Elastic recovery of polyamide 6 matrix nanocomposites and their basalt fiber co-reinforced hybrids

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Abstract
The improved elastic recovery and a wider range of linear elastic behavior of multi-scale hybrid polyamide 6 composites are demonstrated in this study. For the composites basalt fiber was used as micro-sized, and multi-walled carbon nanotubes and surface-treated montmorillonite as nano-sized reinforcement. The materials were melt compounded and then specimens were injection molded. To prove increased elastic behavior, a relatively simple and fast cyclic measurement method was applied, where the load was increased in each cycle and 30 seconds of relaxation time was allowed after unloading. The results showed that both micro and nanoparticles can broaden the range of the elastic behavior of the polyamide 6 significantly, which is reflected in increased elastic recovery and decreased plastic deformation compliance. Nano- and micro-sized reinforcing materials also produce a synergistic effect, which can be explained with the physical crosslinking of the nanoparticles.

Keywords: nanocomposite; hybrid composite; mechanical properties; viscoelastic properties; elastic recovery

1. Introduction

Nowadays the research of multiphase composite structural materials is a leading trend in materials science. Earlier the main target was to improve one or two selected attributes, for instance in the case of polymer composites, it is a common goal to enhance mechanical properties. As fiber strength is already utilized to a high degree in fiber-reinforced composites, the additional increase of mechanical strength may require the application of a third phase. The purpose of a third phase – besides the enhancement of mechanical properties – may be to increase the toughness of a strong but rigid material. In addition, materials can be endowed with new functions as well: electrical or thermal conductivity, gas barrier properties, flame retardancy etc. Materials of this type are currently being developed. In the case of polymer composites the third phase can also be a polymer, e.g. an immiscible polymer blend is employed as matrix. Another possibility is to apply another fiber-like or particle-like material besides the (typically fiber) reinforcement. Polymer matrix hybrid composites containing both fibers and nanoparticles attract particular attention. The main advantage of this three-component system is that the reinforcing materials do not hamper each other and can have different functions. The main reason for this is the very different size of the two fillers (1-9).
Yoo et al (10) investigated the effect of reinforcement content on the mechanical properties of polyamide 6 (PA 6)-based glass fiber and montmorillonite-reinforced composites. They proved that the joint application of reinforcing materials results in more effective reinforcement. It was attributed to the increased apparent viscosity caused by the presence of microfibers, which helped to distribute the nanoparticles more homogeneously during melt processing.

Researchers attribute the synergistic effect on mechanical properties to three effects. The first is that the nanoparticles stiffen the matrix itself. This effect is directly exhibited in the tensile modulus. The second effect is that the nanoparticles make stress distribution in the matrix more homogeneous, thus load is more evenly distributed among the fibers. As a result, both tensile strength and tensile modulus are significantly improved. The third effect appears when the nanoparticles have a high attraction to both the matrix and the fibers. In this case one part of nanoparticles adheres to a fiber, the other part to the matrix. This way they establish better connection between the microfibers and the matrix material by "forming a bridge" between them (6, 11, 12). In PA 6-based hybrid systems, synergy can also produce physical characteristics other than mechanical properties. A good example is reduced flammability. In addition, glass transition temperatures are higher in hybrid systems, widening the applicable temperature range of composites (6, 13).

Nowadays the principles of sustainable development prominently appear in the field of materials science research. For instance in composite science a wide range of natural fiber types are applied and studied as reinforcing material. The main problem in the application of these fibers is reproducibility as the properties of natural fibers greatly depend on the conditions of production, which are usually hard to control. For this reason, reinforcing materials came to the fore that are artificially produced but directly from natural resources. Basalt fiber (BF) is one of the fastest-spreading materials among these new types of reinforcements. Basalt is a common volcanic rock found in most countries around the world and there are basaltic compositions that are directly suitable for fiber manufacturing, without any additives or modification. The experience gained with glass fibers can be used as a basis for basalt fiber manufacturing, due to the very similar structure, melt viscosity and chemical composition of basalt and glass fibers. Overall, it results in high quality and reproducible properties, which are essential for high-tech composite applications (14-17).

