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The Effect of the Addition of Mg-Al LDH Intercalated with Dodecyl Sulfate on the Fire Retardancy Properties of Epoxy

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Summary: Layered double hydroxides (LDH) are chemical compounds that can be added to polymeric resins to confer fire retardant characteristics. The focus of this work is to study the incorporation of LDH intercalated with dodecylsulfate anions into epoxy resins. The mechanical properties were investigated using tensile, flexural and impact mechanical tests. The flame-retardant properties were assessed using horizontal (UL 94 HB) and vertical burning (UL 94 V) tests. The highest tensile strength was obtained for the composite with 3 wt% of LDH, whereas the highest flexural strength was found by incorporating 1 wt% of LDH. All samples containing LDH showed self-extinguishing behavior in the vertical test and lower burning rate than pristine epoxy.

Keywords: composites; epoxy; flame retardancy; layered double hydroxides

Introduction

Epoxy resins are widely used in coatings and polymeric composites due to superior thermomechanical properties and excellent processability.[1] On the other hand, flammability of epoxy resins still represents a limitation for commercial and general uses in whichfire propagation involves both health risks and loss of mechanical properties in structural applications.[2–5]

On this context, the use of nano-scale inorganic fillers has recently drawn great interest due to its potential to improve some properties of pristine polymers, such as thermal stability[6,7] and mechanical [2,5] and flame retardant characteristics[3,7] with a relatively low filler content.[8] Layered double hydroxides (LDHs), are nanofillers that consist of positively charged metal hydroxide layers based on the brucite structure with intercalated hydrated anions which can be represented by the $M^{II}_{x}\ M^{III}_{1-x}(OH)_2A^{n-}_{x/n}.mH_2O$ formula, where M^{II} and M^{III} are bivalent and trivalent metal cations, respectively, occupying octahedral positions within the hydroxide layers, and A^{n-} is an interlayer anion that compensates the charge on the layers.[1,9] Some studies on LDH address their potential use as a non-halogenated and non-toxic flame-retardant nanofiller for polymers.[10,11]

To obtain improved flame-retardancy, good dispersion of nanofillers throughout the polymer matrix is necessary. A recently proposed[12] way of achieve better dispersion regards the organic modification of the LDH surface. The inclusion of organic molecules has the potential of promoting interaction with the polymeric chain, consequently leading to composite with improved properties. The aim of this work is to use Mg:Al LDH intercalated with dodecyl sulfate (HD) to produce intercalated or exfoliated composites with improved flame retardant characteristics.

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Experimental Part

Materials

The following materials were used: Diglycidyl ether of bisphenol A (DGEBA, Araldite LY 1316 - Huntsman); triethylenetetramine (TETA, Aradur HY 1208 - Huntsman) curing agent; $Mg(NO_3)_2.6H_2O$ (Vetec); $Al(NO_3)_3.9H_2O$ (Vetec); sodium hydroxide (Nuclear); intercalated double layered hydroxides with dodecyl sulfate (LDH), which were synthesized in the lab following a previously published methodology.[13] Dimethylformamide (DMF) (Nuclear) was used to aid dispersion (delamination/exfoliation) of the LDHs.

Polymer and LDHs/epoxy Composite Preparation

In order to obtain the composites, the LDHs (0, 1, 2, 3 and 5%) were dispersed (delaminated/exfoliated) in DMF, the desired amount of epoxy resin was added to the LDH suspension and the mixture was sonicated for 10 min. Then, the DMF was evaporated with use vacuum. After that, the curing agent was added to the LDH/epoxy mixture, which was then stirred under sonication for 3 min. The LDH/resin was cast into a silicon rubber mold and cured at room temperature for 24 h. After that, the composite samples were post-cured at 70 °C for 2 h.

To be used as reference, some epoxy resin was treated with DMF and, after that, the DMF was removed and the curing agent was added. The resin was cast into a silicon mold and cured, following the same procedure used for the composites.The samples prepared in this work were called R-HD0, R-HD1, R-HD2, R-HD3 and R-HD-5 according to the respective LDH weight content.

Characterization

Thermogravimetric analysis (TGA) was performed in a TA Instruments 2050, by heating the samples from 25 to 960 °C at a heating rate of 20 °C/min under dynamic flow of O_2. Evaluation of flammability was carried out using the UL 94 tests. Vertical (UL 94 V) and horizontal burning (UL 94 HB) tests were carried out in $130 \times 13 \times 4\,mm^3$ specimens. For each composition, the mean result of five measurements is reported.

