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POLYBENZOXAZINE BASED NANOCOMPOSITES REINFORCED WITH MODIFIED GRAPHENE OXIDE

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The influence of graphene oxide (GO) functionalized with different organic moieties on ring-opening polymerization of bisphenol A- benzoxazine monomer (BA-a) was studied. Polybenzoxazine nanocomposites (PBZ) reinforced with four types of graphene oxide were synthesized. The polymerization behavior of all GO/PBZ nanocomposites was monitored by both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Thermal stability of nanocomposites was investigated by thermogravimetric analysis (TGA) showing a slight increase of temperature at which mass loss is 3% ($Td_{3\%}$) even if only 1% of graphene oxide is added as reinforcing agent. The modification of thermal properties of the studied nanocomposites is mainly attributed to the intermolecular interactions between GO functionalities and benzoxazine matrix.

Keywords: benzoxazine, thermal curing, ring-opening polymerization, intermolecular interactions

1. Introduction

Polybenzoxazine (PBZ) resins are newly developed phenolic resins [1]. The benzoxazine monomers are obtained by the condensation reaction of three main components, phenol, amine and formaldehyde in 1:1:2 ratio [2]. In order to synthesize the PBZ resins, benzoxazine monomers are usually polymerized by a thermal induced ring-opening reaction [3]. Different types of phenols and amines can be used; therefore, the final properties of cured materials can be easily tailored for a wide range of applications such as aerospace [4] or electronics [5]. Polybenzoxazines are ranked as materials exhibiting excellent chemical resistance and low water absorption. Moreover, polybenzoxazines exhibit high thermal resistance and good dimensional stability [6]. However, despite these unique properties for pure benzoxazine-based monomers feature two main drawbacks

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affect their processability: high curing temperature is required, and final materials exhibit high brittleness. To overcome these significant disadvantages of benzoxazine resins, the incorporation of carbon nanofillers into polymer matrix is frequently reported leading to polybenzoxazine-based nanocomposites as high-performance materials [7].

Graphene has recently attracted an extraordinary attention due to its excellent properties. As a one atom thick planar sheet of sp^2 bonded carbon atoms [8], graphene exhibit large specific surface area [9], thermal conductivity [10], high Young` modulus [11] and excellent electrical conductivity [12].

Graphene oxide (GO) is a thin atomic layered graphene sheet functionalized with oxygen-containing functional groups obtained by chemical oxidation of graphite in the presence of strong oxidizing agents and ultrasonic cleavage [13]. The GO sheet exhibits high flexibility. Also, several studies have shown that GO can decrease the polymerization temperature due to its carboxylic groups [14, 15]. For these reasons GO is considered to be a good candidate for partially cancelling the polybenzoxazine drawbacks and obtain exfoliated nanocomposites with high glass transition temperature values (Tg) and also less brittle than usually produced polybenzoxazines.

2. Experimental

2.1. Materials

The bisphenol A benzoxazine monomer (BA-A) was provided by Huntsman. Acetone was purchased from Aldrich (Germany). In this study four graphene oxides with different types of functionalities were used as received from NanoInnova Technologies (Spain).

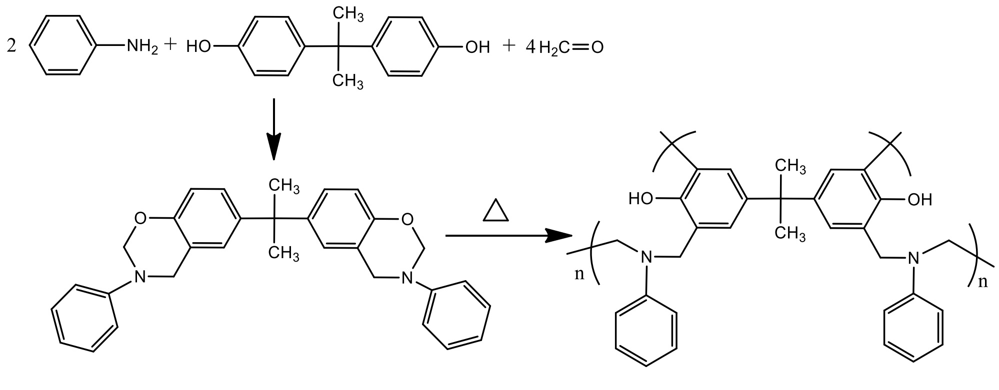
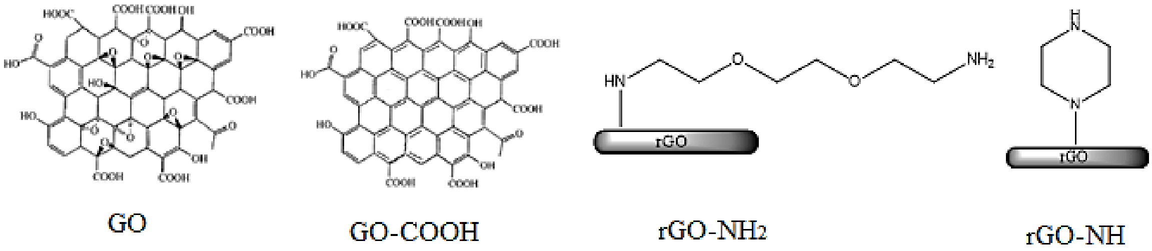


