Ivan BRNARDIĆ, Zvonimir MATUSINOVIĆ, Juraj ŠIPUŠIĆ, Jelena MACAN
University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia

Thermal Properties of Epoxy Resin/Layered Double Hydroxide Intercalated Nanocomposites

Summary

Ca-Al layered double hydroxide (LDH) 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 variation of the rehydration method, by adding benzoic acid and CaO into a mixture of water and acetone used to convert tricalcium aluminate ($Ca_3Al_2O_6$) into final layered structure. Intercalation of benzoate anions within LDH layers was confirmed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Intercalated nanocomposites based on an epoxy resin and LDH-B were prepared by *in situ* polymerisation, with poly(oxypropylene) diamine as a curing agent. Nanocomposites prepared with different contents of LDH-B (5, 10 and 15 phr) were characterised by XRD, FTIR, TGA, differential scanning calorimetry and transmission electron microscopy (TEM). The XRD results indicated formation of intercalated nanocomposites, and TEM analysis confirmed that LDH-B was dispersed within the matrix forming an intercalated structure, which becomes partially exfoliated in the nanocomposite with 5 phr filler. Results of thermal analysis showed detrimental influence on initial degradation temperature in comparison to the neat crosslinked epoxy, while residue at 1,000°C increases, especially for the partially exfoliated nanocomposite. The glass transition temperature decreases in comparison with the neat crosslinked epoxy, indicating poorer crosslinking of the epoxy matrix.

KEY WORDS:
epoxy resin
intercalated nanocomposite
layered double hydroxide (LDH)
morphology
thermal properties

KLJUČNE RIJEČI:
epoksidna smola
interkalirani nanokompozit
morfologija
slojeviti hidroksidi (LDH)
toplinska svojstva

Toplinska svojstva interkaliranih nanokompozita na osnovi epoksidne smole i slojevitog hidroksida

Sažetak

Pripravljen je Ca-Al slojeviti hidroksid (LDH) modificiran benzoatnim anionima ($Ca_4Al_2(OH)_{12}(C_6H_5COO)_2 \cdot x\ H_2O$, LDH-B) modificiranom metodom rehidratacije, tj. dodavanjem benzojeve kiseline i CaO u smjesu vode i acetona, kojom se trikalcijev aluminat ($Ca_3Al_2O_6$) pretvara u konačni slojeviti hidroksid. Interkalacija benzoatnih aniona unutar LDH slojeva potvrđena je rendgenskom difrakcijom (XRD), spektroskopijom u infracrvenom području (FTIR) i termogravimetrijskom analizom (TGA). Interkalirani nanokompoziti na osnovi epoksidne smole i LDH-B pripravljeni su *in situ* polimerizacijom, uz polioksipropilen diamin kao umreživalo. Uzorci s različitim udjelom LDH-B (5, 10 i 15 phr) ispitivani su XRD-om, FTIR-om, TGA-om, razlikovnom pretražnom kalorimetrijom i transmisijskom elektronskom mikroskopijom (TEM). Rendgenska difrakcija pokazala je nastajanje interkaliranih nanokompozita, a TEM analiza potvrdila raspršenje LDH-B unutar matrice i nastajanje interkalirane strukture, uz djelomično raslojavanje u nanokompozitu s 5 phr punila. Toplinska analiza pokazala je smanjenje početne temperature degradacije u usporedbi s nemodificiranim epoksidnim polimerom, dok se ostatak pri 1000 °C povećao, posebice kod djelomično raslojenog nanokompozita. Staklište se snizuje u usporedbi s nemodificiranim epoksidnim polimerom, što upućuje na slabije umreživanje epoksidne matrice.

Introduction

Layered double hydroxides (LDHs) are layered materials consisting of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. They are sometimes referred to as *anionic clays*, due to analogy with the layered structure of clay minerals (such as montmorillonite) which contain intercalated cations and water. This similarity of structure has led to increased research of polymer/LDH nanocomposites in the field of material chemistry in order to obtain materials with improved or novel properties.[1-4]

The general formula of LDHs is $\left(M_{1-x}^{2+}M_x^{3+}(OH)_2\right)^{x+} A_{x/n}^{n-} \cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, and A^{n-} is an anion. LDH layers of varying chemical composition can thus be synthesised: from the most common Mg-Al LDHs,[5,6] through Zn-Al[5] to fairly rare Ca-Al[7] LDHs. Sometimes a monovalent cation can be substituted for the divalent, to prepare Li-Al LDHs[8], and there are also LDHs where the trivalent cation is changed (most commonly to Fe^{3+}).[7,9,10] This wide variety of possible LDHs makes them more flexible than naturally-occurring clay minerals, and influence of cation type on properties of LDHs and polymer/LDH nanocomposites is a subject of research.[5,7,10-12]

Neighbouring sheets in LDH structure 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 M^{2+}/M^{3+} metal salt solution to a base solution of the desired anions.[13] The second is the direct ion exchange method, in which LDHs are stirred in a concentrated solution of desired anions.[14] The third is the rehydration method, in which calcined LDH is added to a solution of desired anions.[15] The intercalated LDH/water-soluble polymer nanocomposites have been prepared successfully,[16-20] 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 presented a greater challenge,[5,6,21-28] and the resulting composite materials rarely show full exfoliation. Most of the research on polymer/LDH nanocomposites has involved thermoplastic polymers, but several research groups worked on the preparation of thermoset (epoxy)/LDH nanocomposites.[24,29-31] In this paper, the preparation of epoxy/Ca-Al LDH intercalated nanocomposites is presented.

