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Synergistic effect of LDH on thermal and flame retardant properties of unsaturated polyester nano-composite containing TXP

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Abstract

In this report, we have explored the thermal stability and flammability of unsaturated polyester resin (UP) nano-composites blended with flame retardant trixylenyl phosphate (TXP) and nano-filler dodecyl sulphate intercalated magnesium aluminum layered double hydroxide (MgAlDS LDH). MgAl LDH was synthesized by co-precipitation method and anion dodecyl sulphate was intercalated by ion exchange method. The XRD analysis denoted the presence of layered double hydroxide crystal lattice which supports the structural conformation. The IR spectra of trixylenyl phosphate (TXP), MgAl LDH and MgAlDS LDH depicted their relevant vibrational transitions. The nano-composites of unsaturated polyester, crossed linked with styrene, were prepared by mixing varying proportions of TXP and MgAlDS LDH. The XRD of the composites reveal the exfoliation of MgAlDS LDH in polymer matrix, which enhances the thermal stability of nano-composite containing 1% MgAlDS LDH along with TXP than the polymer containing TXP alone, was shown by TGA. The Unsaturated polyester (**UP**) resin nano-composite decomposes by two stages. There was 8% reduction in peak mass loss rate of nano-composite containing 1% MgAlDS LDH along with TXP in comparison to nano-composite containing only TXP. UL-94 study shows that MgAlDS LDH had flame retardant properties as confirmed by reduction of burning rate in comparison to virgin unsaturated polyester resin. Morphology analysis by SEM on Charred residue of nanocomposite containing 23% TXP and 1% MgAlDS LDH has shown more compact, hard and without any pin holes upper layer than nanocomposite containing only 24% TXP alone. This can be used in preparation of flame retardant articles of unsaturated polyester resin and will allow use of unsaturated polyester on places where it is avoided due to high flammability and low thermal stability.

Keywords: Layered double hydroxides, polymer, nano-composite, thermal stability, flame retardant.

Introduction

Unsaturated polyester resin (UP) are vastly used for composite manufacturing in industry due to good mechanical properties, low density and low market value. These unsaturated polyester resins are processed by radical polymerization between a pre-polymer that contains unsaturated groups and styrene which acted as a diluent as well as cross linking agent. These UP resins are used as pure or as a fiber reinforced composite in various applications such as naval construction, offshore applications, chemical containers, building construction, automobiles, etc.

As most of the polymers are flammable and so is unsaturated polyester resin, but to make them thermally stable and flame retardant, different flame retardant additives are used **[1, 2]** Mostly halogen based flame retardants were used due to cheap price but they generated toxic gases at the time of combustion. Due to the generation of harmful gases to atmosphere many environmental controlling authorities, have banned the use of halogenated flame retardant additives in preparation of polymer composites. Phosphorus based flame retardants are being used currently as they are comparatively eco-friendly than the halogen based flame retardants. Inorganic flame retardants like magnesium hydroxide and aluminum hydroxide are used but require a very high percentage to get a desired level of flame retardancy which disturbs the mechanical properties of composites [**3**]. To counter these difficulties, another class of inorganic layered materials called Layered double hydroxide (LDH), having the general molecular formula $[M^{2+}_{1-x}M^{3+}_{x}\ (OH)_2]^{x+}\ [(A^{n-})_{x/n}\cdot mH_2O]$ where M^{2+} is a divalent cation like Mg^{2+}, Zn^{2+},Co^{2+},etc. while M^{3+} is a trivalent cation like Al^{3+}, Cr^{3+}, Zr^{3+}, etc. and $A_{x/n}^{n-}$ are charge balancing anions like nitrate, chloride, sulphate etc. They are prepared by different routes and used after intercalation of organic long chain anions like carboxylates, long chain aliphatic sulphate or sulphonate or phosphonate etc. as LDH have ion exchange properties [**4-10**]. Intercalation of organic chain in between the brucite like layers in LDH make them more hydrophobic therefore increases the compatibility with polymers. Secondly, the intercalation of organic chain increases the d-space between the layers allowing monomers/polymers to intercalate easily, resulting in exfoliation of LDH in polymer matrix.

The good dispersion due to exfoliation allows LDH to provide a physical barrier to fire at lower dosing and act as heat sink in polymer nanocomposite [**11-13**]. To pass the industrial standards of flame retardancy, addition of LDH alone is not sufficient so this is used along other flame retardants and combination also gives synergistic effect. Synergistic effect of magnesium hydroxide or aluminum hydroxide and nanoclay in EVA composites were studied and showed that increased thermal stability and charred residue [**14]**.The effect on Fire retardancy of melamine and Zinc aluminum LDH in combination with poly(methyl methacrylate) showed the reduction in dosage of melamine in presence of LDH for good reduction in peak heat release rate [**15]**.The increase in thermal stability and flame retardant properties were reported by the combination of phosphate based Intumescent flame retardant, organic anion intercalated MgAl LDH and graphene with polymethyl methacrylate [**16]**.The homogeneous dispersion along with good thermal stability and flame retardancy was in the study of phosphate derivative intercalated in MgAl LDH with unsaturated polyester resin [**17**]**.**The thermal stability of epoxy resin was increased by MgAlDS LDH in presence of organophosphate**[18]**. In this study, trixylenyl phosphate (TXP) in combination with dodecyl sulphate (DS) intercalated MgAl LDH (MgAl DS LDH) in different percentage are used as flame retardant. The synergistic effect of MgAlDS LDH in presence of TXP on thermal and flame retardant properties of unsaturated polyester (UP) has been investigated systematically. The advantage of this work is to get reduction in loss of decomposed volatile compounds by formation of hard, compact and pin hole free upper surface layer on high temperature resulting in high thermal stability and flame retardancy of unsaturated polyester composite. Further, this work explores the optimization of formulations to use minimum dosage of organophosphate flame retardants in preparation of environmentally safe nanocomposites.

