Thermal Properties of Epoxy Resin/Layered Double Hydroxide Intercalated Nanocomposites

Summary
Ca-Al layered double hydroxide (LDH) modified by the incorporation of benzoate anions (Ca₂Al₉(OH)₁₆(C₆H₅COO)₄ · x H₂O, 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 (Ca₃Al₂O₆) 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) morphogy
thermal properties

TOPLINSKA SVOJSTVA INTERKALIRANIH NANOKOMPOZITA NA OSNOVI EPOXIDNJE SMELE I SLOJEVITOG HIDROKSIDA

Sažetak
Pripriavljen je Ca-Al slojeviti hidroksid (LDH) modificiran benzoatnim anionima (Ca₂Al₉(OH)₁₆(C₆H₅COO)₄ · x H₂O, LDH-B) modificiranom metodom rehidratacije, tj. dodavanjem benzojeve kiseline i CaO u smjesu vode i acetona, kojom se trijalcijskih aluminat (Ca₃Al₂O₆) 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 umrezivač. 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 1,000 °C povećao, posebice kod djelomično raslojenog nanokompozita. Staklište se snizuje u usporedbi s nemodificiranim epoksidnim polimerom, što upućuje na slabije umrezivanje 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. The general formula of LDHs is \( [\text{M}^{2+}, \text{M}^{3+}(\text{OH})_2]^+ \cdot \text{An}^- \cdot x \cdot m\text{H}_2\text{O} \), where \( \text{M}^{2+} \) and \( \text{M}^{3+} \) are divalent and trivalent metal cations, and \( \text{An}^- \) is an anion. LDH layers of varying chemical composition can thus be synthesised: from the most common Mg-Al LDHs, through Zn-Al2+ to fairly rare Ca-Al3+ LDHs. Sometimes a monovalent cation can be substituted for the divalent, to prepare Li-Al LDHs, and there are also LDHs where the trivalent cation is changed (most commonly to Fe3+). 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.

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 M³⁺/M⁺ metal salt solution to a base solution of the desired anions. The second is the direct ion exchange method, in which LDHs are stirred in a concentrated solution of desired anions. The third is the rehydration method, in which calcined LDH is added to a solution of desired anions. The intercalated LDH/water-soluble polymer nanocomposites have been prepared successfully, 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, 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. 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, CaCO₃, p.a. (Kemika, Croatia), aluminium hydroxide, Al(OH)₃, reagent grade (Alrich, USA) and benzoic acid, C₆H₅COOH, 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](image)

SCHEME 1 – Structural formulas of used materials

Initial substance for synthesis of LDH-B, tricalcium aluminate (Ca₃Al₂O₆), has been prepared by firing wet-homogenized stoichiometric slurry of CaCO₃ 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 mixture was poured into a tightly screwed polyethylene flask, and the compound stirred vertically for clarity. X-ray diffraction (XRD) patterns were determined using a Shimadzu XRD 6000 (Japan) with CuKα radiation. Differential scanning calorimetry (DSC) measurements were carried out on a Netzsch DSC 200 (Germany) 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. Benzoic acid, containing aromatic ring, is expected to show affinity with DGEBA.

![Figure 1](image)

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 (20 = 6.03°), in comparison with 0.808 nm (20 = 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\(^3\) 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.\(^4\) Characteristic maxima of LDH-B (\(2\theta = 31^\circ\) and \(36^\circ\), 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 \(6.03^\circ\), \(12.21^\circ\), \(18.63^\circ\) and \(24.41^\circ\)) are further shifted (to \(3.92^\circ\), \(7.78^\circ\), \(11.60^\circ\) and \(15.52^\circ\)). 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.\(^5\)\(^,\)\(^3\(^2\)\(^,\)\(^3\(^3\))

\[\text{COO}^-\] 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. Neat epoxy has several characteristic absorption bands: C-aryl bond stretching at 1,508 and 1,207 cm\(^{-1}\) and CH-in-plane-deformation of aryl group at 825 cm\(^{-1}\), which are all present in spectrum of the composite.

