possibly due to the crystallinity and molecular weight. It seems that adding 0.5 wt% CNF (both pristine and silane

treated) all did not have significant influence on the creep compliance as the creep compliance curves are all close to that of the neat HDPE. However, the ability of the 0.3 wt.% CNF additives (both pristine and silane treated) to increase the creep resistance are noticeable and can be attributed to several factors [16]. First, the confinement effect of the CNFs with high elastic modulus has prevented the deformation of the PE-network. Second, CNFs acted as sites to block the movement of the PE chains and restricted the viscous flow of the amorphous PE when subjected to an external indentation force. Therefore, the 3 wt.% loading level could provide more restriction effect and lead to significant improvement of creep resistance. It was also shown that the silane treated CNFs at 3 wt.% loading level reduced the creep compliance more than the pristine CNFs. This could be due to the fact that the silane coating improved the interfacial bonding between the CNFs and HDPE matrix.

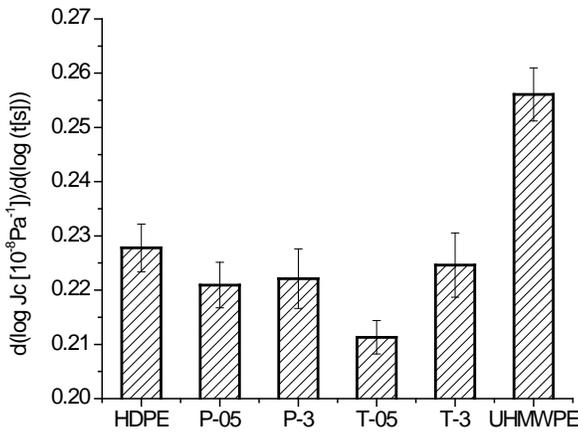


Figure 3: Rates of the creep compliances for the six materials.

Figure 3 shows the average creep rate of each material at steady state (after 1000 s), derived as $d[\log(J_c(t))]/d[\log(t)]$ from the curves in Fig. 2. The creep rates of all HDPE/CNF nanocomposites are lower than that of the pure HDPE and UHMWPE with T1-05 having the lowest creep rate. The major reason for T1-05's low creep rate over steady-state creep might be the uniform distribution of nano-reinforcements. It was found that HDPE with silane treated CNFs at 0.5 wt.% loading obtained the best dispersion as shown in Fig. 4, due to the

lower nanofiller loading level and enhanced adhesion between the modified CNFs and HDPE matrix [10]. During the steady-state creep, uniformly distributed CNFs seemed to be more effective in confining the deformation and restricting the viscous flow of the polymer, resulting in the lower creep rate.

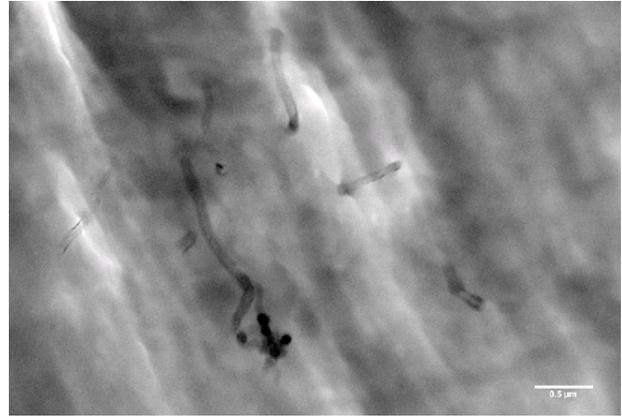


Figure 4: TEM image of HDPE with silane treated CNFs at 0.5 wt.% loading.

