Composites Part B 162 (2019) 685–691

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Fully exfoliated graphene oxide accelerates epoxy resin curing, and results in dramatic improvement of the polymer mechanical properties

Albina Surnova[a], Dinar Balkaev[a,b], Delus Musin[a], Rustem Amirov[a], Ayrat M. Dimiev[a,*]

[a] *Laboratory for Advanced Carbon Nanomaterials, Kazan Federal University, Kremlyovskaya str. 18, Kazan, 420008, Russian Federation*
[b] *Kazan National Research Technical University named after A.N. Tupolev, Karl Marx str. 10, Kazan, 420111, Russian Federation*

ARTICLE INFO

Keywords:
A. Graphene oxide
B. Epoxy composites
C. Thermomechanical properties
D. Thermal analysis
E. Rheology

ABSTRACT

In this study, we propose a new approach for the homogeneous liquid-phase transfer of graphene oxide (GO) into epoxy resin. This makes the process more efficient, while achieving fully uniform distribution of GO flakes within the epoxy matrix. Introduction of as little as 0.4% and 0.6% GO drastically increases the viscosity of the compositions, pointing at the highly exfoliated condition of GO in the resin. A significant accelerating effect of GO on the curing reaction is attributed to reactive groups on the GO surface. The study of the thermo-mechanical properties revealed that the introduction of relatively small amount of GO (0.2 wt%) into the epoxy matrix results in the increase of the storage modulus by 25.4% (3035 MPa) relative to the neat epoxy polymer (2420 MPa). The use of the high-temperature curing agent affords the composites with significantly higher glass transition temperatures, compared to the low-temperature curing agent, broadening the scope of their potential applications.

1. Introduction

Epoxy resin is one of the most broadly used thermosetting polymers in the production of advanced composites due to its excellent properties, including stiffness, durability, light weight, low toxicity and low cost [1,2]. Epoxy resins are used in various industrial fields, such as automotive and aerospace. However, the limitation of epoxy resins is that their stiffness is highly dependent on the crosslinking density, while too high crosslink density can lead to brittle fracture at very low deformations [3]. One of the ways of increasing the strength and the fracture toughness of epoxy resins without compromising their rigidity is the use of various nanofillers.

Nanomaterials in the composite system play an important role in modifying their properties, such as electrical, optical, thermal, and mechanical. Of particular interest are carbon-based nanomaterials such as graphitized carbon, carbon nanotubes, graphene, and graphene nanoribbons [4–7]. Single-layer graphene possesses the highest measured modulus and break strength [8] and the Young's modulus of E = 1.0 terapascals [9]. However, graphitic nanomaterials tend to aggregate in the polymer matrix, especially at high concentrations, which leads to the degradation of the polymers' properties [5,10]. Unlike most of the carbon nanomaterials, graphene oxide comprises numerous oxygen functional groups, which render it soluble in water and some organic solvents, and provide an excellent affinity toward epoxy resin [8,11].

The incorporation of GO into epoxy matrix enhances toughness and stiffness of the epoxy resins. Thus, only 0.1 wt% GO was found to increase the fracture toughness of pristine epoxy by 75% [12]. Liu et al. [13] showed that the introduction of GO has not demonstrated obvious effect on the thermal stability. The researchers emphasize that addition of 0.5 wt% GO provides an increase in the storage modulus by 12% (2061.6 MPa) compared to neat epoxy [14].

As was mentioned above, the critical point in fabricating composites is the uniformity of the nanofiller distribution in the polymer matrix [7]. Concerning the GO/epoxy system, the most important factors in achieving uniform distribution are the choice of the solvent and the method of GO transfer to the resin. In most of the studies, water [4], acetone [8,12–15], ethanol [5,11,16] and curing agent [17] were used as the solvents for preparing GO dispersions. The ability of GO to form dispersions in various solvents and the stability of these solutions have been investigated, and it was found that the dispersions of GO in acetone and ethanol were unstable [18]. At the same time, when the aqueous dispersion of GO is mixed with the resin, it is difficult to achieve the complete transfer of GO into the resin, and to completely remove water from the resin, which leads to the production of poor quality epoxy/GO composites. To overcome these shortcomings, we have recently developed a new method for the liquid-phase

---

* Corresponding author.
E-mail addresses: albin_6767@yahoo.com (A. Surnova), dinar.balkaev@yandex.ru (D. Balkaev), musindelus@gmail.com (D. Musin), ramirov@kpfu.ru (R. Amirov), dimiev.labs@gmail.com (A.M. Dimiev).

https://doi.org/10.1016/j.compositesb.2019.01.020
Received 29 June 2018; Received in revised form 28 November 2018; Accepted 2 January 2019

homogeneous transfer of GO into epoxy resin which affords uniform distribution and highly exfoliated condition of GO in the resin [19]. This leads to preparation of the epoxy/GO composites with improved mechanical properties compared to the neat resin [19]. However, in that work, we did not attain the optimal curing regimes, and thus failed to demonstrate full advantage of the homogeneous transfer method.

In this study, we propose a new peculiar approach for the method of transferring GO into epoxy matrix. This makes the procedure more simple, and allows to further improve the uniformity of the GO distribution in the matrix, and to increase the GO content up to 0.6 wt%, while maintaining nearly fully exfoliated condition of GO in the matrix. A newly used high-temperature amine curing agent allowed to develop the optimal curing regime. The influence of the GO content on the curing reaction and on the rheological properties of the resin was studied. Thermo-mechanical properties of epoxy-GO composites with different GO contents were also evaluated.

