



Hydrothermally resistant thermally reduced graphene oxide and multi-wall carbon nanotube based epoxy nanocomposites

O. Starkova^{a,*}, S. Chandrasekaran^b, L.A.S.A. Prado^b, Folke Tölle^c, R. Mülhaupt^c, K. Schulte^b

^a *Institute of Polymer Mechanics, University of Latvia, Aizkraukles 23, LV-1006 Riga, Latvia*

^b *Institute of Polymers and Composites, Technische Universität Hamburg-Harburg, Denickestraße 15, D-21073 Hamburg, Germany*

^c *Freiburger Materialforschungszentrum and Institut für Makromolekulare Chemie of the Albert-Ludwigs-University Freiburg, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany*

ARTICLE INFO

Article history:

Received 25 October 2012

Received in revised form

3 December 2012

Accepted 4 December 2012

Available online 12 December 2012

Keywords:

Graphene oxide

Nanocomposite

Hydrothermal ageing

Water absorption

Thermo-mechanical properties

ABSTRACT

This study is focused on the investigation of thermo-mechanical properties of an epoxy resin filled with thermally reduced graphene oxide (TRGO) and multi-wall carbon nanotubes (MWCNT) after exposure of samples to hot distilled water. Addition of low contents of TRGO and MWCNTs greatly reduces the water sorption capacity of the epoxy polymer and improves its resistance to hydrothermal ageing. The glassy and rubbery moduli of the neat epoxy decreased for about 20% and 80%, respectively, while TRGO-based epoxy filled with 0.3 wt.% of TRGO showed only 6% reduction of both moduli. Hydrothermal ageing resulted in an enormous drop in the glass transition temperature (T_g) of the neat epoxy, by about 90 °C, while the shift in T_g of the nanocomposites did not exceed 8 °C. After re-drying of samples, the position and shape of the peak was completely recovered for the nanocomposites. Irreversibility of water influence on the neat polymer appeared in the broadened and shifted glass transition region. The improvement of the thermo-mechanical properties of the neat epoxy from the addition of TRGO is higher than that achieved by incorporating MWCNTs. This trend is valid in both unexposed state and after hydrothermal ageing of the nanocomposites.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Polymer nanocomposites have been widely investigated over the past decade, mainly focussing on the development of structure–property relationships and imparting their exceptional mechanical properties [1–3]. Due to the high electrical and thermal conductivity of carbon nanofillers, the polymers filled with carbon black, carbon nanotubes (CNTs), and graphite sheets have also been investigated as multi-functional materials for electrical and thermal applications [1–5]. In recent years, a particular interest is shown to the use of a new class of carbon nanofillers – graphene and graphene oxide nanoplatelets – with a perspective of improving the mechanical and electrical properties of polymers by addition of lower amounts of plate-like nanoparticles compared to already traditional nanotubes [6–13].

Epoxy resins are a very important class of thermoset polymer used in composite industry. They exhibit excellent engineering properties, such as high strength and stiffness, chemical resistance, and good resistance to creep. Different epoxy systems have been

widely used as matrices for polymer composites, e.g. carbon- and glass-fibre-reinforced plastics [14–16]. Many investigations are focused on further improving epoxy materials using nanofillers, and in particular graphene nanoplatelets and carbon nanotubes, able to improve some properties as well as to impart new properties for obtaining multi-functional materials [4–7].

In most applications, polymer composites can be exposed to moisture or be placed in a humid environment. Humid atmosphere and high temperature are one of the common factors, which affect service properties of polymers, including epoxy resins, and their composites. Simultaneous action of these factors (referred as hydrothermal ageing) can essentially deteriorate the structure, physical and mechanical properties of the materials and reduce their service life.

The rate of moisture penetration, and thus the influence of moisture, can be essentially reduced by incorporating nano-sized hydrophobic additives into polymers [17,18]. Fillers with a high aspect ratio can act as efficient barriers against transport of water through the polymer due to the increased path length for molecules diffusing through the material. Another explanation for the reduced water permeability in nanocomposites is that the nano-sized inclusions restrict the molecular dynamics of the polymer chain surrounding the nanofiller, thus retarding the relaxation of

* Corresponding author. Tel.: +371 67543120; fax: +371 67820467.

E-mail address: olesja.starkova@pmi.lu.lv (O. Starkova).

polymeric chains [17,18]. The retarded relaxation, in turn, reduces the diffusion of small molecules through the nanocomposites. Owing to their extremely high specific surface area and two-dimensional geometry, graphene and/or graphene oxide platelets can be regarded as more efficient fillers for improving barrier properties of polymers than CNTs. In literature, there are some reports, where the altered barrier properties of graphene- [8,19] and CNT-based [5,20–22] polymer nanocomposites are studied. However, the efficiency from the addition of both nanofillers cannot be compared due to differences in the chemical nature of polymer systems and processing techniques of nanocomposites. Despite the high interest to investigations of the basic mechanical and physical properties of polymers, including epoxy resins, reinforced with graphene and/or graphene oxide nanoplatelets and CNTs, there are no systematic reports in the literature in which water diffusion characterizations, particularly with regard to hydrothermal ageing, were studied.

