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Epoxy-graphite oxide nanocomposites: Mechanical properties

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ABSTRACT: Graphite oxide (GO) produced by Hummers method was added to epoxy for strengthening purpose. Generally the *E*-modulus was increased due to the GO addition; however, depending on the treatment of the GO an increase or decrease was observed for the glass transition temperature. The change in glass transition was a result of changes in the curing behavior. Addition of GO initially increased the curing speed; however, the final curing degree was lower and was dependent on the type of GO added. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43591.

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INTRODUCTION

Graphene and many graphene-derived carbon compounds like carbon nanotubes have excellent mechanical properties and high electrical and thermal conductance. Graphene, as nanofillers, are used to improve mechanical properties and produce electrical conducting polymers. Due to the much lower price the focus in the research have during the last years shifted from carbon nanotubes toward graphene. Graphene can be produced by various methods, where reduction of graphite oxide (GO) is the dominant route to produce graphene in large quantities.[1] GO is produced from graphite subjected to strong water-free oxidizing agents.[2] Graphene have further advantages making the polymer more flame retardant and decreases the gas permeation.[3]

In this work the idea is to incorporate the graphene into the epoxy network with the purpose of improving the mechanical properties of the composite material. Two routes will be tried. One is adding GO to epoxy in order to form covalent bonds and integrating the GO into the epoxy network. The GO contains many different carbonyl groups, such as carboxylic, hydroxyl, and epoxide groups.[4] In thermosets like epoxy these groups might form covalent bonds to the polymer system. It has also been documented that amines can react with the epoxide groups on the GO.[5] Most experimental works has been studying nanocomposites with graphene produced by several methods including reduction of GO. This is partly because the GO is unstable and start to decompose at temperatures as low as 100 °C but also because GO is electrically insulating so for the production of electrically conducting polymer reduced GO must be used. Incorporation of unreduced GO into epoxy has been done in order to increase the flame retardancy.[6,7] In this study the epoxy being used is a low temperature curing type of epoxy, so it is assumed that no decomposition of the GO is taking place during the curing. The other route to incorporate the graphene into the epoxy network is by grafting the GO with the epoxy resin. In both cases the GO will be added in large quantities (1 and 3% by weight).

Hu *et al.* produced epoxy nanocomposites with dopamine reduced GO (DPA-GO). Adding 1 phr (part per hundred resin) DPA-GO increased the storage modulus and the glass transition temperature.[8] Naebe *et al.* produced thermally reduced and modified GO to enhance the dispersion and the interfacial strength in epoxy. An increase of 22% of the flexural modulus was observed by addition of only 0.1 wt % modified graphene.[9] Rafiee *et al.* observed a 50% increase in Young's modulus and 60% increase in fracture toughness (K_{IC}) when adding 0.125 wt % thermally reduced GO.[10] Tang investigated the effect of dispersion of thermally reduced GO on the mechanical properties of epoxy nanocomposites containing up to 0.2 wt % reduced GO.[11]

Fang *et al.* attached long-chain aromatic amines to GO that was reduced with hydrazine. The attachment was chemically similar to the hardener. In this way they could get good dispersion and also a good interfacial strength between the epoxy matrix and the graphene. They observed increases of flexural modulus, flexural strength and toughness of 60.2, 54.1, and 72.7%, respectively when adding 0.4 wt % amine modified graphene.[12]

GO has been used as catalyst for *in situ* polymerisation.[13–15] Yousefi *et al.* have compared the incorporation of unreduced

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Table I. Epoxy Equivalents for the Resin with GO

	Resin 117	Resin 117 + 1% GO-EtOH	Resin 117 + 3% GO-EtOH	Resin 117 + 1% GO-117	Resin 117 + 3% GO-117
Epoxy equivalent	170	193	230	173	180
Resin/hardener ratio	100:34	100:30	100:25	100:33	100:32

and *in situ* reduced GO in an epoxy resin. They found superior strengthening of the *in situ* reduced GO compared with the unreduced.[16] Wan *et al.* grafted diglycidyl ether of bisphenol-A to unreduced GO for functionalization and observed improved dispersion and mechanical properties in an epoxy resin.[17]