2. Experimental

2.1. Materials

The epoxy resin (NPEL-128, epoxy value 22.6, epoxide equivalent weight is 186.2 g eq.$^{-1}$), which is manufactured from bisphenol-A and epichlorohydrin, was obtained from the “Rus Chemicals Group” (Russia). The 4,4′-diaminodiphenylmethane (DDM) curing agent was supplied by Sigma-Aldrich. Isopropyl alcohol (IPA) and graphite GL-1 were obtained from “TatKhimProduct” LLC (Russia). All reagents and solvents were purchased from commercial suppliers and used as received.

2.2. Preparation of GO

GO was prepared as described in our previous reports [20–22]. Graphite flakes were dispersed in 96% sulfuric acid at room temperature using a mechanical stirrer. After a 10-min stirring, 4 wt equiv. of $KMnO_4$ were iteratively added. After the complete consumption of $KMnO_4$, the reaction was quenched with ice water, and the 30% H_2O_2 was added until the color change. The resulting mixture was centrifuged; the separated GO precipitate was redispersed in DI water, and centrifuged again. Such cycles of GO purification were repeated five more times. The 3% HCl was used instead of water during the last three washing cycles. The GO precipitate was air dried after the last wash.

2.3. Preparation of dispersion of GO in IPA

To prepare the GO solution in IPA (GO-IPA), 100 ml of an aqueous 2 wt% GO solution were mixed with 100 ml of IPA. After the mixture was stirred for 1 h, it was centrifuged for 40 min at 8900 rpm. The clear supernatant was discarded. The precipitated gel was mixed with a fresh portion of IPA, bringing the volume up to 200 ml, stirred for 1 h and centrifuged under the same conditions until GO separates from the supernatant. This procedure was repeated five more times. This sequence of operations resulted in the gradual replacement of water by IPA [19]. The solution remained transparent and resistant to precipitation at all the stages of operation. After the last centrifugation, a GO-IPA gel with the GO content of 2.36 wt% was obtained. According to the dilution factor, this gel should contain 0.048 wt% water. The actual water content was not determined.

2.4. Preparation of the liquid GO/epoxy formulations

In our previous study [19], GO was introduced into the resin directly in the form of the GO-IPA gel with GO content ~2.36%. In this gel, GO might comprise a small fraction of the not fully exfoliated sheets due to the details of the water-to-IPA transfer procedure. In this work, the GO-IPA gel was first diluted with IPA to achieve higher exfoliation degree of GO in IPA, and potentially in the epoxy resin. The Epoxy/GO formulations were prepared as the following. The portions of 0.21 g, 0.42 g, 0.84 g, 1.69 g, and 2.54 g of the 2.36 wt% GO-IPA gel were dissolved in 10 g of isopropanol, using an ultrasonic disperser. Then each solution was blended with 10.0 g of epoxy resin in an ultrasonic bath for 30 min. Upon standing, the mixtures were separated into two phases: epoxy resin with GO on the bottom, and colorless IPA on the top, indicating that all the GO has transferred into the resin. The top IPA portion was decanted, and the GO-epoxy composition was agitated with the over-head stirrer for 18 h at the rate of 500 rpm at 80 °C for complete removal of all the traces of IPA. Thus, the epoxy/GO formulations were obtained with the GO content of 0.05 wt%, 0.1 wt%, 0.2 wt%, 0.4 wt%, and 0.6 wt%, which we will refer to as Epoxy/0.05-GO, Epoxy/0.10-GO, Epoxy/0.20-GO, Epoxy/0.40-GO and Epoxy/0.60-GO, respectively.

2.5. Curing the liquid GO/epoxy formulations and obtaining solid composites

In our previous report [19], we used the polyethylene polyamine (PEPA) curing agent and the curing regime, which lead to a relatively broad sample-to-sample variation in mechanical properties. The complete curing was probably not achieved, and therefore it was not possible to demonstrate all the advantages of the homogeneous liquid-phase transfer method, despite achieving very high GO exfoliation degrees. In this study, we optimized the curing process by using a new hardener DDM, which contributes to the improvement of thermo-mechanical properties. After preparation of GO dispersions in the resin, DDM was added and the mixture was kept with occasional stirring at 80 °C for 40 min. Then, the mixture was poured into a silicone molds and cured 2 h at 80 °C, 2 h at 150 °C, and post-cured for 1 h at 180 °C. This resulted in Epoxy/GO composites with GO content of 0.05 wt%, 0.1 wt%, 0.2 wt%, 0.4 wt% and 0.6 wt%, which we will refer to as Epoxy/0.05-GO-c (c-composite), Epoxy/0.10-GO-c, Epoxy/0.20-GO-c, Epoxy/0.40-GO-c and Epoxy/0.60-GO-c, respectively. Before testing the cured samples, they were conditioned at 23 ± 2 °C at a relative humidity of 50 ± 5% for at least 48 h.

2.6. Characterization of GO and GO-epoxy composites

In this work, we refrain from detailed discussion of the GO characterization as that having no direct relation to the main topic. We prepare GO by the protocol developed in our labs and repetitively conducted in the highly reproducible manner with almost no batch-to-batch variation [19–23]. For the detailed characterization and discussion of the GO chemical structure we refer interested readers to our previous publications [20–23]. The same batch of GO as in ref. [19] was used in this work. The important property of our GO with respect to this study is its oxidation level, allowing complete exfoliation to the single-atomic-layer sheets upon gentle agitation in water, which was repetitively demonstrated befor-e [19–23].

The viscosity of uncured epoxy resin and epoxy/GO blends was examined by the parallel plate rheometer DHR-2 (TA Instruments) in the flow-sweep mode. The samples were tested at 25 °C and shear rate varied between 0.1 and 1000 s^{-1} with the plate diameter 40 mm.