Experimental section

Materials / chemicals

Unsaturated polyester resin with styrene as diluent, Methyl ethyl ketone peroxide as catalyst and cobalt naphthenate as accelerator were purchased from Amtech esters, Delhi, India. Xylenol (purity 99% minimum) was purchased from Sasol chemicals north America LLC, USA. Phosphorus oxychloride was purchased from Tina organics (P) LTD., INDIA with purity more than 95%. Laboratory grade Magnesium nitrate was purchased from Loba. Aluminum nitrate, sodium nitrate and sodium hydroxide were purchased from MERK. Sodium dodecyl sulphate was purchased from Pioneer chemicals Delhi, India.

Synthesis

Synthesis of magnesium aluminum nitrate layered double hydroxide (MgAl LDH)

Magnesium aluminum layered hydroxide was synthesized by earlier reported method [**19]**. In this synthesis, three solutions were prepared; firstly, a solution of magnesium nitrate (2M) and aluminum nitrate (1M) was prepared in water (Solution A). A second solution of Sodium hydroxide (5M) and sodium nitrate (3.4M) solution was prepared (Solution B). Third solution of sodium hydroxide (1.6M) in water (Solution C) was prepared. Solution A and B were added simultaneously in distilled water in a glass reactor with constant stirring, with N_2 gas purged to stop the absorption of carbon dioxide from atmosphere. In all steps, decarbonated distilled water was used. After completion of solution B addition in reactor, solution C was added to maintain the pH of the solution at 10. Magnesium aluminum nitrate layered double hydroxide was precipitated and aged overnight in oil bath at 80°C and then filtered. The white slurry was washed with decarbonated distilled water till pH of filtrate was neutral. The precipitates were dried at 80°C for 24 hours in a vacuum oven under N_2 blanket.

Synthesis of magnesium aluminum dodecyl sulphate layered double hydroxide (MgAlDS LDH)

1M of Magnesium aluminum nitrate layered doubled hydroxide was added in decarbonated distilled water at 80°C in glass reactor under N_2 blanket, which was stirred for 1 hour. 0.34 M of sodium dodecyl sulphate was added and kept for constant stirring for 24 hours. The precipitate was filtered and washed with hot distilled water till the filtrate attained neutral pH. The precipitate is dried at 80°C for 12 hours in N_2 gas blanket.

Synthesis of Trixylenyl phosphate(TXP)

3M of Xylenol was charged in a flask reactor with a condenser, temperature pocket and mechanical stirrer carried out in a heating muffle. 1M of Phosphorus oxychloride was added along with a catalyst and the temperature was gradually raised up to 200°C (**20**). During the course of the reaction, the generated hydrogen chloride was absorbed in water. The crude reacted product is distilled under 1mm Hg reduced pressure. The distilled product was first washed with dilute solution of sodium hydroxide then with distilled water till the pH of the product was neutral and the moisture was removed by heating the washed product up to 120˚C, under reduced pressure (S1).

Preparation of TXP, MgAlDS LDH containing unsaturated polyester Resin blended nanocomposites

Unsaturated polyester (**UP**) resin was blended with TXP and MgAlDS LDH for half an hour by magnetic stirring and later ultrasonicated for 15 minutes. The catalyst and accelerator were added and mixed thoroughly for 5 minutes, which was transferred in to mold. The unsaturated polyester nano-composites containing different concentrations of TXP and MgAl DS LDH were prepared as given in **Table-1**.

Table 1: Composition of unsaturated polyester nano-composite with TXP and MgAlDS LDH.

