SYNTHESIS AND CHARACTERIZATION OF EPOXY RESIN/LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

SINTEZA I KARAKTERIZACIJA NANOKOMPOZITA NA OSNOVI EPOKSIDNE SMOLE I SLOJEVITOG HIDROKSIDA

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Abstract: Ca-Al hydroxide with layered double hydroxide-like structure modified by the incorporation of benzoate anions ($Ca_4Al_2(OH)_{12}(C_6H_5COO)_2 \cdot x\ H_2O$, LDH-B) was prepared by a variant of the rehydration method, by adding benzoic acid and CaO into mixture of water and acetone used to convert tricalcium aluminate ($Ca_3Al_2O_6$) into final layered structure. Modification of layers with benzoate anions was confirmed by Fourier transform infrared spectroscopy (FTIR). Nanocomposites based on an epoxy resin and LDH-B were prepared by *in situ* polymerisation, with polyoxypropylene diamine as a curing agent. Nanocomposites prepared with different contents of the LDH-B (5, 10, and 15 %) were characterised by X-ray diffraction analysis (XRD), FTIR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). XRD results indicated that the characteristic layered structure of the LDH-B had disappeared, and TEM analysis confirmed that LDH-B was partially dispersed within the matrix forming an intercalated structure, which becomes partly exfoliated in the sample with 5 % filler. Results of thermal analysis showed somewhat improved thermal properties in comparison to the neat epoxy resin, while the glass transition temperature initially decreases but then increases to values over that of neat epoxy resin for the sample with 15 % filler.

Sažetak: Slojeviti Ca-Al hidroksid strukture nalik slojevitim dvostrukim hidroksidima (LDH) modificiran je benzoatnim anionima ($Ca_4Al_2(OH)_{12}(C_6H_5COO)_2 \cdot x\ H_2O$, LDH-B) modificiranom rehidracijskom metodom, dodavanjem benzojeve kiseline i CaO u otopinu vode i acetona kojom se trikalcijski aluminat ($Ca_3Al_2O_6$) transformira u konačnu slojevitu strukturu. Prisutnost benzoatnih aniona unutar slojeva potvrđena je spektroskopijom u infracrvenom području (FTIR). Nanokompoziti na osnovi epoksidne smole i LDH-B pripravljeni su *in situ* polimerizacijom, uz poli(oksipropilen)diamin kao umreživalo. Nanokompoziti s različitim udjelima LDH-B (5, 10, i 15 %) karakterizirani su rendgenskom difrakcijom, FTIR-om, razlikovnom pretražnom kalorimetrijom (DSC), termogravimetrijskom analizom (TGA) i transmisijskom elektronskom mikroskopijom (TEM). Rendgenska analiza ukazuje da je karakteristična slojevita struktura LDH-B nestala, a TEM analiza potvrdila je da je LDH-B djelomično raspršen unutar matice tvoreći interkaliranu strukturu, koja postaje djelomično raslojena u uzorku s 5 % punila. Toplinska analiza ukazala je na djelomično poboljšanje toplinskih svojstava u usporedbi s nemodificiranom epoksidnom smolom, dok se staklište isprva snižava da bi postalo više nego za čistu smolu kod uzorka s 15 % punila.

Keywords: epoxy, layered nanofiller, morphology, nanocomposites, thermal stability

Ključne riječi: epoksidna smola, slojevito nanopunilo, morfologija, nanokompoziti, toplinska postojanost

1. INTRODUCTION

Polymer/layered double hydroxide (LDH) nanocomposites have attracted a great interest in the field of material chemistry in recent years due to their novel mechanical, thermal and optical properties [1] which are mainly attributed to the high-degree dispersion of layered inorganic compounds in polymer matrix. LDHs are layered materials consisting of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. The general formula of those materials is $\left(\mathrm{M}^{2+}_{1\text{-}x}\mathrm{M}^{3+}_{x}(\mathrm{OH})_2\right)^{x+}\mathrm{A}^{\mathrm{n}-}_{x/n}\cdot m\mathrm{H}_2\mathrm{O}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, and $\mathrm{A}^{\mathrm{n}-}$ is an anion. In the original structure, the neighbouring sheets strongly attract each other through electrostatic interaction and hydrogen bonding. The gallery distance between LDH layers is generally under 1 nm, preventing monomer or polymer molecules from penetrating into the layers. Furthermore, the hydrophilic surface of the LDH layers is incompatible with hydrophobic polymer molecules, preventing homogeneous dispersion of LDH layers in polymer matrix. Therefore LDH is modified with suitable organic anions to increase the gallery distance and reduce hydrophilic character of the layer surface.

