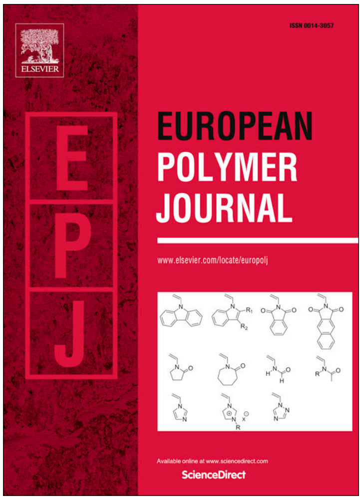

One-step surface modification of graphene oxide and influence of its particle size on the properties of graphene oxide / epoxy resin nanocomposites

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One-step surface modification of graphene oxide and influence of its particle size on the properties of graphene oxide / epoxy resin nanocomposites

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Abstract

Graphene oxide (GO) was synthesized from expanded graphite with particle size of 130 μm (GO130) and 1200 μm (GO1200) and characterized. GO130 was oxidized to a higher degree and contained larger concentration of C=O bonds. After the synthesis, the GO was kept in a form of viscous slurry in methanol to prevent formation of graphite oxide. The slurry was mixed with a hardener and methanol was evaporated. The nanocomposites with GO content from 0.25 to 1.0 wt.% were prepared by mixing the epoxy resin, hardener and hardener/GO mixture and cured. The particles were homogeneously distributed within the polymer matrix as observed by SEM on the plasma etched samples. The glass transition temperature increased from 81 °C to up to

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90 °C. The Young’s modulus increased by 35 % and 30 % with the addition of GO130 and GO1200, respectively, while the tensile strength increased for 10 % only when GO1200 had been added. The optimum concentration of GO in the nanocomposite is from 0.25 to 0.50 wt.%.

Keywords: nanocomposites; epoxy; plasma; graphene oxide; thermal properties; mechanical properties;

1. Introduction

Graphene has attracted great attention during the last ten years since it has unique physical and mechanical properties. Due to its high surface area and high strength it seems to be a good candidate as a nanofiller for the production of high strength, high thermal and electrical conductive polymer nanocomposites. However, the impact of any filler on the physical, chemical and mechanical properties of the polymer composites or nanocomposites depends not only on the fillers properties but also on the filler's particle size, the particle distribution within the polymer matrix and the filler/polymer surface interactions.

There are several routes to prepare graphene like mechanical cleavage, chemical vapour deposition, and epitaxial growth; however, these procedures are not really practical and cheap enough for the mass production needed for the polymer composites preparation,[1] so researchers are seeking for an alternative. The alternative to graphene should have similar properties, especially enormous surface-to-mass ratio, but should be much cheaper. Furthermore, the production procedure should be reliable and scalable up to the industrial level. The best alternative seems to be graphene oxide (GO). It can be synthesized by several methods and most are still being modified and improved [2,3]. Graphene oxide can be covalently or non-covalently modified and/or thermally or chemically reduced into graphene [1]. However, the reduction is never complete so reduced graphene oxide (rGO) still contains some oxygen in its structure. GO is an interesting material not only as a precursor for graphene but as a reinforcing filler in polymer nanocomposites due to its high surface area and strength. Graphene oxide remains in the form of as-produced flakes as long as it is dispersed in a suitable liquid. When dried, it agglomerates rather irreversibly to three-dimensional particles of graphite oxide, so the major property (extremely large surface-to-mass ratio) is lost. Epoxy resins are widely used in various, mostly high-tech applications. However, there is still a need to increase the toughness and strength of such material in order to satisfy the increasing demands in specific applications. Therefore, nanocomposites of epoxy resin with graphene, GO and rGO have been the subject of extensive research during the last few years. The main problem in the preparation of nanocomposites seems to be a dispersion of graphene plates on nanolevel. Three-roll milling appeared to be an effective method to disperse the rGO in the liquid resin, but according to optical microscopy, particles of up to 10 microns were formed [4]. Extraction of GO from water seems to give better results. Yang et al. prepared a homogeneous dispersion of GO in epoxy resin by direct extraction of GO from the water phase into the epoxy resin at 50 °C [5]. At a very low (0.0375 wt.%) loading of GO they increased compressive failure strength and toughness by 48 % and 1185 %, respectively. Other researchers performed extraction from water at room temperature using triglycidyl para-aminophenol (TGPAP) as the surface modifier and phase transfer agent. They claim that without TGPAP the phase transfer is not possible. The highest increase in mechanical properties (50-100%), including elongation at break (15%), was achieved at 20 wt.%

TGPAP and 1 phr of GO [6]. Liu et al mixed the epoxy resin with a dispersion of GO in acetone. After removing acetone in vacuum the mixture was cured. The flexural modulus, strength and impact resistance of the 1 wt.% GO/epoxy nanocomposite increased by 10.1%, 14.7% and 48%, respectively, as compared to the corresponding values of the neat epoxy, while the glass transition temperature (T_g) slightly decreased. Agglomerates of GO particles at the GO concentration of 1.5% were observed, which led to the reduction of mechanical properties [7]. The same research group prepared also a dispersion of GO in dimethylformamide (DMF) and mixed it with the epoxy resin. The highest increase in impact strength (166%) was obtained at a GO concentration of only 0.15 wt.% [8]. It is worth mentioning that in the latter case the particle size of graphite used to synthesize the GO was 50 μm, while in the former case the particle size was only 2 μm, which might be a reason for somewhat different results.