The measurement of the gel point of the liquid Epoxy/GO-DDM formulations was investigated using a parallel plate rheometer DHR-2 (TA Instruments) in the oscillation-step time mode. The samples were tested at 80 °C with the stress of 5% at the frequency of 1 Hz with the plate diameter of 40 mm.

The uniformity of GO distribution in the epoxy matrix was inspected with a BIOLAM M-1 (LOMO, Russia) optical microscope.

Dynamic curing profile of specimens was examined with DSC 214 Polyma (NETZCH Instruments). Freshly prepared uncured sample weighing 5–7 mg was heated at the ramping rate of 5 °C/min in N_2 environment from ambient temperature to 300 °C.

Dynamic mechanical measurements of the epoxy composite samples with the geometry 60 × 12 × 3.2 mm were carried out using the DMA 242 analyzer (NETZCH Instruments) in the 3-point bending mode, with a span length of 50 mm. Samples were tested from 30 to 220 °C at the heating rate of 3 °C/min with frequency of 1 Hz at dynamic load 10 N. Each measurement was repeated at least three times.

Flexural measurements of the neat epoxy resin were carried out with flat bar samples according to the ASTM D 790 protocol with the 5882 universal testing machine (Instron) at 25 °C with a span length of 64 mm and crosshead speed of 2 mm/min. Five specimens of each composite were tested to obtain the standard deviation.

3. Results and discussion

3.1. Dispersion of GO in epoxy systems

The mechanical characteristics of epoxy resin composites are highly dependent on the uniformity of the nanofiller distribution in the matrix [17]. Normally, nanofillers in a highly dispersed state increase the strength and the fracture toughness of the epoxy nanocomposites, as opposed to the poorly dispersed conditions [16]. It is known that GO sheets in a highly dispersed state have different orientations within the matrix that allows GO particles to bind with emerging matrix cracks, the effect that usually is not observed with other types of fillers [8]. It is also noteworthy that the oxygen-containing groups on the GO surface facilitate dispersibility, and enhance the interfacial interaction with the polymer matrix.

To investigate the uniformity of the GO distribution in the resin, i.e. the potential presence of any aggregates in liquid formulations, they were investigated with an optical microscope. Fig. 1 shows the optical image of Epoxy/0.40-GO as compared to that for neat resin. The optical image does not show any visible agglomerates of GO, which indicates a high degree of GO dispersion even at high loading (0.4 wt%). Note, the darker color of Epoxy/0.40-GO as compared to neat epoxy confirms that GO is still there. Importantly, in our previous study [19] we observed several well-visible flakes, which were mistakenly interpreted as single-layer flakes. Now, we realize that those flakes were most likely few-layered, while the single-layer flakes in epoxy matrix are probably not distinguishable with the optical microscope, as it is evident from Fig. 1b. Thus, with the newly-modified transfer method we have attained the higher degree of exfoliation, most likely the fully exfoliated condition.

In most of the literature methods, used to transfer GO into the epoxy matrix, including the chemical modification of GO, degradation of the GO sheets can occur due to specificity of the transfer procedures; this results in an increase in the stress transfer at the GO/epoxy interface, and as a result in the formation of agglomerates, causing poor mechanical properties of the finished composites [24]. The liquid-phase transfer method, used in this work, is softer and retains a highly dispersed state of GO, as shown in Fig. 1.

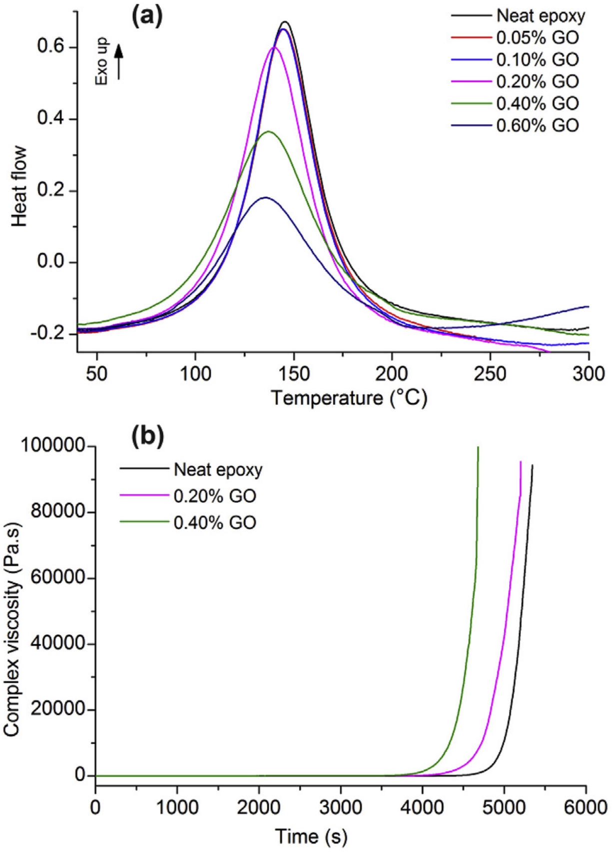

Fig. 2. Non-isothermal DSC thermograms (a), and gel-point measurements (b) for Epoxy/GO/DDM systems.

