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Flexural properties of the epoxy resin filled with single and hybrid carbon nanofillers

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Abstract. The aim of this paper was to estimate the effect of moisture and temperature on the flexural properties of the epoxy filled with single and hybrid carbon nanofillers (CNTs and CNFs) and to reveal the most environmentally stable NC. Water absorption at 70 °C until equilibrium moisture content and heating at 70 °C for 4 weeks were followed by freezing at -20 °C for 8 weeks. Microstructural characterization of optical images revealed homogeneous dispersion of all carbon nanofillers in the epoxy resin at microscale. Positive nanofiller effects were found for sorption, flexural and thermophysical characteristics of the epoxy resin. The most environmentally stable NC was epoxy filled with 0.1 wt. % of CNTs/CNFs hybrid, which had the lowest effect of temperature and moisture on mechanical characteristics, along with the lowest equilibrium water content and diffusivity.

1. Introduction

The rapid development of modern techniques demands new materials having advanced properties. The main advantage of polymer composites over traditional kinds of materials (metals, ceramics, wood etc.) is a unique combination of properties (mechanical, rheological, electrical, frictional, thermal etc.) and a possibility to tune them, by changing composition and processing conditions. To fully take advantage of composite materials, the multifunctionality is introduced, which is nowadays highly investigated [1], [2].

Extensive research on development of multifunctional polymer composites incorporating carbonaceous nanofillers, such as single- and multiwall carbon nanotubes (CNTs) and carbon nanofibers (CNFs) is on-going. The interest of using these nanofillers arises due to unique combination of their mechanical, thermal and electrical properties, which may allow significant weight savings for the products in comparison with micro-filled composites. The addition of optimal amount of such conductive nanofillers, corresponding to electrical percolation threshold, to electrically isolating polymer resins results in the development of electropassive material. These materials incorporate traditional load-bearing properties of composite structural elements and they have nearly the same cost-performance ratio, and supplemental electrical functionality. Such electropassive materials can be widely used for the monitoring of deformation and damage in composite structures under service conditions.

Though, these multifunctional materials are mostly limited to indoor applications due to relative sensitivity of mechanical properties of polymers and polymer composites to the action of environmental conditions, such as moisture and temperature [3]. The issue regarding environmental effects and the estimation of the most stable nanocomposite (NC) could broaden their application to outdoor conditions.

The aim of this paper was to establish the effect of moisture and temperature on the flexural properties of the epoxy filled with single (CNTs and CNFs) and hybrid carbon nanofillers (CNTs/CNFs in the ration 1:1 by weight) and identifying the most environmentally stable NC. Thus, it brings a new concept by addressing a still unsolved problem of environmental consideration for electropassive polymers and composites which could be used for structural health monitoring in outdoor conditions.

2. Materials and methods

The matrix material was a monocomponent RTM6 provided by *Hexcel Composites*. The carbon nanofillers were multiwall CNTs Nanocyl 7000 provided by *Nanocyl* and CNFs SA 719781 provided by *Sigma-Aldrich*. Furthermore, a hybrid nanofiller (HN) loading consisting of both CNTs and CNFs in the ratio 1:1 by weight was prepared. The samples of the neat epoxy and NC at certain electrical conductivity ($\sigma \approx 0.1\text{-}0.01$ S/m) were prepared for the characterization of the flexural and thermophysical properties. Thus, the epoxy was filled with 0.05 wt. % of CNTs, 0.3 wt. % of CNFs and 0.1 wt. % of CNTs/CNFs. The dispersion of all nanofillers within the epoxy matrix was performed by high-shear disperser Ultra Turrax T25 combined with a heating plate RCT basic by *IKA* for 30 min at 90 °C and 20 krpm. Then, the mixtures were degassed at 90 °C and cured for 90 min at 160 °C with a subsequent post cure cycle for 2 h at 180 °C.

