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EVALUATION OF FIRE RETARDANT PROPERTY AND MICROSCOPIC CHARACTERISTICS OF LDH REINFORCED COMPOSITE - AN OVERVIEW

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Abstract:

Fiber Metal Laminate materials comprising of Mg-Al alloy has found recognition for applications for automotive and locomotive body panels. The sandwich materials containing Mg-Al alloy, LDH and nanoclay was prepared using cold forming technique. The prepared sandwich material was tested to evaluate its flame retarding property and microscopic characteristics. The results obtained were compared with sandwich sheet without nanoclay added to it.

Keywords: Sandwich materials, LDH, Epoxy, nanoclay, FML's.

1. INTRODUCTION

A lightweight material plays a major role in commercial and industrial programs due to its periodic material properties. Since strength to weight ratio is a major factor in design and construction, composite materials are mostly preferred. In the combination of right matrix element and reinforcement gives us the required parameters. In the technical paper the preparation of sandwich material is made up of Aluminium as reinforcement over Layered Double Hydroxide (LDH) is taken for finding out its formability characteristics and flame resistance behavior.

A Composite Material is defined as the material that is obtained by judicial combining of two or more different materials, which are having different electrical and physical properties, in such a way that the resultant material properties are superior to any of the parental one. Composite materials are usually made of two phases in which one is reinforcement phase and other one is matrix phase. Composites properties comes as a function of its ingredient materials. As a result an unusual Combination of material properties can be obtained. Aluminium is preferred for all applications demanding materials with strength to weight ratio. In Aluminium especially the 5xxx series has many

beneficial characteristics such as high thermal conductivity and electrical conductivity, superior corrosion resistance, strength, toughness. The presence of Magnesium in 5xxx Aluminium makes it hard and tough.

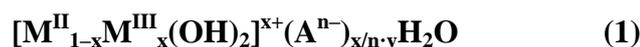
Further the fire resistive properties of the sandwich material are also studied under controlled environment and these materials have wide applications such as automotive body and panels, aircraft shell. The advantage of the specimen is mainly derived from the strength to weight ratio. However, the inclusion of LDH as major constituent creates a threat in case of fire hazardous environments.

2. Fabrication of Sandwich Material

The sandwich material is typically made up of Aluminium and LDH. However epoxy resin is incorporated as a secondary material in order to aid in setting of the sandwich material. The specimen was made using cold forming technique, which is relatively new when considering the fabrication of sandwich materials. The fabrication of the specimen was first preceded by selection of materials. Like all typical sandwich materials, the specimen consists of two thin but stiff material as the skin separated by relatively soft but thick core material. The material chosen for skin of the sandwich is AA 5052 H32. This grade of Aluminium has wide applications ranging from simple household items like cooking utensils, to truck body components to marine applications such as Marine structures. It has good properties such as good strength to weight ratio, formability, weld ability, corrosion resistance in salty atmosphere and also it is cheap. These suits the specifications needed to be used as automotive body structures [1].

3. General Preparation of Layered Double Hydroxide

The core material chosen was Layered Double Hydroxide. According to **Mingdong Dong, et.al.** Layered Double Hydroxide (LDH) is a class of anionic clays with the structure based on brucite (Mg (OH)₂)- like layers in which some of the with trivalent cations occupies the places of divalent cations yielding positively charged sheets. LDHs can be represented by the general formula [2].



where M^{II} and M^{III} cations occupy octahedral holes in a brucite-like layer and Aⁿ⁻ anion is located in the hydrated interlayer galleries.

The identities of the divalent and trivalent cations (M^{II} and M^{III}, respectively) and the interlayer anion (Aⁿ⁻), together with the value of the stoichiometric coefficient (x), may be varied over a wide range, giving rise to a large class of isostructural materials [3]. Considered generally as promising materials in view of their high chemical versatility associated with a tunable anionic exchange capacity.

3.1. Fibre Reinforced Metal Laminates(FML)

Fibre Reinforced Metal Laminates (FML) are hybrid composites consisting of alternating thin layers of Metal Sheets and Fibre-reinforced Epoxy prepreg. The most commonly used metal for Fibre Metal Laminates is Aluminium and the Fibres can be aramid or glass. These laminates possess some of the most desirable properties of both metal and fibrous composite materials [4].

3.2. Epoxy Resin: Epoxy resin is one of the excellent thermosetting polymer resins. The cost-to-performance ratio of epoxy resin is outstanding. Epoxy resins possess characteristics such as high strength low creep, good adhesion to most of the substrate materials, low shrinkage during curing and low viscosity. Due to these reasons epoxy resins are significantly used as matrix material in many applications such as aerospace, structural applications, ship building, and automobile industries and so on[5].

