Creep of high density polyethylene filled with multiwall carbon nanotubes

O Starkova\textsuperscript{1}, J Sevcenko, S Stankevich, O Bulderberga and A Aniskevich

Institute for Mechanics of Materials, University of Latvia, 3 Jelgavas Street, LV-1004, Riga, Latvia

\textsuperscript{1}Corresponding author: olesja.starkova@lu.lv

Abstract. The creep-recovery behaviour of two types of high density polyethylene (HDPE) filled with multiwall carbon nanotubes (MWCNT) is investigated. Nanocomposites with various contents of MWCNT were produced by using a commercially available masterbatch aimed to transfer the gained knowledge to an assessment of properties of industrial-scale products. Nanocomposites are characterized by the improved creep resistance compared to the neat polymers. Incorporation of 10 wt.\% of MWCNT into the polymers resulted in a decrease of creep and residual strains for more than 3 and 5 times, respectively. The reinforcing effect of the nanofiller appeared also in a great increase of the elastic modulus (up to 100\%) and ultimate strength (up to 60\%) as well as a decrease of the coefficient of linear thermal expansion (down to 17\%) of HDPE. Carbon nanotubes, being also good heat conductors, greatly contributed to the improvement of polyethylene’s thermal conductivity (up to 60\%). Electrical percolation is determined below 2 wt.\% of MWCNT. The electrical resistance changes monitored during creep-recovery tests are well correlated with the overall strain changes and residual strains in nanocomposites, that approve their in situ strain sensing capability during inelastic and long-term deformation.

1. Introduction

High density polyethylene (HDPE) is one of the most used and affordable thermoplastics for variety of applications. Thus, search for technical solutions aimed to improve some operational properties of HDPE-based products and introducing them some additional functionalities is an important task. Incorporation of nanofillers is one of the promising ways to improve overall performance of thermoplastic polymers showing high efficiency at relatively low contents, and thus economic feasibility of this approach [1-5]. Owing to their high stiffness, multiwall carbon nanotubes (MWCNT) are considered as good reinforcement particles, while being also electrically conductive these provide “sensing functionality” to polymer nanocomposites [6-9]. Despite high interest on characterization of the mechanical properties of various polyolefin/carbon nanotube nanocomposites during the last decade, there are still a lot of gaps in understanding the mechanisms of deformation of these novel materials. High aspect ratio of nanoparticles, their tendency to form agglomerates and affect crystallization process or polymer microstructure at an interphase result in noticeable changes in deformation behavior of polymer nanocomposites, particularly in their time-dependent response [10-12]. Although creep behavior of various thermoplastic polymers and their nanocomposites is sufficiently highlighted in a number of studies [13-15], these could not give general explanations to some particular phenomena observed in every specific polymer-nanofiller system. Thus, introducing of any novel polymer composite into the real application requires systematic and comprehensive
characterization of creep-recovery behavior and its relation to other properties. Moreover, current studies on strain sensing capability of polymer nanocomposites are mainly based on electrical resistance measurements in the elastic range of deformation, while time-dependent and irreversible effects are rarely reported [7,9,16-18]. The present study is focused on characterization of creep-recovery behavior of HDPE/MWCNT composites and estimation of their strain sensing capability by electrical resistance measurements.

2. Experimental details

2.1. Materials and processing of nanocomposites
Two types of neat HDPE supplied by Ineos (Germany) were studied: Rigidex® K38-20 and Rigidex® HD5502S (denoted as HDPE3820 and HDPE5502S, respectively). These polyethylene copolymers provide an optimum balance of easy processing and properties for use in a wide range of extrusion and blow moulding applications including non-pressure pipes, bottles, and films. HDPE-based masterbatch Plasticyl™ HDPE1501 (Nanocyl, Belgium) containing 15 wt.% of short tangled MWCNT (NC7000™) in the form of pellets was used to produce nanocomposites. Use of commercially available masterbatches allows one easy and repeatable processing of novel nanomodified polymers that will contribute to the effective technology transfer from laboratory to industrial large-scale production [1,2,5].

| Material       | Density (g/cm³) | Melt flow rate (190 °C/2.16 kg) (g/10 min) | Melting temperature (°C) | Elastic modulus, (MPa) | Tensile strength at yield (MPa) | Elongation at break (%) |
|----------------|----------------|------------------------------------------|--------------------------|------------------------|-------------------------------|-------------------------|
| HDPE3820       | 0.938          | 0.2                                      | 129                      | 600 (tensile)          | 19                            | >300                    |
| HDPE5502S      | 0.954          | 0.2                                      | n/a                      | 1050 (flexural)        | 26                            | >350                    |
| HDPE/MWCNT     | 0.977          | n/a                                      | 135                      | 1053 (tensile)*        | n/a                           | n/a                     |

*Tensile modulus is given for neat HDPE used in the masterbatch.