Experimental

Materials used in the synthesis of benzoate-intercalated Ca-Al LDH (LDH-B) were calcium carbonate, $CaCO_3$, p.a. (*Kemika*, Croatia), aluminium hydroxide, $Al(OH)_3$, reagent grade (*Aldrich*, USA) and benzoic acid, 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*, United Kingdom) with the epoxy equivalent weight of 190 g/mol was used, with poly(oxypropylene) diamine (*Jeffamine D230, Huntsman Corporation*, USA) as a curing agent. Structural formulas of used materials are given in Scheme 1.
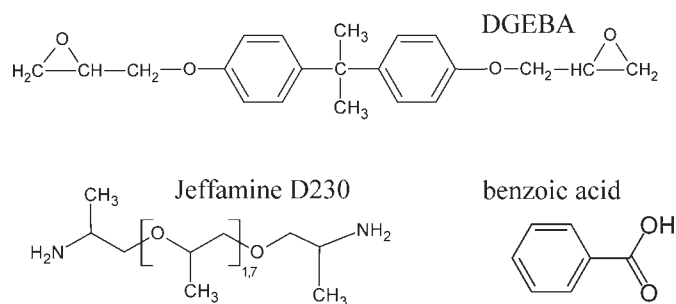
SCHEME 1 – Structural formulas of used materials

Initial substance for synthesis of LDH-B, tricalcium aluminate ($Ca_3Al_2O_6$), has been prepared by firing wet-homogenized stoichiometric slurry of $CaCO_3$ and $Al(OH)_3$ (mole ratio 3:2) at 1,350°C for 3 h. LDH-B was synthesized by a variation 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 $CaCO_3$) and benzoic acid was performed in mixture of deionised 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 (30 phr, parts per hundred parts of resin) 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 phr of filler (equivalent to 3.7, 7.1, and 10.3% of the final material), epoxy resin was compounded with desired amount of LDH-B at 75°C for 24 h and sonicated for 15 min. After cooling the compound to room temperature, a stoichiometric amount of the curing agent *Jeffamine D230* was added and the compound stirred

for 1 h. The compound was then poured into mould and cured at 80°C for 3 h, and then postcured at 120°C for 1 h. Specimens for instrumental characterization were cut from the obtained samples.

Fourier transform infrared (FTIR) spectra of the materials were recorded on a *Bruker Vertex 70* (Germany) FTIR spectrometer in ATR mode. Spectra were obtained using resolution of 4 cm^{-1}, averaged over 16 scans between 400 and 4,000 cm^{-1}. The X-ray diffraction (XRD) patterns were determined using a *Shimadzu XRD-6000* (Japan) with CuK$_\alpha$ radiation. Differential scanning calorimetry (DSC) measurements were carried out on a *Netzsch DSC 200* (Germany) operating in a nitrogen atmosphere, at the heating rate of 10 K·min^{-1}, with specimen size ~20 mg. Each specimen 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* (USA), under a nitrogen (inert atmosphere) or synthetic air (oxidative atmosphere) flow of 150 cm³·min^{-1}, at the heating rate of 20 K·min^{-1}. Additional TGA was performed on powdered specimens in atmosphere of air, under the same conditions. The transmission electron microscopy (TEM) images were obtained on a transmission electron microscope *JEOL JEM-200CX* (Japan) with accelerating voltage of 200 kV. The specimens were cut to thickness of 80-110 nm on an ultratome *Leica Ultracut R* (Germany) with a glass knife.

Results and discussion

In order to facilitate the entry of polymer matrix in between LDH layers, it is important to increase its organophilicity (by preparation of LDH-B) and increase the interlayer distance. The chosen approach, of simultaneously forming the double-layered structure and modifying it by saturating the positively charged layers with bulky organic anions, is an adaptation of procedure by Wang et al.[25] Benzoic acid, containing aromatic ring, is expected to show affinity with DGEBA.
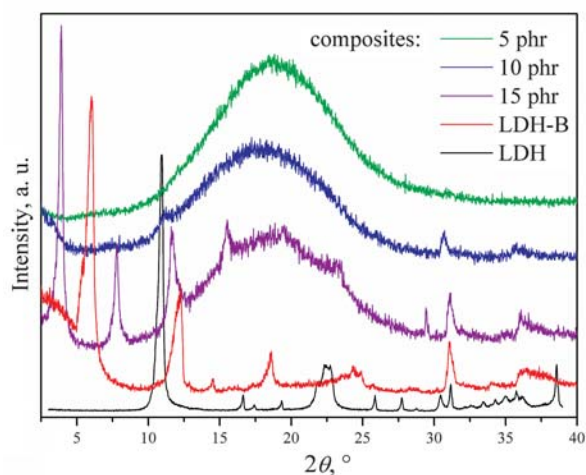