EXPERIMENTAL

Production of GO-EtOH

GO was produced by a modified Hummers method.[18] About 40 mL of concentric $H_2SO_4 + 6.6$ mL of 65% HNO_3 was mixed in a 150 mL beaker and cooled in ice-water bath. Stirring was maintained during the whole time, that is, about 4 h. About 1 g of graphite was added and was stirred for 30 min. Six grams of $KMnO_4$ was added slowly to avoid excess heating. Ice was removed from ice-water bath and mixture was slowly allowed to heat to room temperature. Mixture was slowly heated to 40 °C for about 1 h. Water was added slowly to the mixture up to approximately 6–800 mL. About 10 mL of 30% H_2O_2 was added slowly and the solution became yellowish-brown. Suspension sedimented until next day and excess solution were decanted and new water up to 6–800 mL was added. The mixture was bath sonicated for 1 h and ultra-centrifuged to remove water. The addition of water, bath sonication and ultra-centrifuged was repeated several times. After this ethanol (EtOH) was used instead of water and cleansing with ethanol was repeated twice. After ultracentrifugation GO-EtOH was achieved. No drying was done as it was observed that dispersion in solvents afterward was problematic if the sample had been dried.

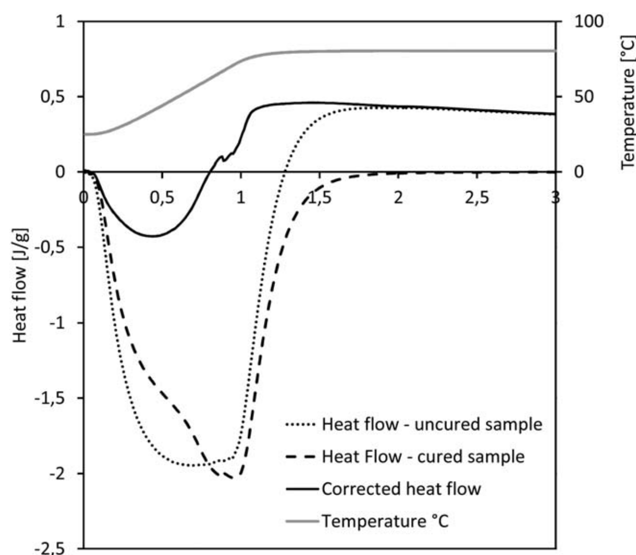

Figure 1. Heat flow during curing of epoxy.

Production of GO-117

GO-EtOH was modified by reaction with the epoxy resin, that is, Bisphenol A/F Diglycidyl Ether according to the recipe by Eitan *et al.*[19] The GO-EtOH was dispersed in acetone and epoxy resin Proset 117 was added. Two NaOH pellets were added as a catalyst and the mixture were heated to 70 °C for 1 h for the GO-EtOH to react with the resin. The mixture was cleansed three times with ultrasonication in acetone followed by ultracentrifugation, and finally once in tetrahydrofuran. The modified GO is called GO-117 in the article.

Epoxy Composites Fabrication

The nanocomposites were fabricated using the respective GO and a commercial epoxy Proset-117/229PF. The epoxy resin Proset 117 contains 30–60% Diglycidyl Ether of Bisphenol A (DGEBA), 30–60% Diglycidyl Ether of Bisphenol F resin, and 10–30% butanendioldiglycidyl ether. The epoxy hardener Proset 229PF contains 60–100% Polyoxypropyleneamine and 10–30% Methylene-di(cyclohexylamine). The mixing ratio is 100:34 by weight. This epoxy is used for infusion processes and has a viscosity of 220 mPa s at 25 °C right after mixing.

The required amount of GO were dispersed in acetone for 0.5 h using an 80 W ultrasonic rod generator to form a suspension; an ice bath was used to keep the suspension cold during sonication. The nanotube suspension was then poured into 100 parts by weight of epoxy resin, and ultra-shear mixed for 30 min. Afterward the acetone was evaporated at 45 °C until all the solvent were evaporated which was verified by weighing the blend.

The epoxy equivalent was measured according to ISO 3001. For the neat epoxy the resin/hardener ratio is 100:34; knowing the

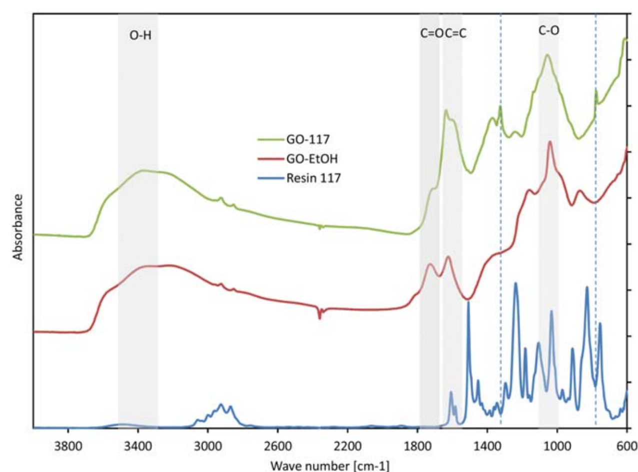

Figure 2. FTIR spectra of the produced GO, the modified GO and epoxy resin 117. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

