Effect of Carbon Nanotubes Concentration on Creep Behaviour of Polypropylene-Carbon Nanotubes Nanocomposites

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The goal of this paper is to study the creep behaviour of multi-walls carbon nanotubes (1, 3, 5 wt.% MWCNTs) filled polypropylene (PP) through the instrumented indentation technique. Two types of the 3-step indentation test were considered to analyse viscoelastic behaviour through sharp indentation at room temperature. Under the loading conditions, the PP/MWCNTs samples present a time-independent plastic behaviour which must be considered not to under/overestimate the viscoelastic properties. The ratio of residual indentation depth to the maximum indentation depth at peak load calculated from the initial portion of the unloading curve was over 0.7 and demonstrated the plastic character of tested materials. The indentation hardness and modulus calculated from the slope at the unloading curve were changed due to the presence of plastic deformation from the loading phase, to the load intensity and hold time. The local distribution of carbon nanotubes lead to the variation in creep response and also, in the mechanical properties of material. Calculating the creep rate, a better creep response was offered by the higher concentration of carbon nanotubes during the indentation test at peak load of 1 N. A 3-step standard indentation test (Oliver and Pharr method) was considered to avoid the influence of the duration from the holding phase on the mechanical parameters. We found that a holding phase of 40 seconds was enough to have a negligible influence of creep on the indentation modulus for 5 wt.% of MWCNTs sample.

Keywords: indentation, creep, carbon nanotubes, indentation hardness, indentation modulus.

The Instrumented Indentation Technique (IIT) is a standard method used to accurately measure the local mechanical properties (indentation hardness, H_{IT}, indentation modulus, E_{IT}) of engineering materials. Due to the local character of the analysis, the indentation testing is suited to the analysis of polymers, whose properties can vary substantially from point to point. This variation could be due to the variation in local composition, microstructure and time-dependent behaviour. Indentation is a non-destructive technique used to study the polymeric composite materials at reduced scale (micro or nano) contact testing. The indentation method was simultaneously developed with the standard analytic technique for mechanical property deconvolution (the Oliver and Pharr method [1]). The Oliver and Pharr method takes into account the elastic recovery and the changing in contact area during the unloading segment of the indentation curve. The Oliver and Pharr analysis applied to polymers is time-independent assuming that the unloading response is purely elastic while the mechanical behaviour of polymers is time-dependent [2-6]. Thus, the indentation test must be performed under hold time to reduce the time-dependence effect during the unloading phase and to extract the mechanical properties of the polymeric materials. The holding phase at fixed peak load allows the material to deform sufficiently for the indentation creep test and to be insignificant during the unloading phase. This paper studied the creep influence on the mechanical features extracted from the indentation curves.

The increasing interest in the applications of indentation methods in the field of polymers led to evaluate the indentation creep response with the viscoelastic or plastic regime which corresponds to thermoplastics. In order to measure the indentation hardness and modulus of polymeric materials by the IIT method, the indentation test should be performed under hold time at peak load. Most of the polymers exhibit creeps when subject to a constant load in long-term creep. Thus, the creep behaviour must be studied before extracting and evaluating the mechanical properties of polymeric materials. The creep process can be characterized as the result of a solid material that is slowly and permanently deformed under the influence of the constant load. As a function of time and temperature, the creep measurement provides important information about the materials with applications on long-term durability and reliability [7].

Thermoplastic polymer nanocomposites filled with the carbon nanotubes with multifunctional properties for science and engineering application were still intensively studied. Polymers are the versatile materials with unique properties like low density, reasonable strength, flexibility etc. Blending of polymer materials with different kinds of fillers have been used to improve the strength and stiffness. From all type of nanofillers the carbon nanotubes were the most promising nanofillers which considerably enhanced the mechanical, magnetic, and electrical properties of the polymer nanocomposites [8-16]. During the last two decades, more experimental studies established that the carbon nanotubes are an ideal reinforcement agent which influence the functional composite properties due to their excellent features such as large interfacial contact area, high aspect ratio, and low mass density [17-26].

It is known, that there is the tendency of the nanofillers to form agglomerates due to the large surface area. Thus, two tasks are required from the nanofillers to ensure a good dispersion within the polymer matrix and an efficient