Fig. 1 Synthesis of BA-a monomer and its thermal polymerization process

2.3. Synthesis of polybenzoxazine – graphene oxide nanocomposites

In order to synthesize the polybenzoxazine- graphene oxide nanocomposites the solvent method was employed. 1 wt % of different GO types was dispersed in 5 mL acetone for 15 min. After that 1.5 g of bisphenol A benzoxazine monomer (BA-a) were added and sonicated for 15 min and finally poured in a rectangular Teflon matrix. The solvent was evaporated. The samples were cured for 2 h at 200°C.



GO GO-COOH rGO-NH2 rGO-NH

Fig. 2. Chemical structures of graphene oxides employed

2.4. Characterization techniques

Differential Scanning Calorimetry (DSC) was performed on DSC 402 F1 equipment from Netzsch. The samples were scanned using the non-isothermal method from 20 to 300°C with 10°C/ min heating rate under nitrogen.

The dynamic mechanical analyses (DMA) were recorded on a TRITEC 2000 B instrument. Samples were analyzed in bending mode at 1 Hz frequency. Data were collected from room temperature to 250°C using a heating rate of 5°C/min.

The thermogravimetric analyses (TGA) were recorded on Q500 TA Instruments equipment under air atmosphere using a heating rate of 10°C/min from room temperature to 800°C.

3. Results and disscusion

3.1. Differential scanning calorimetry (DSC)

DSC is a highly sensitive tool which may provide a detailed thermodynamic characterization of neat polymers or polymer composites. In this study, DSC was employed in order to show the influence of different types of graphene oxide on the curing behavior of BA-a.

The typical DSC curing curves as a function of temperature for benzoxazine monomers and benzoxazine/GO nanocomposites are depicted in Fig. 3. By heating up to 300°C the BA-a monomer and the BA-a/GO mixtures were converted into 3D networks. From the thermograms a single exothermic curing signal for all compounds was noticed. As shown in Fig. 3, BA-a exhibited an exothermic peak at 241.5°C assigned to the ring – opening polymerization of the oxazine structure. The incorporation of the four types of GO visibly shifted the curing exothermic peak of BA-a towards a relatively lower polymerization temperatures.