The anions are typically intercalated into LDH interlayers by one of three approaches. The first is the coprecipitation method, which requires the addition of an $\mathrm{M}^{2+}/\mathrm{M}^{3+}$ metal salt solution to a base solution of the desired anions [2]. The second is the direct ion exchange method, in which LDHs are stirred in a concentrated solution of desired anions [3]. The third is the rehydration method, in which calcined LDH is added to a solution of desired anions [4]. The intercalated LDH/water-soluble polymer nanocomposites have been prepared successfully [5-7], either by the direct intercalation of polymeric anions into LDH, or by intercalation of monomeric anions into LDH followed by *in situ* polymerization. The intercalation of hydrophobic monomers or polymers is much more difficult [8-11]. In this study, preparation of epoxy/LDH nanocomposites by the *in situ* polymerization is presented.

2. EXPERIMENTAL

Materials used in the synthesis of benzoate-intercalated Ca-Al layered double hydroxide-like structure (LDH-B) were calcium carbonate, $\mathrm{CaCO_3}$, p.a. (Kemika, Croatia), aluminum hydroxide, $\mathrm{Al(OH)_3}$, reagent grade (Aldrich) and benzoic acid, $\mathrm{C_6H_5COOH}$, p.a. (Kemika). The materials were used without further purification. To prepare nanocomposite materials, an epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 828 EL, Shell Chemicals) with the epoxy equivalent weight of 190 g/mol was used, with poly(oxypropylene) diamine (Jeffamine D230, Huntsman Corporation) as a curing agent.

Initial substance for synthesis of LDH-B, tricalcium aluminate ($\mathrm{Ca_3Al_2O_6}$), has been prepared by firing wet-homogenized stoichiometric mixture of $\mathrm{CaCO_3}$ and $\mathrm{Al(OH)_3}$ at 1350 °C for 3 h. LDH-B was synthesized by a variant of the rehydration method, by which tricalcium aluminate is converted to layered tetracalcium aluminate. The reaction between finely milled tricalcium aluminate, additional stoichiometric amount of calcium oxide (freshly prepared by firing $\mathrm{CaCO_3}$) and benzoic acid was performed in mixture of deionized water and acetone. The reaction mixture was poured into a tightly screwed polyethylene flask, vigorously shaken for 24 h at room temperature, then filtered and rinsed with acetone in order to prevent agglomeration and cementing of the freshly prepared filler.

To prepare the neat epoxy resin system, DGEBA and a stoichiometric amount of Jeffamine D230 were mixed and stirred at room temperature in a closed vessel for 1 h. To prepare the composite systems with 5, 10 and 15 % of filler, epoxy resin was mixed with desired amount of LDH-B at 75 °C for 24 h and sonicated for 15 min. After cooling the mixture to room temperature, a stoichiometric amount of the curing agent Jeffamine D230 was added and mixture stirred for 1 h. The mixture was then poured into mould and cured at 80 °C for 3 h, and then postcured at 120 °C for 1 h.

Fourier transform infrared (FTIR) spectra of the materials were recorded on a Bruker Vertex 70 FTIR spectrometer in ATR mode. Spectra were obtained using resolution of 4 cm^{-1}, averaged over 16 scans between 400 and 4000 cm^{-1}. X-ray diffraction (XRD) patterns were determined using a Philips PW1730 generator and PW1860 goniometer using CuK_α radiation. Differential scanning calorimetry (DSC) measurements were carried out on a Netzsch DSC 200 operating in a nitrogen atmosphere, at the heating rate of 10 K min^{-1}, with sample size ~20 mg. Each sample was scanned twice, first from room temperature to 180 °C, then cooled back to room temperature and heated to 500 °C. The thermogravimetric analysis (TGA) was performed on a Perkin Elmer thermobalance TGS-2, under a nitrogen gas flow of 150 cm^3 min^{-1}, at the heating rate of 20 K min^{-1}. The transmission electron microscopy (TEM) images were obtained on a transmission electron microscope JEOL JEM-200CX with accelerating voltage of 200 kV. The samples were cut to thickness of 80-110 nm on an ultratome Leica Ultracut R with a glass knife.

3. DISCUSSION OF RESULTS

Characteristic maxima of LDH-B (2ϑ = 31° and 36°) are present in XRD spectra of all epoxy/LDH-B systems indicating successful incorporation of LDH-B into polymer matrix (Figure 1). On the other hand, the disappearance of maxima at 6°, 12°, 18° and 24°, which originate from the layered structure of the filler, indicate intercalation and possibly exfoliation of LDH-B to form the nanocomposite.