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incorporation to prevent re-aggregation of the filler [27]. A real problem consists in the formation of the aggregates during the manufacturing process. Choosing the carbon nanotubes functionalization method, the proper polymer matrix, the suitable synthesis method and the working parameters (temperature, shear rate, shear force, mixing time) are the key for the development of high performance carbon nanotubes composites [28]. Melt mixing is the most common commercial method used to prepare carbon nanotubes-polymer composites such as carbon nanotubes/polypropylene (PP) [29-31], high density carbon nanotubes/polyethylene (PE) [32], carbon nanotubes/polycarbonate (PC) [33-34], etc. The disadvantage of this method is that the dispersion of carbon nanotubes in a polymer matrix is poor as compared to that achieved by solution mixing. In addition, the carbon nanotubes must be lower due to the high viscosities of the composites at higher loading of carbon nanotubes. The PP as semi-crystalline polymer is a common polyolefin used in the food industry and industrial engineering due to its excellent properties and low cost manufacturing [35]. Researchers have reported an improvement of Young's modulus and strength after the incorporation of carbon nanotubes into the PP matrix [36]. Instead, the problem of difficult dispersion of carbon nanotubes-filled thermoplastic nanocomposites which could affect their viscoelasticity needs to be established. The PP is known for low interaction with the carbon nanotubes and dispersion of them [18,37]. Xia et al. prepared PP/MWCNTs (multi-wall carbon nanotubes) composites with good dispersion using a novel solid-state mechanochemical pulverizing process [38]. A modest increase in tensile modulus, E_{comp}, was observed in a composite with 3 wt% of MWCNTs. A good dispersion method with a poor reinforcement effect could involve a weak bonding between the MWCNTs and the matrix.

Both positive and negative effects of the fillers on the creep resistance of polymers have been reported. For instance, the carbon nanotubes incorporated into the thermoplastic matrix decrease the creep deformation of the nanocomposite [39,40]. To improve time-dependent creep response of polymeric materials, one is still trying to establish the mechanisms which explain the advantages and disadvantages of the carbon nanotubes incorporated to thermoplastic.

During this research, the behaviour of multi-walls carbon nanotubes filled polypropylene (PP/MWCNTs) to a constant load was described through the creep indentation procedure. The influence of the concentration by the weight of the carbon nanotubes on time-dependent behaviour was investigated.

Experimental part

Materials and methods

PP filled with 1, 3 and 5 wt.% MWCNTs have been supplied by Nanocyl (Sambreville, Belgium). According to the supplier, the MWCNTs (type Nanocyl™ NC7000) have the diameter of 9.5 nm, the length of 1.5 μm, the carbon purity above 90% in weight, and the metal oxide of 10% [41]. The specimens were obtained by injection moulding; for further details see [42].

Indentation procedure

Creep tests have been carried out by CSM Micro indentation Combi Tester equipment (Switzerland) equipped with a Vickers diamond tip indenter (with an equivalent cone angle of 70.29°), at room temperature.

At least ten measurements were performed on each sample to check the reproducibility of the data. The indentation locations were separated by a distance of 2 mm. A 3-step indentation test was performed on PP/MWCNTs to evaluate the creep response as a function of carbon nanotubes concentration and applied load. The experiment was conducted under load-controlled conditions providing a constant load during the holding phase of the indentation test and no thermal drift correction needed. The loading history of the 3-step indentation test includes linear loading to maximum indentation loads of 1 and 2 N with a constant rate of 2 N/min, holding at the maximum load during 300 s , and unloading with a constant rate of 2 N/min. A standard indentation procedure at a maximum load of 2 N with a hold time of 40 s was considered to eliminate the time influence on the mechanical properties. Then, the parameters extracted from all the obtained indentation curves were compared. The Poisson's ratio for all samples was set at 0.4.

Data analysis

The indentation hardness is a measure of the resistance to permanent deformation or damage. However, hardness may be different if the methods used for the measurement are different.

Instrumented hardness, H_{IT} [MPa], provided by the IIT technique is calculated from its general definition (the ratio between the applied load and the contact area) following the equation [1,43,44]

$$H_{IT} = \frac{P_{\max}}{A_p}, \quad (1)$$

where P_{max} [mN] is the maximum load, and A_p [nm^2] is the projected contact area between the indenter and the specimen at the maximum depth and load.

If the geometry of the indenter is known, the Vickers hardness, *HV* [HV], can be calculated [1,43-46]

$$HV = \frac{P}{A_c}, \quad (2)$$

with A_c as contact area

$$A_c = 4\tan^2(\alpha)h_c^2, \quad (3)$$

where α is the angle between the axis of the indenter and one of the faces of the pyramid (α = 68° for Vickers indenter), and h_c [nm] is the contact depth [47].

Finally, for a Vickers indenter [43]

$$HV_{IT} = 0.0945 \cdot H_{IT}, \quad (4)$$

The reduced elastic modulus, E_R [GPa], is used to account for elastic displacements occurring in both the indenter and the surface and combines the modulus of the indenter and the specimen in a way given by Giannakopoulos [1,47]

$$\frac{1}{E_R} = \frac{(1-\upsilon^2)}{E} + \frac{(1-\upsilon_i^2)}{E_i}, \quad (5)$$

where: ν is the material Poisson's ratio; E [GPa] is the elastic modulus for the sample; E_i [GPa] and ν_i are the elastic modulus and Poisson's ratio, respectively, of the indenter.

