Synthesis and characterization of polybenzoxazine/layered double hydroxides nanocomposites

C. Andronescu [a], S.A. Garea [b], E. Vasile [c], H. Iovu [b],*

[a] Department of Bioresources and Polymer Science, University "Politehnica" of Bucharest, Calea Victoriei 149, 010072 Bucharest, Romania
[b] Advanced Polymer Materials Group, University "Politehnica" of Bucharest, Calea Victoriei 149, 010072 Bucharest, Romania
[c] Department of Oxide Materials Science and Engineering, University "Politehnica" of Bucharest, 1-7 Gh. Polizu, 011061 Bucharest, Romania

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ABSTRACT

New polybenzoxazine/LDH nanocomposites were synthesized using three types of LDH (layered double hydroxides) and various LDH concentrations (1, 5, 10 and 30% wt.). Microcomposites were obtained if unmodified LDH (LDH A or LDH B) was used, while exfoliated nanocomposites were produced if modified LDH with sodium dodecyl sulfate (SDS) was employed. The influence of LDH on the benzoxazine polymerization was investigated by DSC showing a catalytic effect on the polymerization process, which is quite significant if LDH–SDS is used, a decrease with ∼20° of the temperature corresponding to the maximum rate of polymerization being noticed. XRD, SEM and TEM were employed to determine the morphology of the composite materials. Thus high exfoliation degree was revealed for 5% LDH–SDS. The introduction of LDH in the polybenzoxazine matrix decreases the thermostability of the neat resin considering the value of the temperature at which the mass loss is 1% ($T_{d1\%}$), but stabilizes the composite material at higher degradation stages promoting the residual char formation. The best thermal properties were achieved for the exfoliated nanocomposites containing 5% LDH–SDS, a good interaction between LDH–SDS and polybenzoxazine being the key factor for the overall properties of the nanocomposites.

1. Introduction

Polybenzoxazine resins were first obtained in 1994 by Hatsuo Ishida and Xin Ning who synthesized a difunctional benzoxazine monomer from Bisphenol A, methyl amine and formaldehyde [1] following a procedure described by Holly and Cope in 1944 [2]. The crosslinked resin presented a Tg over 200 °C. The polymerization of the benzoxazine monomers can be done either by thermal or catalytic ring-opening process [3,4]. Different benzoxazine monomers were developed since then and polybenzoxazine with improved properties were reported [5].

Various nanocomposites based on polybenzoxazine resins were developed using different reinforcing agents like montmorillonite (MMT) [6], graphene oxide [7], carbon nanotubes [8] or polyhedral oligomeric silsesquioxane [9].

For polybenzoxazine/MMT nanocomposites it was shown that the compatibility of the polybenzoxazine matrix with the modified MMT dictates the effect of the clay on the mechanical properties of the resin. Thus if a good compatibility is achieved the Tg may increase [10]. The studies revealed that the organophylic clay may act as catalyst for the benzoxazine polymerization process, the starting polymerization temperature decreasing even with 50 degrees [11].

Layered double hydroxides (LDH) exhibit a chemical structure of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}]^{x+}[A^{m-}]^{x-}_{x/m}\ 2H_2O]$, including a divalent metal ion M^{2+} (Mg^{2+} or Zn^{2+}), a trivalent metal ion M^{3+} (Al^{3+} or Cr^{3+}), an anion A^{m-} having the valence "m" (CO_3^{2-}, Cl^- or NO_3^-), the value of x ranges from 0.2 to 0.33 being equal to the molar ratio between M^{3+} and ($M^{2+} + M^{3+}$) [12]. LDH show anionic exchange capacity making thus possible the removal of interlayer ions without destroying the LDH structure. LDH are similar to MMT showing: similar geometries, high aspect ratio, nanometer – thin layered platelet particulates. LDH have opposite charges and higher charge density than MMT. The high charge density arises from the strong interlayer electrostatic interactions between Mg and Al oxide platelets. The intercalation of organic molecules is quite difficult due to this high charge density and also due to the low rate of the anionic exchange reaction. Other important properties of these anionic clays are the easy synthesis, high bond water content, no toxicity and "memory effect".

LDH were used as reinforcing agent in different polymeric matrix like: polypropylene [13,14], polyethylene [15,16], polyurethane

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* Corresponding author. Tel.: +40 21 402 3922; fax: +40 21 311 1796.
E-mail address: iovu@tsocm.pub.ro (H. Iovu).

[17], ethylene propylene diene terpolymer [18], poly (vinyl alcohol) [19], epoxy [20], poly (methyl methacrylate) [21]. Usually LDH were used to improve the flame retardant properties of nanocomposites compared to the neat polymer. Also an enhancement of mechanical properties for the polymer matrix was reported.

Until now no study regarding the synthesis of polybenzoxazine/ LDH nanocomposites was published. The aim of our work was to synthesize new polybenzoxazine/LDH nanocomposites in order to combine the properties of polybenzoxazine matrix with those of LDH. Three different types of LDH, two commercial ones and one modified with organic anion were used in this study. The influence of different amounts of LDH on the benzoxazine polymerization was studied. Also the effect of LDH on the Tg and thermostability of the polybenzoxazine was investigated.