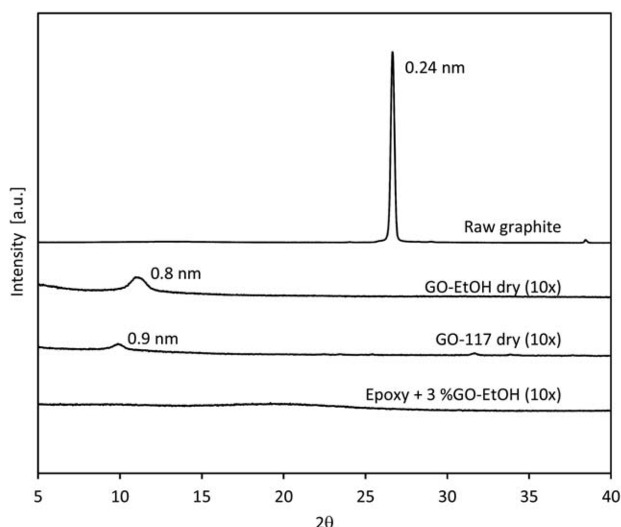

Figure 3. XRD spectra of graphite, the two GO types, and epoxy + 3% GO-EtOH.

epoxy equivalent of the resin and the mixtures the right resin/hardener ratio for the mixtures was calculated and shown in Table I. After adding the hardener the GO/resin mixture were stirred under vacuum to prevent introduction of air bubbles. Dog bone test specimens (ISO 527-2, specimens type 1BA) were obtained by casting the resin/hardener mixture in a silicon mould, specimens was pre-cured at room temperature for 24 h and post cured at 80 or 120 °C for 16 h. The cured samples were 80 mm long, 4.8 mm wide, and 2–3 mm thick. The samples were finally ground to a uniform sample thickness of approximately 1.4 mm.

FTIR Analysis

FTIR analyses were performed using a Bruker LUMOS FT-IR microscope in ATR mode with a germanium crystal.

XRD Analysis

XRD analysis was performed on a Panalytical Empyrean XRD using Cu *Kα*.

Tensile Testing

For the tensile testing the ground samples were used. The measured data are the average of five samples. The tensile testing

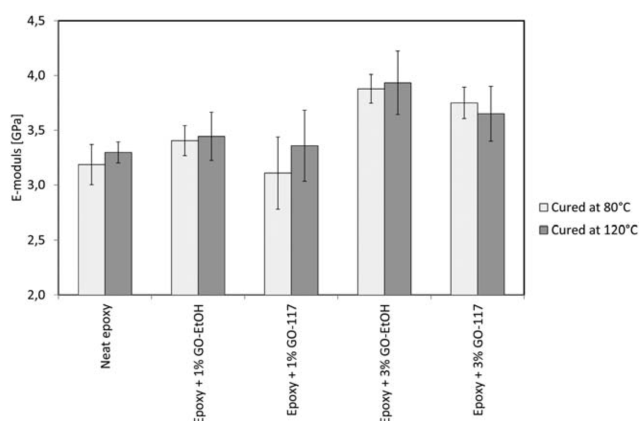

Figure 4. *E*-modulus of the cured neat epoxy and the epoxy composites.

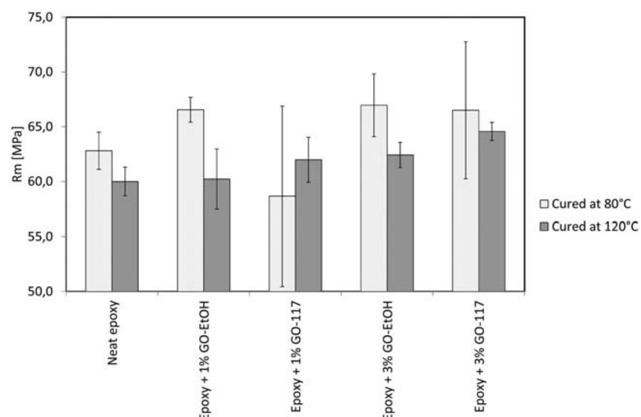

Figure 5. Tensile strength of the cured neat epoxy and the epoxy composites.

machine was a Zwick Z100 equipped with a 5 kN load cell and an incremental clip-on extensometer. The strain rate was 1 mm/min with a sample length of 65 mm.