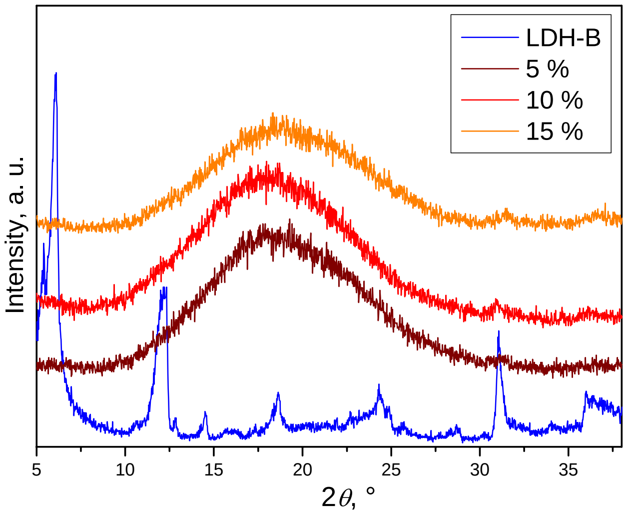

Figure 1. XRD spectra of investigated samples

Figure 2 shows FTIR spectra of benzoic acid, LDH-B, neat epoxy and an epoxy/LDH-B nanocomposite. Benzoic acid shows C=O stretching vibration at 1700 cm^{-1}, and CH-out-of-plane bending of the phenyl ring at 900-600 cm^{-1}. In the spectrum of LDH-B characteristic bands of COO^- asymmetrical and symmetrical stretching vibrations are observed at 1650-1550 and 1450 cm^{-1}, respectively, indicating the presence of benzoate anions within the LDH-like layers. Phenyl ring bands at 900-600 cm^{-1} are observed in the spectra of both LDH-B and the composite. Neat epoxy has several characteristic absorption bands: C-aryl bond stretching at 1505 and 1205 cm^{-1} and CH-in-plane-deformation of aryl group at 825 cm^{-1}, which are all present in spectrum of the nanocomposite.

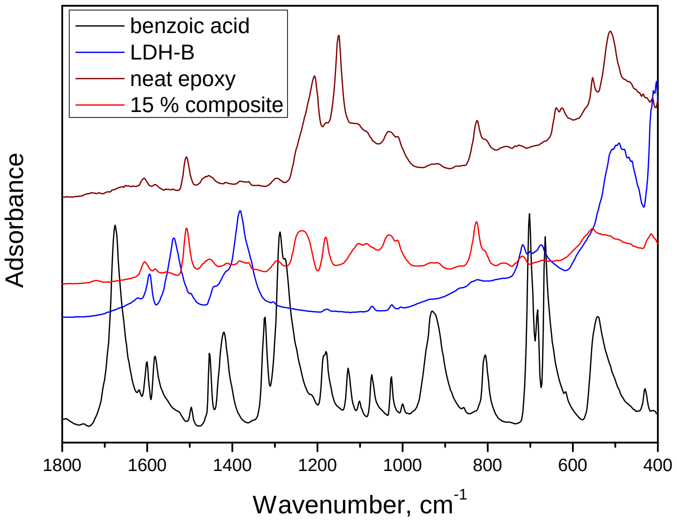

Figure 2. FTIR spectra of listed samples

Morphology of epoxy/LDH-B nanocomposites was further studied by the TEM analysis (Figure 3). With smaller magnification (Figure 3a) it can be seen that LDH-B is homogeneously dispersed within the epoxy matrix. Larger magnification confirms intercalation of polymer matrix within layered structure of LDH-B, but no complete exfoliation in any of the nanocomposites. Only nanocomposite with 5 % of filler shows partial exfoliation.

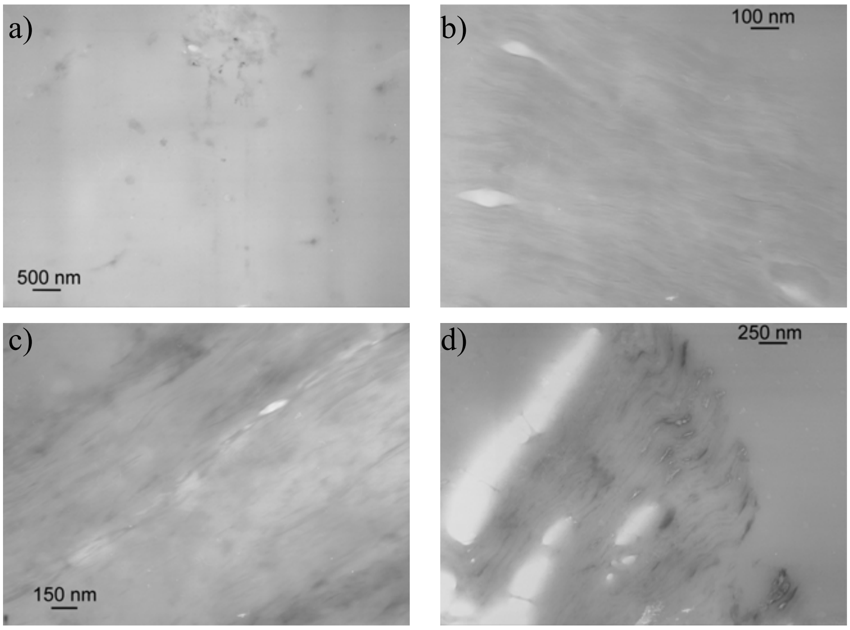

Figure 3. TEM photographs of epoxy/LDH-B nanocomposites with a, b) 5 %, c) 10 % and d) 15 % filler.