FIGURE 1 – XRD spectra of investigated specimens; curves shifted vertically for clarity

From XRD spectra (Figure 1) it can be seen that the intercalation of benzoate anions influences the interlayer distance, which can be determined from the position of the first maximum. Positions of diffraction maxima for all the investigated specimens and interlayer distances calculated from them (*d*) are given in Table 1. The interlayer distance of LDH-B increases to 1.465 nm ($2\theta = 6.03°$), in comparison with 0.808 nm ($2\theta = 10.95°$) for LDH saturated with hydroxide anions, synthesized in a parallel procedure with no benzoic acid in the reaction mixture. This is comparable to Mg-Al

LDH modified by benzoic acid[32] which had interlayer distance of 1.55 nm after modification, and the difference may be explained by changes in anion orientation due to change in LDH composition.[11] Characteristic maxima of LDH-B ($2J$ = 31° and 36°, indices 110 and 201 in Table 1) present in all epoxy/LDH-B systems indicate successful incorporation of LDH-B into polymer matrix. The intensity of these maxima increases with increasing filler content. In systems with 10 and 15 phr filler, maxima originating from the layered structure of the filler (at 6.03°, 12.21°, 18.63° and 24.41°) are further shifted (to 3.92°, 7.78°, 11.60° and 15.52°). This is a result of intercalation of LDH-B with the epoxy matrix and formation of intercalated nanocomposites, with interlayer distance of the filler increasing to 2.25 nm in the composite with 15 phr filler and to 2.54 nm in the one with 10 phr filler. Nanocomposite with 5 phr of filler does not show maxima originating from the layered structure. This may be due to exfoliation of the filler, but may also be caused by large distribution of interlayer distances caused by various levels of intercalation.[5,32,33]
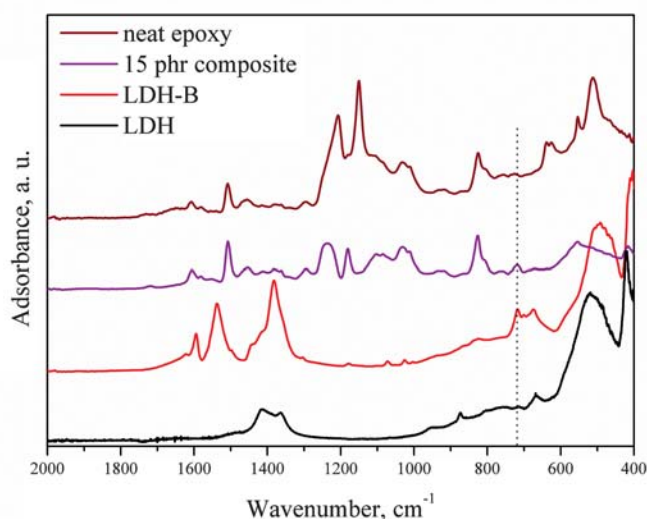

FIGURE 2 – FTIR spectra of listed specimens, phenyl band at 715 cm^{-1} marked with the dotted line; curves shifted vertically for clarity

Figure 2 shows FTIR spectra of LDH, LDH-B, neat epoxy and an epoxy/LDH composite. LDH shows bands at 1,416 and 1,360 cm^{-1}, 874, 667, 519 and 420 cm^{-1}. Some of these bands, with minor shifts (519 to 490 and 420 to 401 cm^{-1}) are also present in the spectrum of LDH-B, so they may be assigned to the inorganic layers of LDH. The bands at 1,420, 1,350 and 667 cm^{-1} overlap with new bands in LDH-B spectrum, while the band at 874 cm^{-1} completely disappears: it is likely a band of CO_3^{2-} interlayer ions that are difficult to completely avoid when synthesizing pure LDH. The bands of COO- symmetrical stretching are present at 1,450-1,350 cm^{-1} (with a pronounced band at 1,380 cm^{-1}), while the bands of asymmetrical

COO- stretching are present at 1,600 and 1,537 cm^{-1}, indicating the presence of benzoate anions within the LDH-B. CH-out-of-plane bending of the phenyl ring bands at 717 and 675 cm^{-1} are observed in the spectra of LDH-B. The band at 717 cm^{-1} can also be observed in the composite, while the other characteristic LDH-B bands are not visible. Neat epoxy has several characteristic absorption bands: C-aryl bond stretching at 1508 and 1207 cm^{-1} and CH-in-plane-deformation of aryl group at 825 cm^{-1}, which are all present in spectrum of the composite.
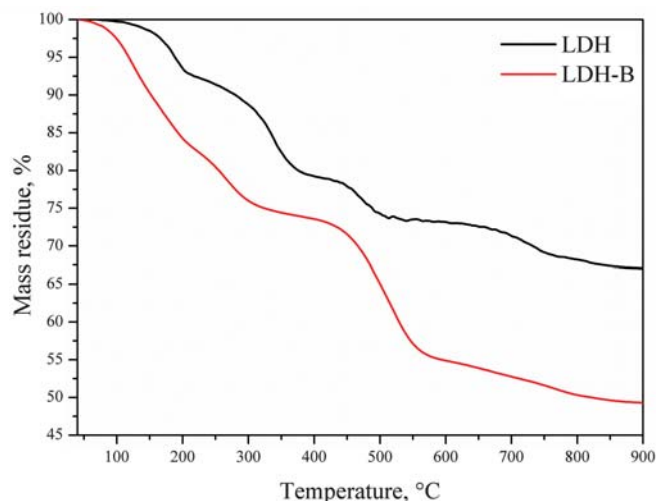