A method of mixing the acetone dispersion of GO with the epoxy resin was used also by other researchers [9,10]. They also reported about10-36% increase in the tensile or flexural modulus and strength at the 0.1-0.5 wt.% of GO. More significant improvements were observed in the fracture toughness and fatigue life.

The surface modification has long been used for improvement of filler/ epoxy matrix interactions. Surface amination seems to be a preferred method and various techniques, including wet-chemistry and plasma treatment have been reviewed recently [11].

To increase the compatibility between the GO and the epoxy resin Li et al. synthesized the amino- and epoxy-functionalized GO using two differently terminated silane coupling agents. A dispersion of functionalized GO in acetone was mixed with the epoxy resin, dried and cured. Optimum mechanical properties were obtained for the nanocomposites containing 0.2 wt.% of GO. Better tensile properties were obtained with the amine-functionalized GO, while ductility was better with the epoxy-functionalized GO [12]. The best mechanical properties at that concentration were also obtained by adding GO modified by successive grafting of first Jeffamine 2000, than epoxy resin and curing agent, as a filler to epoxy resin [13]. Comparison of mechanical and other properties of nanocomposites prepared with pristine and modified GO showed better performance with the modified-ones [14].

Several other methods of surface functionalization of GO have also been developed with various success. Diglycidyl ether of bisphenol-A [15], various silanes [16,17], poly (ether ether ketone) [18], 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide [19], poly(vinyl imidazole) [20] have been used for surface modification of GO.

Sonication of GO in acetone, and mixing this dispersion with epoxy resin seems to be the most popular method for GO/epoxy nanocomposite preparation. However, mechanical mixing of powdered GO or modified GO into the epoxy resin had also been used to prepare nanocomposites [6,14,21,22]. Improvement in mechanical properties was obtained, but micrometre sized particles were sometimes observed [21,22].

The aim of our work was threefold; first, to prepare nanocomposites without drying the GO after its synthesis. Graphite oxide is formed on drying of graphene oxide, which can only be redispersed in a form of nanoplatelets in water. By using the GO as synthesized it is possible to achieve better dispersion of the nanoplatelets and mixing it with the amine crosslinker enables *in situ* surface modification.

The second goal was to investigate the influence of GO particle size on the properties of the epoxy nanocomposites. Although it is known that the specific surface of the filler has the impact on the composite properties, this topic has not been widely studied. There are only two papers, one dealing with the influence of GO particle size on the curing kinetics and thermal stability of epoxy resins [23], and the other one with the influence of particle size on the toughening of the epoxy/GO nanocomposite [24].

The third goal was to apply selective plasma etching [25] for GO/polymer morphology characterization. This technique has already been successfully used to evaluate the distribution of pigments and inorganic fillers in coatings [25].

2. Experimental

2.1 Materials:

Expanded graphite Sigratherm® GFG 130 (average particle size 130 μm) and GFG1200 (average particle size 1200 μm) are the products of SGL Group, Germany. Epoxy resin Araldite LY 1564 and hardener Aradur 3487 are the products of Huntsman Advanced Materials. H_2SO_4 (95-97%), H_3PO_4 (85%), H_2O_2 (30%), $KMnO_4$ and methanol (MeOH) were purchased at Aldrich and used as received.

2.2 Preparation of Graphene Oxide (GO)

GO was prepared according to the modified Hummer method [2]. In a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (500 mL for GO130 and 800 ml for GO1200) 10 g (1 wt. equivalent) of graphite flakes and 50 g (5 wt. equivalent) of $KMnO_4$ were added. The $KMnO_4$ was added in a 1 equivalent portion, after the reaction mixture turned from green to violet, when all the $KMnO_4$ equivalent had been reacted. At the end of reaction, the mixture was cooled to room temperature and ice (≈1 kg) was added, followed with 5 mL of 30 % H_2O_2. The product was centrifuged and washed several times with 10 % HCl, water and MeOH. It was either dried or kept as MeOH dispersion (≈8 wt.% of GO), and stored in fridge. The yield was ≈16 g of dried GO. The dispersions were designated as GO130 (from GFG130) or GO1200 (from GFG1200).

2.3 GO particle size determination

The size of graphene oxide particles in DI H_2O was measured by dynamic light-scattering (DLS) using a Malvern Zetasizer Nano-ZS. Scattering was measured at an angle of 173°. The GO samples were diluted with DI H_2O to a concentration of 1 mg/ml. The carbon black and H_2O refractive indices of 1.470 and 1.3317, respectively, were used in calculations.

2.4 Preparation of GO/Aradur 3487 (AGO) mixture

≈15 g of GO dispersion and ≈25 g of Aradur 3487 were weighed in 50 mL round bottom flask and stirred on a magnetic stirrer for 30 minutes. Then, the mixture was transferred to rotatory evaporator for few hours to remove most of the MeOH at 40 °C. Small quantity of MeOH that remained in the flask was removed using a vacuum dryer. The presence/absence of the methanol was determined by ^1H NMR.

