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Homogeneous Liquid Phase Transfer of Graphene Oxide into Epoxy Resins

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Keywords: graphene oxide, epoxy resin, polymer composite, phase transfer, viscosity

Abstract

Quality of polymer composite materials depends on the distribution of the filler in the polymer matrix. Due to the presence of the oxygen functional groups, graphene oxide (GO) has strong affinity to epoxy resins, providing potential opportunity for the uniform distribution of GO sheets in the matrix. Another advantage of GO over its non-oxidized counterpart is its ability to exfoliate to single-atomic-layer sheets in water and in some organic solvents. However, these advantages of GO has not yet been fully realized due to the lack of the methods efficiently introducing GO into epoxy resin. Here we develop a novel homogeneous liquid phase transfer method that affords uniform distribution, and fully exfoliated condition of GO in the polymer matrix. The most pronounced alteration of properties of the cured composites is registered at the 0.10%-0.15% GO content. Addition of as little as 0.10% GO leads to the increase of the Young's modulus by 48%.. Moreover, we demonstrate successful introduction of GO into the epoxy matrix containing an active diluent-modifier; this opens new venues for fabrication of improved GO-epoxy-modifier composites with a broad range of pre-designed properties. The experiments done on reproducing the two literature methods, using alternative GO introduction techniques, lead to either decrease, or insignificant increase of the Young's modulus of resulted GO-epoxy composites.

1. Introduction

Carbon nanomaterials are broadly used as fillers for a polymer matrix to improve the properties of resulted polymer composite materials.[1-9] The key point in attaining high quality polymer composites is the uniform distribution of the filler in the matrix, which in turn, depends, in large part, on the affinity of the filler toward the polymer matrix. Intact graphitic carbon has very low affinity toward the most of the known solvents, and does not readily disperse in the most known polymers. This is true for all the macro- and nano-forms of graphitic carbon, such as carbon fiber, carbon nanotubes, graphene nanoplatelets, etc. In polymer composites, they tend to form aggregates, especially at higher loadings, which degrades mechanical properties of as-prepared composite materials.[3] The most common strategy to resolve this issue is the functionalization of carbon nanofillers to improve their adhesion with polymer matrix.[3,8] Thus, Liu et al. used this method to introduce partially reduced GO into epoxy resin.[10,11] With GO, however, the situation is different from other forms of carbon. Due to its highly oxidized nature, GO forms stable colloidal solutions in water and in several organic solvents by exfoliating to single-atomic-layer sheets. However, this does not mean yet that GO will spontaneously disperse in a polymer matrix. The solid GO does not dissolve in any solvent other than water. However, it can be transferred from the aqueous into the alcoholic phase by gradual replacement of water by alcohols.[12,13] During this transfer, GO does not coagulate, and remains in exfoliated condition. This is the key point for preparing polymer composite materials with GO, if one intends to keep GO exfoliated and uniformly distributed in the matrix. In the ideal situation, GO should remain in the form of the single-atomic-layer sheets. This will provide the most efficient distribution of GO in the matrix with the highest interface area for a given GO/epoxy ratio.

GO has the functional groups, of the same nature as the functional groups of epoxy resin. Thus, based on the principal "Like dissolves Like", GO should form stable dispersions in epoxy resin, as it does in water and in some low-molecular-weight organic liquids. However, as we mentioned above, solid GO does not dissolve directly in anything other than water. The remaining challenge is to introduce GO into the polymer matrix, keeping it exfoliated. Here we propose the liquid phase transfer of GO into epoxy resin that keeps GO exfoliated during the entire process, and in the resulted solid GO-epoxy composite. We will refer to this transfer method as the homogeneous liquid phase transfer (HLPT) method. Epoxy resin is not miscible with water, thus the direct transfer from aqueous solution to the epoxy phase would not be possible. Subsequently, one needs to develop a chain of the solvents affording such transfer. As an intermediate solvent between water and epoxy resin, we used isopropyl alcohol (IPA) that is miscible with both water and epoxy resin.

In literature, there are several studies reporting successful fabrication of the GO-epoxy composites.[14-26] In most cases, GO is introduced into the epoxy resin through the GO dispersion in acetone.[19-24] After mixing the GO-acetone dispersion with the resin, the solvent is evaporated.[19-24] According to another approach, GO is introduced into epoxy resin in the form of an aqueous solution, and afterwards water is evaporated.[25,26]

From the perspectives discussed above, in theory, these two methods should not afford uniform single-layer dispersion of GO in the epoxy matrix. First of all, GO does form stable solutions in acetone, as it does in several other solvents. Moreover, it cannot be even transferred into acetone from water by the gradual solvent exchange method.[12,13] Thus, in the acetone-transfer method, GO is introduced into the polymer matrix in the aggregated state, i.e. it is not properly exfoliated from the very beginning. Water, in turn, is not miscible with epoxy resin. Subsequently, in the aqueous-transfer method, GO should coagulate after blending two immiscible liquids: aqueous GO solution and epoxy resin. Nevertheless, in many works, authors declare significant improvement in mechanical properties of as-made composite materials. For example, in the reference [15] (the acetone-transfer method), the authors report the 9% and 18% enhancement for the flexural modulus and strength, respectively, at 0.1 wt % GO content; for the 1 wt % GO content this increase is by 12% and 23%, respectively. In the reference [21] (the aqueous-transfer method), the authors declare the increase of the compressive failure strength and toughness by 48.3% and 1185.2% (!) respectively, with only 0.0375 wt% GO loading.

Being intrigued by these data, and for comparison purposes, we tried to reproduce these two techniques, in parallel with developing our own method. This would potentially help one to understand the factors guarding the process of dispersing GO in the epoxy matrix, and the factors influencing the quality of resulted solid GO-Epoxy composites.

2. Results and discussion

Figure 1 represents characteristics of GO that was used in fabricating the GO-Epoxy composites. The most important factor with respect to composite materials is probably the size of the GO flakes. The flakes' diameter varied from 0.5 μm through 30 μm, with the most typical size 5 μm - 20 μm (Fig. 1a, Fig. S1). It is apparent from the SEM images that all the GO flakes are one-atomic-layer thick. This demonstrates that in the aqueous solution, used to prepare the SEM sample, GO is in fully exfoliated condition. Note, no sonication is required for dispersing our GO sample in water; GO dissolves spontaneously within 30 min with gentle magnetic stirring. The thermo-gravimetric analysis data (TGA) and the C1s spectra of the X-ray photoelectron spectroscopy (XPS) show that GO has the oxidation level typical for GO samples prepared by the modified Hummers methods.[27-30] The C/O ratio obtained from the XPS data is 2/1, which is the characteristic of a sufficiently oxidized GO. The FTIR spectrum of GO (Fig. 1d) is also typical for GO.[27-30] Thus, the GO sample used in this work, had the typical oxidation level sufficient for spontaneous exfoliation to single-atomic-layer sheets upon dissolution in water.