3.2. Effects of GO on the curing behavior and rheological properties

Next, we investigate the effect of GO on the kinetics of the curing reaction in the Epoxy/DDM system by Differential Scanning Calorimetry (DSC) in the non-isothermal mode [8]. The addition of GO to the resin can exhibit a catalytic effect on the ring-opening reaction due to the presence of reactive hydrogen atoms in hydroxyl and carboxyl groups on the GO surface. This leads to a decrease of the initial and peak temperatures on the DSC thermograms. Another story is the epoxy groups of GO itself, which can participate in the same ring-opening reactions as the epoxides of the resin. When compared with neat epoxy, the peaks of the curing curves become broader and lower (Fig. 2a) with increasing the GO content. Such changes in the curves

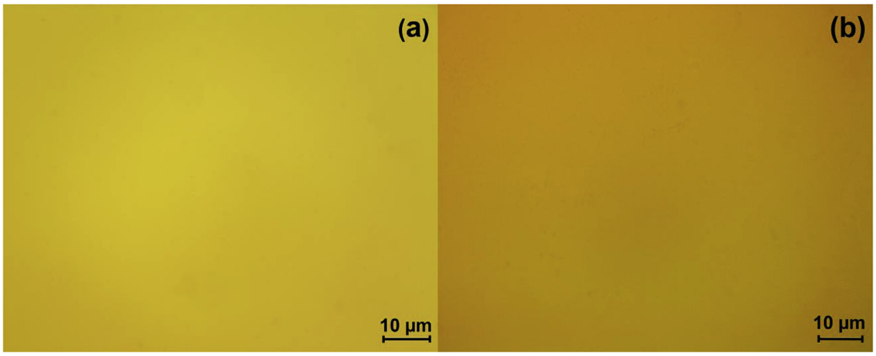

Fig. 1. Optical micrographs of (a) neat epoxy and (b) Epoxy/0.40-GO. A thin layer of liquid formulations was sandwiched between a microscope glass and a coverslip; acquired in the transmitted light mode.

Table 1
DSC curing parameters of neat epoxy resin and Epoxy/GO compositions.

Samples	T_{onset} (°C)	T_{peak} (°C)	T_{end}(°C)	ΔH (J/g)
Neat epoxy	115.6	145.3	174.6	348.9
Epoxy/0.05-GO	114.5	144.9	174.6	338.4
Epoxy/0.10-GO	114.7	144.3	175.9	346.8
Epoxy/0.20-GO	108.4	140.3	172.5	341.3
Epoxy/0.40-GO	96.9	136.9	178.3	258.2
Epoxy/0.60-GO	94.7	136.0	185.6	205.9

Onset temperature of curing (T_{onset}), peak exothermic temperature (T_{peak}), end temperature of curing (T_{end}) and total heat of cross-link reaction (ΔH), as measured by DSC for neat epoxy and Epoxy/GO compositions.

point at a less uniform network due to the accelerating effect of the reaction [25]. In addition to the GO functional groups, the curing reaction can be also accelerated by residual water at GO surface [26].

Epoxy/0.60-GO, with the highest content of reactive groups, expectedly shows the strongest accelerating effect on the curing reaction. The heat of the curing reaction decreases with increasing the GO concentration, especially for Epoxy/0.40-GO and Epoxy/0.60-GO, the samples with the highest GO content (Table 1). In Ref. [27], this was explained by a decrease in the degree of conversion of epoxide groups during the reaction [27].

Introduction of 0.6 wt% GO reduces the enthalpy of reaction from 348.9 J/g to 205.9 J/g. The enthalpy reduction can be attributed to the fact that GO reacts with amine groups of DDM, and, such a modified GO can participate in the curing reaction. Epoxy resin units, bound to GO, or simply situated at the GO interface, possess lower mobility, which leads to a decrease in the conversion of epoxy groups. With the increase in GO content, the number of DDM molecules reacting with GO increases, causing a significant steric effect on the curing reaction [17,28]. At the same time, the curing reaction might partially progress already during the preparation step, i.e. 40 min stirring at 80 °C to dissolve DDM, due to the accelerating effect of GO, thus the part of the reaction heat might be not registered in the DSC thermograms. To check this hypothesis, we measured the gel points of the liquid Epoxy/GO/DDM formulations and compared them to that for neat Epoxy/DDM (Fig. 2b). Indeed, the gel points decreased from 85 min for neat epoxy through 81 min for Epoxy/0.20-GO, and 72 min for Epoxy/0.40-GO. This confirms the hypothesis made above.

The viscosity is a very informative characteristics of epoxy resins with various nanofillers [29,30]. Fig. 3 demonstrates the viscoelastic properties for the Epoxy/GO formulations.

The viscosity decreases with increasing the shear rate, and increases with the content of GO in the resin (Fig. 3a). Epoxy/GO compositions exhibit non-Newtonian or pseudoplastic fluid behavior [30,31], which is associated with the formation of a GO network that remains intact at rest. As the GO content increases, the viscosity value also increases, which provides a more solid-phase behavior. At 0.1 1/s shear rate, the viscosity of Epoxy/0.6-GO is about 100-fold with respect to that for neat resin. The high viscosity of the Epoxy/GO formulations is indicative of the degree of GO exfoliation, as it is observed in aqueous solutions [30,31].

The shear-thinning indicates the destruction of the GO network [32–38]. GO can form liquid crystals also in some polar organic solvents, and the transition from isotropic to nematic phase occurs at the same GO concentration as it occurs in water, at about 0.1 wt% [38]. This is why formation of a nematic phase in epoxy resin is also not surprising. The rheological properties of the Epoxy/GO systems with GO in a highly exfoliated state [19] are very different from those in which GO is not fully exfoliated and/or forms agglomerates [33]. The high viscosity of our Epoxy/GO formulations (Fig. 3) point at the highly exfoliated condition of GO in the uncured resin. GO sheets having a large number of oxygen-containing groups form a uniform dispersion, which effectively affects the viscoelasticity.

