

Effects of dwell time and loading/unloading rate on the nanoindentation behavior of polyethylene-based nanocomposites

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ABSTRACT

The purpose of this paper is to investigate the effects of parameters like loading, unloading rates, and dwell period on the depth-sensing indentation properties is. A bowing out or nose is the most common behavior for polymeric materials in nanoindentation tests due to the viscoelastic behavior. This leads to the negative slope and consequently, significant errors in the calculations of hardness and elastic modulus values using depth-sensing indentation techniques. A common practice to minimize this effect is to apply a creep at maximum indentation load or increase the unloading rates as considered in this work. The results showed that these parameters have significant impact on the nanoindentation hardness and elastic modulus. The hardness and elastic modulus increase with increasing the loading rate during nanoindentation testing. The elastic modulus values reduce significantly by increasing the unloading rate. Contrarily, hardness increase with increasing the unloading rate. Hardness and elastic modulus values are significantly affected by increasing the dwell period. The hardness reduces by 20% after increasing creep time and elastic modulus increases with increasing the dwell time.

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1. Introduction

Depth sensing indentation (DSI) is an advanced technique, which is capable of providing valuable information about the near-surface properties of solid polymer, such as indentation elastic modulus, indentation hardness, elastic-plastic, viscoelastic (creep) and viscoplastic behavior (Fischer-Cripps, 2002). Recently, this technique has become increasingly popular in the investigation of the near-surface properties of polymer nanocomposites and their correlation to the nanoparticle loading (Aldousiri et al., 2011; Yusoh et al., 2010; Wang et al., 2010). Up to date, no work was carried out to evaluate the dispersion of the nanoparticle, the creep behavior, the scratch and wear resistance of polyethylene nanocomposites employing DSI. Therefore, in this paper, the dispersion of carbon nanotube (CNT) and inorganic nanoclay in the UHMWPE/HDPE blend matrix using two different

mixing methods was evaluated by DSI. The effects of the nanoparticle addition on the creep behavior, scratch and wear resistance were also investigated.

The use of the DSI technique with polymers is a challenge due to the complex structure and deformation mechanisms involved. Both time-independent and time-dependent deformation can be seen in the indentation of polymers. The calculation of the indentation hardness and the indentation elastic modulus in the DSI technique depends on the assumption that the initial unloading part is elastic. A bowing out or nose is the most common behavior for polymers in nanoindentation tests due to the viscoelastic behavior (Altaf et al., 2012; Briscoe et al., 1998; Ngan and Tang, 2002; Cheng et al., 2005b; Lu et al., 2009). This can lead to a negative slope (Oyen and Cook, 2003), which invalidates the assumption of elastic unloading, and leads to a major error in the calculation of contact depth and contact stiffness. Therefore, applying appropriate loading and unloading rates and holding times at maximum load are essential factors that should be considered to minimize the effect of viscoelastic behavior in the unloading curve when testing polymers (Yang et al., 2004). Therefore, it is common practice to eliminate or minimize the creep effect through a rapid unloading rate (Cheng et al., 2005a) or a long dwell/holding time at maximum

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load (Briscoe et al., 1998; Chudoba and Richter, 2001). In the current study, various loading and unloading and dwell periods were applied to find the optimum test parameters to obtain an initial elastic segment during the unloading. The effects of these parameters on the hardness and elastic modulus were analyzed.

2. Experimental methods

2.1. Materials

The materials tested in this study were UHMWPE/HDPE blended polymers with two types of nanofillers, which are carbon black (CB) and carbon nanotubes (CNTs). Nascent UHMWPE powders (Sabic@UHMWPE3548) were purchased from SABIC (Dhahran, Saudi Arabia) which had an average molecular weight of 3×10^6 mol/g. HDPE powders (ExxonMobil™ HDPE HMA014) were purchased from ICO Ltd (ExxonMobil Chemical Europe, Belgium). Carbon black (CB) powder with the commercial product name, black pearls® 4040 (BP4040) and average particle diameter of 28 nm was provided by the Cabot Corporation (Cabot Corporation, USA). Multi-wall Nanotubes (MWNT) with diameters in the range of 5 nm to 50 nm, were provided by Nanocyl (Nanocyl, Belgium). Butylated hydroxytoluene and Tris (nonylphenyl) phosphate, supplied by Sigma-Aldrich (Sigma-Aldrich, UK), were used as primary and secondary antioxidants, to maintain the long-term thermal stability and melt processing stability, respectively.

2.2. 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 CB or carbon nanotubes (CNT) to form nano-filled UHMWPE/HDPE blends with a constant volume fraction of 0.5 wt.% each. A blend of 75 wt. % UHMWPE and 25 wt. % 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 1.