DSC–Glass Transition Temperature

The glass transition temperature and possible post curing of the GO reinforced epoxy composites were measured with Differential Scanning Calorimetry (DSC) using TA Q2000 instrument. The measurements were performed in a nitrogen atmosphere at a heating rate of 3 °C/min using modulated DSC ±0.35 °C every 45 s. The samples were heated from 20 to 250 °C, then cooled to 20 °C and second time heated to 200 °C. The glass transition temperature (T_g) was measured as the inflection point on the reversing heat flow curve of three samples.

Dynamic Mechanical Analysis (DMA)

The storage and loss modulus and T_g of the GO reinforced epoxy composites were measured with TA DMA Q800 instrument operating in the three point bending mode at a frequency of 1.0 Hz, strain amplitude of 100 μm and sample length (i.e., distance between supports) of 50 mm. Sample dimension were: length: approximately 60 mm, width: approximately 4.8 mm, and height: approximately 1.4 mm. The data were collected from ambient to 100 °C at a scanning rate of 3 °C/min. The

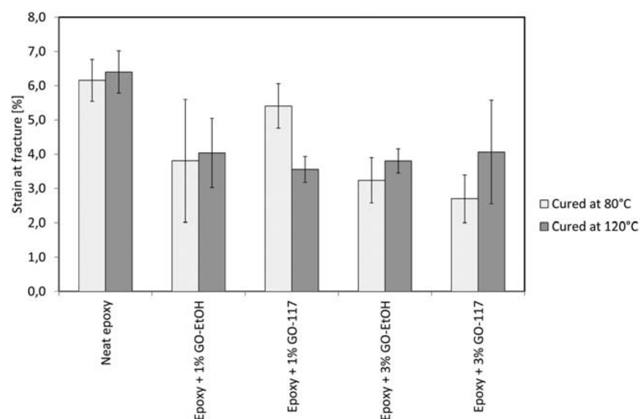

Figure 6. Strain at fracture of the cured neat epoxy and the epoxy composites.

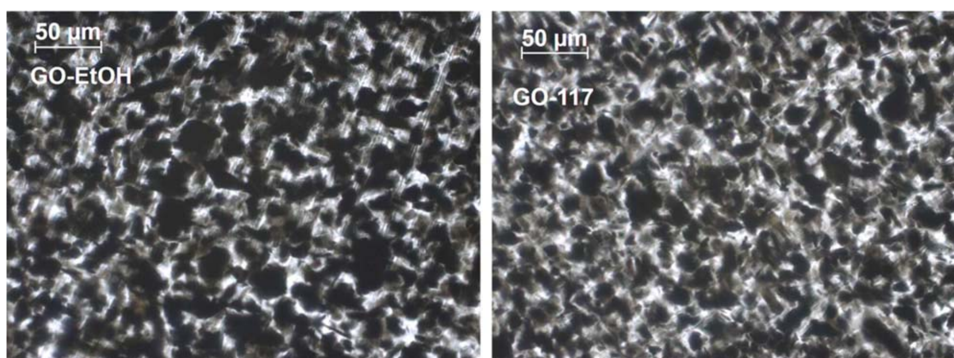

Figure 7. LOM micrographs of the GO epoxy composite with 3% GO. The samples were approximately 30 μm thick. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

glass transition temperature was measured as the peak value of the loss modulus.

DSC–Curing Behavior

The curing behavior of the epoxy–GO mixtures were measured with (DSC) TA Q2000 instrument with the weight of the sample being about 7 mg. The measurements were performed under a nitrogen atmosphere. The samples were heated from 25 to 80 °C at 60 °C/min and held at 80 °C for 1200 min. Then the sample were cooled to 0 °C and second time heated to 200 °C with a heating and cooling rate of 20 °C/min to measure the glass transition temperature and possibly heat of post curing. Finally the sample was again heated from 25 to 80 °C at 60 °C/min and held at 80 °C for 1 h to measure the heat flow necessary to heat the resin during the first curing step. In this way we might be able to extract the heat flow from the heating of the sample from the total heat flow and eventually isolate the heat flow for the curing process itself. During the initial heating from room temperature to the curing temperature heat is used for both heating the sample and the exothermic curing reaction. The heat flow for heating the cured sample at the same experimental conditions can afterward be subtracted from the heat flow of the uncured sample resulting in a corrected heat flow resembling the heat flow due to the curing reaction. However, after curing and especially below the glass transition temperature the heat capacity of the cured sample is lower resulting in an endothermic peak in the corrected heat flow during heating. The endothermic peak is omitted in the further analysis of the curing heat flow. The heat flow of the uncured, the cured sample together with the corrected heat flow can be seen in Figure 1.