3.3. Optimization of curing modes

Before the Epoxy/GO composites were fabricated, the optimal temperature-time curing mode for the neat epoxy was selected. The purpose of this optimization was to achieve the uniform and the highest, at the given conditions, crosslinking density. This was needed to minimize the sample-to-sample variation, the problem that we faced in our previous report [19]. The curing procedure constitutes three steps: 1) pre-curing, to fully homogenize the curing agent in the epoxy matrix, 2) curing, where the main reaction occurs, and 3) post-curing to ensure complete reaction. Based on the DSC curve for the curing of neat epoxy (presented on Fig. S1), the three temperature-time curing modes were selected for testing: Epoxy-DDM-1: 2 h at 60 °C, 1 h at 120 °C and 1 h post-curing at 180 °C; Epoxy-DDM-2: 2 h at 70 °C, 2 h at 150 °C and 1 h post-curing at 180 °C; Epoxy-DDM-3: 2 h at 80 °C, 1 h at 150 °C and 1 h post-curing at 180 °C. The purpose of the first step at 60–80 °C is to uniformly dissolve DDM in the Epoxy/GO matrix. The temperature fork reflects the compromise between the difficulty to dissolve DDM at temperatures below 80 °C from one side, and an attempt to impede the curing process on this step, from another side. The lower temperatures are also needed to keep the initial GO chemical structure intact, which starts changing at ~70 °C. The second step, curing, occurs at 150 °C. At the same time, massive decomposition of GO begins already at ~140 °C, and the choice of 120 °C was an attempt to keep GO from decomposition during the curing reaction to possibly involve it in the crosslinking. Flexural test of the neat epoxy polymers (Table 2) showed that the best strength characteristics with the lowest standard deviation were achieved by using the Epoxy-DDM-3 curing mode (Fig. S2). At such difference in the flexural properties of the three epoxy resins, obtained by the three tested modes, any potential gain from the possible GO participation in the crosslinking would be probably obscured by the loss, caused by the lower crosslinking density in the epoxy resin itself, and by poor sample-to-sample variation. This is why, the Epoxy-DDM-3 curing regime was selected for the rest of the experiments.

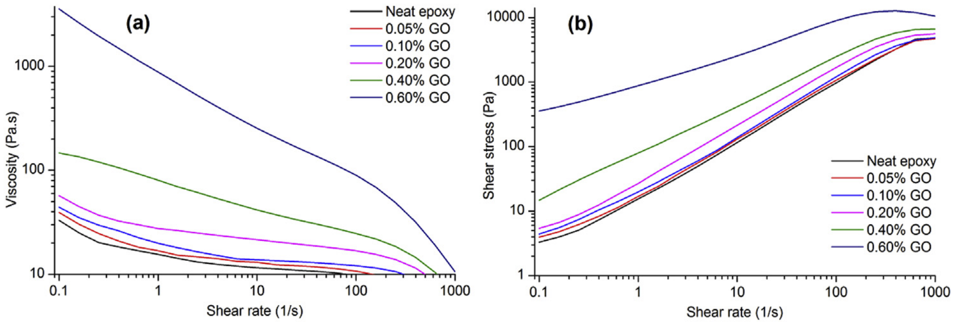

Fig. 3. (a) Steady shear rate flow behavior of the Epoxy/GO compositions at different concentrations, (b) shear stress-shear rate curves. Measured at 25 °C.

Table 2
Flexural properties of neat epoxy polymers obtained at different curing procedures.

Samples	Flexural modulus 0.2–1% (MPa)	Flexural stress max (MPa)
Epoxy-DDM-1	3019 ± 83	68 ± 1.60
Epoxy-DDM-2	2863 ± 276	66 ± 4.05
Epoxy-DDM-3	3270 ± 76	74 ± 1.58

3.4. Thermo-mechanical properties

The mechanical properties of Epoxy-GO composites were evaluated using dynamic mechanical analysis (DMA), which is considered to be a convincing method for describing the interaction between GO and epoxy matrix [5,6,8,13–16,28]. DMA provides information on the storage modulus, the loss modulus and tan delta (tan δ) within the measured temperature range [15]. Fig. 4 demonstrates the three characteristics of the neat epoxy and Epoxy/GO composites at varying GO content.

The storage modulus reflects the elastic properties of materials. It depends on the strength of the interfacial interaction between the filler and the resin matrix, on the mechanical properties and geometric parameters of the nanofiller, and on its concentration [17]. Fig. 4a demonstrates that the storage modulus of neat resin and its composites decreases with temperature due to the softening of the polymer chains. Compared to neat epoxy, all Epoxy/GO composites show an increase in the storage modulus in the glass transition area even at low GO content. The increase of storage modulus is due to the fact that covalent bonding between GO and epoxy matrix limits the mobility of the polymer chains. This restriction is most evident for Epoxy/0.20-GO-c and Epoxy/0.40-GO-c. An important contribution might be from GO itself, which has a higher storage modulus than the epoxy matrix [11]. Highly dispersed GO layers can create a strong interaction with the epoxy matrix, resulting in an effective stress transfer at the interface, which contributes to the growth of the storage modulus [6]. However, for the 0.60 wt% GO content, the storage modulus decreased, which may be due to the not full conversion of the epoxy groups, and/or formation of GO associates. Here under the word “associate” we mean the areas of space where the previously exfoliated GO flakes are arranged sufficiently close to each other with a thin epoxy layer still present between them.

Wan et al. [15] prepared the GO-containing composites by modifying GO surface by DGEBA, which resulted in notably higher values (16.2%) of the storage modulus at 0.25 wt% loading, as compared to composites containing pristine GO, which was similar with neat epoxy. Here, our Epoxy/GO composites demonstrate a larger increase in the storage modulus 25.4% (3035 MPa), compared to the neat epoxy, at only 0.2 wt% loading without any modification of GO. This is especially impressive when compared to 2061.6 MPa (12% increase at 0.5%), reported in ref. [14].