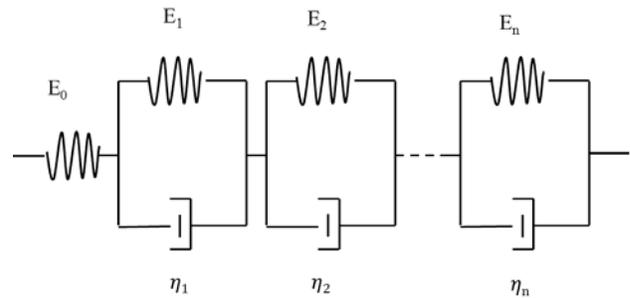


Figure 5: Viscoelastic model used in this study: Kelvin Chain Model

3.2 Creep compliance model

The viscoelastic behavior of the polymers can be described by the well-known Kelvin Chain Model [4, 17]. The model consists of a spring and a series of parallel-connected dashpots and springs as shown in Fig. 5. The creep function based on the Kelvin Chain Model was derived in [4, 17] in detail and can be described as:

n=2	J_0	J_1	τ_1	J_2	τ_2	Residual sum of squares
HDPE	8.70E-05	0.01815	1529.03968	0.01377	88.92099	1.69E-06
P-05	7.12E-05	0.01823	1515.44882	0.01437	84.50271	1.45E-06
P-3	7.18E-05	0.01288	89.97773	0.01695	1466.02871	1.20E-06
T-05	7.98E-05	0.01511	85.92284	0.0173	1523.96512	1.75E-06
T-3	9.59E-05	0.01521	1467.58896	0.0113	99.86467	1.20E-06
UHMWPE	1.58E-04	0.03051	1635.66836	0.01944	98.46553	3.27E-06

Table 2: Fitting parameters of the second order Kelvin Chain Model from Eq. (2) for the six materials.

$$J_c(t) = J_0 + \sum_{i=1}^n J_i(1 - e^{-t/\tau_i}) \quad (2)$$

where J_0, J_1, \dots, J_n are compliance numbers, n is a positive integer, and $\tau_1, \tau_2, \dots, \tau_n$ are retardation times. $\tau_i = \eta_i/E_i$, where E_i is a modulus of elasticity and η_i is the viscosity shown in Fig. 5. In this study, the parameters of a second-order Kelvin Chain Model were determined by a nonlinear curve fitting of the experimental data (Fig. 2) using the least nonlinear least squares regression method and the results are listed in Table 2.

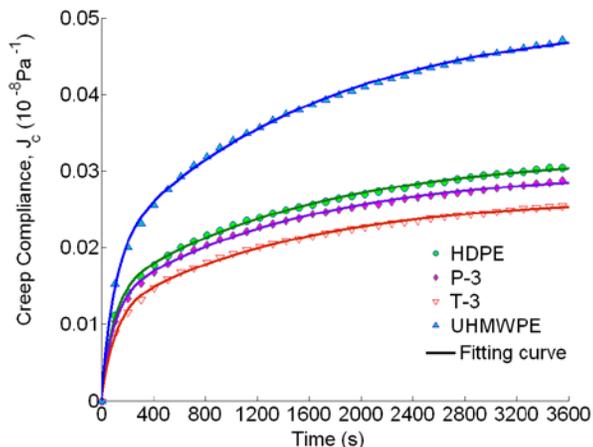


Figure 6: Fitting curves for the four materials using Eq. (2) of the second order Kelvin Chain Model.

The typical fitting curves for the HDPE, P-3, T-3 and UHMWPE are plotted in Fig. 6. The applied second-order Kelvin Chain Model can fit the experimental data of the creep compliances well with very small residual sum of square as exhibited in the last column of Table 2. It can be expected that the higher order of Kelvin Chain Model used in Eq. (2), the less the error between the experiment data and the fitted curves. In addition, the compliances J_i and retardation time τ_i in Table 2 can be further applied to determine other mechanical properties, such as the loss modulus and storage modulus of the polymers.

4 CONCLUSION

This study employed the depth-sensing indentation method to evaluate the time dependent properties of UHMWPE, HDPE and HDPE/CNF nanocomposites. The addition of 3 wt.% CNFs (both pristine and silane treated) enhanced the creep resistance of the nanocomposites noticeably. Compared with pristine CNFs, silane treated CNFs at 3 wt.% loading improved the creep resistance of HDPE more effectively. In addition, the silane treated CNFs at 0.5 wt.% loading resulted in the lowest creep rate among the six materials due to good dispersion. The indentation creep behavior of polyethylene family can be

reasonably predicted by the Kelvin Chain Model with very small error.

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