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

<table>
<thead>
<tr>
<th>Miller indices</th>
<th>LDH</th>
<th>LDH-B</th>
<th>10 phr</th>
<th>15 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>(002)</td>
<td>10.95</td>
<td>0.808</td>
<td>6.03</td>
<td>1.465</td>
</tr>
<tr>
<td>(004)</td>
<td>21.83</td>
<td>0.407</td>
<td>12.21</td>
<td>0.724</td>
</tr>
<tr>
<td>(006)</td>
<td>33.48</td>
<td>0.268</td>
<td>18.63</td>
<td>0.476</td>
</tr>
<tr>
<td>(008)</td>
<td>--</td>
<td>--</td>
<td>24.41</td>
<td>0.365</td>
</tr>
<tr>
<td>(0010)</td>
<td>--</td>
<td>--</td>
<td>31.07</td>
<td>0.288</td>
</tr>
<tr>
<td>(0012)</td>
<td>--</td>
<td>--</td>
<td>37.77</td>
<td>0.238</td>
</tr>
<tr>
<td>(110)</td>
<td>31.17</td>
<td>0.287</td>
<td>31.07</td>
<td>0.288</td>
</tr>
<tr>
<td>(201)</td>
<td>36.13</td>
<td>0.249</td>
<td>35.99</td>
<td>0.250</td>
</tr>
</tbody>
</table>
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, \( t_{\text{max}} \), as determined from derived TGA curve, is \(-20^\circ\text{C}\) 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 \( (t_i, \text{determined from TGA curves as the temperature of 5\% weight loss}) \) 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\(^\circ\text{C}\) and 230-300\(^\circ\text{C}\). 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\(^\circ\text{C}\), \( w_{(\text{residue})} \), 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 \( t_i \) and \( t_{\text{max}} \) 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 \( t_{\text{max}} \) decreases significantly only for neat epoxy and is similar to \( t_{\text{max}} \) for nanocomposite materials, as illustrated in Figure 6a. For nanocomposite materials there is little influence of atmosphere on \( t_{i} \), 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.
at temperatures above 500°C (Figure 6b). Grounding of the materials to increase their free surface decreases \( t_{\text{max}} \) 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 \( t_{\text{max}} \) 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,24,25 and smaller content of filler (< 5 phr) should be used.

**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 unmodified resin: glass transition and degradation temperatures of all nanocomposites have worsened in comparison to the PMMA/LDH systems, Polymer Degradation and Stability, 94(2009), 705-711.

Acknowledgments

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To je važno jer mala djeca rado stavljaju igračke u usta i pri tome ih grizu. Ova površina otpornu na grebanje i ugriz te je fi ziološki potpuno neškodljiv.

Putadien-stiren, ABS. Taj glatki polimerni materijal vrlo je čvrst i ima

Od 1963. godine za izradbu lego-kocaka rabi se kopolimer akrilonitril-kao osnovom mogu kombinirati u bezbroj inačica.

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vom povezivanja izbočine i cijevi, koji je i danas osnova za oko 2 700

u prosjeku 80 lego-kocaka.

od najuspješnijih plastičnih proizvoda. Danas svaki čovjek u svijetu ima

nu, patentirao je kocku

1958. O. K. Christiansen, osnivač tvrtke

Krajem siječnja 2013. lego-kocke slave 55. obljetnicu. Na dan 28. siječnja

Priredila: Đurđica ŠPANIČEK

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Lego-kocke obilježavaju 55. obljetnicu

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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 tisućine milimetra, tako da elementi svih boja i veličina mogu ostati čvrsto povezani i izgrađivati čitave gradove. Lego-kocke koje se napravljaju sadrže se u paketima od 1 000 komada.

Lego-kocke se koriste u različitim oblicima, od igračkih uzoraka preko stolnih igara do predmeta za kreativne prilike.

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