Two processing techniques were selected for mixing the raw polymers with the masterbatch in order to produce nanocomposite samples with various MWCNT contents and evaluate technology-related differences in properties of the produced materials. LabTech Scientific calender (Thailand) was used for mixing via calendering technique (denoted as “c” in the text) with a rotation speed 25/20 rpm and temperature 175/185 °C for the hot/cold rolls, respectively. A gap between the rolls was adjusted as 0.1 mm and the total rolling time was about 7 minutes. The obtained hardened blends in the form of strands were then cut into small pieces and used for compression molding. The other part of samples was produced via extrusion technique (denoted as “ex” in the text). Co-rotating twin-screw extruder Thermo Scientific Prism TSE 16 TC (Germany) with a barrel length of 400 mm and L/D = 16 [19]. Temperature profiles 180 (feed) – 185 – 190 – 195 – 200 (die) and a screw speed of 50 rpm were adjusted during extrusion. The composite strands where then re-pelletized and dried in an oven at 70 °C for 3 hours in order to remove water adsorbed by the strands during cooling. For the neat polymers, the same calendaring and extrusion procedures were applied in order to keep the same processing history compared to their nanocomposites.

Compression molding of the produced pelletized compositions was realized via LabTech Scientific thermal press (Thailand). Load of 105 kN, heating temperature of 210 °C, pre-heating time of 6 min and direct cooling regime were adjusted. Several plates of 120×120×1.5 mm³ dimensions were produced for each composition. Dog-bone samples according to DIN ISO 527-2 1BA (30 mm long and 5 mm wide in the parallel part) were cut from these plates and further used for mechanical testing.
Totally, samples with six various contents of MWCNT were produced: 0, 2, 5, 7.5, 10, and 15 wt.% MWCNT. Samples with the maximal 15 wt.% MWCNT (pure masterbatch) were produced by compression molding only. All samples prior to testing were stored in laboratory conditions.

2.2. Thermal properties

Thermal behavior of the materials was studied by Differential Scanning Calorimetry (DSC) method with a Mettler Toledo device according to ISO 11357-1. The measurements were made on samples of an average weight of 10-12 mg under nitrogen atmosphere, from 25 °C to 220 °C, at a scan rate of ±10 K/min. Three heating-cooling-heating cycles were performed to evaluate the influence of MWCNT on crystallization behavior of the materials. The melting temperatures and crystallinity were evaluated at the second heating runs in order to exclude any thermal history in the materials. For determination of the melting enthalpy $\Delta H$ [J/g] the integration interval between 30 °C and 140 °C was used. The crystalline fraction $X_c$ [%] of the neat polymers and nanocomposites was calculated by equation

$$X_c = \frac{\Delta H}{\Delta H_{PE}(1-\varphi)} \times 100 \tag{1}$$

where $\varphi$ is the weight fraction of the filler in composite, $\Delta H_{PE}$ is the heat of fusion of the perfect crystal of polyethylene and $\Delta H$ is the enthalpy of fusion of the studied samples, respectively. The value of $\Delta H_{PE}$ is 293 J/g [20].

Thermal conductivity of the materials was measured by Hot Disk (ThermTest Inc., TPS500) technique under ambient conditions by applying two-sided configuration and the sensor of 3.189 mm radius. Measurements were made on the produced plates based on the Hot Disk Transient Plane Source method according to ISO/DIS 22007-2.2 standard. Power of 15 mW was applied and time of measurement was set to 40 s. Five repeated measurements were done for each composition and up to five different intervals were chosen for calculation of the mean values of thermal conductivity $K$. The estimated error didn’t exceed 7%.

Thermomechanical analysis (TMA) was performed in order to evaluate the effect of MWCNT on the coefficients of linear thermal expansion (CLTE) $\alpha$ of the neat polyethylene. The tests were performed on Mettler Toledo TMA/SDTA841e device in an expansion mode (through thickness direction) under the force of 0.02 N and a heating rate of 3 K/min. Two heating cycles were monitored and CLTE were estimated at the second heating run in the temperature range of 40 °C – 75 °C. At least two replicate samples of each composition were tested. Data scatter for the mean values of CLTE was in the range of 2 – 5%.

