MOISTURE SORPTION BY EPOXY RESIN FILLED WITH MWCNT OF DIFFERENT THICKNESS

T. Glaskova-Kuzmina[1], A. Aniskevich[1], J. Sevcenko[1], A. Borriello[2], and M. Zarrelli[2]

[1]Institute for Mechanics of Materials, University of Latvia, Aizkraukles 23, Riga, LV-1006, Latvia
Emails: tatjana.glaskova@pmi.lu.lv, andrey.aniskevich@pmi.lu.lv, evgs@inbox.lv, www.pmi.lv
[2]Institute for Polymers, Composites and Biomaterials, National Research Council of Italy, Piazzale Enrico Fermi, Granatello, Portici, 80055, Italy
Emails: anna.borriello@cnr.it, mauro.zarrelli@cnr.it, www.ipcb.cnr.it

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Abstract
The aim of this work was to determine the effect of environmental ageing on sorption and thermophysical characteristics of epoxy and epoxy-based nanocomposites (NC) filled with multiwall carbon nanotubes (MWCNT) with different thicknesses. Two types of MWCNT with average diameter of 140 (aspect ratio - 50) and 9.5 (aspect ratio - 150) nm, respectively, were used. The considered filler content was within the range 0.005-0.1 wt. % for thin and 0.5-2 wt. % for thick MWCNT. For epoxy and NC specimens the moisture absorption and resorption after desorption in silica gel were performed in atmospheres with 47, 73, and 91% RH at room temperature. Dynamic thermal mechanical analysis was employed to evaluate hygrothermal ageing effects in as-produced and “aged” NC samples after moisture ab/de-sorption.
It was experimentally confirmed that the equilibrium moisture content of the NC decreased with filler content for both MWCNT if compared to the neat epoxy resin. The diffusion coefficients for NC filled with 0.1 and 2 wt. % of MWCNT were reduced by 17 and 20%, accordingly. The improved environmental stability of the NC was explained by the reduction of free volume and restriction of polymer chain mobility due to addition of MWCNT to epoxy resin.

1. Introduction

Extensive research on development of multifunctional polymer composites incorporating carbonaceous nanofillers, such as single- and multiwall carbon nanotubes (CNT) [1], graphene nanoparticles [2], and carbon nanofibers [3] 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.

Composites modified by CNT allow tuning the final material properties by changing nanoparticle concentration, and their morphology [4]. CNT have unique mechanical properties like stiffness and strength, respectively, within the range of 100-1000 GPa and 2.5-3.5 GPa, and electrical conductivity of 3000-4000 S/m, thus, making them valuable candidates to develop novel composites characterized as advanced polymer materials [5].

However, up to now such 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 [6]. The consideration of environmental effects and the reveal of the most environmentally stable electropassive nanocomposites (NC) can broaden their application to outdoor conditions.

The aim of this work was to determine the effect of environmental ageing on sorption and thermophysical characteristics of epoxy and epoxy-based nanocomposites (NC) filled with multiwall carbon nanotubes (MCNT) of different thickness. For this purpose moisture ab/de-sorption and resorption tests were performed in atmospheres with different relative humidity and DMTA test were done after moisture ab/de-sorption tests for epoxy and NC samples filled with MWCNT of different thickness and filler content.

2. Materials and Methods

A commercially available monocomponent RTM6 (*Hexcel Composites*) epoxy resin was used as a matrix material. This system is characterized by a low viscosity and a glass transition temperature T_g of about 200 ºC, and is frequently used for infusion processes such as resin transfer moulding or vaccum bag infusion for both industrial and academic purposes.

Two types of MWCNT: 1) SA659258 (*Sigma Aldrich*) with average diameter of 140 nm (aspect ratio is 50) and 2) N7000 (*Nanocyl*) with average diameter of 9.5 nm (aspect ratio is 150) were used as nanofillers to investigate the effect of MWCNT content on sorption characteristics and moisture induced ageing of the NC. The nanofillers were denoted as “SA” and “N”, accordingly. Different content of nanofillers, SA and N, were used ranging from 0.005 wt% to 2 wt%. Taking into account previous experience for dispersion of these nanofillers, different loadings for N (0.005-0.01 wt%) and SA (0.1-2 wt%) nanofillers were added to the hosting matrix [6]-[8] achieving maximally possible nanofiller content and satisfactory dispersion at the same time.