Since the unloading curve is related to the elastic property of the material, the reduced modulus can be determined from the initial part of the unloading indentation curve [1,43-46]

$$E_R = \frac{1}{2\beta}\sqrt{\frac{\pi}{A_c}}\frac{dP}{dh}, \quad (6)$$

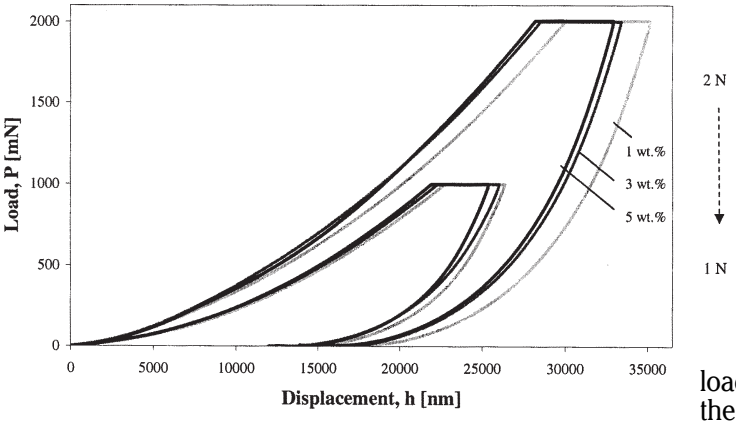

Fig. 1. Load-displacement curves under a 3-segment loading history for PP/MWCNTs nanocomposites for 1 N and 2 N with a 300 s hold period

in which $S = \left(\frac{dP}{dh}\right)_{h=h_{max}}$ is the initial slope of the unloading curve and β a dimensionless factor that accounts for the shape of the cross-section of the indenter (β = 1.0124 for Vickers indenter [48]).

The creep, C_{IT} [%] for the material represents the relative change of the indentation depth measured during the holding phase at fixed peak load [49]

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100, \quad (7)$$

where: h_1 is the indentation depth at time t_1 of reaching P (which is kept constant); h_2 is the indentation depth at hold time t_2 of the constant P.

Results and discussions

Figure 1 presents the average load-displacement curves under a 3-segment loading history at the maximum loads of 1 and 2 N maintained constant during a period of 300 seconds for different MWCNTs concentrations. When the samples are subject to indentation at different loading conditions, they exhibit a different mechanical response in terms of the indentation curve.

During the indentation test, the sharp indenter was kept for a pause of 300 s penetrating the material. The maximum displacement, h_{max}, was reached at the maximum constant load, P_{max}. We found that h_{max} decreased with the increase in the carbon nanotubes concentration. For the samples tested at 2 N, the maximum indentation ranged between $(35 \div 32) \times 10^3$ nm in terms of the increasing concentration. The decrease in the load indentation (from 2 N to 1 N) led to a decrease in the measured indentation depth (from 25.93×10^3 to 25.44×10^3 nm) for 1 N test. This variation corresponds to the viscoelastic behaviour of these materials. Therefore, the residual imprint which remained after the unloading phase contributed to a decrease in the hardness results for all types of samples indented at 2 N to 1 N, respectively (table 1). On the other hand, due to the plastic deformation which occurred during the loading phase, a print area was left in the material. Therefore, the h_{max} parameter varies with the maximum load and carbon nanotubes content in the matrix leading to the variation in the true contact area. Due to the gradual reduction of the contact area caused by the elastic recovery, the unloading part of the P - h curve is nonlinear.

From the initial portion of the unloading curve the h_r / h_{max} parameter was calculated. This parameter represents the ratio of residual indentation depth, h_r, to the maximum indentation depth at peak load, h_{max}. We obtained the homogeneous h_r / h_{max} ratio in the range $0.79 < h_r / h_{max} > 0.86$ under the 3-step indentation experiments for 1, 3 and 5 wt.% of MWCNTs content. For both indentation loads, $h_r / h_{max} > 0.7$ demonstrated the plastic character of the material. The experimental curves were quite similar for all types of tested materials.

The optical microscopy technique was used to examine the indentation imprints in order to obtain qualitative information about the plastic properties of the material. Due to plastic deformations some residual indentation depth, h_r, remains after unloading phase. The residual imprint of these indentations was shown in figure 2 having a clearer outline. The indentations performed at 2 N maximum load for 1, 3 and 5 wt.% MWCNTs were represented in figure 2 (a, b, c). figure 2 (d, e, f) show another set of indentations at 1 N load.

