

# LAYERED DOUBLE HYDROXIDE-EPOXY NANOCOMPOSITES: THE ROLE OF INTERFACIAL ADHESION AND ANION EXCHANGE CAPACITY ON NANOCOMPOSITE PERFORMANCE

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## Introduction

Layered Double Hydroxides (LDHs) represent a class of anion exchanging clays that are easily prepared under normal laboratory settings through a wide selection of divalent and trivalent metal cations. LDHs consists of mixed metal hydroxide layers that are bound together through electrostatic interactions, by charge balancing anions, and extensive hydrogen bonding with the interlayer anions and water[1,2].

The size and anion exchange capacity (AEC) of LDHs can be systematically manipulated during the preparation process by post-precipitation treatments and by varying the divalent: trivalent metal ratios [3,4]. This versatility offers a unique opportunity to systematically investigate synergistic effects that may occur when these two properties are varied along with changing levels of adhesion.

For this study, LDH materials were prepared using a 2:1 divalent:trivalent metal ratio, in which the overall crystallinity and particle sizes were modified by subsequent thermal aging of the newly formed LDH crystallites. The LDH materials were then intercalated with naphthalenecarboxylate anions, and then dispersed into a specific epoxy matrix. The mechanical properties of these nanocomposites were then measured.

The specific epoxy blend consists of diglycidyl ether of bisphenol A (DGEBA) as the bulk

epoxy with a small amount of diglycidyl ether of 1,4-butanediol (DGEBD) added in order to decrease the viscosity of the matrix, enabling easier dispersion of the functionalized LDH.

## Experimental

### Materials

All nitrate salts were used as purchased (magnesium nitrate, Aldrich; zinc nitrate, Fluka, and aluminum nitrate, Sigma Aldrich). Sodium hydroxide (50 % by mass, Aldrich) was used for the deprotonation of 2-naphthoic acid (Fluka,), 6-amino-2-naphthoic acid (6A2N, Aldrich) and for the LDH synthesis.

The DGEBD, DGEBA and 1,3-phenylenediamine were all obtained from Sigma-Aldrich. These chemical structures are shown in Fig.1.

### Preparation of LDH

The LDHs were prepared by precipitating solutions of magnesium nitrate and aluminum nitrate, or zinc nitrate and aluminum nitrate with sodium hydroxide (0.2 mol/L Mg<sup>2+</sup> or Zn<sup>2+</sup>; 0.1 mol/L Al<sup>3+</sup>), such that the hydroxide concentration is six times the aluminum concentrations, in both cases. This procedure

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produces the nitrate version of LDH, or the more commonly referred to “parent LDH”. The nitrate was replaced by the deprotonated acid forms of 2-naphthoate, 6A2N, and a mixture of the two (2/3 naphthoate : 1/3 6A2N; molar ratio).

The suspensions were subjected to overnight stirring under reflux conditions in the presence of a nitrogen blanket (needed to minimize the uptake of adventitious carbon dioxide).

The functionalized products were recovered by centrifugation, washed with deionized water then freeze dried.

### Preparation of LDH-nanocomposites

The LDH-nanocomposites were prepared by adding functionalized LDH (5 % mass fraction) to an epoxy mixture containing a blend of DGEBA and DGEBD (77 % and 23 %, respectively). The LDH was stirred for 2 h with a mechanical stirrer, and then degassed in a 70 °C vacuum oven for 3 h. To the LDH-epoxy mixture, melted m-PDA was added and then mixed in. The LDH/epoxy/m-PDA mixtures were then poured into preheated silicone rubber molds, and the filled molds were immediately placed into a preheated oven, and then cured (60 °C for 3 h, then 121 °C for 2 h).

### Characterizations and measurements

Tensile tests were carried out on the automated tensile testing machine reported in previous research [5]. Before testing, specimens were polished with emery papers No. 800, 1200 and 2400 to remove stress concentration sites at the edges of the samples. The specimens were loaded in tension by the sequential application of strain-steps. Each strain-step was applied at a rate of 85 µm/s and the delay time between the strain-steps was 10 min. The average deformation in the specimen during each strain-step was 85.7 µm.

### Results and discussion

**Table 1** shows the tensile behaviors of the neat epoxy and the LDH-epoxy nanocomposites by applying step loading. The tensile strength of the LDH-epoxy nanocomposites is lower than the neat epoxy, which we attribute to poor interfacial adhesion. The expected standard uncertainty has been calculated to be 1 % of the values reported for the tensile strength measurements.

### Conclusions

LDHs consisting of Mg<sub>2</sub>Al and Zn<sub>2</sub>Al intercalated with 2-naphthoate, 6A2N, and mixtures of the two anions were dispersed into a specific epoxy matrix.

The mechanical properties of the LDH-epoxy nanocomposites were characterized in this study. Preliminary results showed tensile properties of the functionalized LDH-epoxy nanocomposites were not improved over that of the neat epoxy.

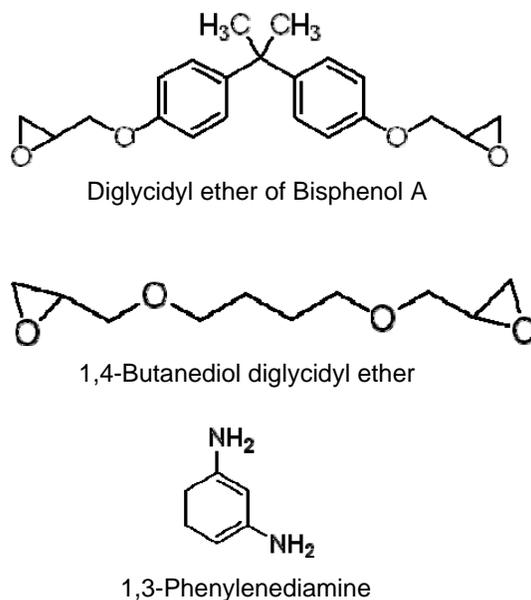


Figure 1. Chemical structures of the epoxy monomer DGEBA, DGEBD and curing agent m-PDA

Table 1. Tensile strengths of the LDH-epoxy samples with the neat epoxy as reference.

LDH-epoxy Sample	Tensile Strength (MPa)
Neat Epoxy	76.3
Mg <sub>2</sub> Al LDH-6A2N	69.6
Mg <sub>2</sub> Al LDH-(2-naphthoate)	61.5
Mg <sub>2</sub> Al LDH-(2-naphthoate + 6A2N)	-
Zn <sub>2</sub> Al LDH-6A2N	62.9
Zn <sub>2</sub> Al LDH-(2-naphthoate)	-
Zn <sub>2</sub> Al LDH-(2-naphthoate + 6A2N)	-

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