NANOCOMPOSITES BASED ON A NEW POLYBENZOXAZINE RESIN AND MMT

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Au fost sintetizate mai multe nanocompozite de tipul polibenzoxazina/argilă utilizând un monomer benzoxazinic difuncțional bis [6-benziloxi-3,4-dihidro-2H-1,3-benzoxazinil] difenil metan. Au fost utilizate două tipuri comerciale de montmorilonit MMT-Na şi MMT_CL 20A. Au fost sintetizate nanocompozite pe bază de răşină polibenzoxazinică utilizând acetonă ca solvent. Monomerul a fost polimerizat în prezența argilei. Analizele XRD şi imaginile TEM arată că nanocompozitele prezintă o structură intercalată. Temperatura de tranziție sticloasă şi termostabilitatea polibenzoxazinei nu sunt influențate de prezența argilelor.

Several types of polybenzoxaine/clay nanocomposites have been synthesized using a bifunctional benzoxazine monomer Bis [6-benziloxy-3,4-dihydro-2H-1,3-benzoxazinyl] diphenyl methane. Two commercial types of montmorillonite were used: MMT-Na and MMT_CL_20A. Polybenzoxazine nanocomposites were prepared using acetone as solvent. The monomer polymerization occurs in the presence of the clay. XRD analysis and TEM images show that nanocomposites exhibit an intercalated structure. The Tg and thermostability of the polybenzoxazine resin are not influenced by the presence of clays.

Keywords: polybenzoxazine, nanocomposites, montmorillonite

1. Introduction

Nanocomposites represent a class of composites where the reinforcing agent has nanometric dimensions. Having nanometric dimensions, nanocomposites exhibit superior properties compared to classical microcomposites due to the high specific surface area of the nanometric reinforcing agent and so, to a possible improved level of adhesion between the two phases.

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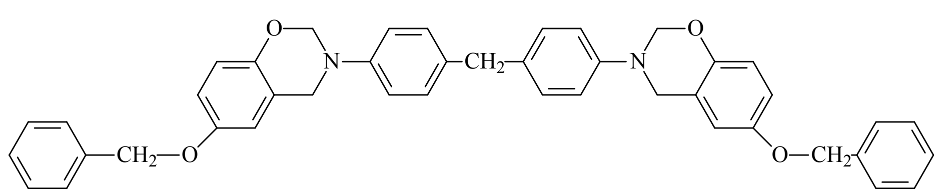
The nanocomposites based on polymers and layered silicates (clays) were developed in the last years due to their properties far superior for those of separated components. Two synthesis routes for the polybenzoxazine/clay nanocomposites were reported: melt [1] and solvent methods [2-6]. Melt method employs the blending of benzoxazine monomer with the modified montmorillonite (clay) above the melting point of the benzoxazine without a solvent followed by in situ polymerization of benzoxazine monomer. The solvent method consists in the dispersion of modified montmorillonite (MMT) in a suitable solvent followed by mixing with benzoxazine monomer. Then the polymerization process occurs [2]. There are two trends observed in the literature regarding polybenzoxazine /clay hybrid nanocomposites. In some cases an increase of the Tg value and thermal stability for the nanocomposites compared with the neat resin was reported [7], and in other studies the presence of MMT had no influence on the Tg or thermal stability [1]. However, it seems the montmorillonite modifier agent plays an important role in achieving a good compatibility between the two phases [3]. Also the addition of organophylic clay to the benzoxazine matrix may reduce the polymerization temperature even with 50 °C. Studies revealed that the surface of the organophylic clay acts as catalyst for the benzoxazine polymerization process [8].

The goal of this work was to synthesize nanocomposites based on polymer like polybenzoxazine resins reinforced with montmorillonite. The influence of the montmorillonite type and concentration on the polybenzoxazine properties was investigated.

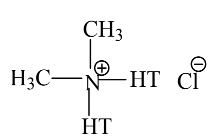
2. Materials and methods

2.1 Materials

The raw materials are presented in Fig. 1.



b.



HT = ~65 % C_{18}, ~30% C_{16}, ~5% C_{14}

Fig. 1. Chemical structures of row materials: a) Bis [6-benziloxy-3,4-dihydro-2H-1,3-benzoxazinyl] diphenyl methane; b) quaternary ammonium salt from MMT_CL_20A.

Bis [6-benziloxy-3,4-dihydro-2H-1,3-benzoxazinyl] diphenyl methane was previously synthesized and characterized from 4-benzyloxyphenol, 4,4'-diaminodiphenylmethane, and formaldehyde solution in p-xylene at 6 h reaction time. According to ^{1}H-NMR, the closed benzoxazine ring content from the monomer is 62% [9].