The tensile storage modulus (E') and loss factor (tan δ) of the epoxy and the composites were evaluated using a dynamic mechanical analyzer DMA 2980 (TA Instruments) at frequency of 3 Hz and heating rate of $10\,^{\circ}C\,min^{-1}$ from room temperature to 200 °C.

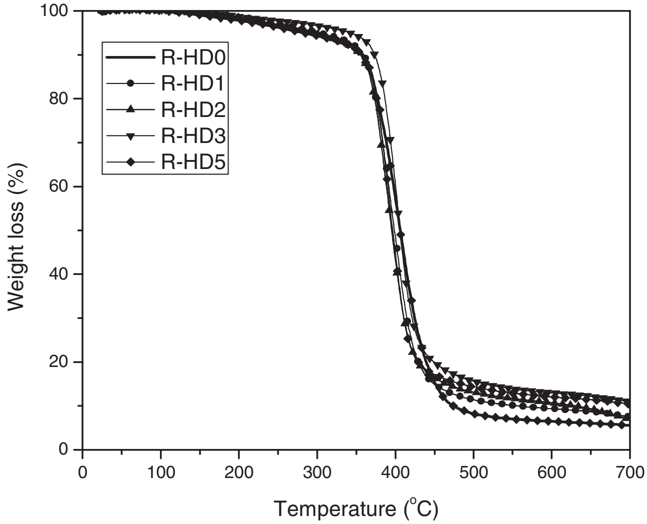

Figure 1.
TGA curves of the epoxy and the composites.

Tensile and flexure strength were evaluated using ASTM D3039 and D790, respectively, in an Emic DL2000 testing machine. Impact properties were evaluated according to ASTM D256 using an IMPACTOR II CEAST equipment and at least five specimens were tested for each composition.

Results and Discussion

Figure 1 and 2 show the thermal analysis (TGA/DTG) curves of epoxy treated with DMF and the composites with 1, 2, 3 and 5 wt% of LDH. The weight loss as a function of temperature shows that the degradation of epoxy resin and of the composites occurs in a single stage at about 374–402 °C. Thermal stability of the composites was slightly higher in comparison with the unfilled epoxy resin and the content residue increased with the LDH content. This behavior suggests that the LDH was effectively dispersed in the polymeric matrix.

Flammability tests were carried out in both vertical and horizontal modes. All composites fell into the classification defined by the UL94 HB, showing much

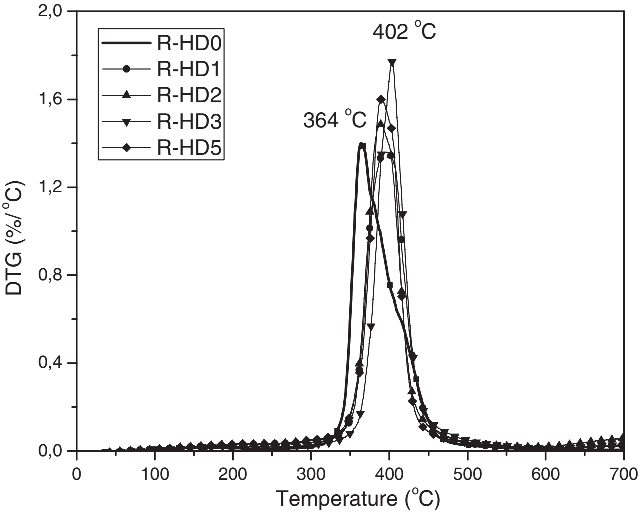

Figure 2.
DTG curves of the epoxy and the composites.

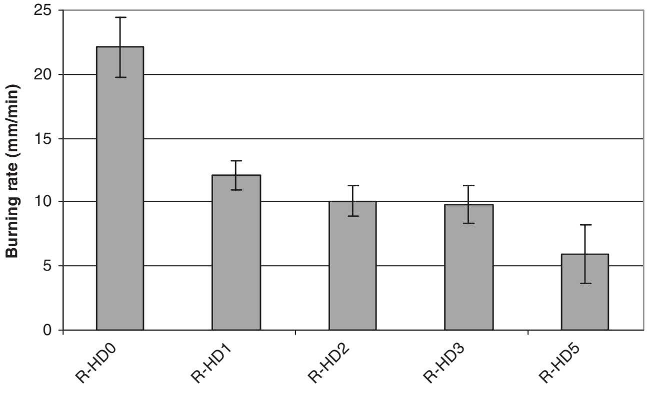

Figure 3.
Horizontal burning rate.

Table 1.
Results of the vertical burning test (UL 94 V).