During the curing reaction, the GO functional groups readily react with the diamine and can bind epoxy matrix units [13]. As a consequence, this reaction results in a stronger interfacial interaction with the epoxy matrix, changing the epoxy resin/DDM stoichiometry and thus reducing the network density in the Epoxy/GO composites [11]. Evidently, if the number of reactive groups on GO surface is changed by a chemical modification, the ratio of amine and epoxide groups will also change [15,28]. The ratio of the loss modulus to the storage modulus is called tan delta (tan δ) (Fig. 4b). The temperature at the maximum value of tan delta is often considered as the glass transition temperature (T_g).

The loss modulus is related to the energy dissipated from the internal friction of the polymer chains. The addition of GO lowers the beginning temperature of the highly elastic-to-glassy transition, and increases the maximum value of the loss modulus (Fig. 4c). This, again, suggests that GO participates in the curing reactions, thus reducing the crosslink density of the epoxy resin [39,40]. On the other hand, the inclusion of GO can provide additional internal friction between GO and polymer chains [17].

All the characteristics shown on Fig. 4 and discussed above, are also presented in Table 3.

All the Epoxy/GO composites up to 0.4% GO content show T_g values similar to that for neat epoxy (Fig. 4b, Table 3). This makes the Epoxy/0.20-GO-c and Epoxy/0.40-GO-c the absolute champions with the highest storage modulus at still high T_g values. A sharp decrease in T_g is observed for Epoxy/0.60-GO-c. In an epoxy matrix, a decrease in the T_g is normally associated with a decrease in the crosslink density [3,15,41]. Subsequently, the observed decrease in T_g can be explained

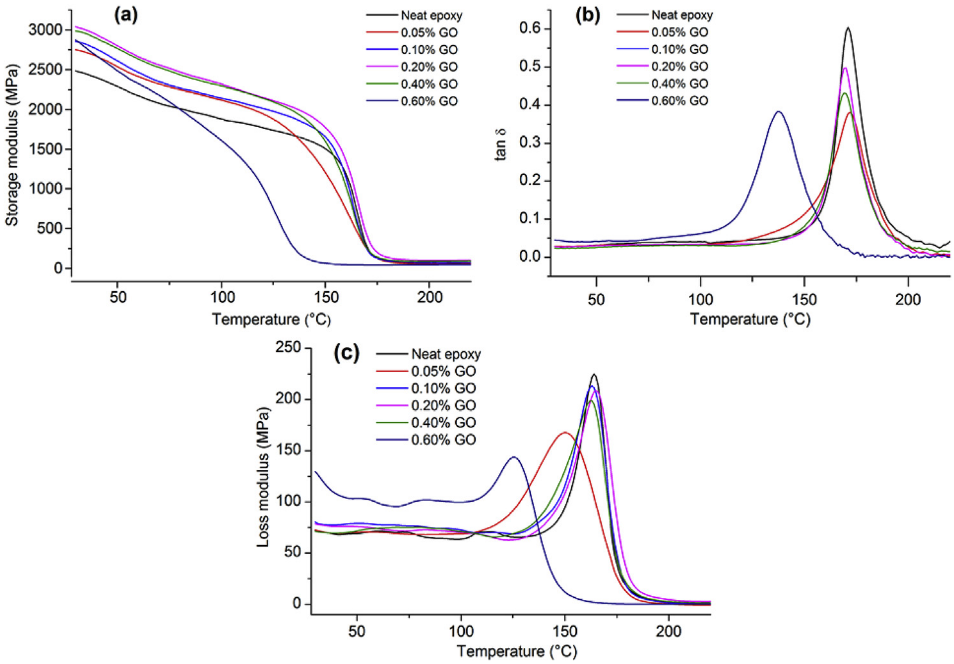

Fig. 4. DMA mechanical properties of neat epoxy polymer and Epoxy/GO nanocomposites: (a) storage modulus, (b) tan δ, (c) loss modulus.

Table 3
Dynamic mechanical properties of neat epoxy polymer and Epoxy/GO composites.

Samples	Storage modulus at 30 °C (MPa)	T_g (°C)	Intensity tan δ
Neat epoxy	2420	170	0.58
Epoxy/0.05-GO-c	2750 (+13.6%)	172	0.38
Epoxy/0.10-GO-c	2855 (+18%)	170	0.50
Epoxy/0.20-GO-c	3035 (+25.4%)	172	0.43
Epoxy/0.40-GO-c	2985 (+23.3%)	169	0.43
Epoxy/0.60-GO-c	2860 (+18.2%)	137	0.38

Storage modulus at 30 °C and glass transition temperature (T_g) as measured by DMA for neat epoxy polymer and Epoxy/GO composites.

by the fact that GO reduces the crosslink density of the epoxy matrix. Interestingly, this contradicts with the study reporting the T_g growth with an increase in the content of nanofiller in polymer composites containing graphene [42].

As compared with neat epoxy polymer, the peak for tan delta of Epoxy/GO composites, especially with 0.4 wt% and 0.6 wt% GO content, become lower and broader, as shown in Fig. 4b. This phenomenon is associated with a wide range of relaxation temperatures in nanocomposites, since GO limits the mobility of neighboring epoxy chains due to strong binding to the surface [41]. This causes the change in the relaxation behavior on comparison to the chains located far from the GO interface. T_g is directly used as a conversion parameter for the analysis of reaction kinetics, and there is a direct ratio between T_g and the degree of curing [43]. The broadening of the tan delta peak may also be due to the fact that a less uniform polymer network is formed due to the excessive reaction rate [25]. Thereby, the introduction of GO changes the epoxy matrix crosslink density and molecular dynamics, thus decreasing T_g and increasing the storage modulus of the resulted composites.