A major challenge in introducing newly developed materials into industrial applications is the lack of knowledge regarding the technically relevant properties of the material. It would be especially important to know the precise time-dependent viscoelastic properties of polymers for the design process. The response of a polymer part to a stress load can be divided into three parts: instantaneous elastic, time-dependent viscoelastic and time-dependent viscous (or relaxation) deformation. The main problem is that the deformation components depend on the load applied, therefore in the case of a polymer or a polymer matrix composite a test has to be performed to characterize deformation at every load level. This characterization method can be quite long, which necessitates the development of shorter tests. In the case of thermoplastic polymers the knowledge of each above-mentioned deformation component is required for the design of a given part, as designing usually entails taking the maximal deformation caused by the given load into consideration. Structural materials must meet an important requirement: after the termination of the load, the remaining deformation should be negligible. This means that instantaneous elastic and time-dependent viscoelastic deformation components do not have to be separated, but can be taken into consideration together. The combined name of these two components is elastic deformation. In order to find the load level where significant remaining deformation appears for the first time, a cyclic test can be done, where the tensile load is increased in every cycle but between each cycle a certain time is allowed for the recovery of time-dependent viscoelastic deformation (elastic deformation). This test helps to find the elastic limit of the material, which will be at the point where significant remaining deformation is experienced. To make it easier to determine, the rate of elastic recovery is introduced (18). It can be assessed for each cycle and can be calculated as the ratio of elastic deformation and total deformation (See Figure 2A).

The purpose of this research was to determine the rate of elastic behavior of polymer matrix nano- and hybrid composites. For the tests injection molded polyamide 6-based nano- and hybrid composites were used, where the reinforcing materials were different nanoparticles and basalt fibers (BF).

2.   Materials and methods

Schulamid 6 MV 13 (PA 6) from A. Schulman GmbH (Germany) was used as matrix material for the composites. Continuous-made chopped basalt fiber, BCS 13.6.KV02 type (BF) made by Kamenny Vek (Russia) was applied as microfiber reinforcement in 30 wt%. The nanoparticles used were montmorillonite and nanotubes. The montmorillonite was organophilic: Nanofil® 919 (Süd Chemie AG, Germany). The montmorillonite was further treated for better dispersion. Montmorillonite was first mixed with (2-hydroxyethyl)-methacrylate HEMA (Merck, Germany) in the ratio of 1:3. The suspension was held at room temperature for 12 hours to swell, and then was spread in a 100 μm-thick layer on a glass plate. After this the MMT-HEMA system was heat treated (of 80°C, 24 hours). The treated montmorillonite (MMT) was also powdered in a mortar. The benefits of this treatment were published in a previous publication [19]. As another nanoparticle reinforcement, multiwalled carbon nanotubes (MWCNT) were chosen. The type of MWCNT was Baytubes® C 150 P (Bayer, Germany) and applied as received without any treatment.

A Brabender Plasti-Corder PL2100 twin-screw extruder was used for continuous melt mixing. Screw speed was 10 rpm, the extrusion temperature was 240°C. For the composites 30 wt% of basalt fiber and 1 wt% of nanoadditive were used. After extrusion, dumbbell type specimens (4x10 mm cross-section) were injection-molded with an Arburg Allrounder 320C 600-250 injection molding machine. The basic mechanical properties and the morphological examination of the materials produced can be found in former publications [20, 21]. It should be noted that in addition to the superior mechanical performance, the morphological characterizations showed a proper dispersion of MMT and MWCNT nanoparticles in hybrid composites.

