

ELASTIC RECOVERY AT GRAPHENE REINFORCED PA 6 NANOCOMPOSITES

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Abstract

In this study tensile-mechanical properties of graphene containing polyamide 6 nanocomposites were deeply analysed via cyclic measurements. Injection moulded specimens with different nanofiller contents (0...1 wt%) were used for the investigations. At the cyclic tests the loading force was increased with 100 N increments in each cycle and the relaxation time was set to be 30 s. After the relaxation time the residual strain was determined in each cycle (plastic deformation). The results showed that the presence of graphene reduced the plastic deformations (i.e. elastic recovery was enhanced compared to the matrix). It results in that the creeping behaviour of nanocomposites becomes considerable just at higher loads. Based on the results it can be stated that the pure linear elastic region of the tensile curves became wider by the incorporation of graphene nanoparticles into polyamide 6 matrix, meaning that the utilization range is also wider regarding the mechanical stresses.

Keywords:

nanocomposite, graphene, mechanical properties, elastic recovery

1. INTRODUCTION

Nowadays there are several types of nanocomposites developed for engineering applications with high mechanical performance. Nevertheless there are few manifested engineering products in our daily life. The reason for that is that nanocomposites are still relatively new types of materials, thus the structural changes caused by mechanical stresses in the nanocomposites are not revealed properly. Without this information it is hard to design a new engineering product. This is particularly true for recently developed nanocomposites, like graphene reinforced thermoplastics [1-5].

Graphene is one of the most recently discovered nanoparticles. Graphene is a single layer of carbon atoms packed densely in a honeycomb crystal lattice. There are numerous processes developed for its production like chemical vapour deposition, chemical conversion or mechanical exfoliation of graphite, etc. Graphene has outstanding properties, such as high thermal and electrical conductivity and superior mechanical performance. Even though physical properties of graphene-like structures are explored deeply, their application as reinforcement in polymer composites is still under intensive research [6-7].

Zhang et al. [8] produced graphene-oxide (GO) reinforced polyamide 6 (PA 6) nanocomposites by *in situ* anionic ring-opening polymerization. They achieved remarkable increase in the tensile strength and Young's modulus at relatively low (0.01-1.00 wt%) GO contents. They exhibited the typical tensile curves of the composites, which suggest that not just the tensile moduli increased but the initial near linear range of the curves also broadened.

Similar tensile characteristics are observable for other nanocomposites, independently from the matrix or reinforcing materials [9-12]. This wider near linear characteristic means that for the designers the utilization range of the material is also wider, however it is hard to characterize the end-point of the near linear segment. This can be explained by the viscoelastic behaviour of the thermoplastics; fundamentally they have three different types of deformation: instantaneous elastic (energy-elastic), time-dependent viscoelastic (entropy-elastic) and time-dependent viscous (relaxation) deformation. The first two components together are elastic deformations. The composites can be used as structural material until these elastic deformations

are overwhelmingly dominant compared to the viscous one. The characterization of the deformation components is quite difficult as they depend on several parameters like the applied load or the loading time. Therefore the researchers introduced the rate of the elastic recovery [13]. This can be calculated from a cyclic measurement where the tensile load is increased by the cycles but between each cycle a certain time is applied for the recovery of the time-dependent viscoelastic deformation. The elastic recovery can be calculated by the ratio of the elastic deformation and the total deformation. As it is shown in Fig 1 the plastic deformation is a cumulative parameter since in this case the reference point is always the zero-point independently from the value where the current cycle begins. The end of the elastic region can be indicated by a significant change in this parameter during the cyclic test. Another possibility is to give the designers a maximum viscous deformation as a set-point for sizing.

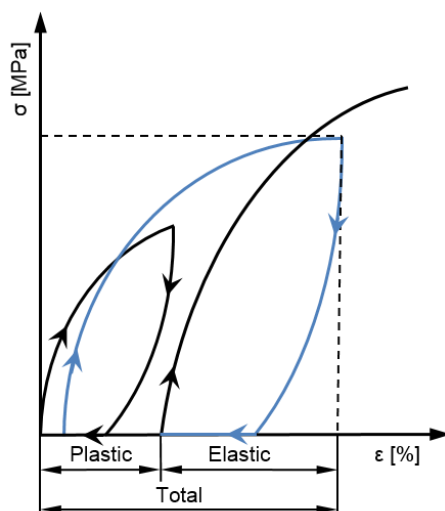


Fig. 1 Strain-stress curves for cyclic loading, at increasing load levels
(the blue coloured curve sign a complete cycle)

The aim of this study is to produce graphene filled PA 6 matrix nanocomposites by melt compounding with different graphene content and the characterization of their tensile-mechanical properties via normal quasi-static and cyclic tensile tests.