The quantitative optical analysis was carried out by optical microscope Olympus BX51. For each type of the NC the filler content 0.1% was chosen as characteristic and representative content for the optical analysis. The test specimens were prepared for optical microscopy by cutting them of size 20x20x0.5 mm with the blazer. The specimens' surface was polished with a paste containing aluminum particles of diameter 1 μm. Three images were obtained for material type and then used for the analysis. The obtained images provided information about dispersion degree in the area of about 3 mm^2 for the lowest magnification (x50).

The flexural properties for the epoxy and the NC were investigated in a three-point bending mode by using Zwick 2.5 universal testing machine and according to ASTM D790. The samples of sizes 3×10×80 mm were tested with a support span of 56 mm and with a strain rate of 1.5 mm/min. The flexural modulus, strength and maximal deformation were evaluated from the stress-strain curves in uncondensed state, during and after the environmental ageing, which consisted of water absorption at 70 °C for 4 weeks, heating at 70 °C for 4 weeks, and freezing at -20 °C for 8 weeks.

The dynamic mechanical thermal analysis (DMTA) was carried out by using a *Mettler Toledo* DMA/SDTA861 in tensile mode for the samples of thickness app. 1 mm at a given force 4 N, frequency 10 Hz and T = 30-280 °C at 3 K/min heating rate to evaluate hygrothermal ageing effects in the epoxy and NC samples.

3. Results and discussion

3.1. Microstructural characterization

For the quantitative estimation of filler dispersion the area of individual filler particles of given systems was determined from the original images obtained from optical microscope using freely available *ImageJ* program. The area of individual filler particles/agglomerates was defined by using binary images and iso-data algorithm for setting the brightness threshold between particles and background. The method of estimation filler dispersion degree was developed for model system and further applied for the epoxy filled with CNTs [4], [5]. Thus, using *ImageJ* software the particle size distribution was obtained and analysed for epoxy resin filled with 0.1 wt. % of CNTs, CNFs and HN

(CNTs/CNFs in ratio 1:1). All data from three independent images for each type of the material were collected together and histogram analysis was carried out to evaluate the distribution of the nanoparticles and their agglomerates by size. The optical micrograph of the epoxy filled with 0.1 wt. % of CNTs is given in Figure 1 and provides only qualitative analysis of CNTs dispersion in the epoxy resin. The results of the quantitative analysis of filler particles distribution by size are summarized in Figure 2.

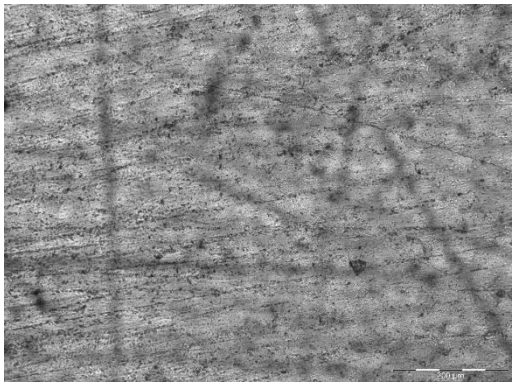

Figure 1. Optical micrograph of epoxy filled with 0.1 wt.% of CNT (scale – 200 μm).

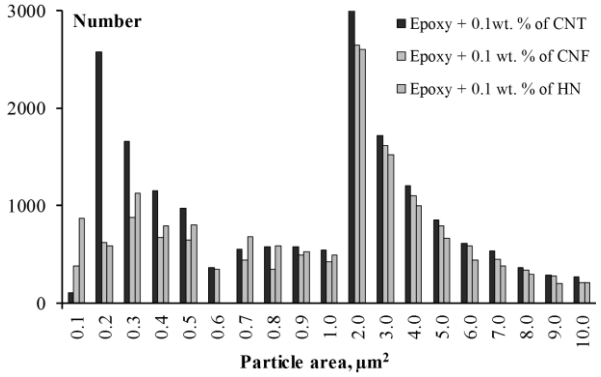

Figure 2. Distribution by particle area for different materials indicated in the figure legend.