Sample	Afterflame time*	Classification
R-HD0	Total burning	Unclassified
R-HD1	~28 s	V-1
R-HD2	~23 s	V-1
R-HD3	~22 s	V-1
R-HD5	~21 s	V-1

*Time required for the flame to self-extinguish.

lower burning rate than epoxy (Figure 3). Besides, the rate of burning decreased with the LDH content in the composites because it undergoes decomposition through an endothermic reaction, which acts as a heat sink, reducing the overall heat generated during combustion.[14,15] Barrier formation during combustion is the general mechanism claimed for fire retardancy using polymer/nanoparticle composites.

The unfilled resin did not pass the UL94 V test (Table 1), i.e. the sample showed sustainable burning upon removal of the flame. However, all the studied composites showed self-extinguishing behavior and were classified as V-1 with decrease in the afterflame time from

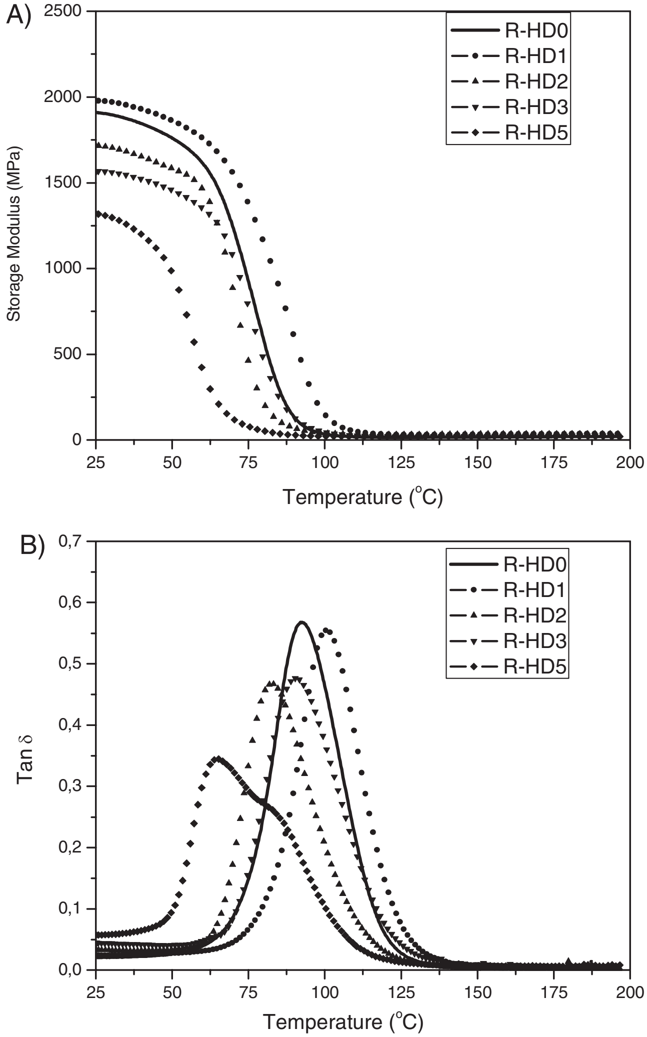

Figure 4.
Storage Modulus (A) and tan δ (B) of epoxy and the composites.

Table 2.
T_g values of epoxy and its composites.

Nanocomposite	T_g as per the tan δ curve (°C)
R-HD0	92.6
R-HD1	100.9
R-HD2	82.9
R-HD3	90.7
R-HD5	65.4

28 s for R-HD1 to 21 s for R-HD5, therefore demonstrating that LDH can be used as an additive to improve the peformance of epoxy resins towards flame exposure.

The storage modulus curve obtained using DMA (Figure 4) of R-H0 and the composites showed similar behavior. The storage modulus decreased with the increase in temperature. Besides, the incorporation of 1 wt% caused an increase in storage modulusbut, above that, this property decreased.

The peak in the tan delta graphs indicates was used to define the glass transition temperature (T_g), which decreased with the addition of LDH (Table 2). This behavior is attributed to the presence of LDH that hinders cross-linking of epoxy having a plasticizing effect on the polymer matrix. Furthermore, the decrease in Tan δ curve peak intensity suggests low toughness of the composites (especially for 5 wt% LDH). In well dispersed nanocomposites, the polymer is intercalated between the lamellae, but without adhesion and, because of that, the chains become more mobile, causing a decrease in T_g.