2. MATERIALS AND METHODS

Schulamid 6 MV 13 type polyamide 6 (PA 6) from A. Schulman GmbH (Germany) was used as matrix material. Graphene xGnP® graphene nanoplatelets - Grade H (GnP) supplied by XG Sciences, Inc. (USA) were used as nano-sized reinforcement. A Labtech Scientific LTE-26-44 twin screw extruder (L/D=44; D=26 mm) was used for continuous melt mixing. The screw speed was set to be 12 1/min and the extrusion temperature was 240 °C. For the composite preparation 0.25; 0.50; 0.75 and 1.00 wt% graphene was used. The dried PA 6 granulates (80 °C; 4 h) were mechanically mixed with the reinforcing materials then extruded and granulated (particle size: 4.5 mm). Dumbbell type specimens (4 x 10 mm of cross section) were injection moulded on an Aurburg Allrounder Advance 370S 700-290 injection moulding machine.

Before the mechanical tests, the specimens were conditioned under 50 % relative humidity and 20 °C for 48 h. Tensile tests were performed on a Zwick Z020 universal testing machine according to EN ISO 527. The tensile moduli were determined in the strain range of 0.1...0.5 %. The cyclic tensile tests were performed also on this machine. The relaxation time was set to be 30 s and the load was increased by 100 N in each cycle. The machine was used in force-controlled mode, the up and the down load speed was set to 100 N/s. Because of the adjustment of the machine, close to the actual target force within a cycle an approaching procedure begins of which original purpose is to avoid the overshoot of the force. This means that in case of thermoplastic polymers at relative high loads the role of the viscous deformation becomes more observable. From a tensile tester point of view it means that it takes more time to achieve the target force. Based on

these considerations the measuring procedure was set to end when at least 1 % additional elongation was detected close to the maximum force, and the force still could not achieve the maximum value. The latter phenomenon meant that the creeping behaviour began to be dominant, that is far away from the elastic deformations.

3. RESULTS AND DISCUSSION

3.1 Tensile characteristic

Fig. 2 a shows the typical tensile curves of the produced materials. It is well visible that the addition of a small amount of graphene (0.25 wt%) enhanced the strength properties of the PA 6, but further addition led to decrease. The 1.00 wt% GnP containing composite has lower tensile strength than the neat PA 6, which refers to not proper dispersion of nanoparticles. It is important to note that, between 0 and 0.75 wt% GnP content, similar phenomenon was observed as it was detailed in the introduction part: it seems that the near linear range of the curves broadened.