Two types of natural montmorillonite were used: CLOISITE 20 A (MMT_CL 20A) and CLOISITE Na (MMT-Na) from Southern Clay Products. CLOISITE Na (unmodified montmorillonite) has an exchange capacity of 92meq/100 g clay. CLOISITE 20 A is a natural montmorillonite modified with a quaternary ammonium salt (HT). The concentration of the modifier agent is 95meq/100 g clay. The basal spacing is 24.2 Å (from XRD)

Acetone was supplied by Sigma – Aldrich and used as a solvent.

2.2. Sample preparation

The polybenzoxazine – based composites were prepared using the following procedure: 2 g of benzoxazine monomer were dissolved in 5 ml acetone. Different amounts of clay (1%, 5%, 10%) were added gradually to the benzoxazine monomer acetone solution and sonicated for 1h. The mixture was added in a teflon matrix. The acetone was eliminated at 55°C for 30 min. The crosslinking process was performed 2h at 170 °C and 2h at 190°C.

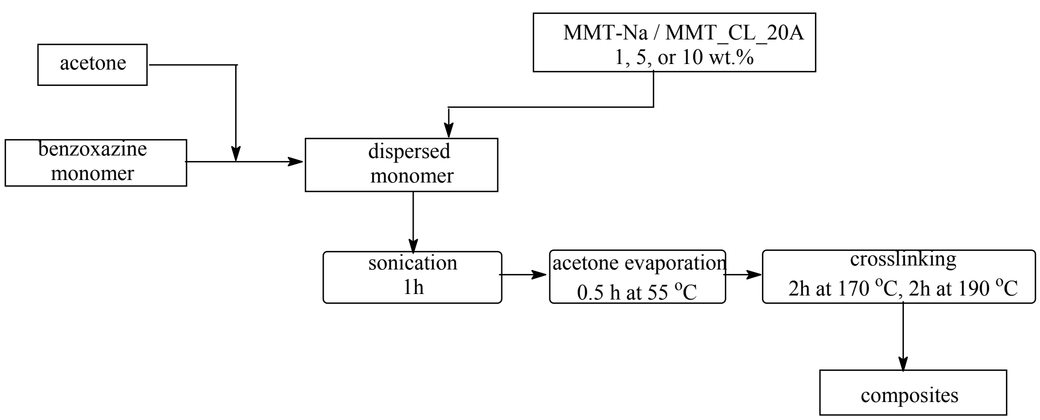


Fig. 2. Procedure used for the composites synthesis

2.3. Characterization

Fourier Transformed – Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70 spectrometer in 4000- 500 cm^{-1} region.

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 temperature range of 25°C to 250°C, the bending mode being considered.

Thermogravimetric analyses (TGA) were performed on a Q500 TA instrument using nitrogen from 30 to 700 °C. The heating rate was 10 °C/min.

The X-Ray Diffraction Analysis (XRD) was done on a XRD 6000 SHIMADZU diffractometer. The test was carried out using the CuKα radiation source filtered with. Ni. The patterns were automatically recorded with scan step of 0.02° and counting time of 0.6 s/step for diffraction angles 2 theta ranged between 3 and 12°, at room temperature.

Transmision electron microscopy characterization (TEM) was performed on a Philips CM 120 ST HR-TEM microscope. Thin specimens of about 50 nm were cut from nanocomposite blocks using an ultramicrotome equipped with a diamond knife at ambient conditions.

3. Results and discussion

More types of polybenzoxazine – based nanocomposites were prepared using two types of montmorillonite (MMT-Na and MMT_CL 20 A). The content of reinforcing agent was varied, 1, 5 and 10 wt. % being used in order to study the influence of the clay type and concentration on the polybenzoxazine properties.