FIGURE 3 – TGA curves of LDH and LDH-B in atmosphere of air

Comparison of TGA curves of LDH and LDH-B in air (Figure 3) also confirms intercalation of organic anions between the layers. Since the degradation of LDH is complex, occurring in at least 4 distinct steps, it is difficult to ascribe a particular mass loss to the interlayer anions. The first step at 100-225°C is the loss of adsorbed water, while further steps at 250-400°C, 430-520°C and 650-800°C are all caused by the degradation of the constituent hydroxides, including interlayer ones. Comparing the two curves, it can be seen that the modified LDH-B has greater mass loss than unmodified LDH in all degradation steps, which indicates that the organic molecules are not present solely inside the double layers, but also on the outer surface of the LDH-B, where they degrade or evaporate at lower temperatures. From the overall mass residue (67.0% for LDH and 49.3% for LDH-B) we have calculated that LDH-B is composed of 75.7 % LDH and 24.3% benzoate.

Morphology of epoxy/LDH-B nanocomposites was further studied by TEM (Figure 4). With smaller magnification (Figure 4a) it can be seen that LDH-B is homogeneously dispersed within the epoxy matrix. Larger magnification confirms intercalation of polymer matrix within the layered structure of LDH-B, but no complete exfoliation in any of the nanocomposites. Only nanocomposite with 5 phr of filler shows partial exfoliation.

TABLE 1 – Comparison of diffraction maxima of LDH, LDH-B and composites with 10 and 15 phr filler

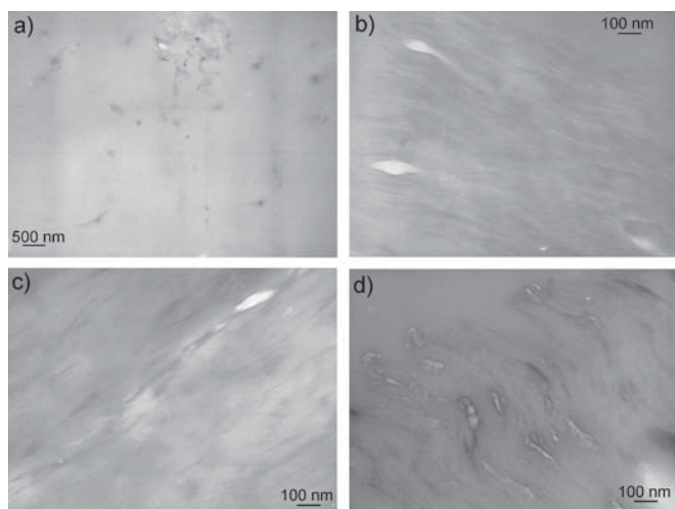| Miller indices	LDH		LDH-B		10 phr		15 phr	
	2θ / °	d / nm	2θ / °	d / nm	2θ / °	d / nm	2θ / °	d / nm
002	10.95	0.808	6.03	1.465	3.48	2.539	3.92	2.254
004	21.83	0.407	12.21	0.724	6.98	1.266	7.78	1.136
006	33.48	0.268	18.63	0.476	11.10	0.797	11.60	0.763
008	--	--	24.41	0.365	--	--	15.52	0.571
0010	--	--	31.07	0.288	--	--	19.50	0.455
0012	--	--	37.77	0.238	--	--	23.50	0.378
110	31.17	0.287	31.07	0.288	30.72	0.291	31.16	0.287
201	36.13	0.249	35.99	0.250	35.70	0.251	36.08	0.249

FIGURE 4 – TEM micrographs of epoxy/LDH-B nanocomposites with a, b) 5 phr, c) 10 phr and d) 15 phr filler

Glass transition temperatures (Table 2) of all epoxy/LDH-B intercalated nanocomposites are lower than that for neat epoxy, and the effect is more pronounced with increasing LDH-B content. Glass transition temperatures increase by 5-8°C in the second measurement, which indicates further curing at temperatures above 120°C used in the preparation of samples. Curing may have been adversely influenced by the increase of viscosity and reduction of the number of reactive groups per unit volume as a consequence of filler addition[34] and possible reaction with organic modifier of the filler.[35,36] Organic modifier may also mix with the matrix and act as a plasticizer.[36,37] Lowering of glass transition of nanocomposites with layered fillers in comparison with neat epoxy may also be caused by a lack of adhesion between the nanolayers and epoxy molecules, which may cause phase separation or increase free volume.[24] Such behaviour was also noticed in epoxy modified by partially exfoliated organically modified montmorillonite (OMMT).[34,38,39]