For the materials in the tests the following abbreviations were used: PA 6: neat polyamide 6; PA 6+MMT: polyamide 6 with 1 wt% HEMA treated montmorillonite; PA 6+MWCNT: polyamide 6 with 1 wt% carbon nanotubes; PA 6+BF: polyamide 6 with 30 wt% basalt fiber content; PA 6+BF+MMT: polyamide 6 with 30 wt% basalt fiber and 1 wt% HEMA treated montmorillonite; PA 6+BF+MWCNT: polyamide 6 with 30 wt% basalt fiber and 1 wt% carbon nanotubes.

Before testing, all specimens were conditioned at 20°C and 50% relative humidity for a month.

Tensile tests were carried out on a Zwick Z020 (Germany) universal testing machine according to EN ISO 527. The tensile speed was 20 mm min^{-1} for the neat matrix and the nanocomposites and 2 mm min^{-1} for the BF and the hybrid composites. The cyclic tensile tests were performed on the same machine. The relaxation time was set to 30 s and the load was increased by 100 N in each cycle. The machine was used in force-controlled mode, the upload and download speeds were set to 100 N s^{-1}. The measurement process ended when there was at least 1% additional elongation before the maximum force was reached. This indicated that the creeping behavior began to be dominant therefore elastic recovery decreased.

3. Results and Discussion

The main purpose of using nanoparticles in polymer matrices is to broaden the range of their applicability. When a new engineering material is developed, first its tensile properties are generally determined, as it happened in earlier research projects for the investigated materials [20, 21]. Based on the results, the optimal reinforcing material compositions and contents can be selected. The tensile properties of the best-performing materials and their references are investigated in depth in this study and their tensile properties are tabulated in Table 1.

In order to better understand how the nano- and microparticles influence tensile properties, the tensile curves themselves can be more deeply examined. Figure 1 shows representative tensile curves for the prepared materials. If the nanoparticles were the only reinforcement in the system, different effects would be experienced. The MMT was well fitted in the matrix and was able to cooperate with it. It is verified by the fact that the specimens sustained large plastic deformation before failure. However, the presence of nanotubes made the material brittle and rigid, due to the remaining agglomerates (see [20, 21] in detail). Hybrid composites behave differently. Compared to neat PA 6 or nanocomposites, they show nearly linear behavior within seemingly broader limits. In addition to

basalt fibers, nanoparticles are also present, resulting in higher strength and a seemingly even broader linearly elastic domain. Presumably, in the case of higher modulus, the material is characterized by the elastic deformation component in a greater proportion. The prepared composites showed modulus growth: nanocomposites had higher moduli than neat PA 6, while hybrid composites had higher moduli than PA 6+BF. Overall, the presence of nanoparticles improved the tensile moduli not just for nano-, but also for hybrid composites and seemingly widened the linear range of the tensile curves. Cyclic tests were carried out to confirm the latter phenomenon, as the change in plastic deformation between the cycles makes it possible to predict the limits of elastic behavior.

A typical cyclic measurement curve of the PA 6+MMT nanocomposite is shown in Figure 2B. It is evident that uploading curves are parallel in the case of small cycle numbers, but this is not typical at higher loads and also the hysteresis areas become larger. The enlarged graph shows that up to a relatively high cycle number, deformation decreases below 0.1% during the relaxation periods. Based on the 110 mm gauge length, this means an elongation of less than 110 μm, which can be considered negligible in the case of thermoplastic polymers and their composites. Similar phenomena were observed for the other investigated materials but of course, the significant increase in residual strain occurred at different cycle numbers.