2.3. Mechanical properties

Uniaxial tensile tests were conducted according to ISO 527 on a Zwick universal testing machine with a load cell of 2.5 kN at a constant crosshead speed of 50 mm/min. Strain was monitored by using clip-on extensometer attached to the parallel part of dog-bone samples. At least three replicate samples for each composition were tested and the mean values of the elastic modulus ($E$), the ultimate stress – maximal stress at yield ($\sigma_y$), and strain at break ($\epsilon_b$) were determined. Low data scatter for $E$ and $\sigma_y$ (about 3%) was observed. The elastic modulus was determined from the slope of the stress-strain curve in the linear range (i.e. from 0.1 up to 0.5% strain). The samples of both the neat and nanomodified HDPE (up to 10 wt.% MWCNT) fractured in a ductile manner with more or less extensive necking related to plastic deformation and orientation effects. Brittle fracture was noticed for samples produced from the pure masterbatch only, i.e. containing 15 wt.% MWCNT. In this study, engineering stress and engineering strain were adopted.

Uniaxial tensile creep tests were performed by using the same Zwick machine. Creep test regimes with different stresses and loading time were applied to cover wide range of strains in the elastic and viscoplastic regions of deformation. Constant load corresponding to 0.25 $\sigma_y$ and 0.5 $\sigma_y$ of the neat polymer or each composition was applied with a constant crosshead speed of 10 mm/min. Creep
period was 30 min or 1 hour, while creep recovery was always three times longer than the active loading. Similar to tensile tests, strain was monitored by using the clip-on extensometer. At least three samples for each composition were tested.

2.4. Electrical properties
The electrical resistance $R$ of all compositions with MWCNT was evaluated by a simple two-point method on the parallel part of the dog-bone sample. Surfaces of samples were cleaned with acetone, polished with sandpaper, and then a conductive silver paint (Electon 40 AC, Amepox Microelectronics, Poland) was applied to ensure low contact resistance to the tips. The measurements were done by using a digital multimeter Tektronix DMM 4020 5-1/2 after complete drying of the silver paint (1 day). The measured resistances $R$ were converted to electrical resistivity using the equation $\rho = R A / l_0$, where $A$ is the cross-section area of the sample in its parallel part and $l_0$ is the distance between two contact points. Average values were calculated for at least three replicate samples of each composition.

Strain sensing capability of the nanocomposites was estimated by monitoring the electrical resistance changes during creep-recovery tests via voltage drop [9]. For electrical insulation against the testing machine, the shoulder parts of dog-bone samples were wrapped with grinding paper.

3. Results and discussion

3.1. Overall characterisation of the materials
Incorporation of MWCNT into HDPE resulted in overall enhancement of thermal and mechanical performance of the nanocomposites. The mean values for some operational characteristics of the produced materials are listed in table 2. As seen from the data, density $\rho$ linearly increases with the addition of nanofillers giving an increment of about 0.6% per 1 wt. % MWCNT that is well correlated with the rule of mixture for similar polymer nanocomposites [8].