The manufacturing procedure of the NC consisted of following steps: 1) ultrasonication of nanofiller and matrix by using a dipping tip sonicator (Misonix S3000) for 60 min at power 20 W and temperature 120 ºC; 2) degassing for 30 min at 80 ºC; 3) curing for 1 h at 160 ºC and post-curing for 2 h at 180 ºC. The processing method was properly designed for a good dispersion of pristine nanotube aggregates [8]. For each filler content 2 discs of diameter 100 mm and thickness app. 2.5 mm were obtained and cut into specimens of average diamensions 70 ± 2, 10 ± 1, and 2 ± 0.2 mm to ensure 1D mode of moisture diffusion through the samples.

Before starting the moisture absorption tests, all test specimens were conditioned in a desiccator with silica gel at relative humidity of 24% to remove the absorbed moisture until all specimens showed no change in mass. Subsequently, they were placed in a desiccators at relative humidity of 47, 73 and 91%, made by using a saturated solutions of KCNS, NaCl, K_2SO_4, accordingly. Moisture desorption and sorption experiments were performed at room temperature (RT) T = 20 ºC. For the investigation of the moisture absorption kinetics, the specimens were periodically removed from the desiccator, air dried for 5 min, and then weighed by using a *Mettler Toledo* XS205DU balance with accuracy 0.05 mg. The results obtained in the moisture sorption experiments were accurately compared for all tested materials. Five specimens were used for each material type, and the averaged values were presented.

For the neat epoxy and NC specimens the moisture kinetics was analysed until equilibrium moisture content was reached. After that, all test specimens were placed in a dry atmosphere again, to analyse the kinetics of moisture desorption until equilibrium moisture content was reached. Then the second sorption-desorption cycle at the same atmospheres was performed again.

DMTA in tensile mode at a given force 4 N was applied by using a Mettler Toledo DMA/SDTA861 instrument to evaluate hygrothermal ageing effects in both as-produced and “aged” NC samples after moisture ab/de-sorption. All experiments were performed at 10 Hz frequency by tensile deformation, scanning from 30 °C to 280 ºC at 3 K/min heating rate. The maximum of tanδ vs. temperature plots was used to identify α-relaxation associated to the glass transition, and the position of the peak was considered to evaluate the glass transition temperature T_g for all test samples. For each “as-produced” and environmentally “aged” samples of dimensions 30×3×1 mm^3 not less than two scans were performed.

3. Results and Discussion

3.1. Moisture sorption

According to free volume approach, two states of water/moisture can exist in polymer-based systems upon water/moisture absorption: unbound free water, which fills the nanovoids (also called free volume), not inducing swelling of the polymer resin, and hydrogen-bounded water, which causes swelling of the polymers [9], [10]. Polymers and composites having a lot of free volume generally are characterized by high moisture uptake, which in turn can induce a more significant reduction of mechanical properties of the polymers and/or composites [7]. The disperion of the nanoparticles having high aspect ratio, e.g. MWCNT, usually leads to the reduction of the free volume with a subsequent mitigation of negative effect associated to the moisture on mechanical behaviour of polymers and composites [7].

The moisture absorption curves in atmosphere with relative humidity 91% obtained for epoxy and NC with 0.1 (N) and 2 (SA) wt. % are given in Figure 1. The moisture content $w(t)$ was defined as the mass difference between moistened m_t (time-varying) and initial m_0 specimens, normalized to the initial mass of specimens according to the relation:

$$w(t) = \frac{m_t - m_0}{m_0} \times 100\,. \qquad (1)$$

Classical Fick’s model was used to describe all sorption curves

$$w(t) = w_\infty - 2\frac{(w_\infty - w_0)}{\pi^2}\sum_{k=1}^{\infty}\frac{(1-(-1)^k)^2}{k^2}\exp\left[-\left(\frac{\pi k}{h}\right)^2 Dt\right], \qquad (2)$$

where w_∞ and w_0 are the equilibrium and initial moisture contents in specimens, D is the diffusion coefficient and h is thickness of the specimens.

According to Figure 1, Fick’s model was in good agreement with the experimental data for all materials tested. Similar results were obtained for the rest atmospheres and filler contents. The moisture absorption isotherms presenting the equilibrium moisture content vs. relative humidity of the atmosphere for moisture absorption and resorption are shown in Figure 2. Obviously, the sorption process finished at lower equilibrium moisture content for the NC filled with the MWCNT in comparison with the epoxy resin. For atmosphere with lowest RH (47%) the equilibrium moisture content was maximally reduced by 0.07% and by 0.11% for N and SA MWCNT, accordingly. For the atmosphere with highest RH (91%), the effect was more pronounced: the equilibrium moisture content was reduced by 0.16% and by 0.26% for N and SA MWCNT, accordingly. This result can be explained by the reduction of the free volume due to the addition of nanofiller particles [11], and as more nanofillers were added, as higher extent of reduction was obtained for the equilibrium moisture content. In fact, the continuos reduction of the equilibrium moisture content for higly filled NC testifies that the dispersion of the MWCNT is good also at high filler content.