To compare the residual strain measured after the relaxation time of the materials (plastic deformation, marked as ε_{30s}) the values were plotted as a function of the cycle number (viz. the stress: as there was no notable difference between the specimen geometries) (Figure 3A). It can be seen that in the case of simple nanocomposites higher residual strains appear at higher cycle numbers, particularly in the case of the PA 6+MMT system. This means that deformation behavior is close to linear up to higher load levels than in the case of the neat matrix. This result correlates with the conclusions in the case of the analysis of the tensile curves. The presence of basalt fibers significantly decreased plastic deformation in the case of small loads. Hybrid composites showed even better performance, particularly nanotube-reinforced hybrids. Nanotubes per se increased elastic properties only to a very limited extent, but hybridization improved properties far more, e.g. plastic deformation was smaller than 0.1% even at a stress of 60 MPa. The nanoparticles caused changes because they altered the microstructure of the material. Decreased plastic deformation can be explained with the physical cross-linking of the nanoparticles (Figure 4). It means that in the case of good dispersion and adhesion conditions the polymer molecules can easily adhere to a nanoparticle or a microfiber but based on the statistical shape and the length of the macromolecules they can also adhere to another nanoparticle or microfiber. On one hand, it leads to decreased deformability, therefore the conformational possibilities of the polymer chains is also limited, which results in enhanced modulus values. On the other hand, it hampers the relative displacement of the molecules, which results in lower viscous deformation.

Figure 3 A shows that the initial part of the curves is close to linear and can be approximated well with the initial tangent of the curves. The slope of the initial tangent characterizes the plastic deformation of the materials well at low stresses. This is a material parameter, which is denominated as plastic deformation compliance, marked with J_m [GPa^{-1}]. The plastic deformation compliance of tested materials is shown in Table 2. If MWCNT is employed as reinforcement in itself, plastic deformation compliance remains virtually unchanged. This was expected based on earlier results, as nanoparticles form large aggregates and have no effect on the structure of the matrix between the aggregates. Contrary to MWCNT, MMT had a greater influence on composite properties due to its better distribution. MMT reinforcement decreased J_m to one-third compared to the neat matrix. The presence of basalt fibers drastically decreased plastic deformation compliance compared to the neat matrix. Plastic deformation compliance is calculated from data measured at very small deformations. Fundamentally the behavior of hybrid composites is not different from that of basalt fiber-reinforced composites at very small stress levels, thus the addition of nanoparticles caused no substantial change in plastic deformation compliance. At the same time the values in the order of a few thousandth GPa^{-1} can be considered very small.

Elastic behavior and its stress domain are well characterized by the percentage of the elastic recovery of the materials, which can be calculated simply from the available measurement data. Results are shown in Figure 3B. In the case of the neat matrix and the composite containing MWCNT elastic recovery decreases intensively at low cycle numbers, then more gradual change was observed at higher cycle numbers. This can be explained with the orientation of the amorphous phase of the matrix. This phenomenon did not occur in the case of the nanocomposite containing MMT. It means that in this case the amorphous region became more elastic, therefore residual deformation was not considerable. It can also be explained with the physical crosslinking effect of the nanoparticles. If viscous deformation is limited due to hampered molecule displacement, it is also more difficult for the molecules in the amorphous phase to become oriented. In the case of the MMT nanocomposites, elastic recovery was still around 95% after 10 cycles (at a load of 25 MPa), while the neat matrix and the MWCNT nanocomposite suffered remarkable residual deformation. In the case of the MMT nanocomposite the decrease of elastic recovery is approximately linear in a wide cycle range, which means that deformation can be calculated relatively easily. The results show that by incorporating nanoparticles into the PA 6 matrix the elastic region can be widened in the case of tensile loads. This means that nanocomposites can be used safely at higher loads compared to the neat matrix. The presence of basalt fibers considerably increased elastic recovery in a wide stress domain. As was experienced in the case of plastic deformation compliance, there is basically no difference between composites reinforced only with basalt fibers and basalt fiber-based hybrid composites. The change in elastic recovery showed that this is only true below a stress of approximately 40 MPa. Over this stress the plastic deformation of composites reinforced only with basalt fibers increases faster than in the case of hybrids, where the rate of growth is unchanged up to a stress of 60 MPa. The time available for the recovery of time-dependent viscoelastic deformation is limited, thus recovery is not complete, which is negligible in the case of low cycle numbers, but influences the measured value more at higher cycle numbers as it cumulates from cycle to cycle. Plastic deformation is never zero in the case of thermoplastic polymers, thus this type of deformation is also cumulated. Based on this, it can be stated that the degree to which elastic recovery decreases nearly linearly characterizes the strength and applicability limits of the material. Among the tested materials, a significant decrease in elastic recovery appeared latest in the case of hybrid composites.