According to Figure 2, all nanofillers' particles mostly have bimodal distribution with peaks located at app. 0.2 and 2.0 μm^2 which corresponds to radius of app. 0.3 μm and 0.8 μm in the case of spherical particles. The bimodality of distribution by particle area means that there is a tendency to form less and more single nanoparticles and their agglomerates. Considering the average sizes of the nanoparticles: 9.5 nm × 1.5 μm (CNTs) and 100 nm×20-200 μm (CNFs) it can be concluded that the filler dispersion is both satisfactory for single and hybrid nanofiller. Noticeably, at the lowest area of 0.12 μm^2 the impact of hybrid nanofiller is the highest of all. It means that the mixing conditions are efficient both for single and hybrid nanofillers. Of course, the efforts can be made to improve it even more, but it should be emphasized that it was not the purpose of current study to get the most efficient dispersion of the nanoparticles within the epoxy resin.

3.2. Moisture absorption

The kinetics of moisture absorption of the epoxy and the epoxy filled with CNTs, CNFs and HN was characterized by using Fick's model for 2D moisture diffusion

$$w(t) = w_\infty - 4\frac{(w_\infty - w_0)}{\pi^4}\sum_{k,i=1}^{\infty}\frac{\left(1-(-1)^k\right)^2}{k^2}\cdot\frac{\left(1-(-1)^i\right)^2}{i^2}\exp\left(-\left(\left(\frac{\pi k}{h}\right)^2+\left(\frac{\pi i}{a}\right)^2\right)Dt\right), \quad (1)$$

where $w(t)$, w_0 and w_∞ are time-varying, initial and the equilibrium moisture contents of a specimen, and D is the diffusion coefficient of the material, a and h are the thickness and width of a specimen, respectively. The equilibrium moisture content was evaluated as maximally achieved moisture content over the sorption test, while the diffusion coefficient was calculated from the initial slope of the curve w vs. $\sqrt{t}$ [6]

$$D = \frac{\pi h^2}{16t}\left(\frac{w(t)-w_0}{w_\infty - w_0}\right)^2. \quad (2)$$

Figure 3 shows the dependence of sorption characteristics, coefficient of diffusion and equilibrium moisture content, on the nanofiller content for different materials indicated in the legend. Obviously,

the epoxy resin was characterized by the highest values of the sorption characteristics. The addition of stiff moisture impenetrable carbon nanofillers caused a slight reduction of equilibrium moisture content by 0.01, 0.06, and 0.23% for the epoxy filled with 0.3 wt. % of CNFs, 0.05 wt. % of CNTs and 0.1 wt.% of HN, accordingly. The diffusivity of the NCs was almost the same as for the neat epoxy resin: 11.0 ± 0.5 10^3×mm^2/h for epoxy resin, 10.9 ± 0.5 10^3×mm^2/h for the epoxy filled 0.05 wt. % of CNTs, 10.08 ± 0.8 10^3×mm^2/h for the epoxy filled with 0.3 wt. % of CNFs and 10.8 ± 0.7 10^3×mm^2/h for the epoxy filled with 0.1 wt. % of HN. Such a small reduction in the sorption characteristics for the NCs can be explained by the high quality, mechanical properties, and resistance to moisture absorption of the epoxy, which is widely applied for aeronautical elements in liquid infusion processes [7].