Thermal stability of epoxy/LDH-B intercalated nanocomposites was studied in inert nitrogen atmosphere by TGA and DSC (Figure 5). All nanocomposites degrade in a single step similar to neat epoxy, but temperature of 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 2). 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. It is known that LDH can act as catalyst for epoxy crosslinking due to the presence of hydroxyl groups.[30] Initial weight-loss temperature (t_i, determined from TGA curves as the temperature of 5% weight loss) is also shifted to lower temperatures. It decreases markedly with increasing filler content, which shows influence of initial degradation of LDH-B that proceeds in two steps at 80-200°C and 230-300°C. The presence of filler somewhat inhibits initial degradation of epoxy network by homolytic bond scission which is not accompanied by weight-loss but is marked by exothermic reaction on DSC curves (Figure 5b). The presence of inorganic filler expectedly increases the weight content of residue after full degradation at 1,000°C, w(residue), and the effect is most marked for nanocomposite with 5 phr filler content, probably due to its partially exfoliated structure. In our previous work on degradation of epoxy/OMMT nanocomposites,[40] addition of filler showed very little influence on t_{max} and t_i, regardless of type of organic modification. In order to achieve significant improvement of thermal stability, full exfoliation of layered fillers is necessary.

In oxidative atmosphere t_i decreases for all specimens, while t_{max} decreases significantly only for neat epoxy and is similar to t_{max} for nanocomposite materials, as illustrated in Figure 6a. For nanocomposite materials there is little influence of atmosphere on t_{max}, indicating that the presence of oxygen from air may have the same overall influence on the mechanism of epoxy degradation as does the presence of LDH filler. The weight content of residue is only slightly larger than the theoretical inorganic content of the nanocomposite materials (Table 2), since organic char oxidizes freely
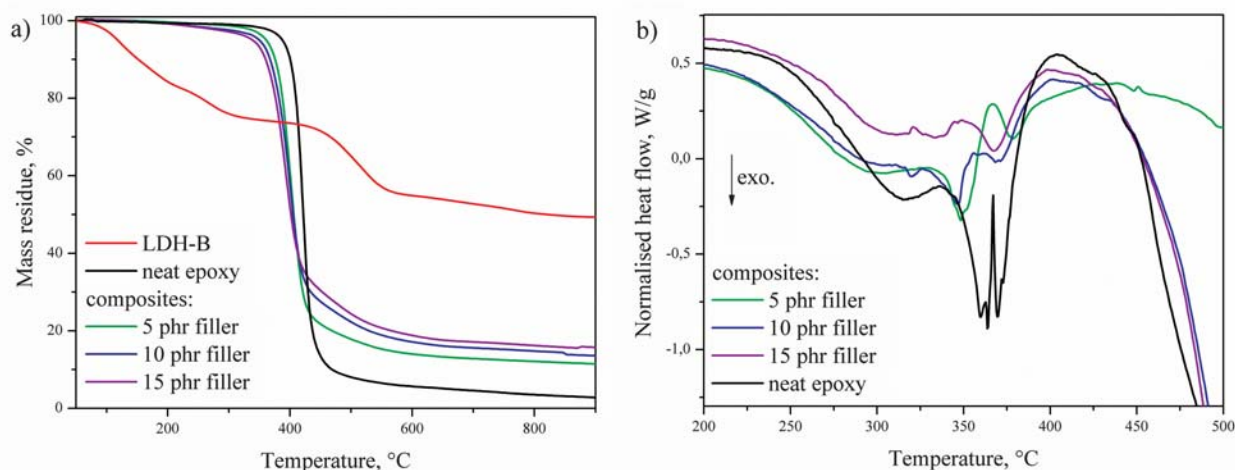

FIGURE 5 – TGA curves (a) and DSC curves (b) for investigated materials in nitrogen atmosphere

TABLE 2 – Glass transition temperature, t_g, initial degradation temperature, t_i, temperature of maximum rate of degradation, t_{max}, and weight content of residue at 1,000 °C, w (residue), for investigated specimens

Material	t_g / °C		t_i / °C		t_{max} / °C		w (residue)		
	1st run	2nd run	N_2	air	N_2	air	N_2	air	theor.
Neat epoxy	79	80	388	354	421	402	1.96 %	0.20 %	0.0 %
5 phr	70	75	361	346	402	402	11.39 %	2.06 %	1.7 %
10 phr	68	76	350	320	400	398	13.07 %	3.80 %	3.2 %
15 phr	67	72	339	330	393	389	15.10 %	5.15 %	4.6 %

at temperatures above 500°C (Figure 6b). Grounding of the materials to increase their free surface decreases t_{max} by ~80°C, as can be seen in Figure 6b. The same shift occurs for oxidative degradation of char (second large peak in DTG curve, above 500°C) of nanocomposite materials, but interestingly not for neat epoxy. DTG curves of all nanocomposite materials show a third, intermediate degradation peak, at ~400°C. The intensity of this peak depends on the filler content (Figure 6b inset) and

its temperature corresponds to t_{max} of bulk specimens, so it is supposed it shows degradation of intercalated polymer, kinetics of which are dictated by diffusion of degradation products.