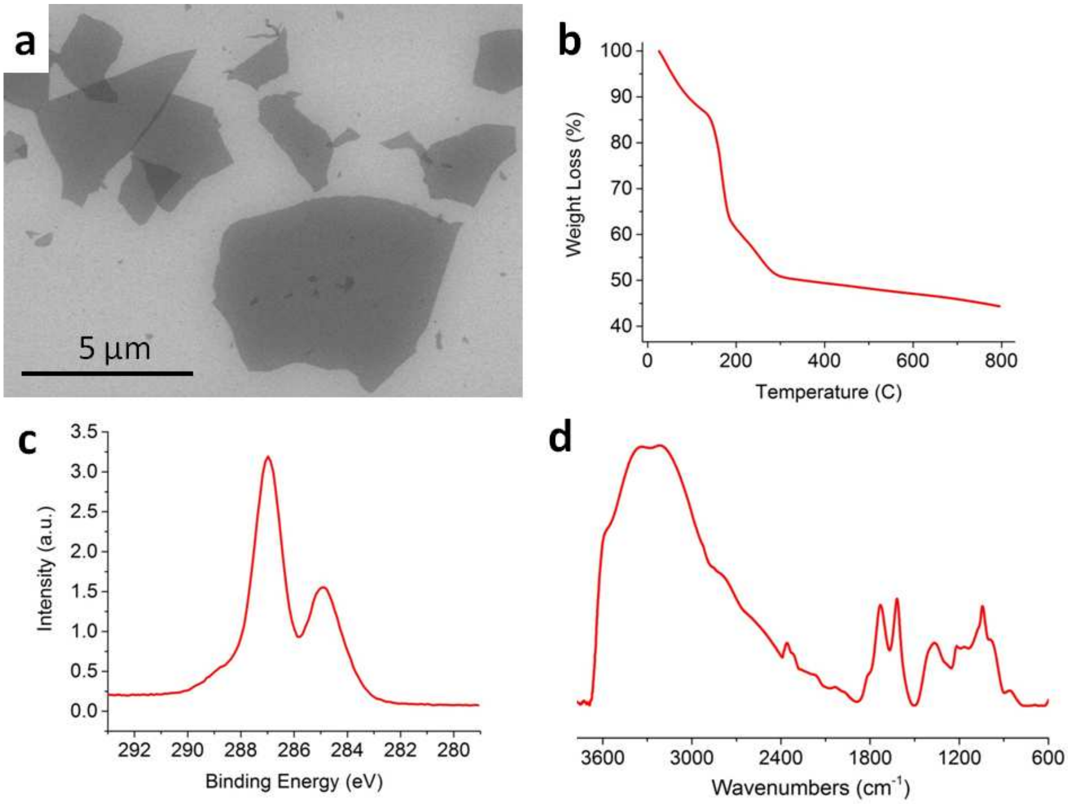

Figure 1. Characteristics of the GO sample used for preparation of the epoxy resin composites. (a) SEM image, (b) TGA data, (c) the C1s XPS spectra, (d) the FTIR spectra. The characteristics of the GO sample are typical for GO prepared by the modified Hummers methods.

On the first step we prepared the system for introducing GO into the epoxy resin, i.e. the GO-IPA solution. The GO-IPA was prepared from the aqueous GO solution by gradual replacement of water by IPA according to the techniques described in the references [12,13]. It is impossible to determine the remaining water quantity in the final GO-IPA with certainty, however, according to the dilution factor it must be 0.048%. The GO-epoxy solution was prepared by addition of GO-IPA into epoxy resin, blending until uniform distribution of GO in epoxy resin, and removing IPA by evaporation. Addition of the uniform and transparent GO-IPA gel into the colorless and transparent epoxy resin (Fig. 2a) resulted in a fully homogeneous and transparent GO-IPA-epoxy mixture (Fig. 2b). After removing IPA, the appearance of the mixture did not change. After curing, the as prepared solid GO-Epoxy samples were absolutely homogeneous and transparent, suggesting that no coagulation occurred during the curing process (Fig. 1c). In this work we are making the accent on the transparency of our samples, because this is the direct evidence of the uniform distribution and for the exfoliated state of GO in the polymer matrix. As an additional confirmation of the exfoliated condition of GO in the matrix we present optical microscopy images of uncured GO-Epoxy solutions (Fig. 2d,e). Figure 2d represents a low magnification image where numerous GO flakes can be seen within the acquisition spot. The actual number of the flakes is probably even larger, since the small-size flakes <1 μm are not resolved by the optical microscopy. Note, all the flakes, except the one, placed in the circle, have similar opacity, suggesting similar number of GO layers, constituting the flakes. SI Figure S2 is the higher resolution image of the same micrograph, where more details are visible. We assume that the number of layers in the majority of the flakes is one, because otherwise they all have to be bi-layer, tri-layer, four-layer, etc., which is not realistic. As the more fulcrum of evidence, Figure 2e represents a large presumably bi-layer GO flake. The flake is partially exfoliated, and one of the layers from the exfoliated area is folded on the top of the non-exfoliated part of the flake. Thus, the flake have the areas of 1, 2, and 3 layers. This image clearly shows the difference in the contrast (opacity) of the different parts of GO flakes. Very few high contrast flakes were registered in the GO-epoxy resin, suggesting that most of the GO flakes are mono-layers, i.e. in the fully exfoliated condition. For the best of our knowledge, very few earlier studies on this topic provided the optical microscopy analysis of the fabricated composites. As an additional evidence for our claims, we stress on the striking difference in the contrast of GO flakes shown in our work (Fig. 2d,e), and the one reported by Wan et al.,[31] suggesting significantly higher exfoliation level attained in our study.