The indentation imprint left in the material for the 2 N test was higher than that for the 1 N test. This fact is due to the decrease in the residual indentation depth along with the load indentation. In terms of increasing the MWCNTs concentration for samples tested at 2 N, the permanent residual indentation depth ranged between $(28 \div 27 \times 10^3)$ nm. A decrease in the load indentation (from 2 N to 1 N) led to a decrease in the measured permanent depth $(22 \div 21 \times 10^3$ nm) for 1 N test. Therefore, the residual imprint which remained after the unloading phase contributed to

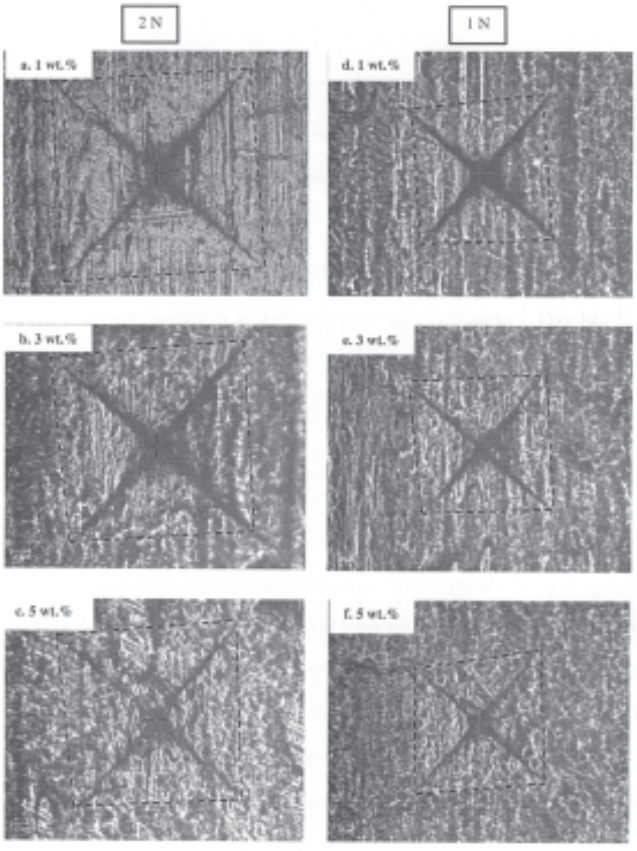

Fig. 2. Optical micrographs of residual indentation imprint at loads of 2 N and 1 N with hold time of 300 secs onds on PP/MWCNTs surface (for 1, 3 and 5 wt.% of MWCNTs) (scaled 15 μm)

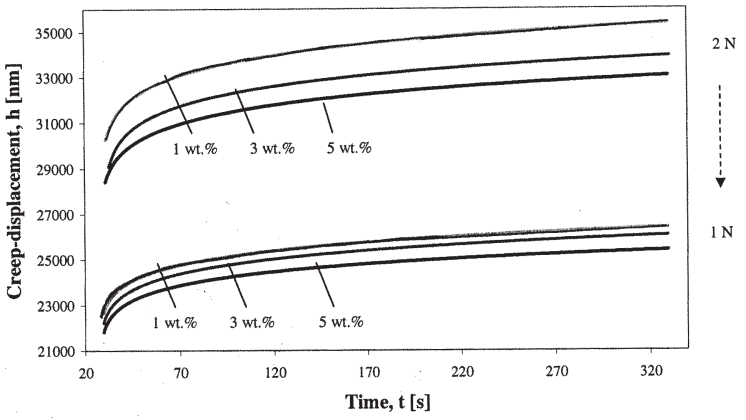

Fig. 3.Influence of the applied load and carbon nanotubes concentration on the creep response for PP/MWCNTs nanocomposites for 1 N and 2 N indent with a loading rate of 2 N/min and a hold period of 300 s.

Parameters		P_{max} = 2 [N], t = 40 [s]			P_{max} = 2 [N], t = 300 [s]			P_{max} = 1 [N], t = 300 [s]		
		MWCNTs (wt.%)			MWCNTs (wt.%)			MWCNTs (wt.%)		
		1	3	5	1	3	5	1	3	5
H_{IT} [MPa]	average	100.70	98.16	119.25	87.64	95.38	96.47	79.97	73.15	81.24
	St. dev.	5.14	7.46	13.26	1.25	1.96	2.98	2.15	7.06	2.54
HV [Vickers]	average	9.51	9.27	11.26	8.27	9.00	9.04	7.55	6.90	7.67
	St. dev.	0.49	0.70	1.25	0.12	0.19	0.31	0.20	0.67	0.24
E_{IT} [GPa]	average	1.81	1.90	1.85	1.44	1.56	1.66	1.31	1.54	1.66
	St. dev.	0.05	0.10	0.06	0.09	0.06	0.05	0.08	0.09	0.25
E_R [GPa]	average	2.15	2.25	2.20	1.71	1.85	2.30	1.55	1.84	1.97
	St. dev.	0.06	0.12	0.07	0.11	0.08	0.29	0.09	0.10	0.30
C_{IT} [%]	average	9.16	8.26	8.93	16.87	16.80	16.47	16.28	16.23	15.89
	St. dev.	0.35	0.40	0.79	0.58	1.27	0.70	0.54	1.09	1.33

Table 1
SUMMARY OF THE MAIN MECHANICAL PARAMETERS OBTAINED FROM THE INDENTATION CURVES FOR PP/MWCNTs COMPOSITES IN DIFFERENT LOADING HISTORIES

a decrease in the hardness results for all types of samples indented at 2 N to 1 N, respectively (table 1).