In order to prepare largely exfoliated epoxy/LDH nanocomposites, LDH should be modified with a reactive anion to promote exfoliation,[24,29] and smaller content of filler (< 5 phr) should be used.
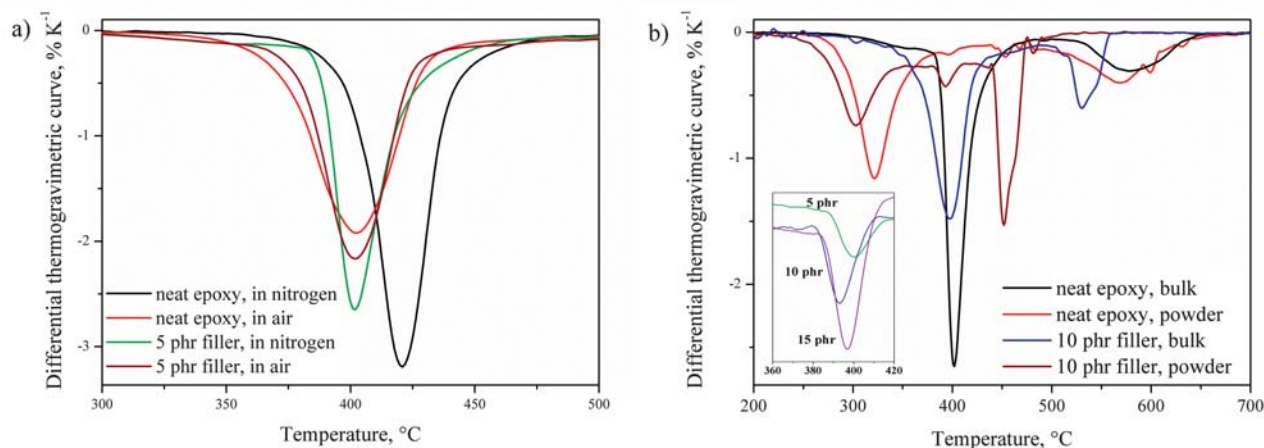

FIGURE 6 – Comparison of DTG curves of neat epoxy and representative nanocomposites in different atmospheres (a) and depending on specimen shape (b)

Conclusions

Benzoate anions intercalated into LDH layers have increased the interlayer distance and the organophilicity of the filler, enabling the preparation of epoxy-matrix intercalated nanocomposites. Successful intercalation has been confirmed by XRD and TEM measurements, and nanocomposite with 5 phr filler shows partial exfoliation. Thermal properties of the intercalated nanocomposites have worsened in comparison to the unmodified resin: glass transition and degradation temperatures of all nanocomposites are lowered, which indicates poorer crosslinking of the epoxy matrix and possible plasticizing effect of the filler. The presence of the inorganic filler does significantly increase weight residue at 1000°C, particularly for partially exfoliated nanocomposite with 5 phr filler. Change to oxidative atmosphere shows little influence on the first degradation step of the nanocomposites, but the char is burned to leave prevalently inorganic ash.

Acknowledgments

REFERENCES

1. Utracki, L. A., Sepehr, M., Boccaleri, E.: *Synthetic, layered nanoparticles for polymeric nanocomposites (PNCs)*, Polymers for Advanced Technologies, 18(2007), 1-37.
2. Evans, D. G., Duan, X.: *Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine*, Chemical Communications, (2006), 485-496.
3. Leroux, F., Besse, J.-P.: *Polymer interleaved layered double hydroxide: A new emerging class of nanocomposites*, Chemistry of Materials, 13(2001), 3507-3515.
4. Forano, C., Hibino, T., Leroux, F., Taviot-Guého, C.: *Layered double hydroxides*, in: Bergaya, F., Theng, B. K. G., Lagaly, G. (ed.): *Handbook of Clay Science*, *Developments in Clay Science*, Vol. 1. Elsevier Ltd., Oxford – Amsterdam, 2006, 1021-1095.