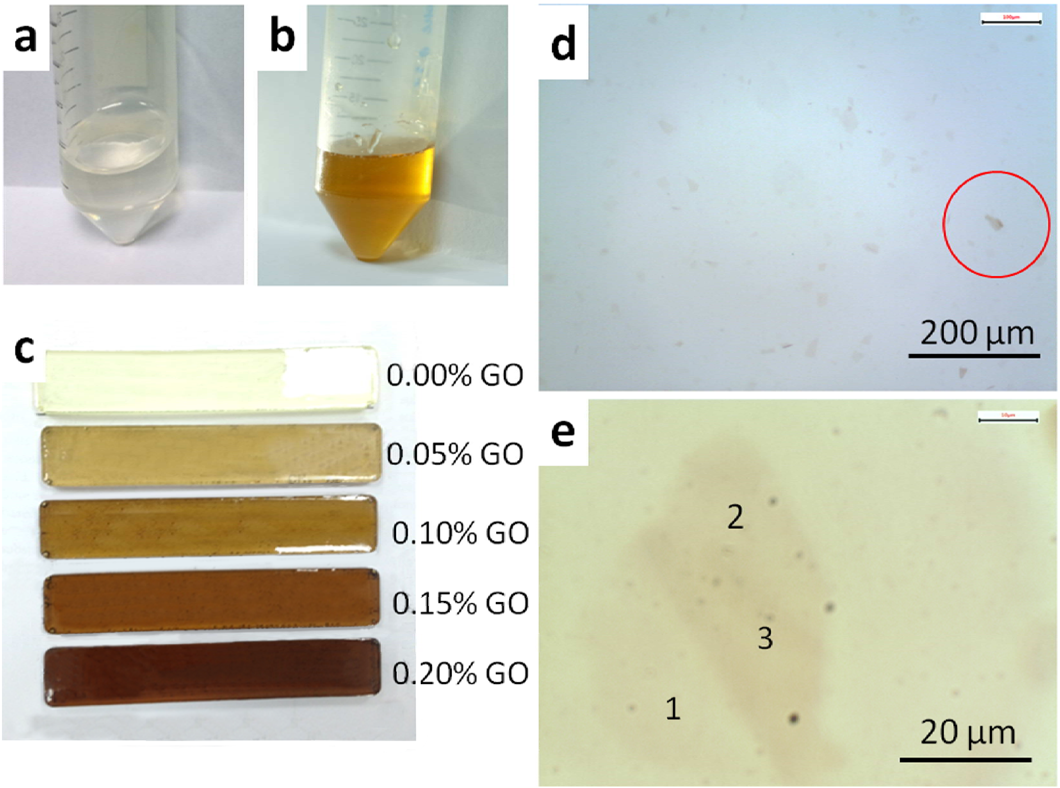

Figure 2. The photographs of (a) neat epoxy resin, (b) the epoxy resin with 0.5% GO , (c) the solid cured GO-epoxy composite samples with different GO content. (d,c) The optical micrographs of the liquid GO-epoxy mixtures before curing. The micrographs are acquired in transmitted light from the liquids sandwiched between a microscope slide and a cover slip. In (d) the red circle shows the flake with higher contrast. (e) The higher magnification image of a partially exfoliated GO flake. The numbers 1-3 represent the number of GO layers in the three different areas of the flake.

In industry, epoxy resins are often used with small amounts of active diluents-modifiers. The modifiers are added to increase shockproof, flexibility, to lower viscosity, to decrease shrinkage, and even to lower the cost.[32,33] In particular, the reactive diluent diglycidyl ether of 1,4-butanediol (DEB) is generally used to improve the fracture toughness of the epoxy resins.[34,35] In the next series of experiments, we incorporated DEB in our formulations, and prepared the tri-component GO-DEB-Epoxy composites. To attain this goal, we first prepared the DEB-Epoxy solutions containing 10% DEB. Next, GO was introduced via GO-IPA gel, similar to the preparation of GO-Epoxy composites. The resulted tri-component mixture GO-DEB-Epoxy was completely homogeneous and transparent at all the tested GO concentrations (Fig. 3a-d).

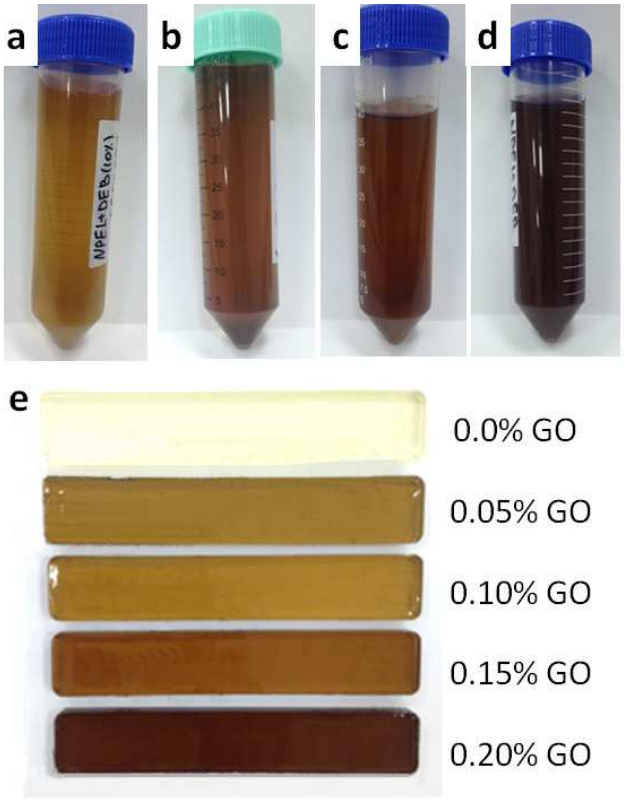

Figure 3. Photographs of the liquid GO-DEB-Epoxy composites at GO content 0.5% (a), 1.0% (b), 1.5% (c), and 2.0%. (d). (e) The photograph of the cured GO-DEB-Epoxy samples with different GO content.

The liquid GO-DEB-Epoxy mixtures were notably less viscous compared to the GO-Epoxy mixtures. This is very important for higher GO loading compositions, since viscosity of the GO-Epoxy solutions increases dramatically already at 0.2% GO loading. Thus, we could not prepare the GO-Epoxy compositions with GO content >0.2%, since their high viscosity did not permit easy flow into the moulds.

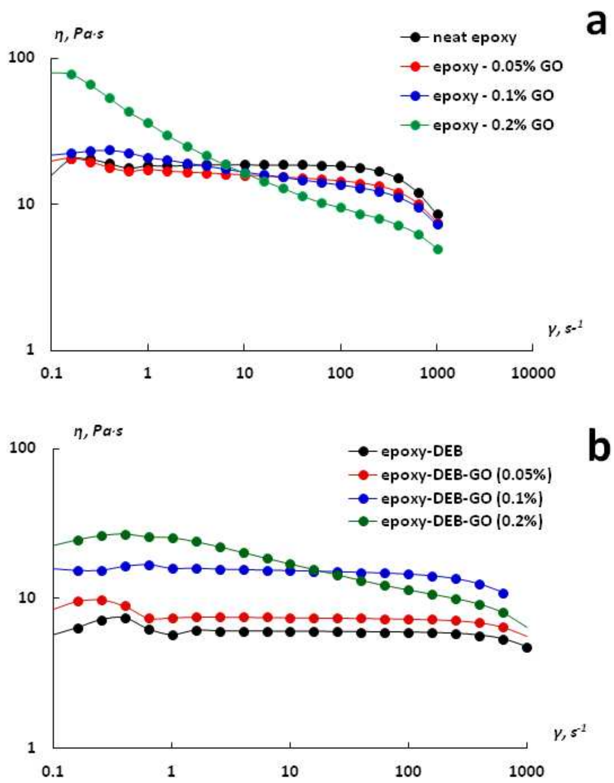

Figure. 4. Dependence of complex viscosity on shear rate for GO-epoxy (a), and GO-DEB-Epoxy (b) solutions at different GO content.