Dynamic mechanical thermal analysis (DMTA) has been shown to be a useful tool to investigate the effect of moisture/water uptake on the viscoelastic response of polymers and composites [14,18,22–24]. Useful information on chain mobility of epoxy and deterioration of its thermo-mechanical properties is obtained from the loss tangent ($\tan \delta$) curve. Moisture uptake causes a shift, broadening and in some cases splitting of the loss factor ($\tan \delta$) peak. By acting as an efficient plasticizer and increasing the polymer chain mobility, absorbed moisture causes a decrease in glass transition temperature (T_g) in epoxy polymers [14,23,24]. DMTA is also employed to detect the interphase effect on the thermal properties of the nanocomposites, as it is convincing approach to provide comprehensive knowledge on the interaction between the filler and matrix [11,14,25].

The aim of the present work is to investigate water uptake under elevated temperature and its effect on the thermo-mechanical response of the epoxy nanocomposites filled with different contents of thermally reduced graphene oxide and multi-wall carbon nanotubes as well as to estimate the potential of using these carbon fillers for improving the polymer's resistance to hydrothermal ageing.

2. Materials and experimental details

The epoxy system used in this study is a commercially available DGEBA-based resin (LY556) cured with an anhydride hardener (CH917) and an imidazole accelerator (DY070) (Huntsman, Switzerland). This epoxy is used in fibre-reinforced composites for aerospace applications and provides good mechanical and chemical properties and is characterized by high T_g .

As-produced multi-wall carbon nanotubes (MWCNTs) (Nanocyl 7000) and thermally reduced graphene oxide (TRGO) were used as fillers. The MWCNTs have average diameter of 10 nm and their length varying from 0.1 to 10 μm with a carbon purity of 90%. Whereas, the TRGO sheets used were prepared using Hummer's method from graphite in Freiburg University [12]. The lateral dimension of the sheets varies from 1 to 4 μm and the carbon content varying from 81 to 97% [13].

The nanocomposites filled with different contents of the fillers – 0.1, 0.3, and 0.5 wt.% – were produced via a common shear-mixing technique [3]. Required amounts of the nanotubes and graphene oxide particles were manually mixed into the resin (LY556) and subsequently dispersed using a lab-scale three-roll-mill (Exakt 120E; Exakt GmbH, Norderstedt, Germany). After dispersing the fillers in the epoxy resin, the hardener and accelerator were added in the ratio 100:90:1. The uncured suspensions were degassed under reduced pressure in a vacuum oven and poured into open aluminium moulds. The curing cycle of the material was 80 °C for

4 h and 140 °C for 8 h, as recommended by the supplier. A detailed description on the processing of the nanocomposites is given in Ref. [13].

The microstructure of cured nanocomposites was analysed by Scanning Electron Microscopy (SEM) using a LEO 1530 FE-SEM (Carl Zeiss, Germany). The cryogenic fracture surfaces were investigated without an additional coating at an acceleration voltage 1 kV.

Bar-shape samples for water sorption and DMTA tests were cut from the plates and polished with sandpaper. The average dimensions of samples were 40 × 5 × 1.5 mm.

The “as-produced” samples were dried in an oven at a temperature 50 °C for 2 days prior to testing in order to remove moisture absorbed from the ambient atmosphere.

Samples were immersed in distilled water and placed in an oven at 80 °C. The water uptake was detected by periodically removing the samples from water and recording their mass using an electronic balance, which has an accuracy of 0.01 mg. Before weighing, the surface of the samples was wiped using a tissue paper. The relative moisture content w [%] was determined as weight gain per unit weight:

$$w = \frac{m_t - m_0}{m_0} \times 100$$

where m_t is the weight of the wet sample at time t , and m_0 is the weight of the dry sample. Three samples of each composition were used for each measurement and the average data are shown in the graphs below. Sample weight changes were plotted versus the square root of time divided by thickness, \sqrt{t}/a , in order to analyse the data in the framework of the Fick's model [26].

Water sorption tests were continued for 2 weeks until saturation was reached. Thereupon, a part of samples – “water-aged” samples – was tested on DMTA to determine the effects of hydrothermal ageing of the materials. To further characterize the reversibility of water influence on the thermo-mechanical properties, the rest of samples were placed back in the oven for re-drying (“re-dried” samples). Desorption was performed at 80 °C until a stable weight of samples was reached, which took about 1 week.

A series of DMTA tests were performed for “as-produced”, “water-aged”, and “re-dried” after water sorption samples in an Eplexor 500 N device of Gabo Qualimeter. The measurements were carried out in tensile mode (1 N) at a frequency of 10 Hz from 20 °C to 200 °C at a heating rate of 3 K per min. T_g was determined from the mechanical loss factor ($\tan \delta$). The measurements were done for two duplicate “as-produced” samples and one-two representative “water-aged” and “re-dried” samples.

3. Results and discussion

3.1. Structural investigations by SEM

The state of dispersion of the fillers in epoxy matrix has been characterised by SEM at a low magnification. The representative SEM micrographs of the epoxy nanocomposites filled with 0.3 wt.% of TRGO and MWCNTs are shown in Fig. 1. The nanofillers were fairly good dispersed in the nanocomposites, although some primary agglomerates can be observed. In the case of TRGO-based epoxy composite (Fig. 1a) though there are a few primary agglomerates, the rest of the secondary agglomerates are distributed uniformly in the matrix, whereas in MWCNT/epoxy composite the network formed by the MWCNT agglomerates is also observed (Fig. 1b). The observed secondary agglomerates are either due to the re-agglomeration process after dispersion or the residue of primary agglomerates.

Download English Version:

<https://daneshyari.com/en/article/5202390>

Download Persian Version:

<https://daneshyari.com/article/5202390>

[Daneshyari.com](https://daneshyari.com)