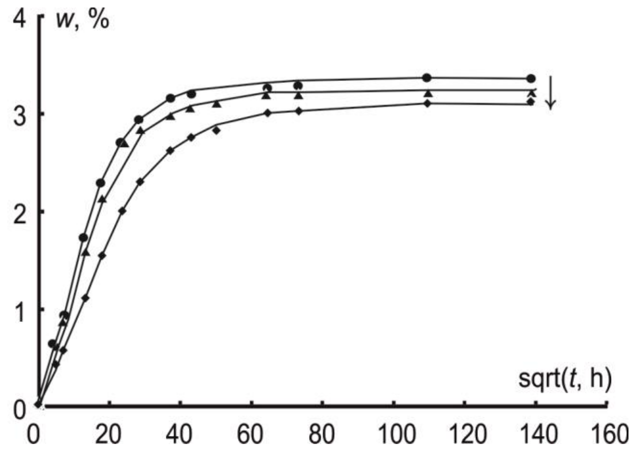

Figure 1. Typical moisture uptake of epoxy (●) and NC filled with 0.1 (▲) and 2 (♦) wt. % of MWCNT in atmosphere with 91 % RH (dots – experimental data, lines are computed by Eq. (2). The arrow indicates the increase of MWCNT content in the NC.

The diffusion coefficient of the epoxy resin was also reduced by the incorporation of MWCNT. For the epoxy resin resin at 91% RH it was about $(1.10\pm0.1)\times10^{-3}$ mm^2/h, while for NC filled with 0.1 (N) and 2 (SA) wt. % of MWCNT it was reduced by app. 17% and 21%, accordingly. It could be explained by improved barrier properties of moisture-impenetrable carbon nanofillers within the epoxy resin, which formed tortous paths, hindering the moisture progress and decreasing the diffusion rate [7], [11], [12]. Moreover, increasing the filler content from 0.1 (thin MWCNT) till 2 wt. % (thick MWCNT), the reduction of sorption properties increased. Of course, it can be attributed to greater overall surface area of the MWCNT within the polymer resin improving the barrier properties of the SA nanofiller parlticles associated with their higher length and filler content. Secondly, the nano-sized inclusions restrict intermolecular movements of the polymers, thus retarding the relaxation of the polymer chains [12], which leads to the reduction of free volume and subsequently the equilibrium moisture content of the composite.

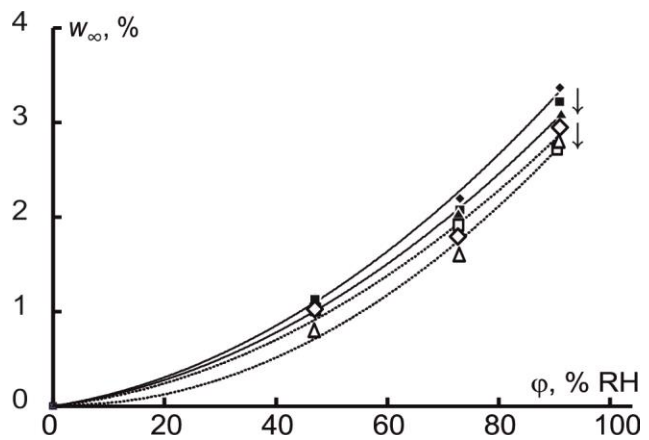

Figure 2. Sorption isotherms for epoxy (♦, ◊) and NC with 0.1 (■, □) and 2 (▲, Δ) wt. % of MWCNT: for moisture absorption (filled symbols) and resorption (open symbols). Lines are approximations by polynoms. The arrows indicate the increase of MWCNT content in the NC.

Moreover, as seen from Figure 2 the moisture absoption and resorption isotherms are slightly different. For both epoxy and NC filled with 0.1 (N) and 2 (SA) wt. % MWCNT the sorption isotherms for resorption lie under the isotherm for sorption. It testifies that sorption process slightly reduced the amount of available free volume within polymer resin, thus changing sorption characteristics of both epoxy and NC. This irreversible moisture effect on thermophysical and mechanical characteristics of the epoxy and NC was also verified by the results of DMTA tests before and after hygro-thermal ageing.