The flow curves for neat epoxy as well as for compositions containing 0.05% and 0.1% GO demonstrate the Newtonian behavior (Figure 4a). The viscosity does not change much with adding GO up to the 0.1% GO content. The solution containing 0.2 wt % GO exhibits very different behavior. At low shear rate its viscosity is significantly higher than that for the other three solutions. However, the viscosity rapidly decreases with shear rate, exhibiting strong shear thinning behavior. This behavior is very similar to that of GO solutions in low-molecular-weight liquids.[35-38] Thus, the GO aqueous solutions begin turning from isotactic to nematic phase at exactly the same 0.1% GO content as in our experiments.[36-38] Apparently, at 0.2% content, GO structurizes epoxy resin with formation of nematic phase. However, with increasing the shear rate the viscosity of this structure rapidly decreases. Such decrease can be explained by desorientation of the established liquid crystalline phase, i.e. due to the rupture of the viscoelastic GO network and acquiring the liquid-like behavior. Interestingly, at high shear rates, viscosity of the 0.2% GO solution goes even lower than that for 0.05% and 0.1% GO solutions, suggesting that GO serves as a sort of lubricant. This observation, in turn, suggests that before adding the curing agent, there is no strong cross-linking interaction between GO and epoxy resin molecules.

Epoxy resin, containing DEB, has a lower viscosity value than the neat epoxy (Fig. 4b). Introducing GO into the DEB-Epoxy system increases viscosity. However, here we do not observe the sharp increase in viscosity between the 0.1% and 0.2% GO content, as for the pure GO-Epoxy solutions. Importantly, the 0.2% GO-DEB-Epoxy mixture remains notably less viscous compared to the 0.2% GO-Epoxy mixture. This is critical for many actual applications of epoxy resins.

Significant increase of viscosity with addition of as little 0.20% GO (Fig. 4) is the additional evidence for a nearly completely exfoliated condition of GO in the epoxy matrix. From all the works on GO-epoxy composites, we had found in literature, only one by Valles et al.[24] provides viscosity values for GO-epoxy solutions. In that acetone-transfer method, addition of 0.5% and 1.0% GO does not notably change the viscosity of the neat resin. Addition of as much as 2.0% and 3.0% GO increases viscosity by only ~25% and ~59% respectively. Note, in our work we registered ~300% increase in viscosity (Fig 4a) with as little as 0.20% GO loading. This apparent discrepancy between the two experiments most likely points at the low exfoliation level of GO in the literature study.[24] Note, in aqueous solutions, where GO is fully exfoliated by definition, viscosity increases more than one order of magnitude with addition of as little as 0.1% GO.[27] The similar level of the increase in viscosity, obtained in our work, suggests that, in general, we attained the same level of GO exfoliation in resin, as in water.

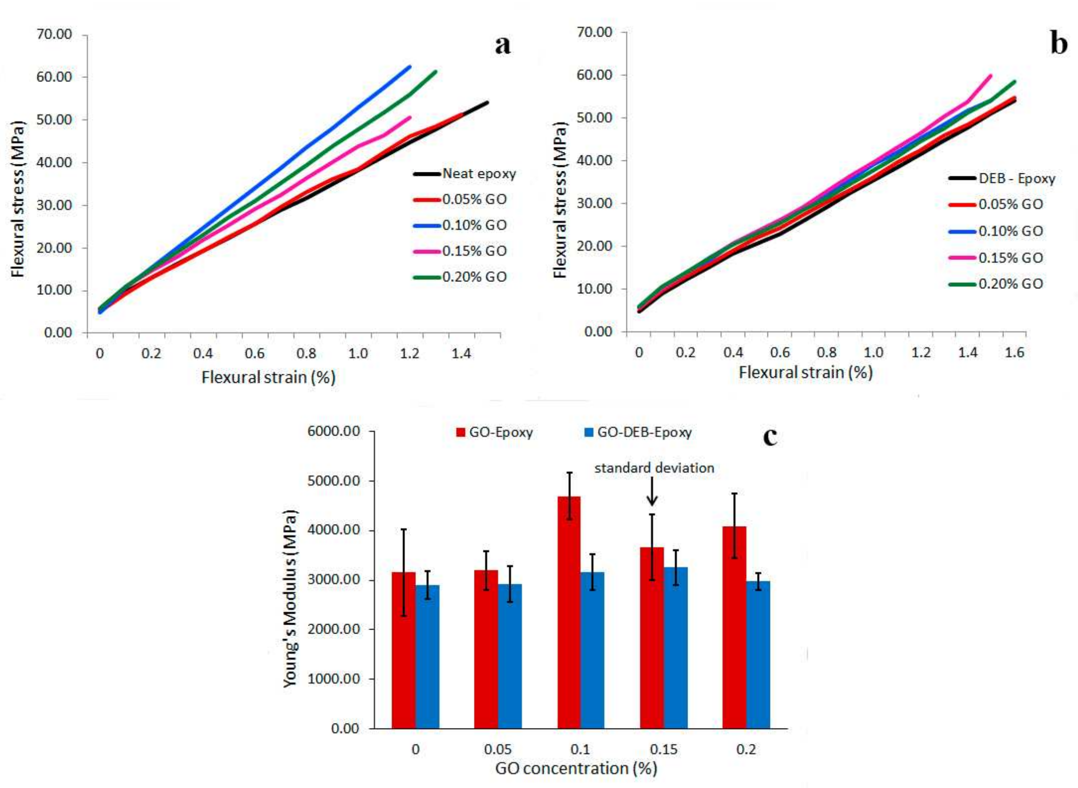

Figure 5. Flexural stress versus strain curves for GO-Epoxy composites (a), and for GO-DEB-Epoxy composites (b) at different GO content. (c) The Young's modulus values for the composites at different GO content.