Rheological Measurements

The curing process of pure epoxy, epoxy + 3% GO-EtOH 100:25, epoxy + 3% GO-EtOH 100:34, and epoxy + 3% GO-117 was studied under isothermal conditions at 80 °C using oscillatory shear measurements. The measurements were performed with a Paar Physica MCR500 rheometer in plate–plate configuration with a 25 mm diameter disk. The heating system consists of a Peltier heating plate and a heating hood ensuring

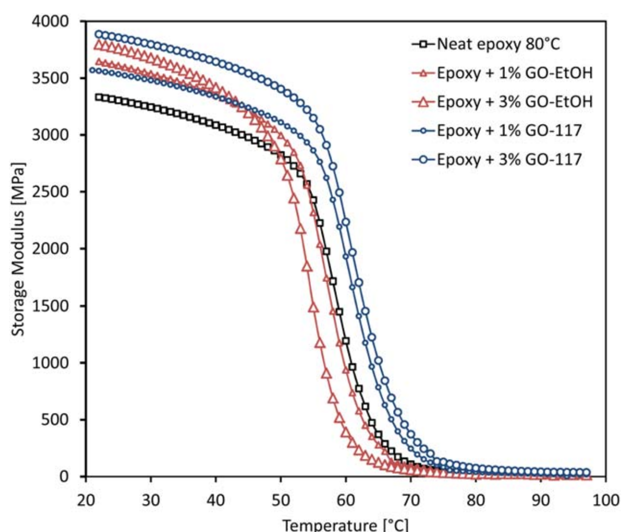

Figure 8. Storage modulus as function of temperature for samples cured at 80 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

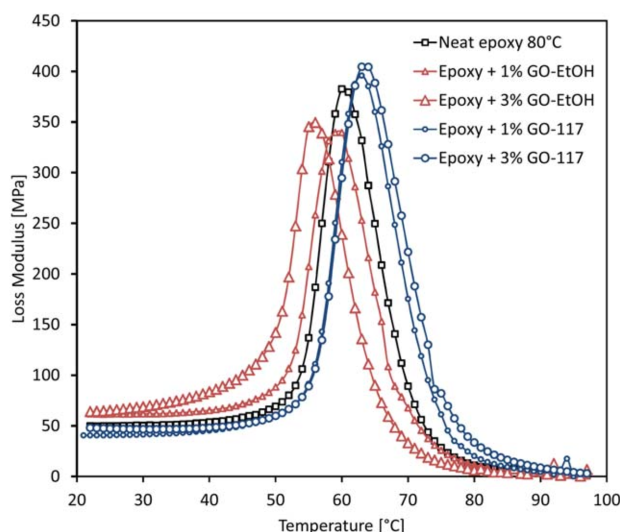

Figure 9. Loss modulus as function of temperature for samples cured at 80 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Glass Transition Temperature from DSC and DMA Measurements together with Residual Heat and the Storage Modulus

	DSC		DMA	
	T_g (°C)	Residual heat (J/g)	Storage modulus @ 25 °C (MPa)	T_g @ peak loss modulus (°C)
Cured at 80 °C				
Neat epoxy	61	0	3304	60.5
Epoxy + 1% GO-EtOH	64	20.4	3612	59.5
Epoxy + 3% GO-EtOH	56	40.1	3736	55.8
Epoxy + 1% GO-117	67	17.8	3535	62.8
Epoxy + 3% GO-117	67	32.7	3856	63.6
Cured at 120 °C				
Neat epoxy	64	0	3323	61.6
Epoxy + 1% GO-EtOH	60	0	3510	61.6
Epoxy + 3% GO-EtOH	52	2.6	3819	55.7
Epoxy + 1% GO-117	65	0	3376	62.8
Epoxy + 3% GO-117	63	0	3734	63.3

isothermal conditions. The development of the storage and loss modulus was recorded during a time test at a frequency of 1 Hz and 5% shear strain; each measured value represents an average over 10 s. The crossover from viscous to elastic dominated behavior is considered to be a measure of the gel point.