2. Experimental

2.1. Materials

The benzoxazine monomer, 6,6′-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine) – Araldite MT 35600 was kindly provided by Huntsman. Hydrotalcite synthetic (MgAl-LDH), $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, sodium dodecyl sulfate (SDS) and acetone were purchased from Aldrich. MgAlZn-LDH was received from Baerlocker Germany. The LDH from Aldrich was noted with LDH A (Mg:Al ratio = 3:1) and the LDH from Baerlocher with LDH B (Mg:Zn:Al ratio = 1.52:0.25:1). Both LDH include carbonate anions inside the galleries.

2.2. Synthesis of modified LDH

The LDH–SDS was synthesized according to a method described in the literature [22]. Thus 9.6 g $Mg(NO_3)_2 \cdot 6H_2O$ and 4.7 g $Al(NO_3)_3 \cdot 9H_2O$ were solved in 45 ml H_2O. 4 g of SDS and 3.4 g of NaOH were solved in 40 ml H_2O. The two solutions were added dropwise to 50 ml H_2O maintaining the pH around 10. After this, the mixture was aged for 18 h at 80 °C. The resultant precipitate was then filtered and washed with hot water (80 °C) and dried for 48 h at 80 °C. The resulted material was noted LDH–SDS (See Scheme 1).

2.3. Synthesis of micro/nanocomposites

The solvent method was used to synthesize the composite materials. Thus 1 g of Araldite 35600 was solved in 5 ml acetone. Different amounts of LDH were added: 1, 5, 10 and 30% wt. The mixture of benzoxazine monomer and LDH was sonicated for 30 min and then poured in a rectangular Teflon matrix. The acetone was evaporated. The samples were cured for 2 h at 180 °C and 2 h at 200 °C.

2.4. Characterization

FT-IR spectra were recorded on a BRUKER VERTEX 70 spectrometer in 500–4000 cm^{-1} region using KBr pellets.

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

The Dynamic Mechanical Analysis (DMA) tests were run on a TRITEC 2000 equipment using 5 °C/min heating rate at 1 Hz frequency in the 25 °C–250 °C temperature region.

Thermogravimetric analyses (TGA) were done on a Q500 TA instrument from 30 to 720 °C using air. The heating rate was 10 °C/min.

X-ray diffraction (XRD) spectra were registered on a Panalytical X'PERT MPD X-ray Diffractometer, in the range 2θ = 1–40. An X-ray beam characteristic to Cu Kα radiation was used (λ = 1.5418 Å).

Scanning electron microscopy (SEM) images were acquired on a Quanta Inspect F (FEI) instrument. Prior to the analysis the materials were fractured in liquid nitrogen. The fresh fractured surface was covered with a gold layer for a better contrast.

Transmission electron microscopy (TEM) images were registered on a Philips CM 120 ST HR-TEM microscope. The sample was embedded in epoxy resin and thin specimens of about 50 nm were cut from nanocomposite blocks. An ultramicrotome equipped with a diamond knife at ambient conditions was employed.

3. Results and discussion

3.1. Influence of LDH on benzoxazine polymerization

The polymerization behavior of benzoxazine monomer in the presence of different types of LDH was investigated by DSC. The DSC curves (Fig. 1) show one exothermic peak which is caused by the benzoxazine polymerization process. For the mixtures containing LDH A and LDH B, the temperature corresponding to the maximum polymerization rate is slightly shifted to a lower temperature if the LDH amount increases. Thus, both types of LDH exhibit a weak catalytic effect on the polymerization reaction probably due to the Al atoms from their surface which may act as Lewis acid sites.

For the mixture of benzoxazine with LDH–SDS a different behavior was observed compared with the other two LDH types. Thus for 1% LDH–SDS the temperature corresponding to the highest polymerization rate is 23 degrees lower than for neat benzoxazine. For higher amounts of LDH–SDS the polymerization process exhibits a maximum rate at higher temperatures (228 °C) but still lower than for single benzoxazine. Generally for LDH–SDS, since a good compatibility is assured by the dodecyl sulfate anion, an interaction between the benzoxazine monomer and the catalytic active centres from LDH is established. If 1% LDH–SDS is used, the dispersion of the LDH in the benzoxazine monomer is better which leads to an increase of the interfacial interaction and thus an enhancement of the LDH catalytic activity on the benzoxazine polymerization process. At higher LDH–SDS amounts the catalytic activity of the LDH–SDS on the benzoxazine polymerization is lower. The suspension benzoxazine monomer – LDH–SDS in acetone is very stable, and its viscosity is increasing. Thus the monomer mobility can be hindered and the penetration of the benzoxazine monomer inside the LDH galleries is not favored leading to a lower interaction between the LDH and the benzoxazine monomer.

3.2. Composite characterization

3.2.1. FT-IR Spectroscopy

The FT-IR spectroscopy was used to identify the changes that occur in the polybenzoxazine structure when different types of LDH are used. The FT-IR spectra are presented in Fig. 2.

The benzoxazine monomer shows the characteristic peaks at 947 cm^{-1} from the oxazine ring attached to the benzene ring, 1232 and 1028 cm^{-1} assigned to the asymmetric and symmetric stretching vibration of C—O—C bond, 1495 cm^{-1} characteristic for disubstituted benzene ring and 754, 692 cm^{-1} attributed to the monosubstituted benzene ring (from aniline). After the polymerization process, the bands from 1232, 1028, 947 cm^{-1} decrease suggesting that the polymerization process took place in the absence or in the presence of LDH using various amounts and different