2.5 Preparation of GO/epoxy nanocomposites

A ratio of epoxy resin to hardener was set to 1 : 0.34 as it is suggested by the producer. 5.0 g of epoxy resin was mixed with the AGO and mixed, first on a magnetic stirrer (400 rpm, 15 min) and then in ultrasound bath (15 min). The rest of the hardener was added and mixed on a magnetic stirrer for another 5 min, and subsequently degassed under vacuum. The concentration of GO was 0.0-1.0 wt.% according to the epoxy resin. Bone-shaped specimens were prepared by curing the mixture at 100 °C for 2 h in a silicone mould.

2.6 Thermal analysis

Curing reaction and T_g were determined by a Mettler Toledo DSC1. 10 mg of epoxy-GO mixture was weighed in a Al pan and heated from 25 °C to 250 °C, cooled to 25°C and heated again to 250 °C. Nitrogen flow was 20 mL/min and the heating/cooling rate was 10 °C/min.

2.7 Scanning electron microscopy

The GO particle size and the surface of fractured samples were studied by scanning electron microscopy (SEM) using a Zeiss Supra 35 VP microscope at an accelerating voltage of 5 kV. Before measurements the samples were coated with gold.

To obtain good images of the GO particles the GO was first dispersed in water and freeze dried. Few milligrams of foam-like product was re-dispersed in dichloromethane. A drop of suspension was put on a thin glass and dried in an air.

SEM microscopy (JEOL FEG-SEM 7600F) was also performed for GO/epoxy composites to see distribution of the GO particles in the epoxy resin. Samples of the composite were first etched in a radiofrequency plasma created at 300 W to remove the surface layer of the epoxy and uncover the under-laying GO particles. Oxygen plasma at 30 Pa was used. The samples were treated with pulsed plasma to avoid heating. Duration of one pulse was 3 s and a delay between pulses was 7 s.

2.8 Mechanical analysis

Tensile testing was performed using a Shimadzu AG-X plus according to the ISO 527 standard.

2.9 X-ray photoelectron spectroscopy

Chemical composition of GO particles was investigated by X-ray photoelectron spectroscopy (XPS) using a model TFA XPS from Physical Electronics. The GO particles were excited with monochromatic Al K$\alpha_{1,2}$ radiation at 1486.6 eV. Survey-scan spectra were measured at a pass-energy of 187 eV and an energy step of 0.4 eV. High-resolution spectra of carbon were measured at a pass-energy of 29.35 eV and an energy step of 0.125 eV. The measured spectra were analysed using MultiPak v8.1c software supplied by XPS manufacturer. Carbon C1s spectra were fitted using a Gaussian-Lorentzian function and a Shirley background subtraction.

3. Results and discussion

3.1 XPS and XRD analysis of GO

The difference in the average size of graphite particles used for a synthesis of GO is large but a relatively small difference in the chemical structure of GO is observed from results of XPS analysis. Namely, the XPS survey spectra were rather similar. Still, they allowed for determination of the O/C ratio: 0.54 for GO130 and 0.51 for GO1200. High resolution spectra allowed for estimation of the individual oxygen-containing functional groups. Table 1 represents results of the de-convoluted high-resolution C1s spectra for both types of materials using best fits. It should be stressed, though, that the peaks corresponding to different functionalities overlap so the exact concentration cannot be determined very precisely.

The XPS survey spectra also showed some impurities such as S, Cl and N, but their concentration was below 1 at.%.

Table 1: Proportions of various carbon bonds together with the oxygen to carbon atomic ratio for the GO130 and GO1200.

	C-C/C=C (%)	C-O (%)	C=O (%)	COOH (%)	O/C
GO130	46	43	9	2	0.54
GO1200	41	50	7	2	0.51

The concentration of oxygen on the graphene oxide influences the thickness of particular GO sheets. Layered structure of the dry GO was observed by XRD for both samples and the result is presented in Figure 1. The layer thickness of the GO130 is larger for 0.06 nm and is attributed to higher oxygen content than for GO1200 samples.

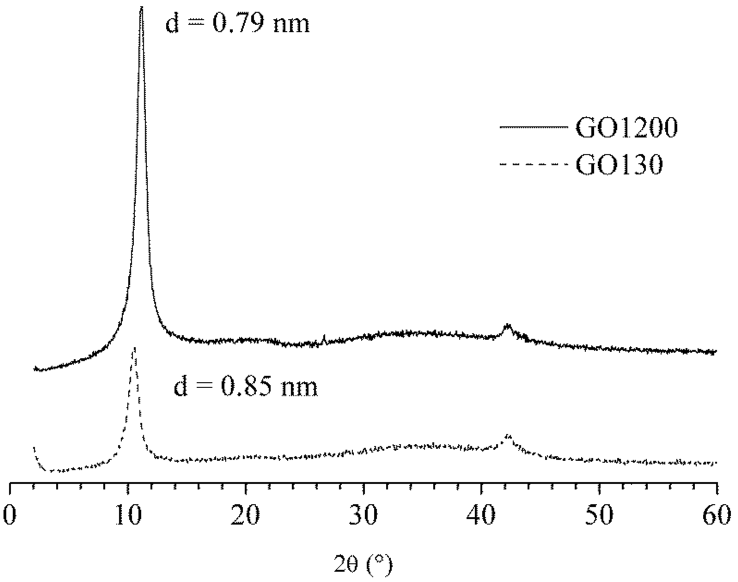

Figure 1: XRD of GO synthesized from graphite with particle size of 130 μm and 1200 μm.