RESULTS AND DISCUSSION

GO Characterization

FTIR-ATR spectra were recorded and is shown in Figure 2, and the following functional groups were identified in all samples: O—H stretching vibrations (3420 cm^{-1}), C=O stretching vibration (1730 cm^{-1}), C=C from unoxidized sp2 C—C bonds (1600 cm^{-1}), and C—O vibrations (1050 cm^{-1}). For the GO-117 the C—H stretching at approximately 2900 cm^{-1} is a bit stronger. The C=O band diminishes and the C=C becomes stronger which can indicate that some reduction of the GO has occurred.

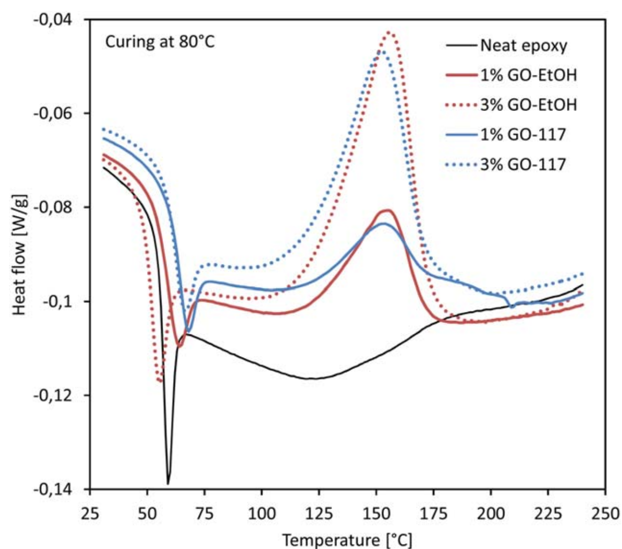

Figure 10. DSC total heat flow for samples cured at 80 °C heated from room temperature at constant heating rate of 3 °C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

XRD in Figure 3 shows the exfoliation taking place from the graphite to the GO. The basal plane (002) reflection at 26° for the graphite disappears and a weak peak appears at 11° corresponding to a layer distance of 0.8 nm. This corresponds to findings by other researchers.[20,21] The modification with 117 gives a slightly larger interlayer distance and the peak intensity weakens indicating further separation. This separation is withheld or perhaps even improved in the composites which can be seen from the absence of peaks in the composite with 3% GO-EtOH.

Mechanical Properties (Tensile Testing)

Adding 3% GO either as GO-EtOH or GO-117 increases the *E*-modulus with 22% for GO-EtOH and 16% for GO-117 as can be seen in Figure 4. Despite the lower degree of curing for the sample with GO-EtOH the largest stiffness is seen with these samples, however the standard deviation is large so the difference between GO-EtOH and GO-117 is not significant.

Looking at the strength the conclusion is not clear partly due to the large standard deviation of the strength values. There might be an increase in tensile strength when 3% GO-EtOH or GO-117 is added. Adding 1% GO-EtOH seems to give a significant increase in the tensile strength; the reason for the behavior is unknown (Figures 5 and 6).

The addition of GO, however, gives a significant decrease in the fracture strain. The standard deviation is generally large indicating that large agglomerates are the cause of the reduced ductility. Looking at the micrographs in Figure 7 the GO is generally well dispersed on a macroscopic point of view. But the size of the GO agglomerates seems to be tenths of micron large. The dispersion is similar to the dispersion observed in other works.[9,19] In these works better dispersion was achieved by using either a surfactant or ball milling of the graphene

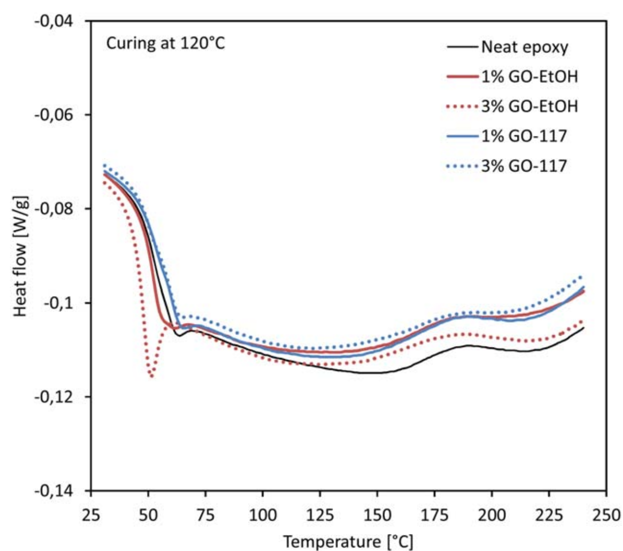

Figure 11. DSC total heat flow for samples cured at 120 °C heated from room temperature at constant heating rate of 3 °C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanosheets. Generally increasing the curing temperature to 120 °C gives no significant change in the mechanical properties.