Next, we analyze how GO addition affects the properties of the cured solid GO-Epoxy composites. One of the most important properties of epoxy resins is the flexural modulus. The flexural properties of the cured composites were measured by the two different methods: 1) with the dynamic mechanical analyzer DMA 242 E *Artemis*, Netzsch, Germany (see Fig. S3, S4), and 2) with the universal Instron 5882 testing machine, according to the ASTM D790 standard (see Fig. 5a,b). Addition of GO to epoxy resin leads to the notable increase in the Young's modulus, but the increase is not monotonous with GO content. The DMA measurements demonstrate the increase of the Young's modulus by 14% and 48% at the 0.05% and 0.10% GO loading, respectively (Fig. S3). The flexural modulus increases until the 0.1% GO loading, after which this parameter does not change: the strain-stress curve for 0.2% GO sample almost overlaps with that for the 0.1% GO sample (Fig. S3). The Instron measurements demonstrated slightly different values for flexural properties (Fig. 5a,c). Importantly, the Young's modulus for all the four GO-loaded samples was higher than that for the neat epoxy. and the maximum increase (48.7% compared to the neat epoxy) was registered at the 0.10% GO content.

Before testing the GO-DEB-Epoxy samples, we first compared mechanical properties of epoxy resin containing 10% DEB with that for neat epoxy resin. The flexural modulus of the two samples was almost the same (see SI Fig. S5). Thus, a small amount of the modifier reduces the viscosity of the uncured resin without degrading mechanical properties of the cured products. Next, we tested mechanical properties of the four GO-DEB-Epoxy samples with different GO content (Fig. 5b, Fig. S4). For this system, addition of GO leads to moderate change in the flexural properties. However, all the curves for GO-loaded samples exhibited higher flexural modulus, compared to that for pure DEB-Epoxy. The 9.1% and 12.1% increase in the Young's modulus was registered for the 0.10% and 0.15% GO loading, respectively (Fig. 5c). According to the DMA method, the alteration of the flexural properties is even higher (Fig. S4).

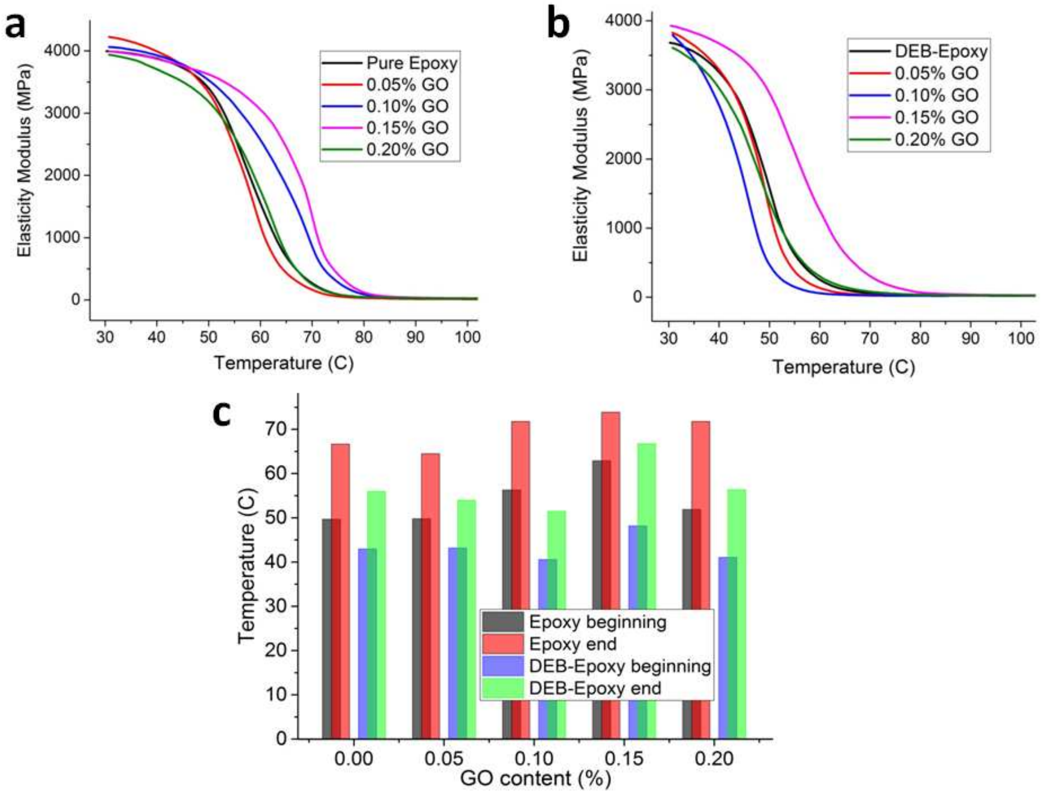

Figure 6. The glass-transition properties for (a) GO-Epoxy composites, and (b) GO-DEB-Epoxy composites. (c) The temperatures showing the beginning and the end of glass-transitions for the curves, shown on the panels (a) and (b).

To further explore the as-prepared composites, we measured their glass-transition temperatures. The pure DEB-Epoxy starts its transition at 43ºC, as opposed to the neat epoxy with 50ºC. Introduction of GO into epoxy resin alters the glass-transition temperatures (Fig. 6), suggesting that GO not only mechanically impregnates the epoxy resin, but also modifies its chemical structure. The function of the glass-transition temperatures on GO content is not linear, passing through the maximal values at around 0.10% - 0.15% GO content (Fig. 6a), i.e. the same concentration range, where the highest alterations in the Young's modulus were registered. Apparently, at this GO content, we reach the highest density of the cross-linking network, that incorporates GO flakes, due to the optimal GO/epoxy ratio. Note, the glass-transition temperature decreases at 0.20% GO content. This is most likely related to the higher viscosity of the uncured resins at this GO loading (Fig. 4). The curing of epoxy resins is in part controlled by diffusion of the curing agent through the matrix. For the 0.20% GO content, the higher viscosity slows the diffusion, which results in the lower density of the cross-linking network. For GO-epoxy this is apparent both for the flexural modulus (Fig. 5a,c), and for the glass-transition (Fig. 6a,c). For the DEB-Epoxy, the viscosity of the 0.20% GO solution is not that high. Subsequently, the difference in the properties of the cured samples is less pronounced (Fig. 5a,c and Fig. 6a,c).

We also tested impact resistance for the prepared composites. Expectedly, the GO-DEB-Epoxy samples demonstrated higher impact resistance compared to the GO-Epoxy samples, which is in line with the literature data.[34,35] In general, addition of GO downgraded the impact resistance of pure epoxy (Fig. S6). In contrast, the impact resistance of the DEB-Epoxy system improved with addition of GO.

