

# Polybenzoxazine – Based Hybrid Composite Materials

## – Summary –

The doctoral thesis includes the following main chapters: 1. Presentation of the doctoral theme. Concepts and methods; 2. Published research articles in extenso; 3. General conclusions; 4. Original contributions; 5. Dissemination; 6. References.

**Keywords:** polybenzoxazine, graphene oxide, polymerization, nanocomposites.

**The first chapter of the thesis** presents the doctoral theme and a critical study of the literature in the field in order to expose the properties of the graphene oxide and polybenzoxazine materials. In the continuation of this chapter the objectives of this doctoral thesis are defined as well as the concepts, respectively the methods used for the development of the original research:

**Objective 1 1:** The influence study of different GO types on benzoxazine thermal polymerization

**Objective 2:** Synthesis of benzoxazine monomers directly onto different GO surfaces

**Objective 3:** Physical and chemical characterization of the novel polybenzoxazine/GO based nanocomposites

In order to achieve the mentioned objectives, *two main synthesis concepts* were used, focusing mainly on the covalent functionalization of benzoxazine monomers directly on the structure of functionalized graphene oxide.

**The first concept** used for the preparation of the nanocomposite materials refers to the use of the physical dispersion method of the graphene oxide layers functionalized with various organic groups in a solvent, followed by their homogenization in the benzoxazine matrix. In this way, nanocomposites based on polybenzoxazines containing 1% wt GO were prepared by directly introducing the reinforcing agent into the polymer matrix.

**The second concept** refers to the chemical modification of the surface of graphene oxide in order to directly form benzoxazine rings by establishing covalent bonds between the two components. In this regard, several types of graphene oxide have been used and several covalent functionalization strategies have been developed for the decoration of graphene oxide with numerous benzoxazine structures that can be subsequently polymerized to obtain new types of nanocomposites with exfoliated structure.

**In the second chapter** of the doctoral thesis are presented the published articles in extenso as a result of the original research:

1. I. Bîru, C.M. Damian, S.A. Gârea, H. Iovu, Benzoxazine-functionalized graphene oxide for synthesis of new nanocomposites, European Polymer Journal, 83 (2016), 244-255, IF=3.862.

2. E. I. Bîru, C. Andronescu, S. A. Gârea, H. Iovu, Polybenzoxazine based nanocomposites reinforced with modified graphene oxide, U.P.B. Scientific Bulletin Series B, 79, 4 (2017), ISSN 1454-2331.
3. E. I. Bîru, S. A. Gârea, A. Nicolescu, E. Vasile, H. Iovu, Advanced Polybenzoxazine Structures Based on Modified Reduced Graphene Oxide, Polymers, 10, 4 (2018), 941, IF=3.426.
4. E. I. Bîru, S.A. Gârea, H. Iovu, Innovative hyperbranched polybenzoxazine-based graphene oxide – poly(amidoamines) nanomaterials, Polymers, 12, (2020), 2424, IF= 3.426.

**In the third chapter** are presented the general conclusions of the doctoral thesis on the synthesis of nanocomposites based on polybenzoxazines and functionalized graphene oxide. Experimental results published in the aforementioned articles have shown that graphene oxide is a reinforcing agent with promising results for improving the thermal or mechanical properties of polybenzoxazines. By introducing only 1% wt. functionalized graphene oxide in the benzoxazine matrix, changes regarding the polymerization temperature of benzoxazine rings were observed during the formation of crosslinked structures containing graphene sheets dispersed in the mass of polybenzoxazine. Moreover, it has been observed that graphene oxide is an optimal platform for the synthesis of new types of benzoxazine monomers directly on the surface of these carbon layers, by using graphene oxide as the main reactant in the synthesis. In this way, studies were performed to improve the compatibility between the polybenzoxazine matrix and graphene oxide in order to obtain nanocomposites with exfoliated structure. Thus, it has been observed that the introduction of chemically modified graphene oxide in the polybenzoxazine matrix influences the thermal properties so that the thermal stability of the materials is considerably increased. Moreover, graphene oxide can catalyze the polymerization process leading to lower temperatures for opening the benzoxazine rings. The arrangement of the graphene layers in the polybenzoxazine matrix and the degree of exfoliation is determined by the type of polymerization performed within these structures. Thus, the benzoxazine monomers formed on the structure of graphene oxide can polymerize either inside the graphene layers (*in-graphene polymerization*) or outside the graphene layers (*out-graphene polymerization*). These two new polymerization concepts have been established based on the experimental results obtained for the synthesized materials and bring major contributions to the field of nanocomposites based on polybenzoxazines and graphene oxide. The polymerization behavior of the synthesized benzoxazine monomers greatly influences the mechanical properties of the materials and new strategies have been developed for the formation of multiple benzoxazine rings on the surface of graphene oxide to improve the final performance of the materials.