DMA and DSC

Generally the storage modulus at RT increases as a function of the added amount of GO (Figures 8 and 9). However epoxy with 3% GO-EtOH softens at significantly lower temperatures than the other samples irrespective of the curing temperature. This is in agreement with the glass transition temperatures shown in Table II. Adding GO-117, however, increases the glass

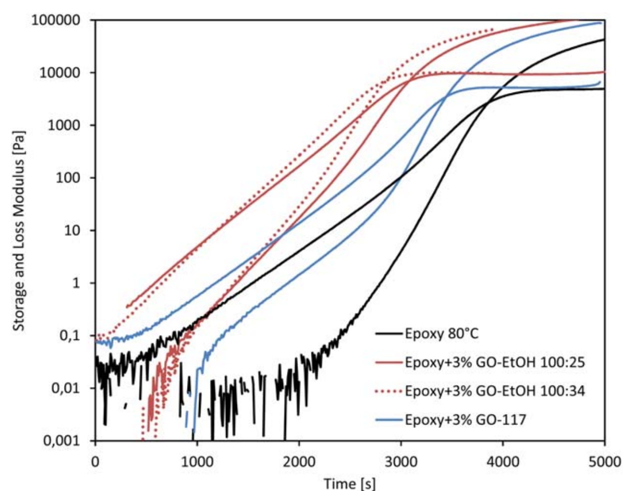

Figure 13. Dynamic mechanical rheological testing of the curing at 80 °C of the epoxy composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transition temperature and the stiffness is retained at higher temperatures. Adding 3% GO-117 results in the best stiffness at high temperature. Srivastiva *et al.*[22] noticed an increase in T_g of 8–10 °C with an addition of as low as 0.125 wt % graphene platelets, whereas we observe only an increase of maximum 6 °C. As can be seen in Table II and Figure 10 adding GO resulted in incomplete curing at 80 °C. From Figure 11 it is clear that curing at 120 °C gives full curing; however, glass transition temperature and the storage modulus were not affected which is evident from Table II. A curing temperature of 120 °C is well above the recommended curing temperature of 80 °C. Possibly some degradation started to take place at low temperatures. In

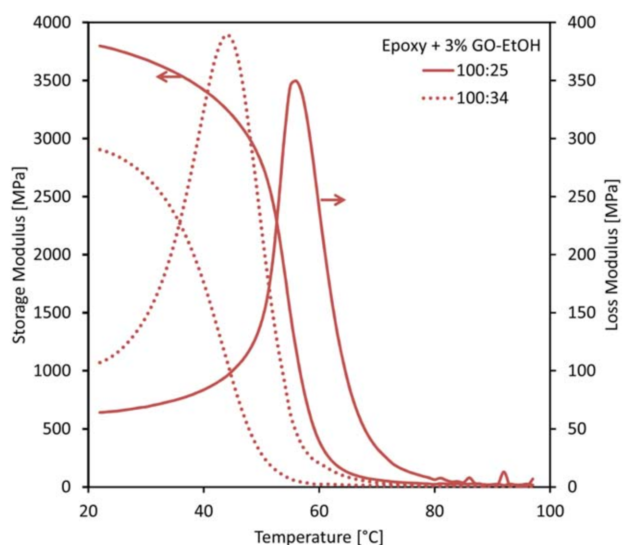

Figure 12. Storage and loss modulus of epoxy with 3% GO-EtOH added the hardener according to the measured epoxy equivalent or the resin specification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