| Material | wt. % | $\rho$ (g/cm$^3$) | $X_c$ (%) | $K$, W/(m·K) | $\alpha$·$10^{-6}$ m/(m·K) | $E$ (GPa) | $\sigma_y$ (MPa) |
|----------|-------|-------------------|-----------|--------------|-----------------------------|-----------|-----------------|
| HDPE5502S-c | 0  | 0.967  | 70.7  | 0.157  | 206  | 1.54  | 29.0  |
| 2       | 0.979  | 73.3  | 0.176  | 195  | 1.66  | 29.8  |
| 5       | 0.998  | 73.5  | 0.225  | 186  | 1.88  | 32.2  |
| 7.5     | 1.012  | 73.8  | 0.243  | 176  | 2.08  | 34.7  |
| 10      | 1.029  | 71.8  | 0.250  | 179  | 2.27  | 36.8  |
| HDPE3820-c | 0  | 0.967  | 61.1  | 0.142  | 229  | 0.98  | 21.3  |
| 2       | 0.966  | 61.9  | 0.174  | 215  | 1.17  | 23.8  |
| 5       | 0.985  | 67.7  | 0.196  | 213  | 1.45  | 27.7  |
| 7.5     | 1.001  | 69.3  | 0.216  | 208  | 1.74  | 31.4  |
| 10      | 1.019  | 70.7  | 0.247  | 191  | 2.04  | 34.6  |
| HDPE3820-ex | 0  | 0.950  | -  | 0.154  | 265  | 0.94  | 20.6  |
| 2       | 0.964  | -  | 0.165  | 241  | 1.12  | 22.6  |
| 5       | 0.981  | 60.7  | 0.194  | 226  | 1.17  | 25.5  |
| 7.5     | 0.995  | 62.4  | 0.226  | 205  | 1.37  | 28.3  |
| 10      | 1.015  | -  | 0.258  | 198  | 1.67  | 33.0  |
| Plasticyl™ HDPE1501 | 15 | 1.045  | 71.9  | 0.321  | 164  | 2.38  | 34.8  |
According to the results of calorimetric tests, melting temperatures were almost not affected by the addition of nanotubes. Variations of $T_m$ were in the range of $\pm 2$ °C with the mean values 132, 130, and 133 for HDPE5502S-c, HDPE3820-c and HDPE3820-ex, respectively. Similarly to other semicrystalline polymers, two competitive processes are affecting the crystalline order of nanomodified polyethylene [2]. MWCNT promote formation of nuclei and facilitate their growth [3], while their high aspect ratio and strong interfacial interactions with the polymer result to conformational restrictions of macromolecules [2,5]. The obtained higher degree of crystallinity in the nanocomposites (up to 15% for HDPE3820-c reinforced with 10 wt.% MWCNT) compared to neat polyethylene is thus attributed to a predominance of the former process.

The reinforcing effect of MWCNT appears in a decrease of CLTE $\alpha$ and great improvement of the mechanical characteristics of HDPE (table 2). A linearly decreasing $\alpha$ with growing MWCNT content in nanocomposites (down to 13-17%) indicates to their enhanced ability to withstand thermal deformations. The elastic modulus $E$ linearly increases with addition of the nanofillers and reach up to 50% and 80-100% growth for compositions with 10 wt.% MWCNT of HDPE5502S and HDPE3820, respectively. Similar trends are observed for the ultimate strength $\sigma_y$: an enhancement for the maximally reinforced samples is in the range of 30-60%.

The strain at break dramatically decreased with the growth of MWCNT content in the polymers (from more than eight hundreds down to a ten), however most of samples still fractured in a ductile manner. Similar results on the improvement of mechanical characteristics for various polyolefine/MWCNT composites have been obtained in a number of studies [4-6].

Carbon nanotubes, being also good heat conductors, greatly contributed to the improvement of polyolefin’s thermal conductivity [23]. With the addition of 10 wt.% MWCNT, the coefficient of thermal conductivity $K$ increased for more than 60% for all HDPE. Electrical percolation threshold is found to be below 2 wt.% MWCNT. The electrical resistivity of maximally loaded nanocomposites decreased for more than four orders of magnitude and reached values 0.02 and 0.04 Ohm-m for HDPE5502S and HDPE3820, respectively.

By comparing the data for two types of HDPE3820 nanocomposites, no obvious beneficial effects on their operational properties from using extrusion or calendering processing technique were revealed. This result could further be useful for selecting an effective method for producing nanomodified polyethylene samples in laboratory conditions and giving a preference to the more simple and energy-consuming calendering method.

3.2. Creep performance

Representative creep-recovery curves of HDPE/MWCNT composites are shown in figure 1. All samples exhibited highly nonlinear viscoelastic-viscoplastic behavior. Incorporation of MWCNT into HDPE resulted in a noticeable enhancement of its creep resistance appeared in lower creep and residual strains. HDPE5502S-based nanocomposites exhibited lower creep strains compared to HDPE3820/MWCNT that is well correlated with higher degree of crystallinity, lower CLTE and higher elastic modulus and yield stress of the former material (table 1). The same correlations are noticed, when compare creep resistances of neat and MWCNT-filled polymers.
The creep strain of HDPE after 30 minutes long loading under stress levels of 0.5 $\sigma_y$ of the neat polymers (15 MPa and 12 MPa for HDPE5502S-c and HDPE3820-ex, respectively) decreased for more than 3 times with the addition of 10 wt.% MWCNT. More extensive effect is noticed for residual strains: their values for nanocomposites decreased down to 5 times compared to the neat polymers (figure 2a). Similar improvements in the creep resistance of various polymer nanocomposites have been reported elsewhere [2,5,10,11-14] and are explained by reinforcing effect of nanofillers and their contribution to changes of polymer microstructure at an interphase. The enhanced creep recovery property of nanocomposites is considered to be particularly important in engineering applications, since high unrecovered strains could result in unpredictable damage of polymer-based products.