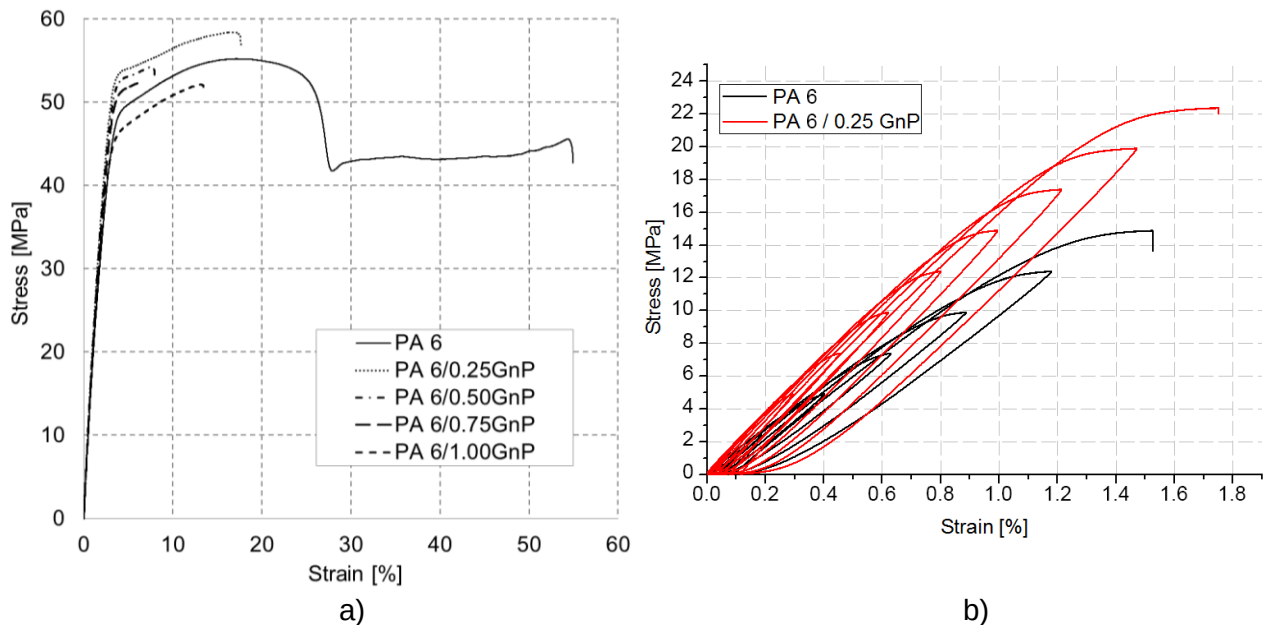


Fig 2 Tensile curves a) and the results of cyclic measurements b)

The exact tensile strengths, tensile moduli and elongation at break values are tabulated in Table 1. The addition of graphene induced some enhancement in the tensile moduli but the effect was less dominant for higher filling rates. The elongation at break decreased when graphene was incorporated. At 0.25 GnP content the decrease was less compared to the other nanocomposites.

Table 1 Tensile properties of graphene containing PA 6 nanocomposites

Materials	Tensile strength [MPa]	Young's modulus [MPa]	Elongation at break [%]
PA 6	56.9 ± 0.7	2054 ± 17	53.5 ± 14.1
PA 6/0.25GnP	59.9 ± 0.7	2244 ± 37	18.5 ± 3.1
PA 6/0.50GnP	57.5 ± 0.9	2259 ± 30	10.9 ± 2.5
PA 6/0.75GnP	56.0 ± 0.9	2220 ± 28	9.9 ± 2.0
PA 6/1.00GnP	53.0 ± 0.1	2123 ± 28	11.0 ± 3.4

Cyclic measurements were carried out in order to evaluate the range of the elastic-dominant behaviour of the materials. The measured curves for PA 6 and PA 6/0.25GnP nanocomposite are shown in Fig 2 b. It is easily observable that the modulus is higher for the nanocomposite compared to the reference. Another important

result is that the measurement ended at higher number of cycles for the nanocomposite; that means that creeping behaviour appeared at higher cycle number.

Fig. 3 a. shows the viscous deformations of the samples after 30 s relaxation time (e.g. the remained deformation before a cycle in proportion to the initial length). PA 6 showed higher viscous deformations compared to the nanocomposites. In addition the measurement ended after 4 cycles, while the nanocomposites achieved seven. This rather elastic-dominant behaviour appeared also in the elastic recovery values (Fig. 3. b). As it was expected, the elastic recovery as a function of cycle numbers decreased faster for the PA 6 than for nanocomposites. For the nanocomposites it can also be concluded that while at the quasi-static measurements the particle content affected the mechanical properties, there were not remarkable differences in case of the cyclic results. It can be explained by that for the cyclic measurements the loads were on a lower level, therefore the presence of the aggregated nanoparticles had less negative influence. This also correlates with the tensile moduli results, where moderate increments were observed compared to the matrix, but there were not significant differences as a function of nanoparticle content.

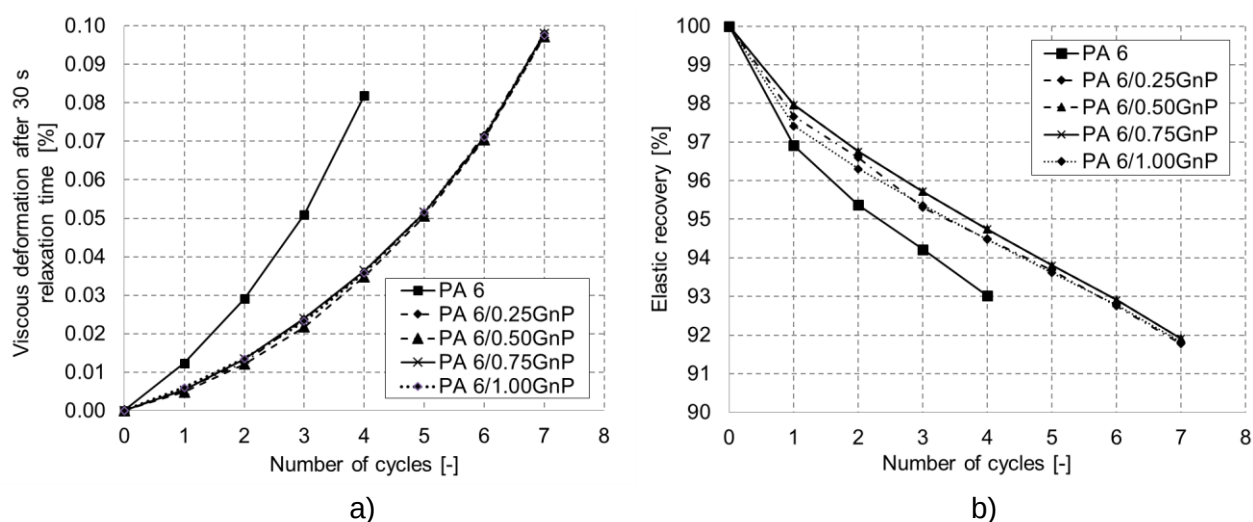


Fig 3 The viscous deformation a) and the elastic recovery b) as a function of cycle numbers