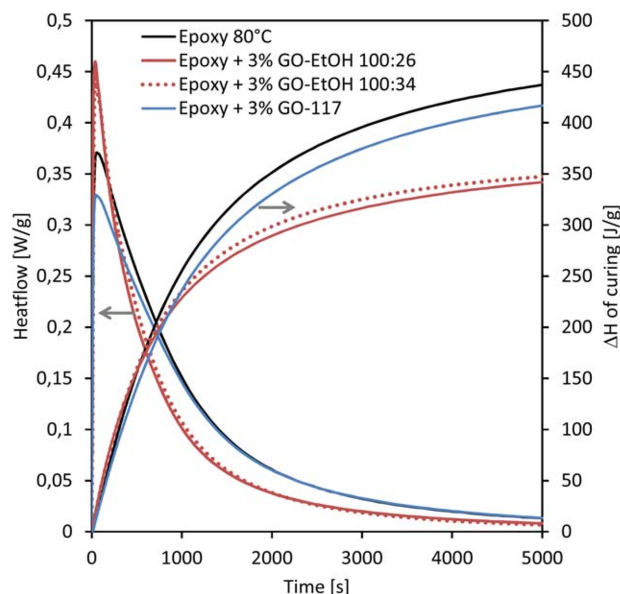

Figure 14. DSC heat flow measured and the integrated heat flow (ΔH) during curing at 80 °C of the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. DSC Measurements Giving Enthalpy of Curing and the Post Curing and Glass Transition Temperature after Curing at 80 °C for 1200 min

	ΔH_{total} at 80°C isothermal curing (J/g)	Residual heat (J/g)	T_g after isothermal curing (°C)
Neat epoxy 80 °C	498.4	–	66.7
Epoxy + 3% GO-117	464.9	18.9	68.0
Epoxy + 3% GO-EtOH 100:26	377.6	27.9	53.9
Epoxy + 3% GO-EtOH 100:34	381.9	23.5	44.4

Figure 11 a small and broad exothermic peak is seen below 200 °C.

The low glass transition temperature of epoxy + 3% GO-EtOH could possibly be explained by the lower degree of crosslinking due to the lower amount of added hardener. It was thus tried to produce epoxy + 3% GO-EtOH with the normal amount of hardener called epoxy + 3% GO-EtOH 100:34. However, the mechanical properties and T_g were inferior as can be seen in Figure 12, where the storage and loss modulus is shown. The extra hardener as compared with the amount according to the epoxy equivalent will probably stay unreacted in the cured sample acting as a plasticizer.

Curing Behavior

Looking at the rheological measurement during curing in Figure 13 it can be seen that the curing proceeds faster for the epoxy containing GO-EtOH—this is also evident from the DSC measurements. In Figure 14 is shown the heat flow and the integrated heat flow, that is, the enthalpy due to the curing reaction and the heat of curing peaks at a higher value for the epoxy with 3% GO-EtOH, but the heat flow decays very fast and is after few minutes lower than epoxy without GO-EtOH. The fast decay can be triggered by the rapid increase in viscosity causing the reaction gradually to be diffusion controlled. Looking at the enthalpy of curing it is clear that the addition of GO-EtOH results in less epoxy bonding being formed which is expected for the blend with less hardener. However, adding the normal amount of hardener has no significant influence on the curing behavior. Adding GO-117 results also in a slightly increased viscosity during the initial stages of curing probably resulting in less curing, but no catalytic effect can be seen. After the isothermal curing at 80 °C the samples were heated to 250 °C at 10 °C/min to see if any post curing took place. Addition of GO results in incomplete curing and some post curing take place during the heating to 200 °C which can be seen from the data in Table III. Adding the heat of post curing to the heat of curing during the isothermal step it can be seen that addition of GO-117 can result in a crosslinking density very close to the neat epoxy, whereas addition of GO-EtOH will result in a lower crosslinking density. Qiu *et al.* using a very different epoxy system [N,N,N′,N′-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) and 4,4′-diaminodiphenylsulphone (DDS)] also noticed a catalytic effect of the curing when adding up to 5 wt % GO to however they noticed no effect of the final degree of curing.[23]

CONCLUSIONS

Adding GO-filler to epoxy increases the *E*-modulus and storage modulus at room temperature. However the fracture toughness decreases probably due to presence of GO-agglomerates.

Addition of unmodified GO accelerates the initial curing of the epoxy; however, it also results in an incomplete curing and, thus, lower glass transition temperature. This might be explained by the higher viscosity of the sample causing the curing to be diffusion controlled at an earlier stage. It might also be caused by a decomposition of the GO during curing.

Adding GO generally lead to an increased epoxy equivalent leading to a lower resin/hardener ratio. The result is a lower crosslinking density. Especially addition of unmodified GO with its large amounts of functional groups changes the epoxy equivalent of the resin mixture and results in lower crosslinking density and lower glass transition temperature and inferior storage modulus at higher temperature. The curing behavior of epoxy with the modified GO (GO-117) is more similar to the curing behavior of neat epoxy and the cured samples have higher storage modulus at higher temperature also compared with the neat epoxy.

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