3.2 Particle size analysis

The GO particle size is related to the particle size of the starting graphite, although quite large size reduction has been observed by other authors, especially when big graphite particles were used [26,27]. These findings are confirmed by our results. Particle size of GO was determined by DLS and SEM. Since GO particles are not spherical the DLS results can be used as semi-qualitative approximation only. For both samples the bi-modal particle size distributions were observed with the particle sizes of 200-1000 nm and 1-7 μm. Smaller particles most probably arise from breaking of larger particles during the synthesis. This might be due to the extensive oxidation during which so-called oxidative debris [28] were formed, or due to mechanical mixing of highly viscous reaction mixture of GO, $KMnO_4$, and acids. The results are shown in Table 2.

Table 2: Average particle size (Z-av.) of the first and second peak, intensities of the peak, and average particle size and polydispersity index (PDI) of the whole GO sample, as determined by DLS and SEM. GO130 and GO1200 samples were prepared from graphite with average particle size of 130 μm and 1200 μm, respectively.

	1st peak		2nd peak		Whole sample		SEM (μm)
	Z-av. (nm)	Intensity %	Z-av. (μm)	Intensity %	Z-av. (μm)	PDI	
GO130	469	15.3	2.69	15.3	1.43	0.51	<80
GO1200	499	13.0	3.57	87.0	2.07	0.51	<100

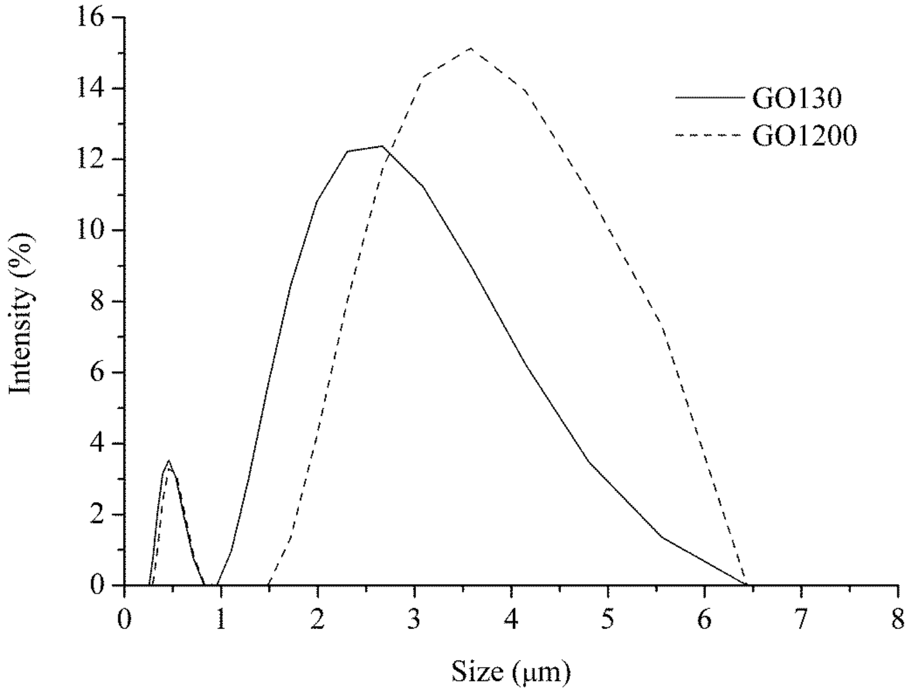

Figure 2: Dynamic light scattering size distributions of GO130 and G=1200.

SEM images may gave more realistic insight into the particle size, although due to bending, overlapping and very big differences in particle size and shape it is practically impossible to determine the average particle size reliably. Nevertheless, from SEM images presented in Figure 2 it is clear that the particles of GO1200 are broken down to the size that is still larger than the particle size of GO130, but not an order of magnitude as was the size of graphite grains. This is most probably a consequence of mechanical mixing of a very high viscosity mixture of GO/acids during the synthesis, the viscosity of which increased with increasing graphite particle size. Actually, the synthesis of GO1200 in 500 mL of acids was not possible since the mixer stopped working due to high viscosity. Although the quantity of acids was increased to 800 mL, it seems that breaking of large particles into smaller ones cannot be avoided. To prepare the GO of very large size one should use much larger amount of acids, which is economically and ecologically questionable. Typical SEM images for comparison of the particle size of the GO130 and GO1200 are shown in Figure 3.