In a separate experiment, we tried to further optimize the curing conditions for the composition with 0.2% GO, which demonstrated the best results, in an attempt to possibly obtain even better mechanical properties. However, the newly prepared samples demonstrated lower glass transition temperatures at almost similar storage modulus (see Fig. S3 for details). This data signifies the importance of the fine tuning of the curing modes.

4. Conclusions

In this work, we further developed the homogenous liquid phase transfer method for introducing GO into epoxy resin. This makes the transfer more efficient, while maintaining the nearly fully exfoliated condition of GO in the matrix. The optical microscopy studies of the liquid formulations point at the uniform distribution and the nearly fully exfoliated condition of GO in the resin. The rheological studies of Epoxy/GO compositions showed a dramatic increase in the viscosity of Epoxy/0.40-GO and especially Epoxy/0.60-GO, indicating a high degree of GO exfoliation.

We optimized the curing process of Epoxy-DDM systems to attain full advantage of the homogeneous liquid phase transfer method. High values of the flexural modulus were achieved with a minimum standard deviation. The study of the NPEL-128 epoxy resin curing by DDM showed that the introduction of GO into the epoxy resin exhibits the accelerating effect on the curing reaction. This effect is more pronounced in the systems with the GO concentration of 0.4 wt% and 0.6 wt%. The introduction of relatively small amount (0.2 wt%) of GO into the epoxy matrix results in the increase in the storage modulus by 25.4% (3035 MPa) compared to the neat resin (2420 MPa). Such an improvement in the mechanical properties of Epoxy/GO composites at relatively low loading is due to the highly exfoliated condition of GO in the matrix, and covalent bonding between GO flakes and epoxy matrix.

As compared to our previous work [19], in this study, we used the new aromatic amine curing agent DDM that allowed to prepare the Epoxy/GO composites with significantly higher glass transition temperatures, broadening the scope of their potential applications. We have also achieved significantly better sample-to-sample variation. The 25.4% increase in the storage modulus due to the introduction of 0.2% GO, additionally demonstrates the superiority of DDM compared to PEPA [19].

Acknowledgements

This research was conducted with support of the Russian Science Foundation, Grant # 16-13-10291.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2019.01.020.

References

[1] Vidil T, Tournilhac F, Musso S, Robisson A, Leibler L. Control of reactions and network structures of epoxy thermosets. Prog Polym Sci 2016;62:126–79.
[2] Wang S, Liang Z, Liu T, Wang B, Zhang C. Effective amino-functionalization of carbon nanotubes for reinforcing epoxy polymer composites. Nanotechnology 2006;17(6):1551–7.
[3] Bao C, Guo Y, Song L, Kan Y, Qian X, Hu Y. In situ preparation of functionalized graphene oxide/epoxy nanocomposites with effective reinforcements. J Mater Chem 2011;21(35).
[4] Yang H, Shan C, Li F, Zhang Q, Han D, Niu L. Convenient preparation of tunably loaded chemically converted graphene oxide/epoxy resin nanocomposites from graphene oxide sheets through two-phase extraction. J Mater Chem 2009;19(46).
[5] Norhakim N, Ahmad SH, Chia CH, Huang NM. Mechanical and thermal properties of graphene oxide filled epoxy nanocomposites. Sains Malays 2014;43(4):603–9.
[6] Ma P-C, Mo S-Y, Tang B-Z, Kim J-K. Dispersion, interfacial interaction and re-agglomeration of functionalized carbon nanotubes in epoxy composites. Carbon 2010;48(6):1824–34.
[7] Liu T, Phang IY, Shen L, Chow SY, Zhang W-D. Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites. Macromolecules 2004;37(19):7214–22.
[8] Bortz DR, Heras EG, Martin-Gullon I. Impressive fatigue life and fracture toughness improvements in graphene oxide/epoxy composites. Macromolecules 2011;45(1):238–45.
[9] Lee C, Wei X, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 2008;321(5887):385–8.
[10] Gudarzi M, Aboutalebi S, Sharif F. Graphene oxide-based composite materials. In: Dimiev AM, Eigler S, editors. Graphene oxide: fundamentals and applications. London: Wiley; 2017.
[11] Shen X-J, Pei X-Q, Fu S-Y, Friedrich K. Significantly modified tribological performance of epoxy nanocomposites at very low graphene oxide content. Polym J 2013;54(3):1234–42.
[12] Wang X, Jin J, Song M. An investigation of the mechanism of graphene toughening epoxy. Carbon 2013;65:324–33.
[13] Liu Q, Zhou X, Fan X, Zhu C, Yao X, Liu Z. Mechanical and thermal properties of epoxy resin nanocomposites reinforced with graphene oxide. Polym Plast Technol Eng 2012;51(3):251–6.
[14] Wan Y-J, Gong L-X, Tang L-C, Wu L-B, Jiang J-X. Mechanical properties of epoxy composites filled with silane-functionalized graphene oxide. Composites Part A 2014;64:79–89.
[15] Wan Y-J, Tang L-C, Gong L-X, Yan D, Li Y-B, Wu L-B, et al. Grafting of epoxy chains onto graphene oxide for epoxy composites with improved mechanical and thermal properties. Carbon 2014;69:467–80.
[16] Tang L-C, Wan Y-J, Yan D, Pei Y-B, Zhao L, Li Y-B, et al. The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites. Carbon 2013;60:16–27.
[17] Wei Y, Hu X, Jiang Q, Sun Z, Wang P, Qiu Y, et al. Influence of graphene oxide with different oxidation levels on the properties of epoxy composites. Compos Sci Technol 2018;161:74–84.
[18] Paredes J, Villar-Rodil S, Martínez-Alonso A, Tascon J. Graphene oxide dispersions in organic solvents. Langmuir 2008;24(19):10560–4.
[19] Amirova L, Surnova A, Balkaev D, Musin D, Amirov R, Dimiev AM. Homogeneous liquid phase transfer of graphene oxide into epoxy resins. ACS Appl Mater Interfaces 2017;9(13):11909–17.
[20] Dimiev AM, Polson TA. Contesting the two-component structural model of graphene oxide and reexamining the chemistry of graphene oxide in basic media. Carbon 2015;93:544–54.
[21] Dimiev AM, Alemany LB, Tour JM. Graphene oxide. Origin of acidity, its instability in water, and a new dynamic structural model. ACS Nano 2012;7(1):576–88.
[22] Amirov RR, Shayimova J, Nasirova Z, Dimiev AM. Chemistry of graphene oxide. Reactions with transition metal cations. Carbon 2017;116:356–65.
[23] Amirov RR, Shayimova J, Nasirova Z, Solodov A, Dimiev AM. Analysis of