The 3-step indentation tests were considered and two maximum loads were selected to study the influence of load and carbon nanotubes content on the creep behaviour of polymer materials.

The variation in the creep-displacement as a function of time was measured. Figure 3 displays a comparison between the creep curves for the three PP/MWCNTs composites tested with different indentation parameters (P_{max} = 1 and 2 N, t_{hold} = 300 s). These curves were generated by averaging five indentation curves.

As it can be seen in figure 3, the creep stage formation for both indentation loads was indicated by the shape of the obtained curves. The initial part of the creep phase had a sudden increase in the creep-displacement which slowly decelerated and no steady-state was yet reached during the holding phase of 300 s.

The creep response of the composites was influenced by the load intensity and local distribution of the carbon nanotubes during the test. The repeatability of the results was high and the difference between the highest and lowest final value at the end of the holding phase of the creep-displacement curve was less than 1.8 ⌈m (for P_{max} = 1 N) and 3 μm (for P_{max} = 2 N), respectively.

The higher the indentation load, the more pronounced creep response. 1 wt.% of MWCNTs was the sample exhibiting the highest creep followed by 3 and 5 wt.% of MWCNTs for both applied loads. Figure 2 shows a significant difference in the creep-displacement curves. In the case of polymeric materials indented at P_{max} = 2 N the creep-displacement decreased with 6.57% from 1 to 5 wt.% of MWCNTs. When the load was reduced at half (from 2 to 1 N), a decrease in creep-displacement with 3.77% from 1 to 5 wt.% of MWCNTs was observed.

The maximum difference between the creep-displacement was found for 1 wt.% of MWCNTs loaded at 2 and 1 N, respectively ($\Delta h \approx 25\%$). For 3 and 5 wt.% of MWCNTs the difference in the creep-displacement was about 23%. Thus, the important plastic deformation which occurred during the loading phase led to this increase in the creep-displacement for samples indented at load of 2 N.

These data have been transformed into displacement-log time plotting to calculate the creep rate (the slope at the linear portion of the creep-displacement-time curve). The indentation at fixed peak load of 1 N induced a variation of creep rate between 7.69÷7.20 nm/s along with the increase of the carbon nanotubes concentration. Also, the creep rate decreased from 10.72 to 9.77 nm/s under the 3-step indentation test at load of 2 N. The higher incorporation of MWCNTs into the polymer matrix, the lower creep rate could indicate the reinforcing effect of the carbon nanotubes.

To minimize the influence of the pause time on the slope at the unloading phase, the mechanical parameters were extracted from the *P-h* curves obtained during a 3-step indentation test with a hold period of 40 s (Oliver & Pharr method). Then, the parameters were compared with those calculated from the indentation curves under a 3-segment loading history (P_{max} = 2 N, t_{hold} = 300 s). Table 1 presented the average value and standard deviation of mechanical parameters (Vickers hardness, indentation hardness, indentation modulus, reduced modulus, and indentation creep coefficient). Also, the parameters extracted from the 3-step indentation test (P_{max} = 1 N, t_{hold} = 300 s) were presented in this table. Before computing the results, the normality assumption for the experimental data was verified.

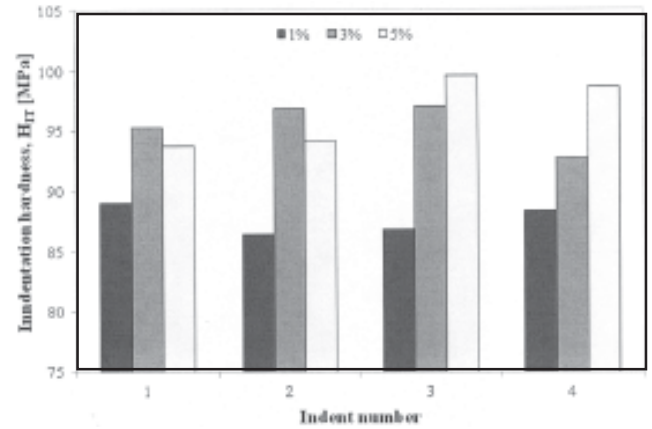

Fig. 4. Indentation hardness as a function of the carbon nanotubes content and the indent sites of PP/MWCNTs nanocomposites under a 3-step indentation procedure (P_{max} = 2 N, t_{hold} = 300 s)