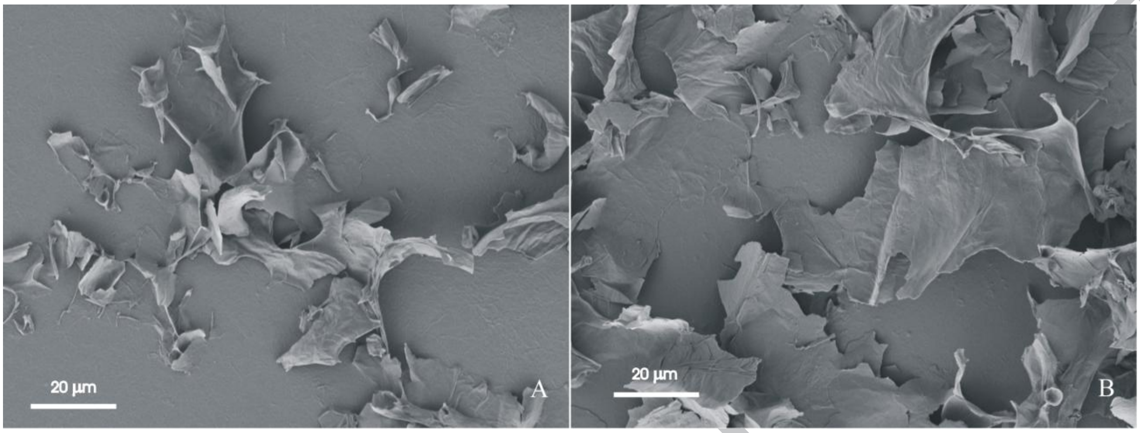

Figure 3: SEM images of GO130 (A) and GO1200 (B) particles.

In Figure 4 SEM images of the GO/epoxy composite, containing 0,25 wt.% of GO1200, at two different magnifications are shown. The surface of as-synthesized composite shown in Figure 4(A) does not reveal any GO particles (spherical features observed are probably just dust particles). Therefore, the sample was selectively etched in pulsed oxygen plasma to remove the surface layer of the epoxy polymer and to uncover the buried GO particles. After etching the composite in oxygen plasma for 2 × 3 s, the polymer surface became rough (Figure 4(B)) what is a known effect of plasma etching of polymers [29]. To prove this statement, additional SEM images of pure epoxy were performed before and after plasma treatment and are shown in Figure 5. It can be observed that originally pure epoxy surface became rough with a similar network-like structure as in Figure 4.

In Figure 4(B), a very few GO particles (marked with arrows) already became visible; therefore, the sample was further etched to reveal more GO particles. In Figure 4(C-D) images for the samples etched in plasma for 4 × 3 and 5 × 3 s, respectively, are shown.

The surface is now fully covered with the GO particles, what is clearly observed at higher magnifications. From these figures we can conclude that GO particles are uniformly distributed in the epoxy resin. However, the thickness of particles is in the range from nanometer scale to few micrometers. Layered structure can be observed in larger particles (Figure 4(C,D).