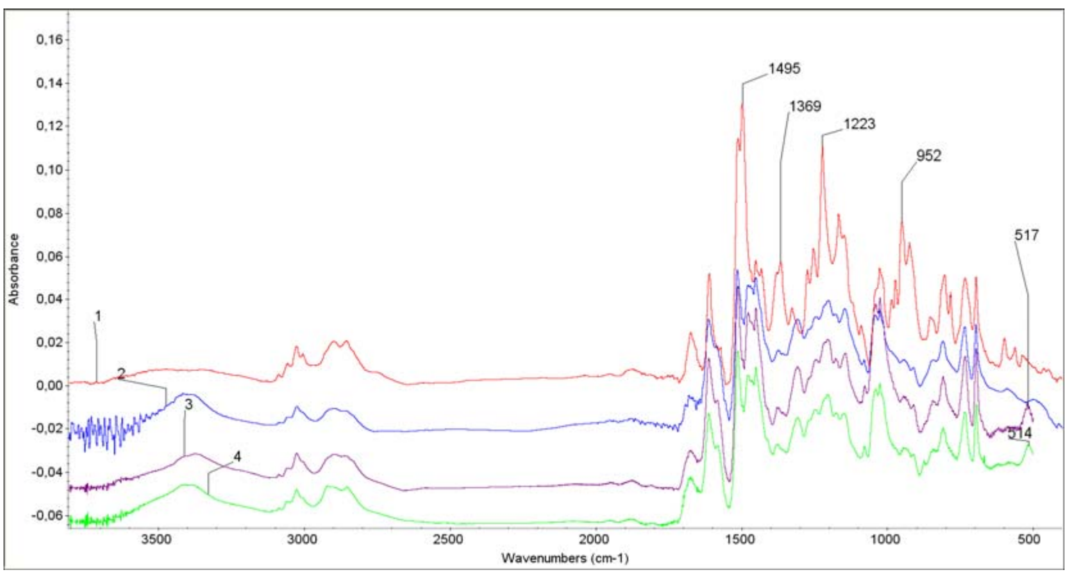


Fig. 3. FT-IR spectra of:1 – benzoxazine monomer, 2- cured polybenzoxazine; 3- polybenzoxazine reinforced with 5 wt.% MMT-Na; 4 – polybenzoxazine reinforced with 5 wt.% MMT_CL 20 A

From Fig. 3 one may observe that the characteristic absorption bands presented in the benzoxazine monomer (952, 1369, 1223 and 1498 cm^{-1}) decrease after the curing 2h at 170 °C and 2h at 190 °C. The presence of the clays MMT-

Na and MMT_CL 20 A in the nanocomposites is proved by the presence of the maximum of absorption at 517 and 514 cm^{-1} respectively attributed to the Al-O stretching and Si-O bending of montmorillonite. Similar results were reported in the literature [10, 11].

Table 1

FT-IR band assignments

Frequency, cm^{-1}	Assignment
952	Oxazine ring
1369	CH_2 from benzoxazine ring
1223	$C_{aliphatic}$-O-$C_{aromatic}$
1498	Trisubstituted aromatic ring
517/514	Al-O stretching/ Si-O bending of montmorillonite

The study of the dispersion of the reinforcing agent within the polybenzoxazine matrix was performed by XRD and TEM.

By XRD the changes of the interlayer distance of the clay gallery in the nanocomposites may be observed.

From Fig. 4 one may observe that for nanocomposites with MMT-Na when 1 and 5 wt. % content is used the diffraction peak is no longer present and at 10 wt. % content the diffraction peak is shifted to lower 2θ values.

The absence of any diffraction peak corresponding to the interlayer basal spacing suggests that the order of the clay layers is perturbated, leading to intercalated or exfoliated nanocomposites.

If high amount of MMT-Na is used (10 wt. %) the diffraction peak is still present this being a consequence of the poor compatibility between the two phases which leads to the reinforcing agent agglomeration.

For nanocomposites with MMT_Cl 20 A the absence of the diffraction peak is observed for all the clay concentration used. This demonstrates that between the two phases a better interaction is achieved due to the higher hydrofobicity of MMT_Cl 20 A compared with MMT-Na.

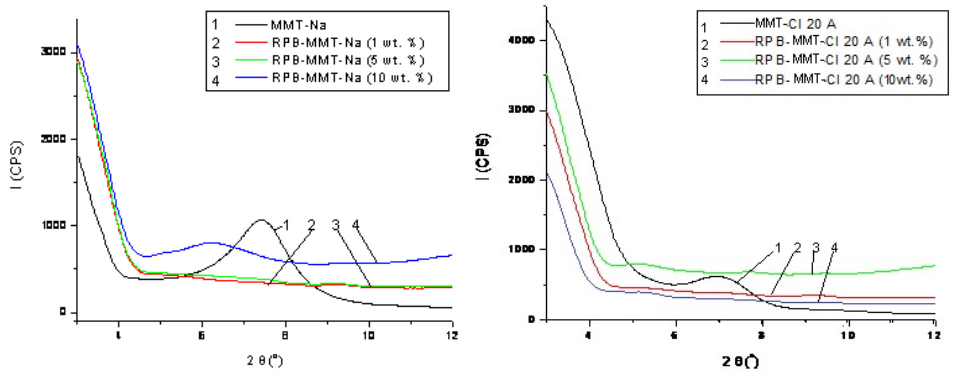


Fig. 4. XRD curves of MMT-Na and MMT_CL_20A and their composites based polybenzoxazine resin

In order to support the results from XRD, TEM images for polybenzoxazine reinforced with 5 wt% MMT-Na and MMT_Cl 20 A are shown in Fig. 5 and Fig. 6.