Compression moulding was used to mould the nanocomposite materials. The raw material was placed into a square mould (100 X 100 X 1.65 mm), and then heated to 190°C, which is higher than the melting point of the composite (approximately 135°C). Various mould pressures (154, 232, 309, and 386 MPa) were investigated to optimize 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 309 MPa and 15 minutes, respectively, which

resulted in the highest 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 into a square shape of 10x10 mm with 1.65mm thickness.

Table 1: Processing method parameters

| Extruder Speed (rpm) | Processing Temperature (°C) | Cooling |
|----------------------|-----------------------------|---------|
| 400 | Zone 1 | 180 |
| | Zone 2 | 190 |
| | Zone 3 | 200 |
| | Zone 4 | 210 |
| | Die | 220 |

2.3. Material testing and characterization

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). The details of these techniques are discussed in this section.

Differential Scanning Calorimetry (DSC), (TA instruments, Shimadzu DSC60) was used to analyze the effect of different compression moulding parameters and nanoparticle type on the crystallinity of the blend and nanocomposites. The specimens, with an average mass of 5 ± 0.2 mg, were sealed in aluminum pans and heated from 20 to 180°C at a rate of 10°C 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 (290 kJ/kg) (Humbert et al., 2009). The surface morphology was investigated using a LEO 440 Scanning Electron Microscopy (SEM) from Leo Electron Microscopy Ltd (Cambridge, UK), and Philips XL30 ESEM-FEG from FEI Company (Eindhoven, The Netherlands). The dispersion of nanoparticles was studied after fracturing the samples in liquid nitrogen, then coating them using platinum. A JEOL 2000FX Transmission Electron Microscopy (TEM) from JEOL Ltd. (Welwyn Garden, UK) was used to analyze the dispersion of nanoparticles into the blend matrix.

Depth sensing indentation (DSI) experiments were performed on the specimens at a controlled machine chamber temperature of 25°C, using a NanoTest 600 from Micro Materials Ltd (Wrexham, UK). A Berkovich indenter, with a face angle of 65.3°, was used to make at least 10 indents with 40 mN maximum load, 600s dwell period and 2 mN/s loading and unloading rates. The results were analyzed using the Oliver and Pharr method (Oliver and Pharr, 1992) and the average curves were plotted using Excel. In this method, the initial portion of the unloading curve is described by the power law relation:

$$P = \alpha (h - h_r)^m, \quad (1)$$

where P is the load, α and m are constants determined by curve fitting, h is penetration depth

and h_r is the depth of the residual impression. The contact stiffness (S) can be obtained by:

$$S = \frac{dP}{dh} (h = h_{max}) = m \propto (h_{max} - h_r)^{m-1}. \quad (2)$$

The contact depth (h_c) at maximum load (P_{max}) can be estimated using:

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S}, \quad (3)$$

where ε is a constant related to the geometry of indenter, which is 0.75 for the Berkovich indenter, h_{max} is the maximum penetration depth. Thus, the projected contact area (A_c) is determined from (h_c) by the following relation:

$$A_{c \approx} 24.5 h_c^2, \quad (4)$$

and hence the indentation hardness (H) is:

$$H = \frac{P_{max}}{A_c} = \frac{P_{max}}{24.5 h_c^2}. \quad (5)$$

The reduced modulus can be calculated from stiffness (S) using the relation:

$$S = \frac{dP}{dh} = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A}, \quad (6)$$

where, $A = 24.5 h_p^2$, E_r is the reduced modulus and β is a correction factor that depends on the type of indenter (1.034 for Berkovich indenter). Consequently, the elastic modulus (E_s) for the specimen can be calculated using the equation:

$$\frac{1}{E_r} = \frac{(1-\nu_s)^2}{E_s} + \frac{(1-\nu_i)^2}{E_i}, \quad (7)$$

where, E_s , ν_s and E_i , ν_i are the elastic moduli and the Poisson's ratios of the specimen and the indenter respectively, ($E_i=1141$ GPa, $\nu_i = 0.07$).

For the materials used in this study, a bulge or (nose) effect was found during the initial portion of unloading as a result of creep, which can lead to errors in the calculation of contact depth and contact stiffness. Therefore, various dwell times of 500 to 2000s was introduced at maximum load to minimize this effect of viscoelastic behavior and to investigate the effect of this dwell time on the nanoindentation behavior. In this study, the Oliver and Pharr method was used to compare the mechanical resistance of the blend and nanocomposites under identical testing conditions. Various loading/unloading rates were applied, 0.1, 0.5 and 1 mN/s to investigate the effects of loading/unloading rates on the mechanical properties at a small scale.