Glass transition temperatures (Table 1) of 5 % and 10 % epoxy/LDH-B nanocomposites are lower than that for neat epoxy, but they increase by 5-10 °C in the second measurement, indicating further curing at temperatures above 120 °C used in preparation of samples.

Table 1. Glass transition temperature, T_g, initial degradation temperature, T_i, temperature of maximum rate of degradation, T_{max}, and weight content of residue at 1000 °C, *w*(residue), for investigated samples.

Material	T_g / °C		T_i / °C	T_{max} / °C	*w*(residue)
	1st run	2nd run			
Neat epoxy	71	72	388	421	1,96 %
5 %	62	67	361	402	11,39 %
10 %	60	70	350	400	13,07 %
15 %	78	86	339	393	15,10 %

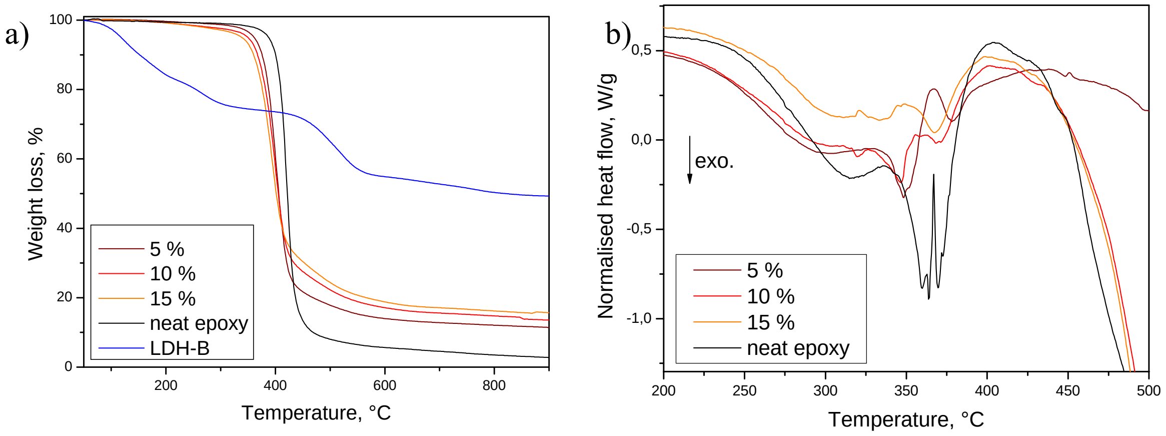

Figure 4. a) TGA curves and b) DSC curves for investigated samples.

Thermal stability of epoxy/LDH-B nanocomposites was studied by TGA and DSC (Figure 4). All nanocomposites degrade in a single step similar to neat epoxy, but maximal rate of degradation, T_{max}, as determined from derived TGA curve, is ~20 °C lower than for neat epoxy and decreases slightly with increased content of filler (Table 1). Intercalated filler does not present a significant barrier for diffusion of volatile degradation products, and presumably even acts as a catalyst for dehydration or chain scission, the two main mechanisms of degradation of crosslinked epoxy. Initial weight-loss (T_i, determined from TGA curves as 5 % weight loss) is also shifted to lower temperatures, but more marked decrease with increasing filler content shows influence of initial degradation of LDH-B that proceeds in two steps at 80-200 °C and 230-300 °C. Presence of filler somewhat inhibits initial degradation of epoxy resin by homolytic bond scission which is not accompanied by weight-loss but is marked by exothermic reaction on DSC curves (Figure 4b). Presence of inorganic filler expectedly increases weight content of residue after full degradation at 1000 °C, *w*(residue), and the effect is most marked for nanocomposite with 5 % filler content, probably due to its partially exfoliated structure.

4. CONCLUSIONS

Benzoate anions intercalated into the LDH-like layers have increased the organophilicity of the filler, enabling the preparation of epoxy-matrix nanocomposites. Successful intercalation has been confirmed by XRD and TEM measurements, and sample with 5 % filler shows partial exfoliation. Thermal properties of the nanocomposites were somewhat improved in comparison to the unmodified resin: glass transition temperature of sample with 15 % filler is higher than for unmodified epoxy resin, and weight residue at 1000 °C is significantly increased, particularly for partially exfoliated nanocomposite with 5 % filler.

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