**The fourth chapter** presents the original contributions of the thesis in the field of nanocomposites based on polybenzoxazines and graphene oxide. The personal contributions made to these subjects are structured as follows:

### *1. Polybenzoxazine based nanocomposites reinforced with modified graphene oxide*

In this study, a di-functional benzoxazine monomer was synthesized by the condensation reaction between aniline, bisphenol A and formaldehyde, and for the first time in the literature the influence of four different types of graphene oxide on the polymerization temperature of the monomer and thermal properties of final nanocomposites was studied.

The originality of this study consists in the introduction in the polybenzoxazine matrix of two new types of reduced graphene oxide functionalized with different amine groups: reduced graphene oxide functionalized with polyethylene glycol chains and primary amines (rGO-NH<sub>2</sub>) and reduced graphene oxide functionalized with groups piperazine (rGO-NH) respectively, containing structures with secondary and tertiary amines. Therefore, the study of the polymerization behavior for the benzoxazine monomer synthesized based on bisphenol-A (BA-a) was extended in order to evaluate the influence of the functionalization nature of graphene oxide on the polymerization process. Thermal properties of polybenzoxazine materials containing 1% wt. reduced graphene oxide functionalized with amino groups were evaluated by thermal analysis TGA, DMA and DSC and compared with polybenzoxazine materials containing 1% wt. graphene oxide with oxidized groups.

In this study it was shown that the nature of organic functionalities from the surface of graphene sheets has a major role in the polymerization process of the monomer. From the DSC results on the synthesized materials, a decrease in the polymerization temperature was observed for the BA-a monomer from 241.5°C to 237.7°C in case of the nanocomposites containing graphene oxide with numerous oxidized groups (GO) and up to 239°C for the nanocomposites containing graphene oxide with carboxyl groups (GO-COOH). On the contrary, this decrease in polymerization temperature is very small when the reduced graphene oxide functionalized with amino groups is introduced into the benzoxazine matrix. From the DSC results it was observed that the graphene oxide (GO and GO-COOH) behave as a catalyst for the opening of benzoxazine rings, contributing to the reduction of the polymerization temperature. In the case of the use of rGO-NH<sub>2</sub> and rGO-NH, no major contributions were observed in accelerating the polymerization, but it was shown that the amine groups are consumed during the reaction with the BA-a monomer, which contribute to the crosslinking of polybenzoxazine materials.

It was also observed by DMA analyzes that the T<sub>g</sub> of the synthesized polybenzoxazine is improved by introducing only 1% wt. graphene oxide for all four nanocomposites. However, differences in homogeneity in the composition of the samples were observed compared to the simple polybenzoxazine-based material. The TGA results showed an increase in the thermal stability of the final nanocomposites, especially for composites containing rGO-NH due to the content of piperazine cycles that can take part in the material crosslinking process. This study contributes to the field of polybenzoxazine materials by establishing the influence of each type of graphene oxide on the polymerization of benzoxazine monomer based on bisphenol-A.

## 2. *Benzoxazine-functionalized graphene oxide for synthesis of new nanocomposites*

In this study, new methods were developed for the synthesis of benzoxazine monomers directly on the surface of graphene oxide functionalized with carboxylic groups (GO-COOH). For the first time, the surface of GO-COOH layers were used directly in the synthesis of benzoxazine monomers and new strategies were established to improve the yield of monomer formation directly on the surface of graphene planes. This study proposes original methods for the synthesis of benzoxazine monomers directly onto graphene oxide surface through covalent bonds.

The carboxyl groups displayed on the GO edges were modified by reaction with a hydroxylamine (tyramine) to form numerous phenolic groups on the surface of the graphene planes. This process was performed using two innovative methods: 1) activation of carboxylic groups in order to react with the amine groups from the tyramine structure, using the EDC / NHS activation system and 2) chlorination of carboxylic groups in the presence of thionyl chloride (SOCl<sub>2</sub>), followed by reaction with tyramine.