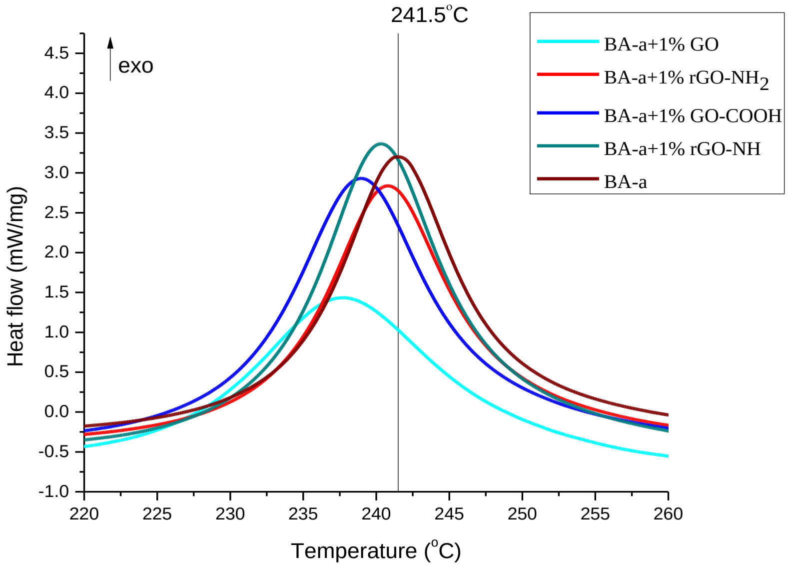


Fig. 3. DSC curves of BA-a resin and different functionalized GO/BA-a compounds

As seen in Table 1 by adding only 1% of GO the curing peak is shifted with ~4°C. As expected, the presence of numerous hydroxyl, epoxy and carboxyl groups from the pristine GO structure acts as a catalyst for the ring-opening polymerization of benozoxazine monomer [16]. Similarly, the addition of GO-COOH led to a lower polymerization temperature of BA-a, but still higher than in the case of GO added due to the small amount of carboxylic groups present on graphene oxide structure.

Table 1

Polymerization temperatures obtained from DSC analysis

Sample	Polymerization temperature (°C)	Polymerization enthalpy (J/g)
BA-a +1% GO	237.7	280.6
BA-a +1% rGO NH_2	240.8	280.7
BA-a + 1%GO-COOH	239	296.3
BA-a +1% rGO-NH	240.3	315.7
BA-a	241.5	307

On the other hand, the DSC results showed that the addition of only 1% reduced amino functionalized graphene oxide did not show a significant change on the polymerization temperature of BA-a as the simple GO or carboxylated GO did. As shown in Table 1 by adding 1% rGO-NH or rGO-NH_2 the polymerization temperature of BA-a decreases with only 1°C or less. Interestingly, even if the curing temperature of BA-a/rGO-NH_2 decreased with less than 1°C, the area exhibited under the exothermic peak is significantly lower than BA-a. This phenomenon could be explained by the fact that the 1% amino-polyethylene glycol functionalities covalently linked to graphene oxide do not catalyze the polymerization of BA-a, but participate as reactants in the crosslinking process.

On the contrary, the incorporation of 1% rGO-NH to the benzoxazine matrix leaded to a notably increase of the polymerization enthalpy compared to rGO-NH_2. This fact is probably due to the more active nitrogen atoms (secondary and tertiary) in the crosslinking process in comparison with rGO-NH_2 which includes only primary nitrogen groups which are less reactive.

3.2. Dynamic mechanical analysis (DMA)

DMA investigation on crosslinking network, molecular motion and glass transition temperature provides valuable information about the intermolecular interaction and thermal properties for all the benzoxazine nanocomposites filled with different types of GO.

The DMA curves of the tan δ as function of temperature for the GO – filled polybenzoxazine nanocomposites are shown in Fig. 4. Tan δ curves were obtained from the ratio of loss modulus (E″) to storage modulus (E′) in a sinusoidal deformation. From Fig. 4 a sharper peak at 193°C attributed to Tg for the neat PBZ was observed, indicating the homogenity of a single polymer networks. Compared to pure PBZ, significantly higher Tg values are noticed for all the graphene – oxide/ PBZ nanocomposites, as shown in Table 2. Intermolecular interactions between functionalized GO and PBZ occurred leading to hydrogen bonds formation between graphene sheets and polymer chains that limit the polymer segment motions for all the studied nanocomposites. Therefore the increase of Tg values may be assigned to the π-π stacking interactions between graphene sheets and benzoxazine matrix. It is also possible that some true crosslinking reactions may occur between amine groups from rGO-NH_2/ rGO-NH and benzoxazine structures which lead to a more rigid network in which nitrogen atoms from rGO-NH_2/rGO-NH are involved in the polymerization of benzoxazine rings. It is noted that all the studied GO/PBZ nanocomposites had relatively broader and lower magnitude of α-relaxation peaks compared to the neat PBZ, indicating a greater network heterogenity in the nanocomposites.