3.2. Thermomechanical analysis

DMTA is widely used to analyze chain mobility for the polymers, deterioration of their thermomechanical properties due to moisture/water uptake and hygrothermal effects [11], [12]. The DMTA curves of the epoxy and NC filled with 0.1 wt. % in as-produced (before environmental ageing) and "aged" (after invironmental ageing in atmospheres with relative humidity 47%, 73% and 91% and subsequent desorption in atmosphere with relative humidity 24%) were analyzed. Based on Figure 3 which combines the change of the storage modulus and loss tangent with temperature for the epoxy resin and NC filled with 0.1 and 2 wt. % of MWCNT, the effect of environmental ageing after sorption in 91% RH and desorption in 24% RH, and resorption in 91% RH can be analyzed. The environmental ageing in this atmosphere having highest relative humidity of the study was characterized by the highest impact on thermomechanical propereties of epoxy and NC, and therefore is emphasided in the paper. The results for the rest tests obtained after environmental ageing in atmospheres with relative humidity 47% and 73 % are inline with those obtained for 91% RH.

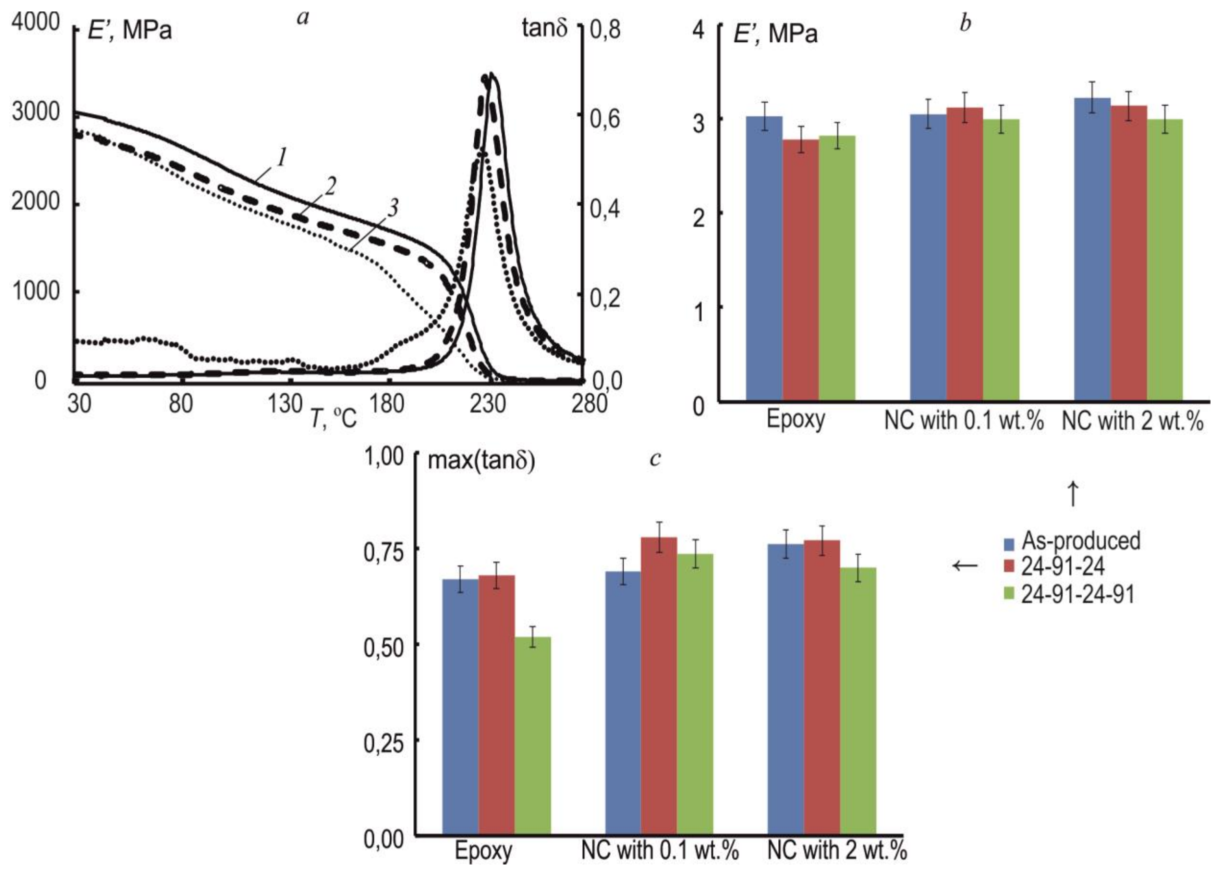

Figure 3. DMTA curves of the epoxy resin (*a*), storage modulus at RT (*b*) and the maximal value of tanδ (*c*) for the neat epoxy and NC filled with 0.1 and 2 wt. % of MWCNT in different states indicated in the legend (*1* – in as-produced state, *2* – after sorption in 91% and desorption in 24% RH, *3* – after resorption in 91% RH).