4. CONCLUSIONS

PA 6 matrix graphene reinforced nanocomposites were successfully produced. Moderate increase of the tensile properties was observed. At the cyclic measurements it turned out that the presence of graphene in PA 6 matrix could effectively enhance the elastic deformation components. This resulted in higher elastic recovery compared to the pure matrix. Overall it can be stated that the presence of nanoparticles could broaden the utilization range of the PA 6 at relatively low filling rates.

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REFERENCES

- [1] KANGO, S., KALIA, S., CELLI, A., NJUGUNA, J., HABIBI, Y., KUMAR, R. Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites - A review. *Progress in Polymer Science*. 2013, year 38, nr. 8, page 1232
- [2] YOUNG, R.J., KINLOCH, I.A., GONG, L., NOVOSELOV, K.S. The mechanics of graphene nanocomposites: A review. *Composites Science and Technology*. 2012, year 72, nr. 12, page 1459
- [3] KIRÁLY, A., RONKAY, F. Effect of graphite and carbon black fillers on the processability, electrical conductivity and mechanical properties of polypropylene based bipolar plates. *Polymers and Polymer Composites*. 2013, year 21, nr. 2, page 93
- [4] YUAN, X.Y., ZOU, L.L., LIAO, C.C., DAI, J.W. Improved properties of chemically modified graphene/poly(methyl methacrylate) nanocomposites via a facile in-situ bulk polymerization. *Express Polymer Letters*. 2012, year 6, nr. 10, page 847
- [5] MAITI, S., SHRIVASTAVA, N.K., SUIN, S., KHATUA, B.B. A strategy for achieving low percolation and high electrical conductivity in melt-blended polycarbonate (PC)/multiwall carbon nanotube (MWCNT) nanocomposites: Electrical and thermo-mechanical properties. *Express Polymer Letters*. 2013, year 7, nr. 6, page 505
- [6] SINGH, V., JOUNG, D., ZHAI, L., DAS, S., KHONDAKER, S.I., SEAL, S., Graphene based materials: Past, present and future. *Progress in Materials Science*. 2011, year 56, nr. 8, page 1178
- [7] KUILLA, T., BHADRA, S., YAO, D., KIM, N.H., BOSE, S., LEE, J.H. Recent advances in graphene based polymer composites. *Progress in Polymer Science*. 2010, year 35, nr. 11, page 1350
- [8] ZHANG, X., FAN, X., LI, H., YAN, C. Facile preparation route for graphene oxide reinforced polyamide 6 composites via in situ anionic ring-opening polymerization. *Journal of Materials Chemistry*. 2012, year 22, nr. 45, 24081
- [9] MONDAL, D., BHOWMICK, B., MOLLICK, M.M.R., MAITY, D., MUKHOPADHYAY, A., RANA, D., CHATTOPADHYAY, D. Effect of clay concentration on morphology and properties of hydroxypropylmethylcellulose films. *Carbohydrate Polymers*. 2013, year 96, nr. 1, page 57
- [10] LIANG, J., HUANG, Y., ZHANG, L., WANG, Y., MA, Y., GUO, T., CHEN, Y. Molecular-Level Dispersion of Graphene into Poly(vinyl alcohol) and Effective Reinforcement of their Nanocomposites. *Advanced Functional Materials*. 2009, year 19, nr. 14, page 2297
- [11] FANG, M., WANG, K., LU, H., YANG, Y., NUTT, S. Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites. *Journal of Materials Chemistry*. 2009, year 19, nr. 38, page 7098
- [12] MASENELLI-VARLOT, K., CHAZEAU, L., GAUTHIER, C., BOGNER, A., CAVAILLÉ, J.Y. The relationship between the electrical and mechanical properties of polymer–nanotube nanocomposites and their microstructure. *Composites Science and Technology*. 2009, year 69, nr. 10, page 1533
- [13] MORTON, W.E., HEARLE, J.W.S. *Physical properties of textile fibers*. London and Colchester: Butterworth & Co. Ltd. and The Textile Institute, 1962.