In addition, we analyzed the fracture surfaces of the samples after the impact resistance test by SEM (Fig. 7). The roughness of the fracture surfaces is often associated with the ability of a material to resist crack propagation,[10,11,19] attributing the rougher surface to improved fracture toughness. In our work, the fracture surface of the GO-Epoxy composite (Fig. 7b) contains more ridges and ravine patterns compared to that for neat epoxy (Fig. 7a), confirming, alteration of the structure and mechanical properties of epoxy resin. On the higher magnification images (Fig. S7, S8), the situation is different: the fracture surface of the GO-epoxy sample looks more uniform compared to that for neat epoxy. Interestingly, no apparent GO flakes are visible, confirming the uniform distribution, and the single-layer character of GO flakes in the matrix.

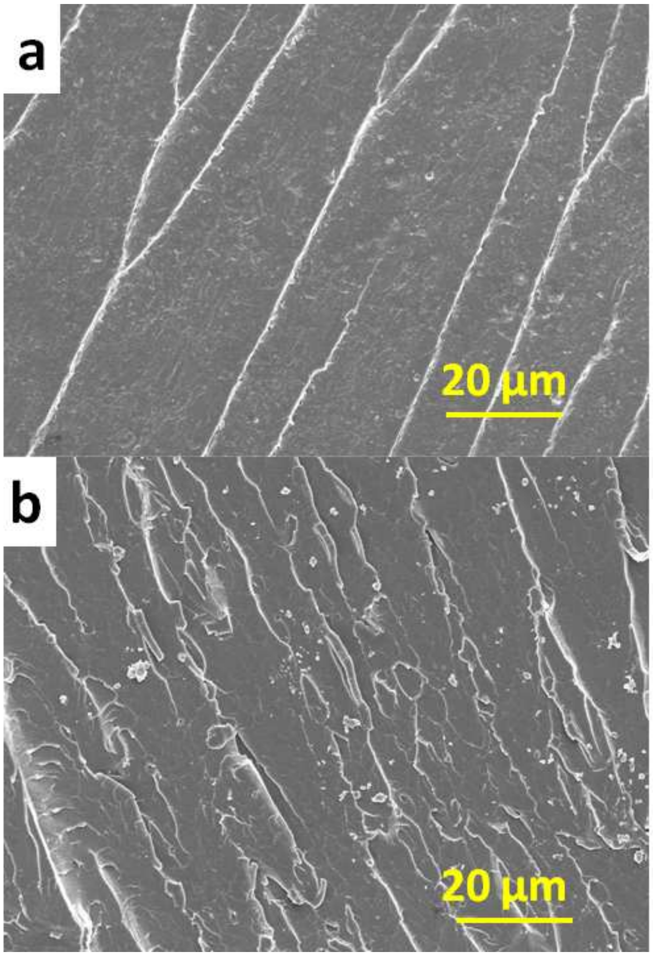

Figure 7. The SEM images of the fracture surfaces for (a) neat epoxy, and (b) 0.1% GO-Epoxy.

Finally, for comparison purposes, we performed some experiments on reproducing two literature methods for preparing GO-Epoxy composites. Since the flexural strength changes with GO loading not linearly, when reproducing the earlier published methods, we used the same GO loadings as it was in the original publications. More precisely, the 0.1% loading was used for the acetone-transfer method,[19] and the 0.0375% loading was used for the aqueous-transfer method.[25] The first number is exactly the same as the 0.1% loading in our experiments, and the second number is close to the 0.05% loading.

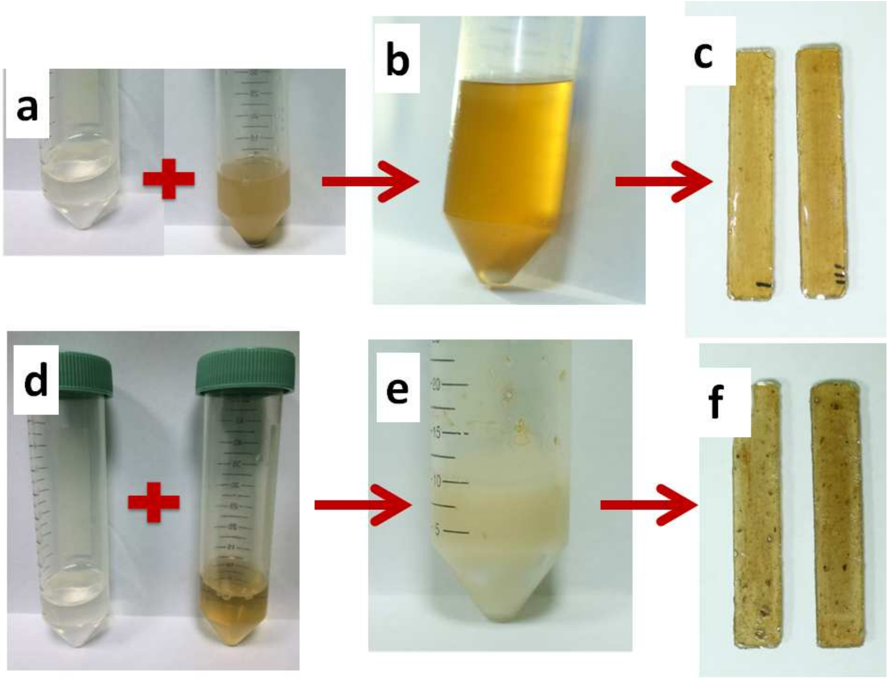

Figure 8. Photographs demonstrating reproduction of the literature methods: (a-c) the acetone-transfer method, (d-f) the aqueous-transfer method. (a) neat epoxy (left) and GO dispersion in acetone (right). (b) the GO-acetone-epoxy resin mixture. (c) the solid GO-epoxy samples after curing; the GO content is 0.1%. (d) neat epoxy resin (left) and 0.2% GO aqueous solution (right). (e) GO-water-epoxy resin mixture. (f) solid GO-epoxy samples after curing; the GO content is 0.0375%.

As it was expected, GO did not dissolve in acetone. Moreover, it cannot even be transferred into acetone by the gradual solvent exchange method.[12,13] In our experiment, direct dispersion of solid GO in acetone yielded a muddy-looking dispersion that precipitated within few minutes after the agitation (Fig. 8a). The non-transparent appearance suggests that GO aggregates have the size comparable with the wavelength of the visible light, i.e. the several hundreds of nanometers. Considering the thickness of a single-layer GO flake of ~1.2 nm, the aggregates must have several hundreds of GO layers. Surprisingly, mixing this dispersion with epoxy resin yielded uniform yellow-colored solution (Fig. 8b). After removing acetone by evaporation, the remaining GO-epoxy resin dispersion remained stable and homogeneous with no signs of coagulation. Curing of this resin yielded uniform and transparent solid GO-epoxy samples (Fig. 8c). The dissolution of GO into epoxy resin from the non-exfoliated state in the acetone dispersion is rather interesting. Some complex phenomenon must be happening on the GO/liquid interface when the acetone-wet GO is introduced into epoxy resin. The strong affinity of GO toward epoxy resin must facilitate the exfoliation, when it is transferred from the phase miscible with the resin. This topic deserves more detailed investigation in future.