The successful modification of GO-COOH with tyramine units containing phenolic structures was confirmed by FT-IR analysis, which showed that using the EDC/NHS method only 12% of the -COOH groups were transformed into amide groups. On the contrary, the use of the SOCl<sub>2</sub> method led to a much higher reaction yield (70%), influencing the properties of the final materials. The formation of benzoxazine monomers was confirmed by <sup>1</sup>H-NMR and XPS analyses that showed important differences between the final materials, the hybrid monomer obtained by the SOCl<sub>2</sub> method exhibiting an increased tendency of polymerization. The thermal properties of the materials were investigated by TGA showing a better thermostability of the benzoxazine functionalized materials compared to raw and intermediary compounds. A more pronounced increase in thermal stability was observed for materials obtained using the SOCl<sub>2</sub> method, due to the introduction of a higher number of aromatic rings in the structure, the results being correlated with the FT-IR analysis. The exfoliation process of the final materials was investigated. A higher tendency of exfoliation of graphene layers in the polybenzoxazine matrix was observed in the case of materials obtained by the SOCl<sub>2</sub> method. These results obtained by XRD analysis and TEM images are consistent with the <sup>1</sup>H-NMR results which showed that the materials obtained by this method have a higher tendency to polymerize by opening the benzoxazine rings.

Moreover, the polymerization behaviour for the final materials was established. It was shown that the benzoxazine monomers located on the same plane of GO layers can polymerize inside the graphene layers (*in-graphene polymerization*) or outside the graphene layers, the polymerization taking place between monomers located on the surface of different graphene sheets (*out-graphene polymerization*). These two new concepts were first introduced in the literature and provide valuable information on the thermal and mechanical behaviour of final materials.

## 3. *Advanced polybenzoxazine structures based on modified reduced graphene oxide*

Hybrid materials based on reduced graphene oxide and benzoxazine monomers were developed in this study. The novelty of this study consists in the use of reduced graphene oxide functionalized with polyethylene glycol and primary amine chains (rGO-NH<sub>2</sub>) and graphene oxide functionalized

with tetra-pentylamine groups (rGO-TEPA) directly in the synthesis of benzoxazine monomers, as an amine component necessary for the formation oxazine cycle. For the first time, these reduced graphene oxide structures were used in the benzoxazine Mannich condensation reaction. Presenting primary amines on the surface, both types of reduced graphene oxide were reacted with phenol and formaldehyde, finally obtaining benzoxazine structures. The success of the functionalization reaction was demonstrated by chemical analyses of FT-IR, XPS and <sup>1</sup>H-NMR showing the presence of signals characteristic of the benzoxazine monomers. The thermal properties of the synthesized materials were investigated by DSC and TGA thermal analyses showing a better thermal stability compared to the raw materials. Moreover, the process of exfoliation of graphene layers after functionalization was investigated by XRD analysis and TEM images. The structural changes of the carbon layers were investigated by RAMAN spectrometry showing a high degree of disorder of the graphene planes in the obtained nanocomposites, the obtained results agreeing with the XRD and TEM analyses.

#### 4. *Innovative hyperbranched polybenzoxazine-based graphene oxide – poly(amidoamines) nanomaterials*

In this study, original strategies for the synthesis of multiple benzoxazine rings on the surface of graphene oxide were developed.

For this purpose, GO was submitted to the carboxylation reaction to form a higher content of carboxylic groups on the surface of the graphene planes. The carboxylated groups thus obtained were further submitted to the amidation reactions in the presence of poly(amidoamine) dendrimers of different generations (G0, G1, G2) to increase the content of primary amino groups on the GO surface. Subsequently, the amino groups obtained on the GO layers were submitted to the condensation reaction with phenol and formaldehyde to form multiple benzoxazine rings.

The formation of benzoxazine rings on the surface of graphene planes was confirmed by chemical analyses of FT-IR, XPS and <sup>1</sup>H-NMR, showing the decoration of the GO layers with covalently bonded benzoxazine rings. Moreover, the thermal behaviour of these materials was analysed by TGA and DSC, showing a higher thermal stability of the raw materials and a lower polymerization temperature compared to conventional benzoxazines, temperature that decreases as the dendrimer generation increases.

The propagation of the polymerization process can take place in this case between the benzoxazines from the structure of the same dendrimer (*in-dendrimer polymerization*) or between benzoxazines located on different dendrimer structures (*out-dendrimer polymerization*). In this study it was shown that the generation of dendrimer used for the functionalization of graphene oxide significantly influences the mechanical properties of the final materials. As the dendrimer generation was increased, multiple benzoxazine rings were obtained, with a tendency to crosslink the final structure, greatly improving the final properties of the nanocomposites.

The doctoral thesis *Polybenzoxazine - Based Hybrid Composite Materials* presents a high degree of originality by developing new strategies for the synthesis of benzoxazine monomers directly on

the surface of different types of chemically modified graphene oxide structures. Several strategies for the synthesis of hybrid monomers have been developed, and the results obtained will greatly influence the methods of obtaining materials on polybenzoxazines and graphene oxide.

**The fifth chapter** of the doctoral thesis presents the publications resulting from this paper and the dissemination of results at national and international conferences.