5. Nyambo, C., Wilkie, C. A.: *Layered double hydroxides intercalated with borate anions: Fire and thermal properties in ethylene vinyl acetate copolymer*, Polymer Degradation and Stability, 94(2009), 506-512.
6. Costa, F. R., Wagenknecht, U., Heinrich, G.: *LDPE/MgAl layered double hydroxide nanocomposite: thermal and flammability properties*, Polymer Degradation and Stability, 92(2007), 1813-1823.
7. Manzi-Nshuti, C., Wang, D., Hossenlopp, J. M., Wilkie, C. A.: *The role of the trivalent metal in an LDH: Synthesis, characterization and fire properties of thermally stable PMMA/LDH systems*, Polymer Degradation and Stability, 94(2009), 705-711.
8. Tsai, T.-Y., Lu, S.-W., Li, F.-S.: *Preparation and characterization of epoxy/layered double hydroxides nanocomposites*, Journal of Physics and Chemistry of Solids, 69(2008), 1386-1390.
9. Ding, Y., Gui, Z., Zhu, J., Hu, Y., Wang, Z.: *Exfoliated poly(methyl methacrylate)/ MgFe-layered double hydroxide nanocomposites with small inorganic loading and enhanced properties*, Materials Research Bulletin, 43(2008), 3212-3220.
10. Sahu, B., Pugazhenthi, G.: *Properties of polystyrene/organically modified layered double hydroxide nanocomposites synthesized by solvent blending method*, Journal of Applied Polymer Science, 120(2011), 2485-2495.
11. Manzi-Nshuti, C., Wang, D., Hossenlopp, J. M., Wilkie, C. A.: *Aluminum-containing layered double hydroxides: the thermal, mechanical, and fire properties of (nano)composites of poly(methyl methacrylate)*, Journal of Materials Chemistry, 18(2008), 3091-3102.
12. Manzi-Nshuti, C., Chen, D., Su, S., Wilkie, C. A.: *Structure–property relationships of new polystyrene nanocomposites prepared from initiator-containing layered double hydroxides of zinc aluminum and magnesium aluminum*, Polymer Degradation and Stability, 94(2009), 1290-1297.
13. Iyi, N., Kurashima, K., Fujita, T.: *Orientation of an organic anion and second-staging structure in layered double-hydroxide intercalates*, Chemistry of Materials, 14(2002), 583-589.
14. Xu, Z. P., Braterman, P. S., Yu, K., Xu, H., Wang, Y., Brinker, C. J.: *Unusual hydrocarbon chain packing mode and modification of crystallite growth habit in the self-assembled nanocomposites zinc-aluminum-hydroxide oleate and elaidate (cis- and trans- [$Zn_2Al(OH)_6(CH_3(CH_2)_7CH=CH(CH_2)_7COO^-)$]) and magnesium analogues*, Chemistry of Materials, 16(2004), 2750-2756.
15. Dimotakis, E. D., Pinnavaia, T. J.: *New route to layered double hydroxides intercalated by organic anions: Precursors to polyoxometalate-pillared derivatives*, Inorganic Chemistry, 29(1990), 2393-2394.
16. Oriakhi, C. O., Farr, I. V., Lerner, M. M.: *Incorporation of poly(acrylic acid), poly(vinylsulfonate) and poly(styrenesulfonate) within layered double hydroxides*, Journal of Materials Chemistry, 6(1996), 103-107.
17. Lin, J. J., Juang, T. Y.: *Intercalation of layered double hydroxides by poly(oxyalkylene)-amidocarboxylates: tailoring layered basal spacing*, Polymer, 45(2004), 7887-7893.

18. Liao, C. S., Ye, W. B.: *Structure and conductive properties of poly(ethylene oxide)/layered double hydroxide nanocomposite polymer electrolytes*, Electrochimica Acta, 49(2004), 4993-4998.

19. Roland-Swanson, C., Besse, J. P., Leroux, F.: *Polymerization of sulfopropyl methacrylate, a surface active monomer, within layered double hydroxide*, Chemistry of Materials, 16(2004), 5512-5517.

20. Vaysee, C., Guerlou-Demourgues, L., Delmas, C., Duguet, E.: *Tentative mechanisms for acrylate intercalation and in situ polymerization in nickel-based layered double hydroxides*, Macromolecules, 37(2004), 45-51.

21. Chen, W., Qu, B..*Structural characteristics and thermal properties of PE-g-MA/MgAl-LDH exfoliation nanocomposites synthesized by solution intercalation*, Chemistry of Materials, 15(2003), 3208-3213.

22. Chen, W., Feng, L., Qu, B.: *Preparation of nanocomposites by exfoliation of ZnAl layered double hydroxides in nonpolar LLDPE solution*, Chemistry of Materials 16(2004), 368-370.

23. Hsueh, H. B., Chen, C. Y.: *Preparation and properties of LDHs/polyimide nanocomposites*, Polymer, 44(2003), 1151-1161.

24. Hsueh, H. B., Chen, C.-Y.: *Preparation and properties of LDHs/epoxy nanocomposites*, Polymer, 44(2003), 5275-5283.

25. Wang, G. A., Wang, C. C., Chen, C. Y.: *The disorderly exfoliated LDHs/PMMA nanocomposite synthesized by in situ bulk polymerization*, Polymer, 46(2005), 5065-5074.

26. Huang, N. H., Wang, J. Q.: *A new route to prepare nanocomposites based on polyvinyl chloride and MgAl layered double hydroxide intercalated with laurylether phosphate*, eXPRESS Polymer Letters, 3(2009), 595-604.

27. Manzi-Nshuti, C., Songtipya, P., Manias, E., Jimenez-Gasco, M. M., Hossenlopp, J. M., Wilkie, C. A.: *Polymer nanocomposites using zinc aluminum and magnesium aluminum oleate layered double hydroxides: Effects of the polymeric compatibilizer and of composition on the thermal and fire properties of PP/LDH nanocomposites*, Polymer Degradation and Stability, 94(2009), 2042-2054.

28. Matusinović, Z., Rogošić, M., Šipušić, J., Macan, J.: *Polymer nanocomposite materials based on polystyrene and a layered aluminate filler*, Polymer Engineering and Science, 48(2008), 2027-2032.

29. Tseng, C., Hsueh, H., Chen, C.: *Effect of reactive layered double hydroxides on the thermal and mechanical properties of LDHs/epoxy nanocomposites*, Composites Science and Technology, 67(2007), 2350-2362.