With the aqueous method, mixing transparent colorless epoxy resin with transparent aqueous GO solution (Fig. 8d) yielded milky looking emulsion of the two immiscible liquids (Fig. 8e). Upon standing, this emulsion separated to the two phases: transparent, almost colorless aqueous phase, and milky epoxy-water emulsion. The aqueous phase was discarded. After removing water from the epoxy-water phase by evaporation, the resulted GO-epoxy resin dispersion became transparent, but with inclusions of coagulated GO. Curing of this resin yielded similar, not fully homogeneous solid GO-epoxy samples with inclusions (Fig. 8f). The tri-component system: GO-water-epoxy forms Pickering emulsion, where GO takes place on the interface between the two phases.[39,40] Most likely, this is the factor preventing GO from being homogeneously transferred into the epoxy phase. Apparently, GO remained between the two phases until the very last portions of water have been removed. This caused accumulation of significant amounts of GO in one point, and, as the result, the inability to dissolve this aggregate in the epoxy phase.

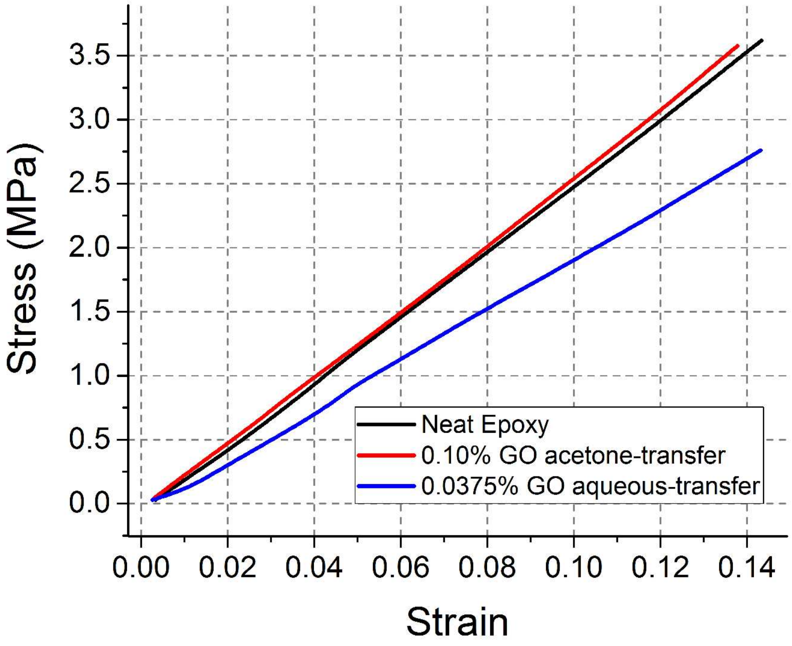

Figure 9. Flexural strength versus strain curves for neat epoxy resin and GO-epoxy composites prepared by the literature methods: the acetone-transfer,[19] and the aqueous-transfer.[25] The 0.1% GO content was used in the acetone-transfer method, and 0.0375% GO was used in the aqueous-transfer method.

The testing of the flexural properties of the as-prepared composite materials was conducted at low deflecting loads with the universal DMA 242 analyzer. The acetone-transfer method resulted in a negligible improvement in the flexural properties of the cured epoxy resin (Fig. 9). This is rather strange, considering that GO was uniformly blended in the resin (Fig. 8b). The possible explanation is that GO might be still not fully exfoliated in the epoxy matrix, being present in the form of few-layer sheets. The few-layer GO flakes have the thickness that will not scatter visible light. However, the efficient content of GO in the matrix, i.e. the area of the GO/epoxy interface will be lower compared to the case of the full exfoliation. This data emphasizes the advantage of our GO transfer method that affords significant improvement of the flexural properties at the same 0.10% GO content. The aqueous transfer method resulted not in improvement, but in degrading the flexural properties of the resin; the value of the Young's modulus was decreased by 23.7% (Fig. 5). This is in line with the non-uniform distribution of GO in the composite. Thus, we couldn't reproduce the fantastic improvement of mechanical properties declared by the authors.[25]

The main task of this study was to demonstrate the range of the possible alterations of the properties of epoxy resins with GO addition, while maximally preserving the fine chemical structure of GO. The curing of epoxy resins is a very complex process, and depends on numerous parameters. In this study we might not completely reached the maximal density of the polymer network, especially at higher GO loadings. Thus, the tested properties might not fully attained their maximal values. Optimization of the curing conditions with the goal of attaining the best possible results will be the subject of our next study.

3. Conclusions

We developed the HLPT method for introducing GO into the epoxy resin matrix, affording uniform distribution of GO in the resin. The homogeneously transparent appearance of as-prepared samples, the optical microscopy and rheology studies of uncured resins suggest that we attain nearly complete exfoliation of GO in the epoxy matrix. This affords significant alteration of several mechanical properties of the as-prepared cured composites. The tested properties change not monotonously with GO content, exhibiting peak values around 0.10% - 0.15% GO content. The use of the HLPT method affords the 48% increase of the Young's modulus at the 0.10% GO loading, compared to uncured resin. The further increase in GO loading does not lead to the increase of the Young's modulus. When the DEB additive is used, the Young's modulus was increased for 9.1% and 12.1% at 0.10% and 0.15% GO loading respectively. The glass-transition temperatures also demonstrate significant alterations with GO additions, with the peak values around 0.10% - 0.15% GO loading. The experiments done on reproducing two literature methods, using GO introduction techniques other than HLPT, lead to either decrease, or insignificant increase of mechanical properties of the resulted GO-epoxy composites.

4. Experimental Part

4.1. Materials

The epoxy resin (NPEL-128, epoxy value 22.6,) which is manufactured from bisphenol-A and epichlorohydrin was obtained from the "Rus Chemicals Group" (Russia). The polyamine-based hardener (Polyethylene polyamine (PEPA) from the "Chimex Limited", Russia) was always used in the ratio of epoxy resin : curing agent = 10:1. Reactive diluent diglycidyl ether of 1,4-butanediol (DEB) was from the "Chimex Limited" (Russia).