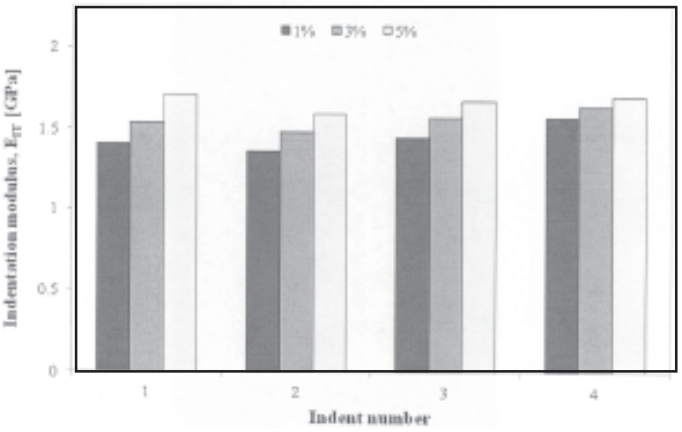

Fig. 5. Indentation modulus as a function of the carbon nanotubes content and the indent sites of PP/MWCNTs nanocomposites under a 3-step indentation procedure (P_{max} = 2 N, t_{hold} = 300 s)

The indentation hardness and modulus calculation was affected by the indentation load intensity and period from the holding phase. For the same load intensity, the average H_{IT} and E_{IT} increased along with the carbon nanotubes concentration. A decrease of parameters was observed when the hold period increased from 40 to 300 s. The results obtained showed that the effect of creep on the E_{IT} can be neglected after only 40 s as holding phase for 5 wt.% of MWCNTs sample. Instead, for 1 and 3 wt.% of MWCNTs samples a hold period more than 150 s could be necessary to minimize the influence of creep on the H_{IT}.

When comparing the results obtained in two different conditions of the hold time, the highest value of hardness (119.25 Mpa for 5 wt.%) was recorded after 40 s at peak load. At the same time, the C_{IT} (8.93%) determined during indentation with a hold time of 40 s was twice lower than C_{IT} (16.47 %) picked-up after 300 s of holding phase for 5 wt.% carbon nanotubes. In the case of indentation with a holding phase of 300 s, the creep phenomenon developed. Thus, PP/MWCNTs composites exhibit a time-dependence behaviour which will decrease their mechanical performance.

The uniform dispersion of MWCNTs into the polymeric matrix appeared from figures 4 and 5. Figure 4 showed the indentation hardness variation as a function of the carbon nanotubes content and the indent site. From distinctive indent points, an increasing trend in H_{IT} with the carbon nanotubes content was shown.

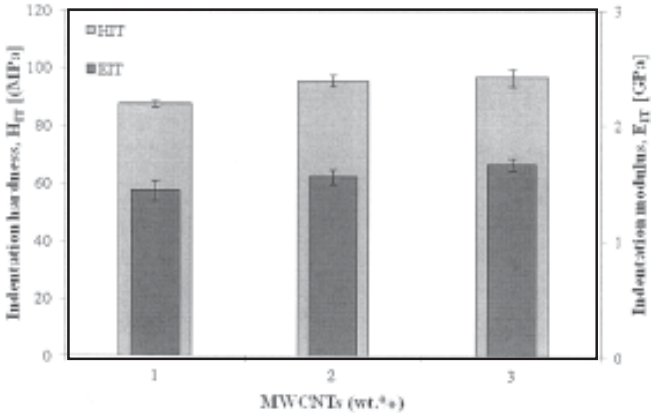

Fig. 6. Average indentation hardness and modulus as a function of the carbon nanotubes content for PP/MWCNTs nanocomposites (P_{max} = 2 N, t_{hold} = 300 s)

Due to the local character of the analysis, the results indicate a variation in the hardness from one site to another for each carbon nanotubes concentration. The indenter tip could be possible to be driven into a micro-region with poor dispersion of carbon nanotubes. An increase in the content from 1 to 5 wt.% of the carbon nanotubes led to the formation of tightly packed agglomerates of several MWCNTs increasing the hardness. The continuous agglomerates area became bigger at the higher injection pressure [41,42]. Researchers have shown a tendency of the carbon nanotubes agglomeration at higher content (above 3 wt.% of MWCNTs) depending on the polymer type matrix [18,20].

Generaly, the E_{IT} of the samples has the tendency to increase with the MWCNTs content (table 1). The variations in the E_{IT} as a function of the carbon nanotubes content and the indent site were shown in figure 5.

Figure 6 presents the variation of the instrumented hardness and modulus as a function of the carbon nanotubes concentration. Each column from the graph below was generated by averaging four parameters obtained from the indentation curve.

The average indentation hardness for 3 and 5 wt.% of MWCNTs was quite close with 95.38 MPa and 96.47 MPa and the standard deviation was 1.96 MPa and 2.98 MPa. The average value of the indentation modulus for 1, 3 and 5 wt.% of MWCNTs was quite close with 1.44 GPa, 1.56 GPa and 1.66 GPa whereas the standard deviation was lower than 0.09 GPa. The H_{IT} and E_{IT} have increased with the weight percentage of the carbon nanotubes incorporated into the polymeric matrix.