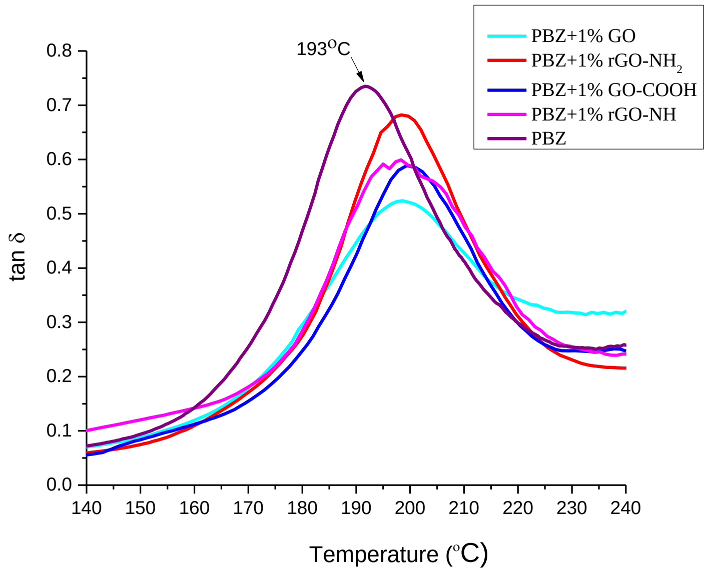


Fig. 4. DMA curves comparing tan δ for BA-a based polymer (PBZ) and different functionalized GO/PBZ compounds

Also it is worth noting that most of the functionalized GO/PBZ nanocomposites exhibit higher values of loss modulus (E″) compared to pure polybenzoxazine which is explained by the contribution of GO functionalities to the polymerization and even crosslinking leading to a dense structure of PBZ. The only exception is rGO-NH/PBZ which exhibits a much lower value of E″ probably due to the heterogeneous structure of rGO-NH/PBZ nanocomposite given by the bulky piperazine rings. The results are in accordance with DSC observations.

Table 2

Glass transition temperatures (Tg) and loss modulus (E″) obtained from DMA

Sample	Tg (°C)	E″ (°C)
PBZ +1% GO	198.6	173.8
PBZ +1% rGO NH$_2$	198.4	168.1
PBZ + 1%GO-COOH	199.4	171.7
PBZ+1% rGO-NH	198.3	148.6
PBZ	193	167

3.3. Thermogravimetric analysis (TGA)

The thermal stability of all functionalized GO/PBZ nanocomposites and neat PBZ was monitored by TGA (Fig. 5) and the results are summarized in Table 3.

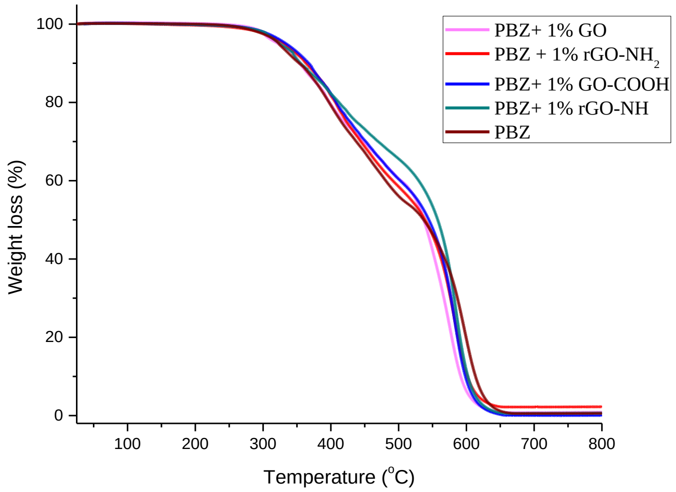


Fig. 5. TGA curves for BA-a based polymer (PBZ) and different functionalized GO/PBZ compounds

Compared to the neat polybenzoxazine, the incorporation of only 1% functionalized GO shows better thermal stability. For all the studied GO/PBZ nanocomposites the TGA curves showed a similar behavior except rGO-NH/PBZ which exhibit a higher thermal stability than all other composites due to the more crosslinked structure obtained in this case (also proved by DMA tests) with large involvement of secondary and tertiary nitrogen atoms in the polymerization process of BA-a (Fig. 5). As shown in Tab. 3 the weight loss temperatures at 3%, 5% and 10 % respectively for nanocomposites exhibit much higher values than neat PBZ due to the higher content of aromatic rings from the graphene oxide structure.

Table 3

Weight loss temperatures for BA-a based polymer (PBZ) and different functionalized GO/PBZ compounds

Sample	Td$_{3\%}$ (°C)	Td$_{5\%}$ (°C)	Td$_{10\%}$ (°C)
PBZ +1% GO	305	322.2	354
PBZ +1% rGO NH$_2$	310.5	330.7	363.4
PBZ + 1%GO-COOH	314.6	334.3	367.5
PBZ+1% rGO-NH	309	325	355.4
PBZ	303.2	316.8	349.4

5. Conclusions

The polybenzoxazine-based nanocomposites synthesized by including various types of GO/rGO showed the major influence played by the GO/rGO type against the polymerization process of benzoxazine and also to the thermal stability of the resulted nanocomposites.