For both nanocomposites an increase of the interlayer basal distance is observed with almost 3 nm for MMT-Na and 3 to 5 nm for MMT_CL 20 A. The clays are not homogenous dispersed within the polybenzoxazine matrix which confirms the intercalation of the polybenzoxazine resin into the silicates galleries.

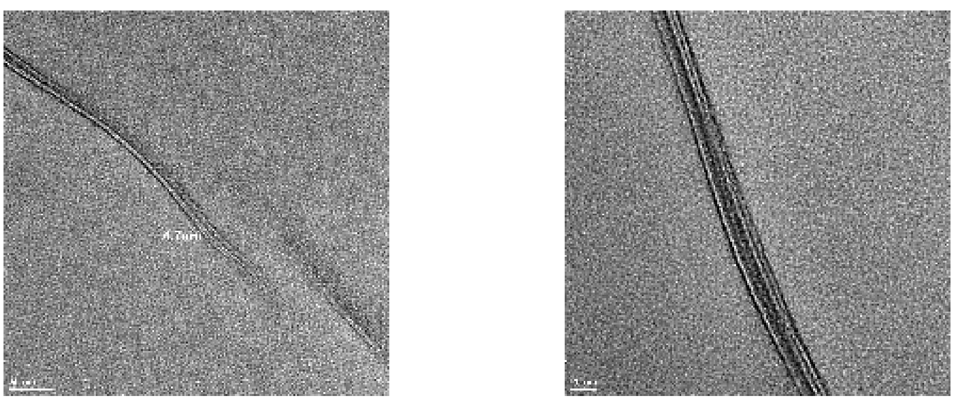


Fig. 5. TEM images of polybenzoxazine – MMT-Na (5wt.%)

From the data shown in Table 2 it may be observed that the inclusion of the two types of montmorillonite in the polybenzoxazine resin exhibits no significant effect on the Tg as results from DMA measurements, and on the onset ($T_{d5\%}$ or $T_{d10\%}$) of the degradation of the polybenzoxazine resin, this being a consequence of the poor compatibility between the two phases, which was also observed in TEM images.

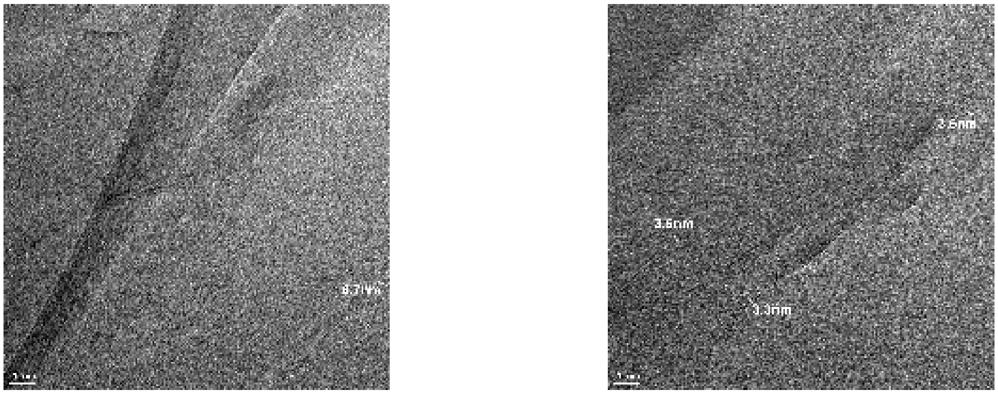


Fig. 6. TEM images of polybenzoxazine – MMT_CL 20A (5wt.%)

The thermal properties of the nanocomposites given by the TGA and DMA techniques are summarized in Table 2.

Table 2

Thermal properties of composites

Reinforcing agent, %	Tg (°C)*	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)
0	149	289	308
MMT-Na, 1%	147	286	301
MMT-Na, 5%	147	278	301
MMT-Na, 10%	147	288	308
MMT_CL 20A, 1%	150	283	301
MMT_CL 20A; 5%	148	281	300
MMT_CL 20A, 10%	-[1]	288	308

* 0,316 HZ frequency
[1] – the sample was

4. Conclusions

New nanocomposites based on polybenzoxazine resin and two types of commercial montmorillonite were synthesized.

The nanocomposites exhibit intercalated structures, this being proved by XRD and TEM analyses.

The presence of the clays in the poybenzoxazine matrix does not increase the resin properties due to the poor interaction between the polybenzoxazine and the reinforcing agents, even if intercalated nanocomposites are finally obtained as revealed by XRD.

Acknowledgements

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