4. Conclusions

In sum, it can be stated that relatively simple cyclic measurement characterizes the behavior of polymers and their composites well. The method was used for the qualification of polyamide 6-based nano and hybrid composites. The application of MMT and basalt fibers expands the applicable stress domain of the material in the case of tensile loads, while the joint employment of nanoparticles and BF provided even further growth. Reinforcements also decreased plastic deformation compliance. The decrease in the rate of elastic recovery with increasing stress was less substantial in the case of basalt fiber-reinforced and hybrid systems than for nanocomposites. The significant increase in plastic deformation appeared at a higher stress in hybrid composites than in basalt fiber-reinforced composites. The decrease of plastic deformation was connected to the physical crosslinking effect of the nanoparticles.

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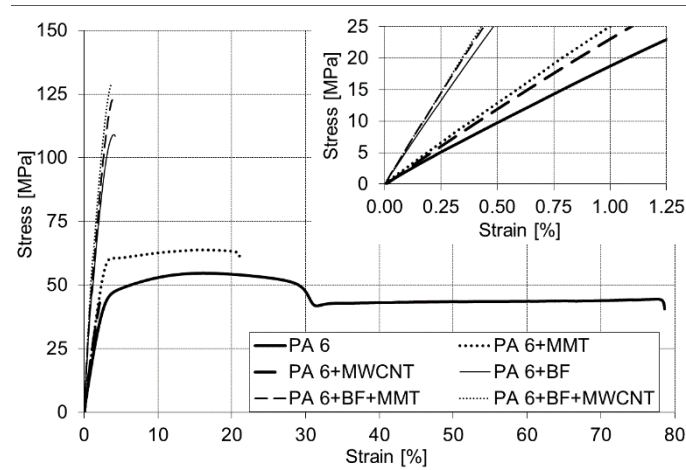
Figures

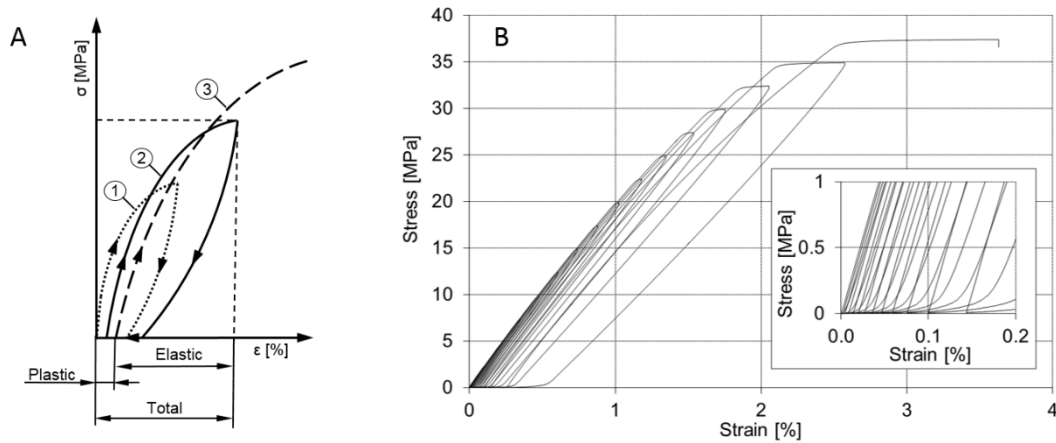*Figure 1.* Stress-strain curves for PA 6 nano- and hybrid composites