4. Flame-Retardant Properties of Epoxy/MG-AL LDH Composites.

- i. The modern flame retardant methods should not be toxic to human, animals and plants.
- ii. The migration should not occur. Which means after the finished product should not release any harmful evaporating gases. This can be achieved by using reactive flame retardants which will react with the polymers.
- iii. Developed flame retardants should not release any additional toxic, harmful or corrosive smoke gases during the case of fire.
- iv. Recycling properties of the flame retardant should not be negatively affected.
- v. Flame retardant must be environmental friendly either neutral or bio-degradable.

4.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, Araldite LY 1316–Huntsman) and triethylenetetramine (TETA, Aradur HY 1208 – Huntsman) curing agent were used. $Mg(NO_3)_2 \cdot 6H_2O$ (Vetec), $Al(NO_3)_3 \cdot 9H_2O$ (Vetec), sodium hydroxide (Nuclear) and glycine (Vetec), all in analytical grade, were employed to synthesize the glycinate intercalated layered double hydroxides (LDH). Three different solvents were used to aid dispersion (delamination/exfoliation) of the LDH, namely, acetone (Vetec), chloroform (Synth) and dimethylformamide (DMF) (Nuclear).

4.2. Polymer and LDH/EPOXY Composites Preparation

The pristine epoxy polymer was obtained by mixing the epoxy monomer (Araldite LY 1316) with the curing agent (Aradur HY 1208) at room temperature for 3 min, degassing the mixture using an ultrasonic bath, casting into a

silicon rubber mold, curing at room temperature for 24 h, then post curing it at 70 C for 1 h. For the composites, solvents were used to aid dispersion (delamination/exfoliation) of the LDH crystals. In order to investigate the effect of the solvent itself on the epoxy resin, some epoxy samples were mixed with acetone, chloroform or DMF followed by evaporation and curing. Identification of all samples prepared in this work is shown in table below.

The following five-step route was selected, after experimental optimization, for the preparation of the composites[6 to 8]:

- a) LDH (1, 3 or 5 wt.%) were dispersed in one of the solvents (as described above) using strong sonication for 20 min to achieve homogeneous dispersion.
- b) The desired amount of epoxy resin was added to the LDH suspension and the mixture was sonicated for 20 min.
- c) The mixture was placed on a vacuum assisted rotary evaporator and heated in a water bath at 50, 60 or 100 °C for acetone, chloroform or DMF, respectively, in an attempt to promote a thorough evaporation of the solvent. These temperatures were chosen based on the boiling temperature of each solvent (56, 61 and 153 °C, respectively).
- d) The curing agent was added to the LDH/epoxy mixture, which was then mechanically stirred under sonication for 3 min.
- e) The LDH/resin was cast into a silicon rubber mold and cured at room temperature for 24 h. After that, the composites were post-cured at 70 °C for 1 h.



Fig. 1. Schematic presentation of Fibre Metal Laminate (Courtesy- CPRI, Bangalore).

4.3. Characterization

X-ray crystallography is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density

of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

X-ray diffraction was conducted at a scanning speed of 1/min using a Shimadzu (XRD-6000) diffractometer with a Cu Ka source (1.5418 Å). Data was collected in a step scan mode between 3 and 50 (for 2hours) using the flat samples directly on the sample holder.

A Scanning Electron Microscope (SEM) is a type of electron microscope instrument that pictures of a sample by scanning it with a focused beam of electron particles. The electrons work together with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography structural information and composition. The electron beam is generally scanned in a raster (is a sequence of horizontal lines that are scanned rapidly with an electron beam from left to right and top to bottom) scan pattern. The resultant image is produced by combination of deflected signal to beam's position. Specimens can be observed in high vacuum, in low vacuum, in dry conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures. The morphological characteristics of the` composites were studied with a Jeol JSM 6060 scanning electron microscope (SEM) after coating of the samples with a thin layer of gold.

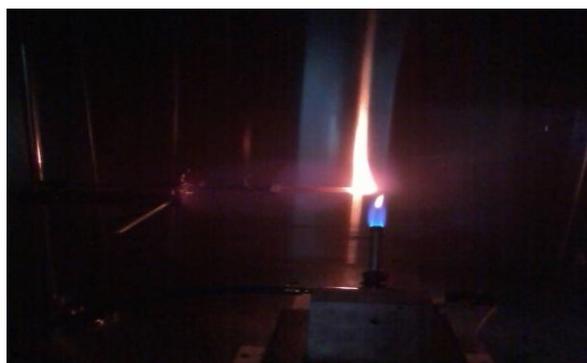


Fig. 2. Burning test(Courtesy-CPRI-Bangalore).