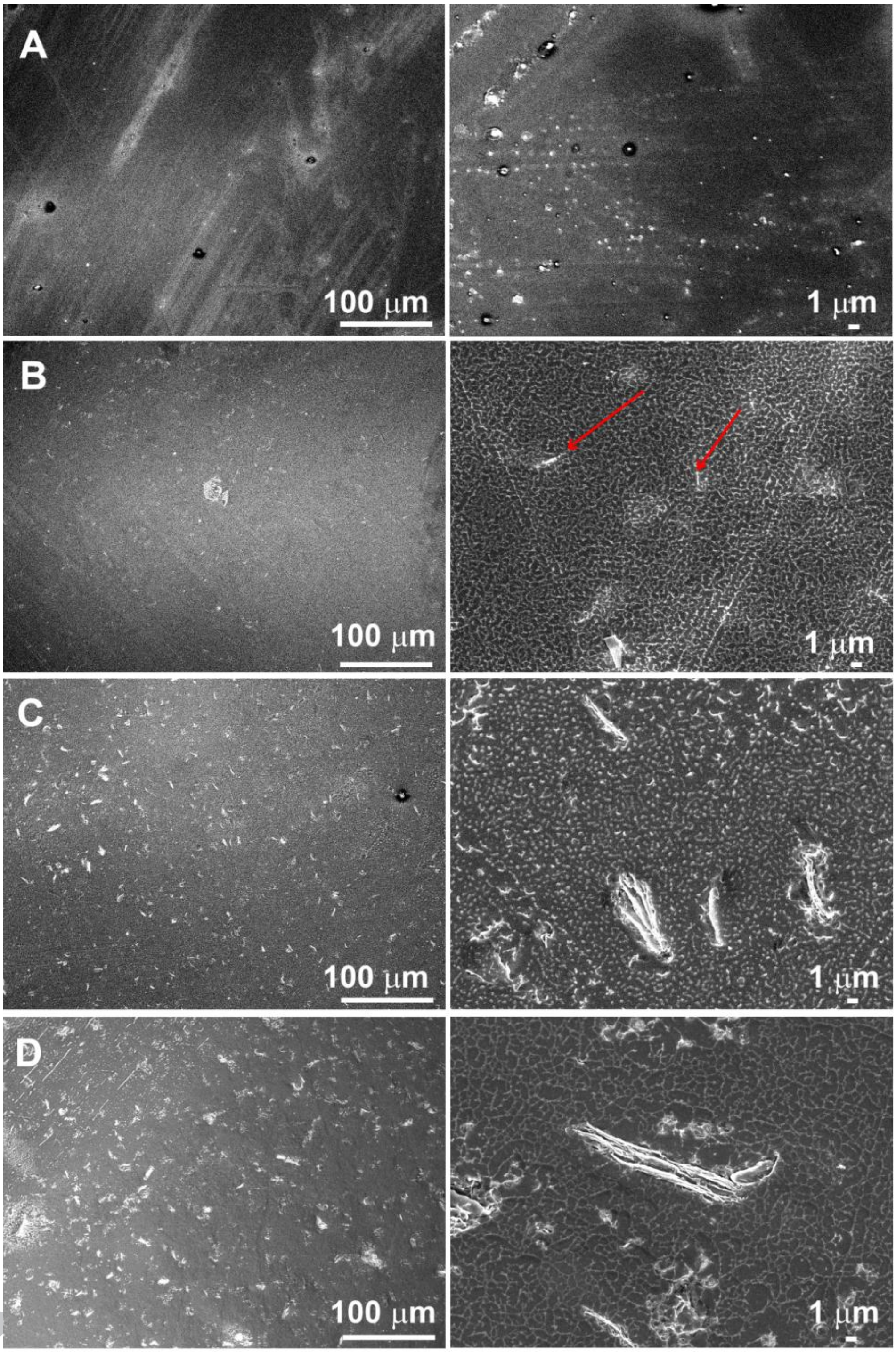

Figure 4: SEM images of GO/epoxy composite at two different magnifications: 250× (left) and 3000× (right). Figure (A) is for as-synthesized GO/Epoxy resin, whereas other figures are for plasma-etched samples: (B) 2 × 3 s, (C) 4 × 3 s and (D) 5 × 3 s.

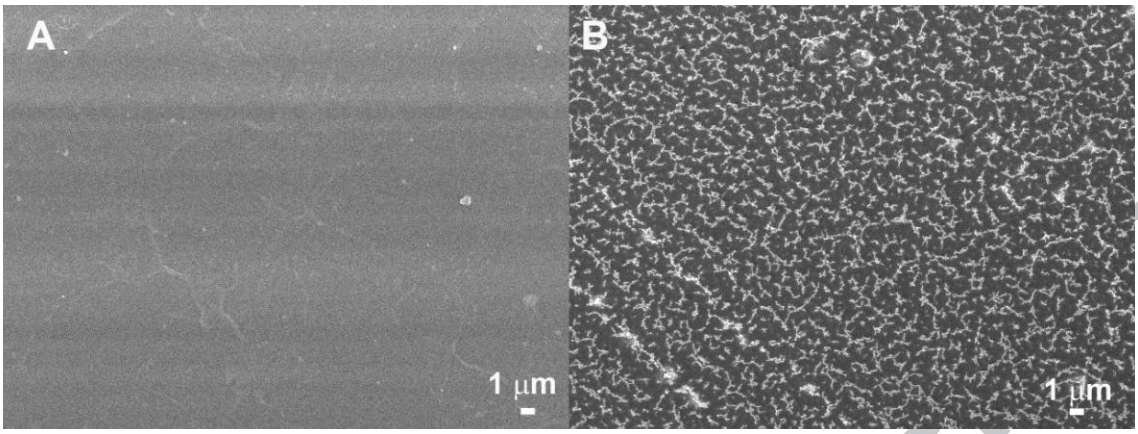

Figure 5: SEM images of pure epoxy: (A) before and (B) after plasma treatment.

3.3 Influence of GO on the curing reaction and the composite's glass transition temperature

There are several publications reporting the influence of GO on the curing reaction of epoxy resin. Among them there is only one paper dealing with the influence of the size of graphene oxide sheets on the curing reaction [23]. Composites with GO particle sizes (D_{50}) of 0.7 μm, 1.72 μm and 10.79 μm were prepared, mixed with the epoxy resin and isothermally cured by DSC. It was found out that the activation energy was reduced for all samples and the most pronounced reduction was observed for the medium sized particles [21]. Other authors investigated the influence of the GO quantity added to the epoxy resin on the curing kinetic and very diverse results have been reported. Bortz et al. observed the catalytic effect of GO that was exhibited as a decrease in onset of the cure reaction, while the peak heat flow slightly increased (for 1.5 °C) with increasing GO concentration up to 1 wt.%, and the reaction enthalpy increased from -209 J/g to ≈-230 J/g (for 0.25-1.0 % GO) [9]. Park and Kim reported on the catalytic effect exhibited by a decrease in peak heat flow temperature for 3 °C [30]. Contrary to that, the addition of the thermally reduced graphene oxide decreased the enthalpy (from -129 to -93 J/g) and shifted the peak heat flow for 6 °C to higher temperatures by addition of

0.25 wt.% of rGO only. A retardation effect on the curing reaction was explained by a steric hindrance due to increased viscosity [31]. Retardation effect was also observed by Galpaya et al. who reported on the decreased enthalpy while the peak temperature remained unaffected. They suggested that retardation effect of GO could arise from the reaction of oxygen functional groups of GO with the amine groups from curing agent [10]. Similar results were observed in our work and are summarized in Table 3. The peak heat flow was noticed at ≈116 °C for all the samples, while the enthalpy of reaction decreased. The decrease in enthalpy was somewhat higher (for 8 %) when GO1200 was admixed as compared to the reaction for the case of GO130 (5 %) as shown in Table 3. This observation can be attributed to higher contents of the epoxy and/or hydroxyl groups at the surface of the GO1200 (see Table 1). Epoxy groups on the GO probably reacted with the amine groups during AGO preparation, leaving less amine groups available to react with the epoxy resin.