3. Results and discussion

3.1. Nanoparticle dispersion

Nanofillers dispersion and distribution in the neat polymer matrix is a vital factor in the production of nanocomposites that can significantly

influence the mechanical and rheological properties of the composite. In a previous work, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to analyze nanoparticle dispersion in the U75H25 matrix. Homogenous dispersions of CB and CNT at the constant volume fraction (0.5 wt. %) were observed, with no large aggregates of nanoparticles. Further evidence of the good dispersion of CNT and CB nanoparticle was obtained by using the TEM, which showed the presence of CB and CNT in the polymer matrix (Alghamdi, 2017; 2019).

3.2. Effects of loading rate

Fig. 1 shows the effect of loading rate on the hardness and elastic modulus values of polyethylene polymeric material and its nanocomposites. It can be seen that increasing the loading rate resulted in an increase in both hardness and elastic modulus values of the U75H25 and U75H25-0.5 wt. % CNT polymeric materials. A slight reduction in these values is observed at 0.5 mN/s loading rate for the U75H25 polymeric material.

The addition of CNT nanoparticles into the polyethylene matrix resulted in an increase in the hardness value at all loading rates. This can be attributed to the 2D shape of these nanotubes, the good distribution of nanofillers and the excellent interaction between the nanofillers and the polyethylene matrix. The embedding of CB nanoparticles into the polyethylene matrix shows an increase in both hardness and elastic modulus values at a high loading rate of 1 mN/s compared to the neat polymer. Therefore, selecting the appropriate loading rate is critical when conducting a nanoindentation test for polymeric materials and their nanocomposites.

3.3. Effects of unloading rate

It is known that the slope of the unloading curve at the maximum displacement point of the nanoindentation loading/unloading behavior has grate effects on the hardness and elastic properties of materials. These effects can be reduced by applying a suitable unloading rate. It can be seen in Fig. 2 that the hardness values increased with the increase in the unloading rate. However, a reduction in the elastic modulus values is observed at a high unloading rate for all polymeric materials. The addition of CB nanoparticles resulted in a significant increase in the elastic modulus at a slow unloading rate.

3.4. Effects of dwell time

The application of the dwell period at maximum indentation load is one way to reduce the impact of nose on the nanoindentation results. Fig. 3 shows the influence of dwell time on the hardness and elastic modulus properties. Increasing dwell time (creep)

resulted in a significant reduction in hardness values.

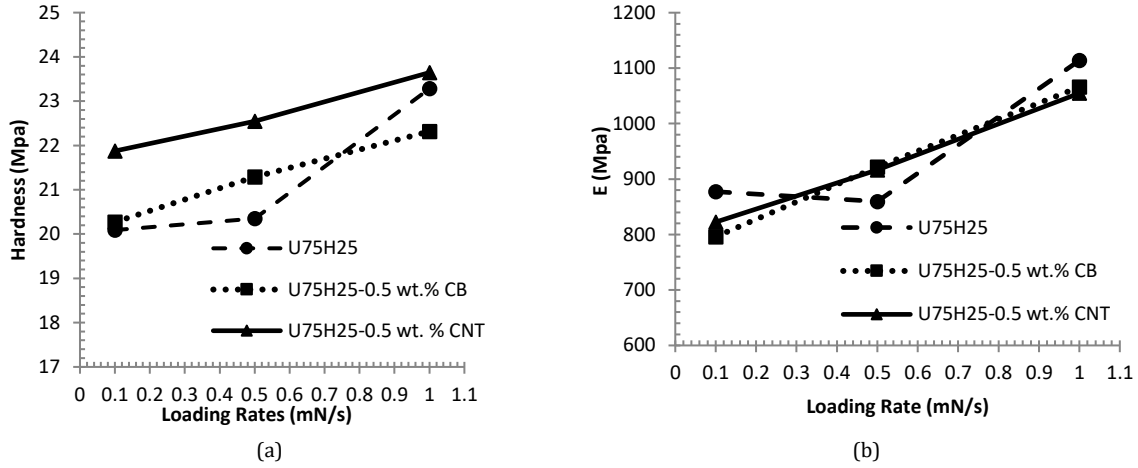


Fig. 1: Effect of loading rate on (a) the hardness value and (b) the elastic modulus