Conclusions

This paper analyzed the viscoelastic behaviour of multi-wall carbon nanotubes filled polypropylene, using a sharp indentation.

In order to investigate the influence of the plastic deformation which occurred during the loading phase on the creep response of materials, two types of 3-step indentation tests were considered.

From the experimental indentation curves, the viscoelastic behaviour of materials resulted in an increase in the maximum indentation depth with the decrease in the carbon nanotubes concentration, even if the load was constant during the holding phase of 300 s.

We discovered that the measured creep-displacement during the 3-step indentation test with an applied load of 2 N introduced a significant plastic deformation as compared to the 3-step indentation results obtained at load of 1 N. In these conditions, the highest difference in the creep-

displacement of $\Delta h \approx 25\%$ was obtained for 1 wt.% of MWCNTs. More pronounced creep response was found at lower concentration of 3 and 5 wt.% of MWCNTs indented at the lower load of 1 N.

Another parameter which demonstrated the plastic character of the materials was the ratio of residual indentation depth to the maximum indentation depth at peak load ($h_r / h_{max} > 0.7$).

The influence of MWCNTs concentration on the creep behaviour resulted in the creep rate calculated from the displacement-log time plot. A higher creep rate was noticed to vary between 10.72 nm/s (for 1 wt.% of MWCNTs) and 9.77 nm/s (5 wt.% of MWCNTs) under a 3-step indentation test at load of 2 N. The creep rate increased along with load intensity and decreased with carbon nanotubes concentration.

The Oliver and Pharr method was used to extract the mechanical properties of polymeric materials from the unloading phase of the indentation curve after 40 s. The influence of duration of the holding phase on some parameters such as indentation hardness and modulus was studied.

Mechanical parameters obtained from the indentation curves after 40 s were compared to those obtained after 300 s at peak loads of 1 and 2 N. An increase in load intensity led to an increase in H_{IT} (81.24 ÷ 119.25 MPa for 5 wt.%) and E_{IT} (1.66 ÷ 1.85 GPa for 5 wt.%) along with the carbon nanotubes concentration.

The behaviour of time-dependent materials reduced the H_{IT} and E_{IT} parameters. The effect of creep on the E_{IT} can be neglected after only 40 s as holding phase for 5 wt.% of MWCNTs sample. Instead, for 1 and 3 wt.% of MWCNTs samples, a hold period more than 150 seconds could be necessary to minimize the influence of creep on the H_{IT}. To get a steady-state, an increase in hold time was necessary.

The local character of the analysis determined a variation in the H_{IT} with the carbon nanotubes concentration from one site to another. The presence of few agglomerates led to an increase in the hardness from 1 wt.% (86 MPa) to 5 wt.% (99.55 MPa) of MWCNTs. Also, the EIT increased along with the concentration. A higher dispersion of carbon nanotubes into the polymer could improve the creep resistance of materials and their mechanical performance.

To describe the response of time-dependent materials under sharp indentation an analytical model must be established as long as the plastic deformations during the loading phase must be isolated using an appropriate loading history.