Since a fraction of the amino groups of the curing agent reacted with the GO the actual ratio between the amine and epoxy groups was lower than 0.34/1. Lowering the amino/epoxy ratio decreases the T_g, however, on the second heating scan the T_g increased from 81.5 °C for the pure epoxy to up to 90.7 °C for all the nanocomposites (Table 3). Relatively high increase in T_g at the low GO loading can be attributed to a strong covalent bond between the GO nanoparticles and the epoxy matrix and to an increased crosslink density that was determined by the swelling of GO/epoxy nanocomposites in DMF for 5 days. Uptake of DMF of the GO/epoxy nanocomposites was 25-30 % (higher for the lower GO contents), while for the neat epoxy resin it was 38 %.

Table 3: Enthalpy of curing reaction (ΔH), peak heat flow ($T_{\max}$), and the glass transition temperature (T_g) of epoxy resin and epoxy resin/GO nanocomposites.

	ΔH (J/g)	$T_{\max}$ (°C)	T_g (°C)
Pure epoxy resin	-565.6	116.3	81.5
GO130-0.25 %	–566,7	116.0	85.0
GO130-0.50 %	–557.1	116.3	86.8
GO130-0.75 %	–555.1	116.4	88.3
GO130-1.00 %	–535.7	115.9	87.8
GO1200-0.25 %	–560.9	116.0	83.3
GO1200-0.50 %	–561.9	116.2	86.7
GO1200-0.75 %	–537.0	116.2	88.4
GO1200-1.00 %	–518.6	116.6	90.7

3.4 Mechanical properties of GO/epoxy GO/epoxy nanocomposites

The influences of GO particle size on the mechanical properties of GO/epoxy nanocomposites have rarely been investigated. Wang et al. found that the GO particle size had no influence on the Young’s modulus, but it influenced fracture toughness of epoxy resin as well as the curing mechanism. Fracture toughness increased with decreasing particle size and was the highest at the 0.05-0.1 wt.% content of GO, while a catalytic effect on the curing reaction was the highest for the medium sized (1.7 μm) particles [23,24]. However, the increase [32] as well as the decrease [27] in mechanical properties with the increasing GO particle size was observed in other polymers. Addition of GO130 increased the Young’s modulus of epoxy resin for 35 %, while the tensile strength remained unaffected at the GO concentrations of up to 0.5 wt.%, but it dropped for 20 % at the GO130 content of 1 wt.% (Table 4). Addition of the GO1200 increased the Young's modulus for 30 % but the tensile strength increased for ≈10 % irrespective of the GO concentration. The strain at break slightly increased for both GO types at the addition of 0.25-0.50 wt.% only. At higher concentrations it was reduced and the scattering of results increased. The addition of the GO130 increased brittleness more than the addition of the GO1200. Larger particles seem to connect more epoxy matrix together, transfer more stress and improve the mechanical properties.

Table 4: Dependence of Young's modulus, tensile strength and strain at break on the addition of GO.

	Young's modulus (GPa)	Tensile strength (MPa)	Strain at break (%)
Pure epoxy resin	1.92 ± 0.20	60.1 ± 2.7	4.20 ± 0.29
GO130-0.25 %	2.40 ± 0.69	61.6 ± 2.5	4.61 ± 0.31
GO130-0.50 %	2.63 ± 0.42	61.9 ± 4.9	4.54 ± 0.67
GO130-0.75 %	2.68 ± 0.40	54.3 ± 4.9	3.15 ± 0.42
GO130-1.00 %	2.56 ± 0.32	48.9 ± 5.5	2.75 ± 0.47
GO1200-0.25 %	2.17 ± 0.14	67.0 ± 1.01	5.18 ± 0.25
GO1200-0.50 %	2.36 ± 0.17	66.1 ± 6.84	4.00 ± 0.78
GO1200-0.75 %	2.52 ± 0.49	63.5 ± 8.40	3.30 ± 1.00
GO1200-1.00 %	2.46 ± 0.19	66.6 ± 3.48	3.32 ± 0.49

Tensile fractured surfaces were analysed by SEM. The surface of pure epoxy resin (Figure 6 A) is quite rough, which is not really the characteristic of epoxy resin. However, similar was observed by Joshi et al., who used the same epoxy resin [33].

Very different fracture morphology was observed in nanocomposites with GO130 and GO1200. The fractured surface of nanocomposites with 0.25 and 1 wt.% of GO1200 are shown as example (Figure 6 B and 5C, respectively).