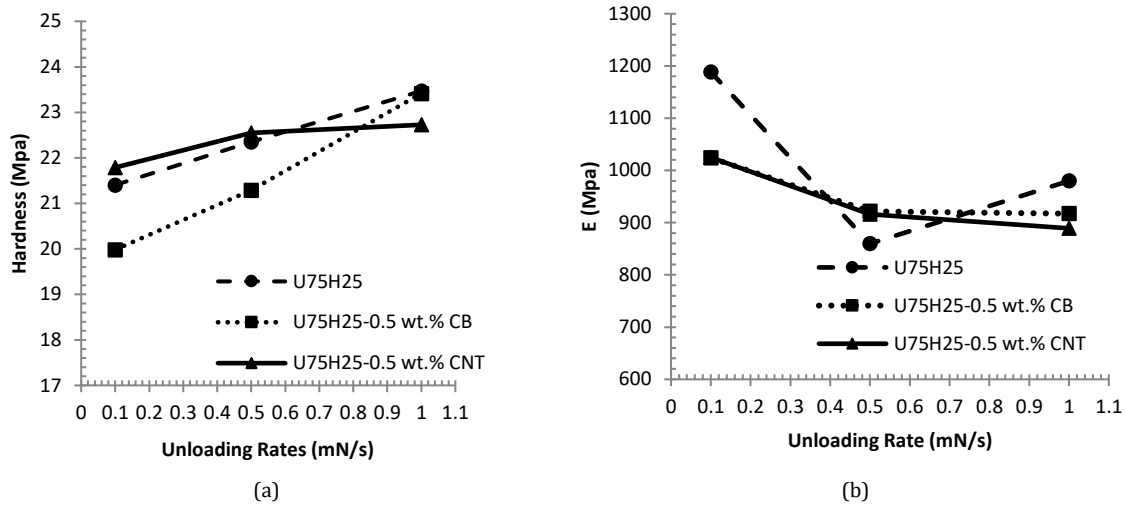


Fig. 2: Effect of unloading rate on (a) the hardness value and (b) the elastic modulus

This behavior is also found by [Yasin et al. \(2019\)](#) during their work on investigating the effects of experimental parameters on the indentation behavior of low-density polyethylene. However, the presence of nanofillers shows grate effects on the nanoindentation properties. The hardness value is reduced by 20% for the U75H25-0.5 wt. % CB after

increasing the dwell time from 500s to 2000s. On the other hand, an increase in the elastic modulus is obtained with the rise of the dwell time for more than 1000s for all polymeric materials. The addition of CNTs and CB nanofillers resulted in a slight reduction in the elastic modulus compared to the blended U75H25.

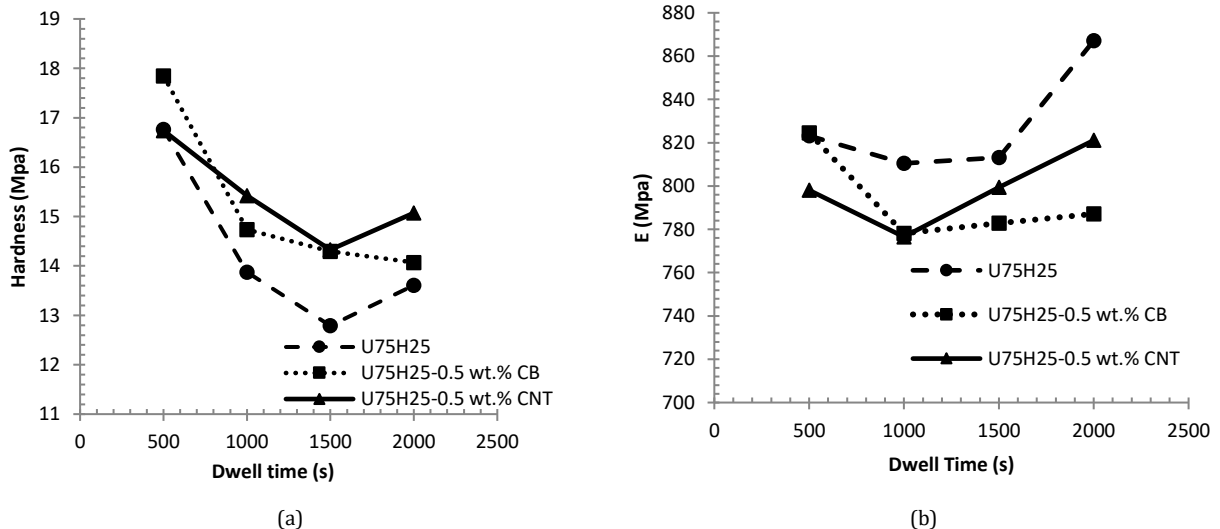


Fig. 3: Effect of dwell time on (a) the hardness value and (b) the elastic modulus

4. Conclusion

In this paper, the effects of loading, unloading rate and dwell period on the depth-sensing indentation properties are investigated. It is found that these factors have noticeable effects on the hardness and elastic modulus properties at the micro-level. The hardness and elastic modulus increase with increasing the loading rate of the nanoindentation testing. The elastic modulus values reduce significantly by expanding the unloading rate. Contrarily, hardness increase with increasing the unloading rate. The best practice for reducing the effect of noise during the unloading of polymeric materials is applying dwell time. However, this study indicates that dwell time can play a significant role during nanoindentation tests. Hardness and elastic modulus values are significantly affected by the increasing dwell period. The hardness reduces by 20% after increasing creep time and elastic modulus increases with increasing the dwell time.

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Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

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