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References

1.OLIVER, W.C., PHARR, G.M., J. Mater. Res., **7**, nr. 6, 1992, p. 1564
2.BRISCOE, B.J., FIORI, L., PELILLO, E., J. Phys. D, Appl. Phys., **31**, nr. 19, 1998, p. 2395
3.CHUDOBA, T., RICHTER, F., Surf. Coat. Technol., **148**, 2001, p. 191
4. LU, H., WANG, B., MA, J., HUANG, G., VISWANATHAN, H., Mech. Time-Depend. Mater., **7**, 2003, p. 189
5.HUANG, G., LU, H., Exp. Mech., **47**, 2007, p. 87
6.PALADE, L.I., REIMANIS, I.E., GRAHAM, A.L., Mat. Plast., **50**, no. 2, 2013, p. 97
7.KREMPL, E., KHAN, F., Int. J. Plasticity, **19**, nr. 7, 2003, p. 1069
8.ALIG, I., LELLINGER, D., DUDKIN, S.M., POTSCHKE, P., Polymer, **48**, 2007, p. 1020
9.BAO, H.D., GUO, Z.X., YU, J., Polymer, **49**, 2008, p. 3826
10. KANAGARAJ, S., VARANDA, F.R., ZHIL'TSOVA, T.V., OLIVEIRA, M.S.A., SIMOES, J.A.O., Compos. Sci. Technol., **67**, 2007, p. 3071
11. SONG, B., CHEN, W.N., LIU, Z.S., ERHAN, S., Int. J. Plasticity, **22**, 2006, p. 1549
12. ZHANG, W.X., WANG, T.J., CHEN, X., Int. J. Plasticity **26**, 2010, p. 957
13. BIKIARIS, D., Materials, **3**, 2010, p. 2884
14. SATHYANARAYANA, S., HÜBNER, C., Thermoplastic Nanocomposites with Carbon Nanotubes, J. Njuguna (ed.), Structural Nanocomposites, Engineering Materials, Springer-Verlag Berlin Heidelberg, (2013)
15. ISHIKAWA, H., FUDETANI, S., HIROHASHI, M., Appl. Surf. Sci., **178**, 2001, p. 56
16. KRACKE, B., DAMASCHKE, B., Appl. Phys. Lett., **77**, 2000, p. 361
17. BREUER, O., SUNDARARAJ, U., Polym. Compos., **25**, nr. 6, 2004, p. 630
18. COLEMAN, J.N., KHAN, U., BLAU, W.J., GUNKO Y.K., Carbon, **44**, 2006, p. 1624
19. ESAWI, A.M.K., FARAG, M.M., Mater. Des. **28**, 2007, p. 2394
20. MOHAMMED, AL-SALEH, H., SUNDARARAJ, U., Compos. Part A – Appl. Sci., **42**, 2011, p. 2126
21. HAYASHI, T., ENDO, M., Compos. Part B – Eng. **42**, 2011, p. 2151
22. EITAN, A., Compos. Sci. Technol., **66**, nr. 9, 2006, p. 1162
23. LEE, G.W., JAGANNATHAN, S., CHAE H.G., MINUS M.L., KUMAR S., Polymer, **49**, 2008, p. 1831
24. PANTANO, A., MODICA, G., CAPPELLO, F., Mater. Sci. Eng. A – Struct., **486**, 2008, p. 222
25. CAI, L., TABATA, H., KAWAI, T., Appl. Phys. Lett., **77**, 2000 p. 3105
26. RUIZ, F., SUN, W.D., POLLAK, F.H., VENKATRAMAN, C., Appl. Phys. Lett., **73**, 1998, p. 1802
27. HIRSCH, A., Angewandte Chemie International Edition, **41**, 2002, p. 1853
28. WANG, S., QIU, J., Compos. Part B–Eng., **41**, nr. 7, 2010, p.533
29. LOPEZ MANCHADO, M.A., VALENTINI, L., BIAGIOTTI, J., KENNY, J.M., Carbon, **43**, 2005, p. 1499
30. VALENTINI, L., BIAGIOTTI, J., KENNY, J.M., SANTUCCI, S., Compos. Sci. Technol., **63**, 2003, p. 1149
31. ZHANG, H., ZHANG, Z., Eur. Polym. J., **43**, 2007, p. 3197
32. TANG, W., SANTARE, M.H., ADVANI, S.G., Carbon, **41**, 2003, p. 2779
33. POTSCHKE, P., BHATTACHARYYA, A.R., JANKE, A., Polymer, **44**, 2003, p. 8061
34. POTSCHKE, P., BHATTACHARYYA, A.R., JANKE, A., Eur. Polym. J., **40**, 2004, p. 137
35. MIHAELA, M., OLARU, A., In: Cornelia V, editor. Handbook of polyolefins. Marcel Dekker, Inc., (1993)
36. ZHAO, P., WANG, K., YANG, H., ZHANG, Q., DU, R., FU, Q., Polymer, **48**, nr. 19, 2007, p. 5688
37. BAO, S.P., TJONG, S.C., Mat. Sci. Eng. A–Struct., **485**, 2008, p. 508
38. XIA, H., WANG, Q., LI, K., HU, G.H., J. Appl. Polym. Sci., **93**, 2005, p. 378
39. GANß, M., SATAPATHY, B.K., THUNGA, M., WEIDISCH, R., POTSCHKE, P., JANKE, A., Macromol. Rapid Commun., **28**, nr.16, 2007, p. 1624
40. PEGORETTI, A., KOLARIK, J., PERONI, C., MIGLIARESI, C., Polymer, **45**, 2004, p. 2751
41. Nanocyl, Technical Data Sheet. <www.nanocyl.com>
42. STAN, F., SANDU, L.I., FETECAU, C., Composites: Part B, **59**, 2014, p. 109
43. FISCHER-CRIPPS, A.C., Nanoindentation, Springer, New York, 2nd edition, (2004)
44. STAN, F., MUNTEANU, A.V., FETECAU, C., Mat. Plast., **48**, no. 1, 2011, p. 1
45. SNEDDON, I.N., Int. J. Eng. Sci., **3**, nr. 1, 1965, p. 47
46. STAN, F., FETECAU, C., Mech. Time-Depend. Mater., **17**, 2013, p. 205
47. GIANNAKOPOULOS, A.E., LARSON, P.L., SODERLUND, E., ROWCLIFFE, D.J., VESTERGAARD, R., Int. J. Solids and Structures, **31**, nr. 19, 1994, p. 2679
48. KING, R.B., Int. J. Solids Struct., **23**, nr. 12, 1987, p. 1657
49. *** CSM Instruments SA Indentation software manual R0.1.5b (Apr. 11) 107/112

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