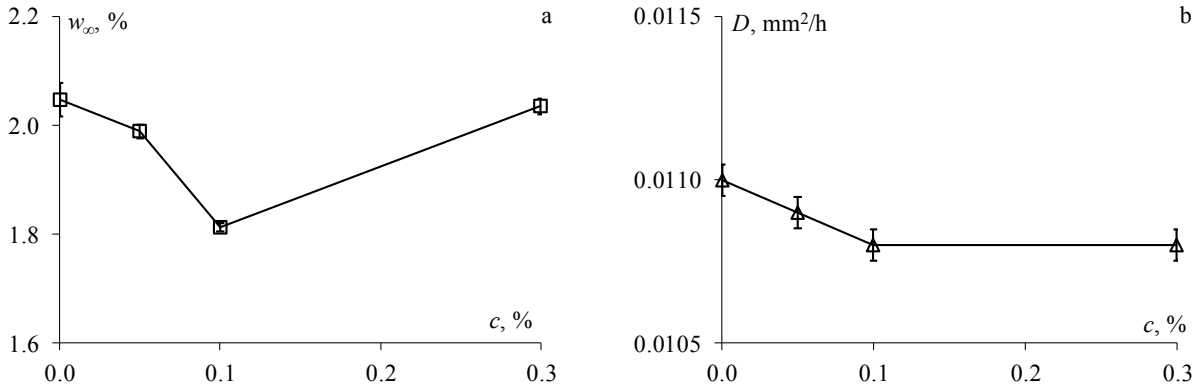

Figure 3. Diffusivity (*a*) and equilibrium moisture content (*b*) vs. nanofiller (-s) content.

3.3. Flexural properties

The flexural tests were carried out for all investigated systems, e.g. neat and filled epoxy resin respectively at 0.05 wt. % of CNTs, 0.3 wt. % of CNFs and 0.1 wt. % of HN, before and after the conditioning with and without water.

The flexural stress in the outer surface of the test specimen was calculated using the standard equation for homogeneous elastic material tested in flexure as a simple beam supported at two points and loaded at the midpoint

$$\sigma = \frac{3PL}{2ah^2}, \tag{3}$$

where P is applied load at a given point on the load-deflection curve, L is the support span, a and h are the width and thickness of the specimen tested.

The flexural strain was considered as a nominal fractional change in the length of an element of the outer surface of the test specimen at midspan, where the maximum strain occurred and was calculated using formula

$$\varepsilon = \frac{6dh}{L^2}, \tag{4}$$

where d is the deflection of the centre of the specimen in the middle of the support span.

The flexural strength for all the materials tested was defined as the maximal achieved value of stress in the specimen, and flexural (chord) modulus was calculated from the slope of a secant line between 0.05% and 0.25% strain on a stress–strain plot.

In uncondensed state, before environmental ageing, the flexural properties were almost the same for all materials studied: flexural modulus was 2.9±0.1 GPa, strength was 140±5 MPa, maximal deformation was 6.5±0.5%. Though the addition of CNTs and CNFs should increase the nanofiller/epoxy interfacial strength and should produce an increase of the shear component of the flexural modulus [8] the evident effect of single and hybrid carbon nanofillers on flexural modulus of epoxy in the uncondensed state wasn't observed. One of the reasons for found negligible improvement

in flexural characteristics, could be the relatively low filler content and the possible aggregation of nanofillers which cause weak nanofiller-matrix interfacial interactions.

Then, as it evident from Figure 4, due to environmental ageing with and without water the flexural properties have changed for all materials analyzed, revealing a different induced effect in all cases. It is well known that environmental ageing of polymer materials should be considered as a process of accumulation of different kinds of damages: microcracks, volume defects and pores, delamination etc., induced by the complex and combined action of environmental factors such as moisture, temperature, UV radiation, temperature variation or gradient etc. Obviously, the increase in defectiveness of the material led to decrease in the flexural properties such as strength and maximal deformation.