Fourier transform infrared spectroscopic (FTIR) studies were carried out using a Perkin Elmer Spectrum 1000 FTIR spectrometer in the 4000 to 400 cm^{-1} wavenumber range, using the transmission mode, KBr pellets and accumulation of 32 spectra.

Thermogravimetric analysis (TGA/DTG) was performed in a TA Instruments 2050 equipment, by heating the samples from 25 to 96 °C at a heating rate of 20 °C/min under O_2 atmosphere. Tensile properties (strength, modulus and strain at failure) were evaluated according to ASTM D638 using an Emic DL 2000 testing machine coupled with an extensometer. Flexural properties were evaluated using rectangular samples and the same testing machine, following ASTM D790. At least five specimens were tested for each composition.

Table 1: Identification of the samples and the solvents used to disperse the LDH[9].

Sample Name	LDH (% wt.)	Solvent used
R-H0 (pristine)	0	Acetone
R-H0A	0	Chloroform
R-H0C	0	DMF
R-H0D	0	Acetone
R-H1A	1	Chloroform
R-H1C	1	DMF
R-H1D	1	Acetone
R-H3A	3	Chloroform
R-H3C	3	DMF
R-H3D	3	Acetone
R-H5A	5	Chloroform
R-H5C	5	DMF
R-H5D	5	Chloroform

Evaluation of flammability was carried out using the UL 94 tests. Vertical burning (UL 94 V) and horizontal burning (UL 94 HB) tests were carried out in 130 * 13 * 4 mmspecimens. For each composition, the mean result of five measurements is reported.

5. Flame Retardant Properties of LPDE/LDH nanocomposite.

5.1. Preparation of LPDE/LDH NANOCOMPOSITE

The pristine Mg-Al LDH was modified with SDBS by regeneration method and used for the preparation of LDPE/LDH nanocomposites. The detail description of the method and the characterization the SDBS modified LDH (henceforth designated as LDH-DBS, where DBS means dodecylbenzenesulfonate) are already reported in our earlier communications[10].

The nanocomposite compositions were prepared following two steps.

- a) In the first step, LDH-DBS was meltcompounded with PE-g-MAH at a weight ratio of 1:1 (based on the approximate metal hydroxide content of LDH- DBS) to prepare a masterbatch.
- b) This masterbatch in the second step was diluted with LDPE through melt compounding.

Both the steps were carried out in a tightly intermeshing and co-rotating twin-screw extruder (Leistritz Micro 27) having screw diameter 27 mm and L/D ratio of 36. The conditions used for melt-compounding steps were 160-210 °C

temperature profile along the extruder barrel from the feed section to the die section with 200 rpm screw speed and 6 kg/h feed rate. The concentrations of LDH in the nanocomposite were determined based on an approximate metal hydroxide content of the filler. LDH-DBS prepared in the present study contains about 46.0% of its weight as metal hydroxide. Its approximate composition based on average sulfur content (determined from elemental analysis and the average of three measurement was taken for calculation) and the value of 'x' is given by the formula[11].



5.2. Characterization of LPDE/LDH Nanocomposite

The morphological analysis was carried out using transmission electron microscopy (TEM) with microscope LEO 912. The conditions used during analysis were room temperature, 120 kV acceleration voltage and bright field illumination. The ultra-thin sections of the samples were prepared by ultramicrotomy at 120 °C with a thickness of a section 80 nm. Thermal analysis was carried out with a thermogravimetric analyzer (TGA 6 from Perkin Elmer) using a constant heating rate of 10 K/min both under air and nitrogen atmospheres.



Fig. 3. “UL 94” Horizontal Burning test apparatus (Courtesy-CPRI-Bangalore).

The flammability properties were investigated using the tests methods such as cone-calorimeter analysis (with the cone-calorimeter from Fire Testing Technology Ltd., United Kingdom), limited oxygen index (LOI) determination (LOI instrument from Raczek Scientific Instruments, Germany) and UL94 vertical and horizontal burn testing (Horizontal Vertical Flame Chamber made by Atlas Material Testing Solutions formerly known as Atlas Electric Devices)[12].



Fig. 4. Experiment of Horizontal burning (Courtesy-CPRI-Bangalore).

The LOI measurements were carried out following ASTM D 2863 with specimen size 120x10x4 mm. The cone-calorimeter investigations were made the horizontal positioning of the samples having dimension 100x100x4 mm and with an external heat flux of 30 kW m². The cone-calorimeter results were averaged over four measurements for each composition. All the samples were preconditioned at 23°C and 50% relative humidity for 24 h. The UL94 V and UL94 HB testing were carried out with 130x13x4 mm specimens and averaged over five measurements for each composition. The test specimens used for flammability investigation were injection molded under identical conditions.