The GO/rGO species generally act as catalysts for the benzoxazine polymerization leading to lower polymerization temperatures. In the case of rGO species with nitrogen based groups, it was noticed that these groups may be involved even in the chemistry of benzoxazine polymerization. This is obviously when considering the Tg values of the obtained nanocomposites, showing higher Tg values for modified GO/rGO included in the final structures.

The contribution of modified GO/rGO to the overall thermal stability of polybenzoxazine-based nanocomposites was pointed out from TGA data showing even possible crosslinking reactions to occur through nitrogen species from rGO-NH_2/rGO-NH.

R E F E R E N C E S

[1]. *H. Ishida, T. Agag*, Handbook of Benzoxazine Resins, Elsevier, Amsterdam, 2011, pp. 3-81.

[2]. *N.N. Ghosh, B. Kiskan, Y. Yagci*, “Polybenzoxazines –new high performance thermosetting resins: Synthesis and properties”, Progress in Polymer Science, **vol. 32**, 2007, pp. 1344-1391.

[3]. *B. Kiskan, Y. Yagci M. Imran*, "Concise synthesis and characterization of unsymmetric 1,3-benzoxazine by tandem reactions," Tetrahedron Letters, **vol. 54**, 2013, pp. 4966-4969.

[4]. *B. Kiskan*, “Adapting benzoxazine chemistry for unconventional applications”, Reactive and Functional Polymers, in press 2017, doi.org/10.1016/j.reactfunctpolym.2017.06.009.

[5]. S. Rimdusit, H. Ishida, “Development of new class of electronic packaging materials based on ternary systems of benzoxazine, epoxy, and phenolic resins”, Polymer, **vol. 41**, 2000, pp. 7941-7949.

[6]. *H. Ishida, D. Allen*, Physical and mechanical characterization of near-zero shrinkage polybenzoxazines, Journal Polymer Science B: Polym. Phys. **vol. 34**, 1996, pp. 1019–1030.

[7]. *H. Ishida, F.H.J. Maurer, C.R. Arza*, "Quantifying dispersion in graphene oxide/reactive benzoxazine monomer nanocomposites," Macromolecules, **vol. 47**, 2014, pp. 3685-3692.

[8]. *A.K. Geim, K.S. Novoselov*, “The rise of graphene”, Nature Materials, **vol. 6**, 2007, pp. 183–191.

[9]. S.*V. Morozov, K.S. Novoselov, A. K. Geim*, “Giant intrinsic carrier mobilities in graphene and its bilayer”, Physical Review Letters, 2000**, vol. 100**, article 016602.

[10]. *A.A. Balandin, S. Gosh, W. Bao*, “Superior thermal conductivity of single-layer graphene”, Nano Letters, **vol. 8**, 2008, pp. 902-907.

[11]. *C. Lee, X. Wei, J.W. Kysar, J. Hone*, “Measurement of the elastic properties and intrinsic strength of monolayer graphene”, Science, **vol. 321**, 2008, pp. 385-388.

[12]. *W. Cai, Y. Zhu, X. Li, R.S. Ruoff*, “Large area few-layer graphene/graphite films as transparent thin conducting electrodes”, Applied Physics Letters, **vol. 95**, 2009, pp. 123115.

[13]. *S. Park, C.W. Bielawski, R.S. Ruoff, D.R. Dreyer*, "The chemistry of graphene oxide", Chemical Society Reviews, **vol. 39, 2010**, pp. 228-240.

[14]. *A.A. Abdala, C.W. Macosko, H. Kim*, "Graphene/polymer nanocomposites," Macromolecules, **vol. 43**, no. 16, 2010, pp. 6515-6530.

[15]. *S.P. Lonkar, A. A. Abdala*, “Applications of Graphene in Catalysis”, Journal of Thermodynamics & Catalysis, **vol. 5**, 2014, pp. 132.

[16]. *J. Dunkers, H. Ishida*. „ Reaction of benzoxazine-based phenolic resins with strong and weak carboxylic acids and phenols as catalysts”, Journal of Polymer Science A: Polym Chem, **vol 37**, 1999, pp. 1913–21.