In order to reveal the origin of the improved creep resistance of nanocomposites, some creep-recovery tests were performed at stress levels equivalent to 0.25 $\sigma_y$ and 0.5 $\sigma_y$ for each series of samples (table 1). Interestingly, reduction of the creep and residual strains due to addition of MWCNT in these tests was not as extensive as in the case when the same stress is applied for both neat polymer and nanocomposites (figure 1, figure 2a). As seen from figure 2b, the residual strains remain almost unchanged with increasing content of MWCNT. It should also be pointed out rather high data scatter of the strain values that increases with the applied load and time of loading and is related to microstructural inhomogeneity of the materials.

The residual strain as a function of the total creep strain for all tested samples is shown in figure 3. Interestingly, the data fit on a common dependence independently on testing conditions. Increase of applied stress or time of loading in creep-recovery tests appears in a shift along the dependence towards higher residual and creep strain values, while an opposite trend is noticed for growing content.

**Figure 1.** Representative creep-recovery curves of HDPE5502S-c (a) and HDPE3820-ex (b) based nanocomposites at a stress level equivalent to 0.5 $\sigma_y$ for corresponding neat polymers.

**Figure 2.** Residual strains of nanocomposites as a function of MWCNT content for HDPE5502S-c and HDPE3820-ex determined after 30 min/90 min creep-recovery tests at stress levels corresponding to 0.5 $\sigma_y$ of the neat polymer (a) and for HDPE3820-c determined after 1 h/3 h creep-recovery tests at stress levels corresponding to 0.25 $\sigma_y$ and 0.5 $\sigma_y$ for each series of samples (b).
of MWCNT in nanocomposite samples. These data could be useful for selection of an appropriate material and easy prediction of residual strains accumulated in polymer-based products under specific operational conditions.

![Figure 3](image.png)

**Figure 3.** Residual strain as a function of total creep strain for all materials and testing conditions.

The electrical resistance changes monitored during creep-recovery tests are shown in figure 4 by example of HDPE3820-c nanocomposites tested at stress levels equivalent to 0.5 $\sigma_y$. Similar dependences were observed for other series of samples and loading conditions.

![Figure 4](image.png)

**Figure 4.** Creep-recovery curves (a) and related electrical resistance changes (b) of HDPE3820-c nanocomposites.

As seen from figure 4, electrical resistance changes vs. time follow the same shape as creep-recovery curves. The higher are the creep and the residual strains, the higher the corresponding electrical resistance changes are. These data approve applicability of HDPE/MWCNT nanocomposites for in-situ strain monitoring including inelastic deformation regions and relatively long terms. Moreover, the data can further be used for an assessment and modeling of viscoplastic strain evolution and related structural changes in MWCNT-filled polymers.

**4. Conclusions**

Two types of HDPE, neat and filled with various contents of MWCNT incorporated by using a commercially available masterbatch, were studied. Incorporation of up to 10 wt.% MWCNT into HDPE resulted in a slight increase of their crystallinity (up to 15%), while melting temperatures became almost unchanged. Reinforcing effect of the nanofiller appeared in a great increase of the elastic modulus (up to 80%) and ultimate strength (up to 60%) as well as decrease of the coefficient of
linear thermal expansion (down to 17%) of HDPE. Carbon nanotubes, being also good heat conductors, greatly contributed to the improvement of polyethylene’s thermal conductivity (up to 60%). Electrical percolation is determined below 2 wt.% MWCNT.

Nanocomposites are characterized by the improved creep resistance compared to the neat polymers: the creep strains decreased for 3 times with the addition of 10 wt.% MWCNT. All the materials exhibited highly nonlinear viscoelastic-viscoplastic behavior and development of both viscoelastic and viscoplastic deformation was highly restricted by the nanofillers. The residual strains of maximally reinforced nanocomposites are fivefold lower than these for the neat polymers. A common dependence of the residual strain on the total creep strain is determined from the whole set of data on creep-recovery tests. The electrical resistance changes are well correlated with the overall strain changes and residual strains in nanocomposites.

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