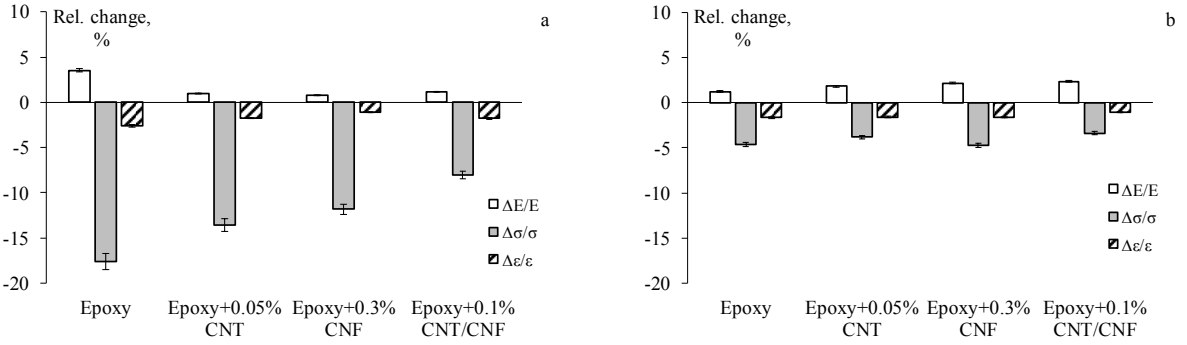

Figure 4. Relative change of the flexural modulus, strength and maximal deformation after the environmental ageing for different materials in water (*a*) and without water (*b*).

According to Figure 4 after the environmental ageing, the flexural modulus of all materials slightly increased due to possible post-curing of the epoxy resin as also previously reported in [7]. Obviously, the environmental ageing in water had more influence on flexural strength and maximal deformation as compared with the environmental ageing without water. The maximal decrease was observed for the flexural strength of the epoxy (-17.5%) upon the environmental water conditioning. The extent of this change was minimal for the epoxy filled with 0.1 wt. % of HN. The maximal deformation of all materials was also reduced after two different environmental ageing processes (with and without water) indicating that the post-curing play a critical role over plastization [10]. Moreover, the addition of single and hybrid carbon nanofillers to the epoxy resin resulted in a lower decrease of the flexural properties thereby improving the stability of the epoxy resin to environmental factors such as temperature and moisture.

3.4. Thermophysical properties

The maximum peak of the tanδ vs. T plots was used to identify the α-relaxation associated with the glass transition and the corresponding temperature was assumed to evaluate T_g for all tested samples. The results are provided in Table 1 for the samples before and after the environmental ageing in water and without water. Similarly, as for flexural properties the glass transition temperature for the epoxy and the epoxy filled with single and hybrid carbon nanofillers was almost the same before the environmental ageing T_g = 235±3 °C. This can be attributed to several contrary acting factors such as existence of interphases/interfaces on the surface of the nanoparticles, agglomerates, changes in crystallinity and cross-link density of the epoxy resin.

The environmental ageing in water has resulted in a slight decrease of the glass transition temperature both for the epoxy and for the NCs. Contrary, the environmental ageing without water had almost no effect for all materials studied proving that such aeronautical epoxy resin is very stable to moisture and temperature effects and can be safely applied in the outdoor applications.

Table 1. Glass transition temperature of the investigated materials before and after environmental ageing in water and without water.

Material	T_g, °C (in initial state)	T_g, °C (after env. ageing in water)	T_g, °C (after env. ageing without water)
Epoxy	235.3 ± 1.0	231.5 ± 0.5	235.7 ± 0.7
Epoxy +0.05 wt. % of CNTs	237.5 ± 0.7	235.5± 0.6	236.2 ± 0.5
Epoxy +0.1 wt. % of HN	237.5 ± 0.5	236.8 ± 1.0	236.6 ± 0.8
Epoxy +0.3 wt. % of CNFs	238.4 ± 0.7	237.8 ± 0.8	238.0 ± 0.5

4. Conclusions

Efforts were being made to evaluate the effect of environmental ageing on the flexural properties of the epoxy resin and the epoxy resin filled with single and hybrid carbon nanofillers (CNTs and CNFs). It was experimentally confirmed that in initial state before the environmental ageing the effect of the addition of carbon nanofillers is insignificant perhaps due to relatively low filler content and possible aggregation of the nanofillers causing weak nanofiller-matrix interfacial interactions.

Nevertheless, after environmental ageing in water and without water the flexural characteristics of the epoxy and the NCs essentially decreased and the extent of this decrease was smaller for the NCs proving that the addition of carbon nanofillers resulted in improved stability of the epoxy resin to the environmental factors such as temperature and moisture. Based on experimental results the most environmentally stable NC was epoxy filled with 0.1 wt. % of HN, which had the lowest effect of temperature and moisture on flexural modulus and strength along with the lowest equilibrium water content and diffusivity.

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