competitive binding of several metal cations by graphene oxide reveals the quantity and spatial distribution of carboxyl groups on its surface. Phys Chem Chem Phys 2018;20(4):2320–9.
[24] Mohan VB, Lau K-t, Hui D, Bhattacharyya D. Graphene-based materials and their composites: a review on production, applications and product limitations. Composites Part B 2018;142:200–20.
[25] Monteserín C, Blanco M, Aranzabe E, Aranzabe A, Vilas JL. Effects of graphene oxide and chemically reduced graphene oxide on the curing kinetics of epoxy amine composites. J Appl Polym Sci 2017;134(19).
[26] Choi S, Janisse AP, Liu C, Douglas EP. Effect of water addition on the cure kinetics of an epoxy-amine thermoset. J Polym Sci, Part A: Polym Chem 2011;49(21):4650–9.
[27] Wang S, Tambraparni M, Qiu J, Tipton J, Dean D. Thermal expansion of graphene composites. Macromolecules 2009;42(14):5251–5.
[28] Jiang T, Kuila T, Kim NH, Ku B-C, Lee JH. Enhanced mechanical properties of silanized silica nanoparticle attached graphene oxide/epoxy composites. Compos Sci Technol 2013;79:115–25.
[29] Del Giudice F, Shen AQ. Shear rheology of graphene oxide dispersions. Curr Opin Chem Eng 2017;16:23–30.
[30] Vallés C, Young RJ, Lomax DJ, Kinloch IA. The rheological behaviour of concentrated dispersions of graphene oxide. J Mater Sci 2014;49(18):6311–20.
[31] Kumar P, Maiti UN, Lee KE, Kim SO. Rheological properties of graphene oxide liquid crystal. Carbon 2014;80:453–61.
[32] Khandelwal V, Sahoo SK, Kumar A, Manik G. Electrically conductive green composites based on epoxidized linseed oil and polyaniline: an insight into electrical, thermal and mechanical properties. Composites Part B 2018;136:149–57.
[33] Vallés C, Beckert F, Burk L, Mülhaupt R, Young RJ, Kinloch IA. Effect of the C/O ratio in graphene oxide materials on the reinforcement of epoxy-based nanocomposites. J Polym Sci, Part B: Polym Phys 2016;54(2):281–91.
[34] Chang-Jian C-W, Cho E-C, Lee K-C, Huang J-H, Chen P-Y, Ho B-C, et al. Thermally conductive polymeric composites incorporating 3D MWCNT/PEDOT: PSS scaffolds. Composites Part B 2018;136:46–54.
[35] Martin-Gallego M, Bernal MM, Hernandez M, Verdejo R, Lopez-Manchado MA. Comparison of filler percolation and mechanical properties in graphene and carbon nanotubes filled epoxy nanocomposites. Eur Polym J 2013;49(6):1347–53.
[36] Shang Y, Zhang D, Yang C, Liu Y, Liu Y. Effect of graphene oxide on the rheological properties of cement pastes. Constr Build Mater 2015;96:20–8.
[37] White KL, Yao H, Zhang X, Sue H-J. Rheology of electrostatically tethered nanoplatelets and multi-walled carbon nanotubes in epoxy. Polymer 2016;84:223–33.
[38] Valles C. Rheology of graphene oxide dispersions. Dimiev AM, Eigler S, editors. Graphene oxide: fundamentals and applications, vol. 4. London: Wiley; 2017. p. 121–46.
[39] Kim K-S, Jeon I-Y, Ahn S-N, Kwon Y-D, Baek J-B. Edge-functionalized graphene-like platelets as a co-curing agent and a nanoscale additive to epoxy resin. J Mater Chem 2011;21(20).
[40] Liu W, Koh KL, Lu J, Yang L, Phua S, Kong J, et al. Simultaneous catalyzing and reinforcing effects of imidazole-functionalized graphene in anhydride-cured epoxies. J Mater Chem 2012;22(35).
[41] Wang S, Liang Z, Liu T, Wang B, Zhang C. Effective amino-functionalization of carbon nanotubes for reinforcing epoxy polymer composites. Nanotechnology 2006;17(6):1551–7.
[42] Fang M, Zhang Z, Li J, Zhang H, Lu H, Yang Y. Constructing hierarchically structured interphases for strong and tough epoxy nanocomposites by amine-rich graphene surfaces. J Mater Chem 2010;20(43).
[43] Zhao H, Gao J, Li Y, Shen S. Curing kinetics and thermal property characterization of bisphenol-F epoxy resin and MeTHPA system. J Therm Anal Calorim 2003;74(1):227–36.