Figure 2. Strain-stress curves for cyclic loading, at increasing load levels A shows an idealized curve (the solid curve (2) is a complete cycle) and B shows a real measurement curve in the case of PA 6+MMT
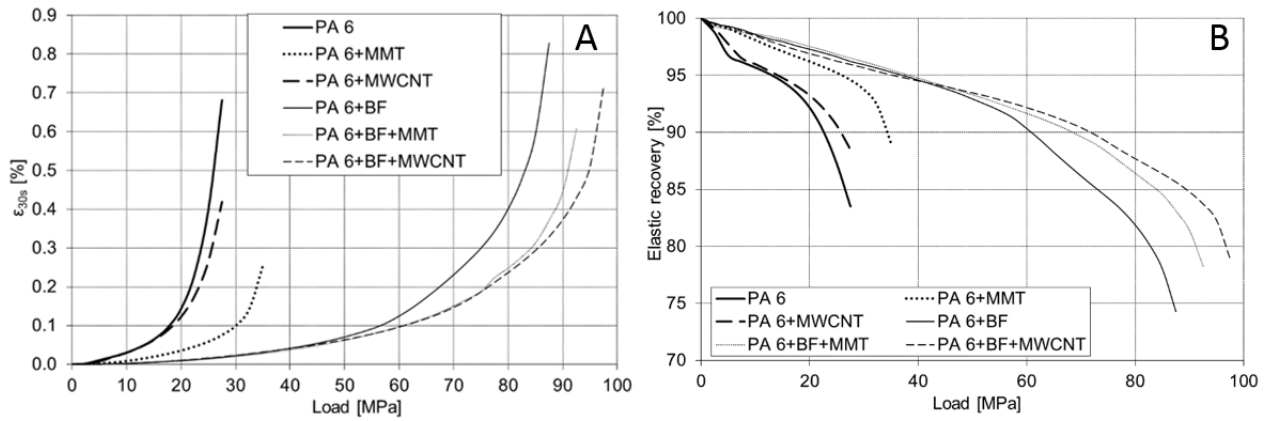
Figure 3. The residual strain measured after the relaxation time (30 s) (A) and the elastic recovery of nano- and hybrid composites (B)
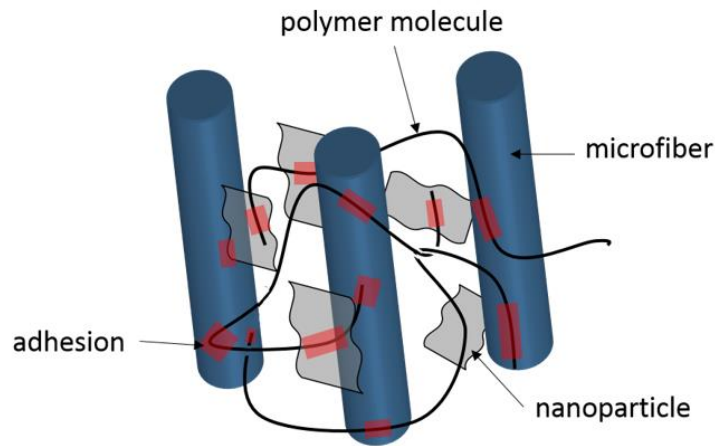

Figure 4. Schematic model of the crosslinking effect of the nanoparticles.

Tables

Materials	Tensile strength [MPa]	Tensile modulus [MPa]	Elongation at break [%]
PA 6	51.1±0.3	1816±55	80.0±24.0
PA 6+MMT	63.2±1.2	2567±47	15.2±7.5
PA 6+MWCNT	40.5±1.8	2200±50	2.1±0.1
PA 6+BF	109.2±0.1	4814±560	4.3±0.4
PA 6+BF+MMT	123.7±1.0	5875±95	3.8±0.3
PA 6+BF+MWCNT	118.2±0.3	5517±154	4.0±0.3

Table 1. Tensile properties of the investigated materials (16, 17)

Materials	J_m [1/GPa]
PA 6	0.042
PA 6+MMT	0.013
PA 6+MWCNT	0.044
PA 6+BF	0.004
PA 6+BF+MMT	0.003
PA 6+BF+MWCNT	0.006

Table 2. Plastic deformation compliance of the tested materials