4.2 Preparation of GO and dispersion of GO in IPA

GO was prepared as described in our previous reports.[23,24] Graphite flakes (10 g, 832 mmol) were dispersed in 96% sulfuric acid (680 mL) at room temperature using a mechanical stirrer. After 10 min of stirring, 1 wt equiv of $KMnO_4$ (10 g, 63.2 mmol) was added. The mixture became green due to the formation of the oxidizing agent MnO_3^+. Additional portions of $KMnO_4$ (10 g, 63.2 mmol each) were added when the green color of MnO_3^+ was diminished, indicating that the oxidizing agent was consumed. A total of 4 wt equiv of $KMnO_4$ were sequentially added. The end of the oxidation was always determined by the disappearance of the green color after each $KMnO_4$ addition. After complete consumption of $KMnO_4$, the reaction was quenched with 1400 mL of ice-water mixture, and 16 mL of 30% H_2O_2 solution was added to convert manganese by-products to soluble colorless Mn (II) ions. The reaction mixture was centrifuged 15 min at 8900 rpm to separate GO from acid. For purification, the GO precipitate was redispersed in DI water, stirred 30 min, and centrifuged 20 min at 8900 rpm to separate purified GO from washing waters. This constituted one purification cycle. Four more purifications were performed consecutively: one time with DI water and three times with 4% HCl. The GO precipitate after the last washing was dried in air. 18.2 g of air-dry GO was obtained.

To prepare GO solution in IPA (GO-IPA), 100 mL of the 2 wt% GO aqueous solution was blended with 100 mL IPA. After stirring the mixture for 1 h, it was centrifuged for 40 min at 8900 rpm. The clear supernatant was discarded. The precipitated gel was blended with fresh portion IPA, to bring the volume up to 200 mL, stirred for 1 h, and centrifuged at the same conditions. This procedure was repeated five more times. This sequence of operations afforded the gradual replacement of water by IPA. The solution stayed transparent and stable against precipitation at all stages of operation. After the last centrifugation, we obtained GO-IPA gel with GO content 3 wt%. According to the dilution factor, this gel should contain 0.048 wt% water. The actual content of water was not determined.

4.3 Preparation of nanocomposites

4.3.1 "Aqueous-transfer method". The aqueous-transfer method was performed exactly as it was described in the reference [21]. 7.5 mL of 0.5 mg/mL aqueous GO solution was introduced into 10.0 g epoxy resin. The mixture was stirred for 4 h at 50°C; then it was left standing for 8 hours to separate for two phases. Upon standing, this emulsion separated to the two phases: transparent, almost colorless aqueous phase on the top, and milky epoxy-water emulsion on the bottom. The aqueous phase was discarded. The bottom portion was not transparent, suggesting formation of emulsion; thus water was not completely removed. Next, the emulsion was additionally stirred for several hours at 50°C for complete removal of water. This resulted in formation of transparent, but not fully homogeneous GO-epoxy composite; the particles of solid GO aggregates were visible with bare eye. After adding curing agent and curing, this resulted in solid GO-epoxy composites with ~0.0375% GO content. The samples were transparent, but not uniform: solid GO inclusions were visible with bare eye.

4.3.2 "Acetone method". The 10.0 g of the 0.2% GO dispersion in acetone was prepared by directly dispersing solid GO in acetone by sonication with tip sonicator for 30 min The as-prepared dispersion was not transparent, having muddy appearance. The dispersion precipitated within 10 min after sonication, suggesting non-exfoliated, aggregated nature of GO flakes in acetone. 10.0 g of the agitated GO-acetone dispersion was introduced into 20.0 g epoxy resin. The mixture was blended manually until homogeneous solution was formed, and acetone was removed by evaporation under vacuum with constant stirring. This resulted in the homogeneous and transparent 0.1% GO-epoxy solution. The curing agent was added and mixed with epoxy resin, and cured in teflon moulds for 6 hours at 60°C

4.3.3. Proprietary method

The GO-epoxy composites were prepared as the following. The 0.15 g, 0.30 g, and 0.60 g of the 3 wt% GO-IPA gel was introduced into 10.0 g epoxy resin and blended for 30 min. IPA was evaporated under vacuum until the constant weight. Then, curing agent was added and blended with epoxy resin. The mixture was cured in Teflon moulds for 6 hours at 60°C. This resulted in GO-epoxy composites with GO content of 0.05%, 0.1%, and 0.2%.

To prepare GO-DEB-Epoxy composites, the 3 wt% GO-IPA gel was introduced into the epoxy-DEB solution, containing 10% DEB. The rest of the procedures was the same as described above for GO-Epoxy composites.

4.4 Characterization of GO and GO-epoxy composites

The scanning electron microscopy (SEM) images were acquired with a field-emission high-resolution scanning electron microscope Merlin from Carl Zeiss at accelerating voltage of incident electrons of 5 kV and a current probe of 300 pA. Rheological measurements were conducted in a flow mode with the DHR-2 rheometer (TA Instruments Inc, USA) equipped with the 20 mm parallel plate geometry. Viscosity of the GO-epoxy mixtures was measured as the function of shear rate. The flexural modulus was measured with two different methods: 1) with the universal Instron 5882 testing machine, according to the ASTM D790 standard, and 2) with the dynamic mechanical analyzer (DMA 242 E *Artemis*, Netzsch, Germany). For the first method, the samples were molded into the 80 mm × 12.7 mm × 4.0 mm rectangular specimens; the support span distance was 64 mm. Five samples were measured for each GO content, and the average values were reported. For the second method, the specimen size was 60 mm x 10.0 mm x 2.3 mm. The support span distance was 50 mm. The test results are shown on the Fig. S3 and S4.

The glass-transition measurements were conducted with a dynamic mechanical analyzer (DMA 242 E *Artemis*, Netzsch, Germany) by the three-point geometry bending test. The sample's dimensions were 60 mm x 12.7 mm x 3.2 mm. The support span was 50 mm; the frequency was 1Hz under sample dynamic loading. Before the heating, the samples were thermostated for 30 min at 30ºC. The heating rate was 3K/min from 30ºC through 180ºC. The impact resistance was measured with the pendulum impact tester TSKM-50 from the "TestSystems", Russia, according to the ASTM D6110 standard. The sample's dimensions were 60 mm x 12.7 mm x 3.2 mm. The hammer strike energy was 7.5 J. Five samples were measured for each GO loading, and the average values were presented on Fig. S6.

Supporting Information. SEM image of GO flakes, optical microscopy image of GO-epoxy composite, strain-stress curves, SEM images of the fracture surfaces.

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Conflict of Interests

The authors declare no competing interests.

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