To investigate the mechanical properties of the composites, tensile, flexural and impact tests were performed. Figure 5 shows the tensile strength results. Comparing pristine epoxy with the composites with 1 and 2 wt% of LDH, it can be noticed that the incorporated LDH failed to serve as reinforcement. Although, the tensile strength slightly increases when 3 wt% of LDH content is reached, it again decreases for 5 wt% of LDH content, showing that, above a certain concentration, LDH may act as stress concentrators, probably leading to premature failure. This observation suggests that the LDH was not exfoliated in the polymer matrix and there were cluster formation occurs at high LDH content. The flexural strength (Figure 6) increases with the addition of 1 wt% of LDH and decreases above that concentration, whereas, for impact strength the higher the LDH content the lower the strength (Figure 7), confirming that LDH failed to serve as reinforcement.[16,17]

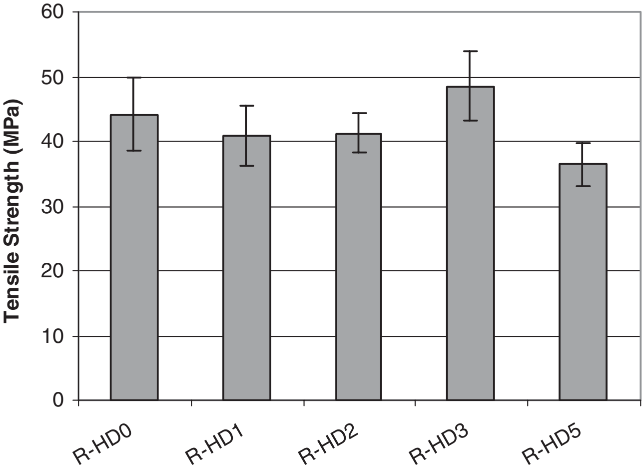

Figure 5.
Tensile strength of the various samples.

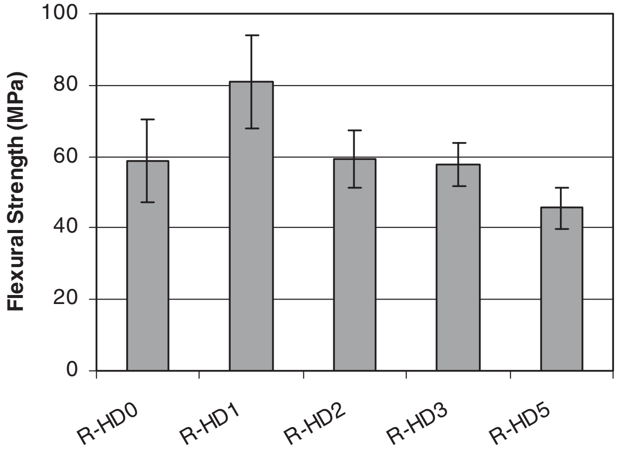

Figure 6.
Flexural strength of the sample.

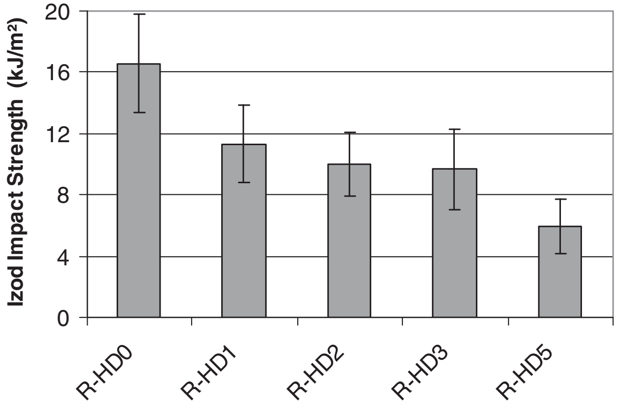

Figure 7.
Izod impact strength of the samples.

Conclusion

In this work, layered double hydroxide/epoxy resin nanocomposites were obtained and the effect of the LDH content on resin properties was studied. Based on the results, it was found that the layered double hydroxides slightly increased the thermal stability of the epoxy resin. Moreover, all the studied composites showed much lower burning rate and attained self-extinguishing behavior compared to pristine epoxy, confirming that Mg-Al LDH can be used to confer flame retardancy to epoxy matrices.

The composites presented an increase in storage modulus at 1 wt% of LDH and a decrease in T_g compared to pristine epoxy that was attributed to a possible decrease in reticulation degree created by the LDH incorporation in the polymer matrix.

The results of the mechanical tests showed that LDH is not very effective as reinforcement, especially regarding impact behavior, what suggests that the LDH was not exfoliated in the polymer matrix or it has low adhesion to the polymer matrix.

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