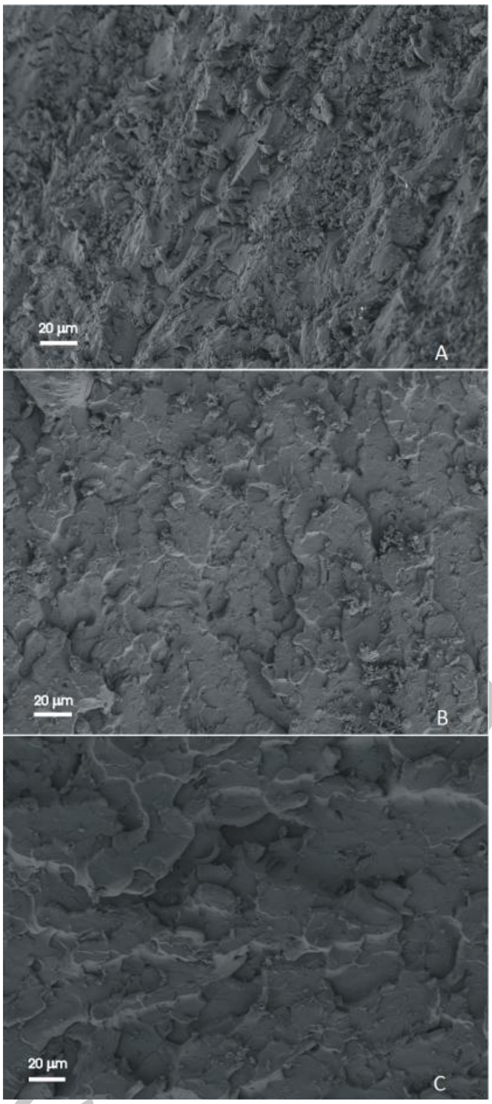

Figure 6: SEM images of fractured surfaces of pure epoxy (A), epoxy with 1.0 wt.% of GO1200 (B), and epoxy with 0.25 wt.% of GO1200 (C).

4. Conclusions

An innovative method for synthesis of GO/epoxy composites suitable for upscaling to industrial size has been presented. In the final stage of the GO synthesis a viscous suspension of GO in water or another highly polar solvent can be obtained and applied directly for preparation of the composite. This is extremely important since dried graphite oxide can only be re-dispersed on nanoscale in water, usually with the application of ultrasound, so the unique properties such as a high surface-to-mass ratio are lost. Using the as-prepared dispersion to prepare polymer nanocomposites is therefore a much better solution.

GO samples were synthesized and prepared as the dispersions in methanol with a concentration of about 8 wt.%. The dispersion was mixed with the amine hardener and methanol was then removed in vacuum. The amine groups from the hardener reacted with the epoxy groups on the surface of GO, what was confirmed by the reduced reaction enthalpy during curing with epoxy resin. Nevertheless, the modified GO particles increased the crosslinking density, resulting in the smaller solvent uptake and increased glass transition temperature of the nanocomposite. The size of the GO nanoparticles influenced the mechanical properties of the nanocomposites. Young’s modulus increased more when smaller GO particles were added to the epoxy resin, while the tensile strength increased for about 10 % only by the addition of larger particles. The optimum concentration of GO was found to be 0.25-0.50 wt.% since above this concentration the material became more brittle. The technique is rather easily scalable and represents an alternative to classical methods for preparation of epoxy composites with improved mechanical properties.

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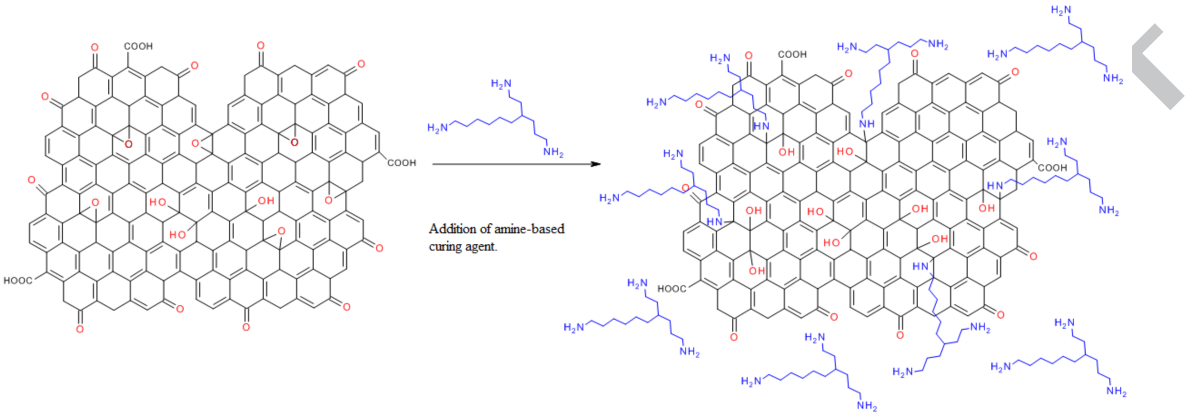
Graphical abstract



Slurry of graphene oxide in methanol after the synthesis.

Slurry of modified graphene oxide in curing agent after methanol removal.

Highlights

Graphene oxide is used without drying after the synthesis.
Surface of GO is modified with curing agent.
Selective plasma etching was used to characterize GO dispersion in epoxy.
The influence of GO particle size on properties of nanocomposites is determined.