Generally, the thermomechanical behavior of epoxy (see Figure 3a) and NC samples filled with different content of MWCNT was similar. According to Figure 3b, the storage modulus at RT for epoxy (3.03 GPa) was lower than for the NC filled with 0.1 wt. % (3.05 GPa) and 2 wt. % (3.23 GPa). Slight increase of the storage modulus for epoxy resins due to the addition of MWCNT was expected, and is a frequent result in the literature [11], [12]. It is explained by the improvement of the crosslink density and the reduction of the molecular mobility of the polymer chains due to incorporation of stiff MWCNT. The higher content of MWCNT resulted in higher improvement of the storage modulus (by 6.6%) at RT proving again that the dispersion of the MWCNT within the epoxy resin was satisfactory. However, not great difference was obtained for the storage modulus of the epoxy and NC in the rubbery region indicating that the crosslinking degree of matrix was similar.

Figure 3b shows that the environmental ageing (moisture absorption in 91% RH and desorption in 24% RH) leads to slight irreversible changes in the thermomechanical properties: for epoxy resin (Figure 3a) the storage modulus of the “aged” specimens was reduced by 8% in comparison with as-produced state. As it was expected, after moisture resorption the storage modulus of the NC (see Figure 3b) is reduced to lower extent (by app. 6.1%) in comparison with the epoxy at room temperature. Thus, absorbed moisture caused plastization increasing polymer chain mobility and decreasing the glass transition temperature for both epoxy and epoxy-based NC.

The loss tangent curves for all the material studied both in as-produced and “aged” state was similar having a slight shift of the peak to lower temperatures. Using the position of this peak T_g of epoxy and NC samples was evaluated and analyzed. Negligible variations of the glass transition temperature for the epoxy (226 ± 3 ºC) and NC (230 ± 3 ºC) were obtained which could be explained by counterbalancing the restricted mobility of the polymer chains and lower cure degree of the NC [12]. The shift to lower temperatures due to environmental ageing is around 3-5 ºC for all of the materials studied, but similar height of the peak (see Figure 3c) can be related to similar degree of mobility of the polymer chains at the glass transition for both epoxy and NC specimens in “aged” state. The decrease of the height of the relaxation peak for the samples after moisture resorption in 91% RH is attributed to higher degree of mobility of polymer chains due to the presence of water in the free volume. Notably, the NC (Figure 3b and Figure 3c) are less affected by the environmental ageing. In fact, the equilibrium moisture content for NC was also reduced that together with restricted mobility of the polymer chains contribute to the enhanced environmental stability of the NC.

4. Conclusions

First of all, it was experimentally confirmed that sorption characteristics of both NC filled with thin (N) and thick (SA) MWCNT were slightly reduced. Since the maximally available nanofiller content was used for both types of MWCNT the effect of thickness cannot be evaluated directly due to different nanofiller content in the epoxy resin. For this purpose additional independent tests are required for the NC filled with MWCNT of different thickness at the same filler contents. Nevertheless, the indirect evaluation of the effect of thickness of MWCNT on sorption characteristics allows concluding that the main contribution was exactly the total surface area of the nanofiller which increased by increasing the filler content from 0.1 till 2 wt. %.

Secondly, the reduced sorption characteristics of the NC in comparison with epoxy resin were attributed mainly to the reduction of free volume of the polymer resin available for the impenetration of water molecules. Moreover, slight improvement of the storage modulus and the glass transition temperature was obtained for the NC filled with both thick and thin MWCNT which was explained by the improvement of the crosslink density and the reduction of mobility of the polymer chains due to incorporation of stiff MWCNT.

Finally, it was proved that the effect of environmental ageing for NC filled with both thick and thin MWCNT was slightly reduced in comparison with the epoxy resin. After moisture ab/de-sorption and resorption in all atmospheres both storage modulus and glass transition temperature for the NC were reduced less comparing to the epoxy resin. The storage modulus and glass transition temperature of environmentally “aged” NC specimens was app. 3.00 ± 0.1 GPa and 230 ± 3 ºC in comparison with “aged” epoxy specimens having 2.82 ± 0.1 GPa and 226 ± 3 ºC, accordingly. Thus, not full recovery of thermophysical properties for epoxy and epoxy-based NC was registered during the study. Nevertheless, the addition of stiff moisture impenetrable MWCNT could allow minimizing the negative effect of environmental ageing on mechanical properties of polymer-based composites.

Acknowledgments

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