Table 2: LDPE/LDH nanocomposite prepared following melt-compounding method [13].

LDPE/LDH nanocompositions	Metal hydroxide content, wt%
PE-LDH1	2.43
PE-LDH2	4.72
PE-LDH3	6.89
PE-LDH4	8.95
PE-LDH5	12.75
PE-LDH6	16.20

5.3. Cone Calorimeter Investigation

The cone calorimeter investigation is a very popular and standard method for ranking and comparing the flammability properties of polymeric materials. During the entire combustion process of the sample in a cone calorimeter, a constant external heat flux is maintained to sustain the combustion of the test sample i.e. the test method creates a forced flaming combustion scenario. Therefore, the test results from cone calorimeter are very important in flammability evaluation of any polymeric materials. In contrary, sustained combustion of the test samples in the test methods, like LOI, UL94, etc. depend on material's heat of combustion. The results from the cone calorimeter investigations of the LDPE/LDH nanocomposites are summarized.

The cone-calorimeter investigation reveals that the Mg/Al LDH is indeed very efficient to reduce the heat release rate and total heat released during combustion, which are important to reduce the tendencies for quick fire growth and for large-scale fire formation. Mg/Al LDH also facilitates the formation of carbonaceous char on the burning surface

causing less emission of carbon monoxide during the initial phase of burning. At LDH concentration above about 10 wt%, the nanocomposites not only burn at extremely slow rates, but also show low dripping tendency. However, LDH alone, at these concentrations, is not sufficient to obtain high LOI value or V0 rating in UL94 testing. We believe that improved dispersion of Mg/Al LDH in polyethylene in comparison to conventional metal hydroxide fillers (like MH, aluminum trihydrate, etc.), can be helpful to reduce the overall filler loading for obtaining satisfactory flammability rating.

5.4. Flammability Study By UL 94

UL94 testing was carried out following two standards: one is the vertical burn test (UL94 V) and the other is the horizontal burn test (UL94 HB). The LDPE/LDH nanocomposites containing up to 16.2 wt% LDH did not pass any of the UL94 V specification. All the samples start burning spontaneously after first 10 s flame application, which continues until the test specimen is completely burnt up to the sample holding clamp. This means that the nanocomposites are not self-extinguishing. However, UL94 V gives useful information regarding the dripping behavior of the nanocomposites. The dripping of burning melts directly influences the spread of flame through secondary flaming during real life burning situations. Although all the samples show dripping while burning, the time at which dripping starts is significantly increased by the presence of LDH. A parameter called time to start dripping was defined as the time after first 10 s flame application at which first dripping occurs that ignites a piece of cotton kept underneath.

The time to the first dripping increases steadily with increasing LDH concentration in the nanocomposites and becomes more than 10 times at 16.2 wt% LDH (PE/LDH6). Similar, trend was also observed in case of polypropylene/layered silicate based nanocomposites where none of the composition achieved any UL94 V rating, but showed improved dripping behavior compared to the unfilled polypropylene. The slow and much delayed dripping tendency in LDPE/LDH nanocomposites can be related to the high melt viscosity of the nanocomposite composition. As can be seen, higher the viscosity of the LDPE/LDH nanocomposite higher is its resistance against dripping during burning. While in the case of unfilled polyethylene dripping starts in the form of a continuous stream of burning melt due to low viscosity, that in presence of LDH takes place in the form of chunks of glowing residue or ash. The LDPE/LDH nanocomposites pass UL94 HB rating and shows much better performance in terms of rate of burning compared to the unfilled polyethylene. It has been found that the rate of burning (expressed in mm/min) steadily decreases with increasing LDH concentration in the nanocomposites. This also qualitatively related to the

cone-calorimeter investigation results, where the nanocomposites containing higher amount of LDH are found to burn for longer duration. At LDH concentration above 10 wt%, the nanocomposite burns extremely slowly resulting in very slow rate of mass loss by the materials.

Applications

- LDHs are widely used in commercial products as adsorbents, catalyst support precursors, anion exchangers, acid residue scavengers, flame retardants and polymer stabilizers.
- LDH has many applications depending upon the additives selected to create it. The many applications of LDH includes: catalyst, water treatment, biology, medicine, cement and flame retardant. Powdery LDH is also commercially promising as an additive in flame retardants. Compared to other flame retardants, LDH is a new type of material due to high smoke suppression, non toxicity or low toxicity.
- Clinical Applications of Lactate Dehydrogenase Isozymes: Alterations in Malignancy[15].
- Powdery LDH is also commercially promising as an additive in flame retardants. Many flame retardants are considered harmful, having been linked to liver, thyroid, reproductive/developmental, and neurological effects [16].

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