30. Chan, Y.-N., Juang, T.-Y., Liao, Y.-L., Dai, S. A., Lin, J.-J.: *Preparation of clay/epoxy nanocomposites by layered-double-hydroxide initiated self-polymerization*, Polymer, 49(2008), 4796-4801.

31. Zammarano, M., Franceschi, M., Bellayer, S., Gilman, J. W., Meriani, S.: *Preparation and flame resistance properties of revolutionary self-extinguishing epoxy nanocomposites based on layered double hydroxides*, Polymer, 46(2005), 9314-9328.

32. Nyambo, C., Chen, D., Su, S., Wilkie, C. A.: *Variation of benzyl anions in MgAl-layered double hydroxides: Fire and thermal properties in PMMA*, Polymer Degradation and Stability, 94(2009), 496-505.

33. Kornmann, X., Lindberg, H., Berglund, L. A.; *Synthesis of epoxy-clay nanocomposites: Influence of the nature of the clay on structure*, Polymer, 42(2001), 1303-1310.

34. Ivanković, M., Brnardić, I., Ivanković, H., Mencer, H. J.: *DSC study of the cure kinetics during nanocomposite formation: Epoxy/poly(oxypropylene) diamine/organically modified montmorillonite system*, Journal of Applied Polymer Science, 99(2006), 550-557.

35. Kornmann, X., Rees, M., Thomann, Y., Necola, A., Barbezat, M., Thomann, R.: *Epoxy-layered silicate nanocomposites as matrix in glass fibre-reinforced composites*, Composites Science and Technology, 65(2005), 2259-2268.

36. Gârea, S.-A., Iovu, H., Voicu, G.: *The influence of some new montmorillonite modifier agents on the epoxy–montmorillonite nanocomposites structure*, Applied Clay Science, 50(2010), 469-475.

37. Liu, W. P., Hoa, S. V., Pugh, M.: *Organoclay-modified high performance epoxy nanocomposites,* Composites Science and Technology, 65(2005), 307-316.

38. Brnardić, I., Ivanković, M., Ivanković, H., Mencer, H. J.: *Isothermal and nonisothermal cure kinetics of an epoxy/poly(oxypropylene)diamine/octadecylammonium modified montmorillonite system*, Journal of Applied Polymer Science, 100(2006), 1765-1771.

39. Triantafillidis, C. S., LeBaron, P. C., Pinnavaia, T. J.: *Thermoset epoxy-clay nanocomposites: The dual role of α,ω-diamines as clay surface modifiers and polymer curing agents*, Journal of Solid State Chemistry, 167(2002), 354-362.

40. Brnardić, I., Macan, J., Ivanković, H., Ivanković, M.: *Thermal degradation kinetics of epoxy/organically modified montmorillonite nanocomposites*, Journal of Applied Polymer Science, 107(2008), 1932-1938.

CONTACT
Prof. dr. sc. Jelena Macan
University of Zagreb
Faculty of Chemical Engineering and Technology
Marulićev trg 19, p.p. 177
HR-10000 Zagreb, Croatia
E-mail: jmacan@fkit.hr

Lego-kocke obilježavaju 55. obljetnicu

Priredila: Đurđica ŠPANIČEK

Krajem siječnja 2013. lego-kocke slave 55. obljetnicu. Na dan 28. siječnja 1958. O. K. Christiansen, osnivač tvrtke *Lego*, sa sjedištem u Kopenhagenu, patentirao je kocku *Lego*. Time je postavljen kamen temeljac jednom od najuspješnijih plastičnih proizvoda. Danas svaki čovjek u svijetu ima u prosjeku 80 lego-kocaka.

Godine 1958. O. K. Christiansen razvio je kocku *Lego* s poznatim sustavom povezivanja izbočine i cijevi, koji je i danas osnova za oko 2 700 različitih lego gradbenih elemenata. Ti se gradbeni elementi s kockom kao osnovom mogu kombinirati u bezbroj inačica.

Od 1963. godine za izradbu lego-kocaka rabi se kopolimer akrilonitril-butadien-stiren, ABS. Taj glatki polimerni materijal vrlo je čvrst i ima površinu otpornu na grebanje i ugriz te je fiziološki potpuno neškodljiv. To je važno jer mala djeca rado stavljaju igračke u usta i pri tome ih grizu.

Za njih se izrađuju posebne kocke *Lego Duplo*, koje su dvostruko veće od uobičajenih pa se ne mogu progutati.

Lego-kocke danas se proizvode u Danskoj, Čečeniji i Meksiku. ABS se dobavlja u obliku granula, od kojih se injekcijskim prešanjem pri temperaturi taljevine od 232 °C silom zatvaranja od 1 500 MN i vrlo preciznim temperiranjem kalupa prave vrlo precizni otpresci. Naime, svaki otpresak ima toleranciju od tisućinke milimetra, tako da elementi svih boja i veličina mogu ostati čvrsto povezani i izgrađivati čitave gradove. Lego-kocke koje ne zadovoljavaju ponovno se rastale i oblikuju. Na taj se način smanjuje otpad i čuva okoliš.

Lego-kocke mogu se naručiti u 58 različitih boja i ukupno 9 000 kombinacija boja i oblika. Tijekom godina proizvedeno je više od 600 milijardi lego-elemenata.

plasticker.de