Sample code	UP Resin (Wt. %)	Catalyst (Wt. %)	Accelerator (Wt. %)	TXP (Wt. %)	MgAlDS LDH (Wt. %)
UP-1	95	2.5	2.5	—	—
UP-2	71.5	1.75	1.75	25	—
UP-3	71.5	1.75	1.75	24	1
UP-4	71.5	1.75	1.75	23	2
UP-5	93	2.5	2.5	—	2

Characterization

The FTIR was recorded on Prestige 21-Shimadzu spectrometer within 400-4000cm^{-1} spectral range with resolution of 5 cm^{-1}. The compounds were palletized using KBr(1%) solid state pelletizer.The XRD was recorded on Shimadzu XRD 6000 diffractometer with CuK source (λ = 0.15418nm) using scanning speed (10°/ min), recorded in step scan mode between 4-70°(2θ) using flat powdered sample on holders.The SEM images and EDX spectra were recorded on JEOL model JSM6360 with a magnification (30,000X) ranging within1µm. All TXP and MgAlDS LDH unsaturated polyester nanocomposites were coated with conductive layer of gold. The flammable property was analysed by American standard UL-94 using instrument make by SA associates, Delhi. The flammability was recorded in horizontal position for HB classification using 130mmx13mmx4mm specimens for each composite. Thermogravimetric analysis curves were recorded on Netzschtg 209F1 under oxygen environment from 100°C to 700°C with heating rate of 10°C/min. Muffle furnace model TIC 4000 of Thermotech was used for charring of nanocomposite samples in air.

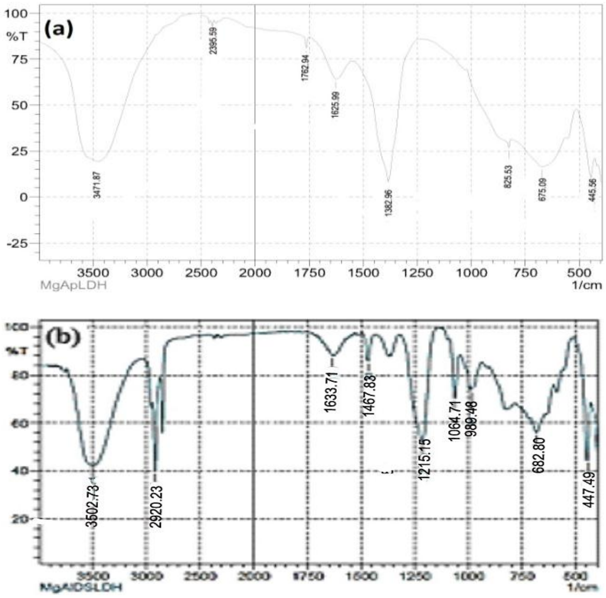

Fig. 1(a) FTIR spectra of MgAl LDH **1(b).** FTIR spectra of MgAl DS LDH.

Results and discussion

Characterization of MgAl LDH and MgAlDS LDH

The IR spectra of MgAl LDH, in **Fig. 1(a),** shows a absorption peak at 3471.87cm^{-1} which corresponds to the hydroxyl groups present on MgAl LDH lattice and free water molecules within the inter-gallery space. The absorption peak at 1382.96cm^{-1}corresponds to the nitrate ions within MgAl LDH. In **Fig. 1(b)**, the appearance of absorption peak at 1215.15cm^{-1} corresponds to sulphate ions, confirming a selective anionic exchange in MgAl DS LDH with comparison to MgAl LDH **[21]**. The absorption peak at 2920.23cm^{-1} corresponds to -CH_2-bonds in dodecyl sulphate units. This clearly shows that the intercalation had taken place and confirms the formation of MgAlDS LDH.

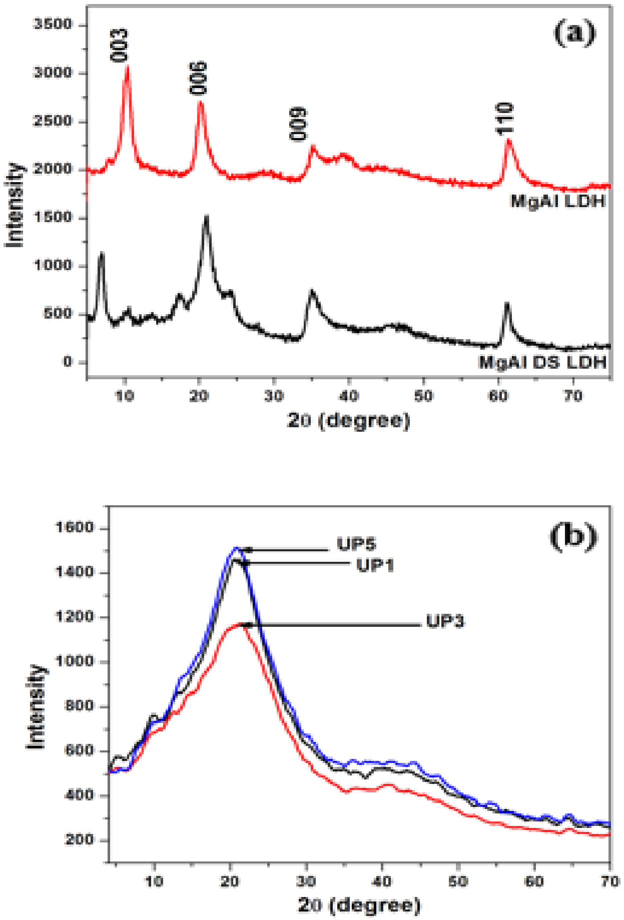

Fig. 2(a) The XRD pattern of MgAl DS LDH and MgAl LDH shows a shift at 003 planes due to anionic exchange **(b)** The exfoliation of UP blended composites.

In **Fig.2**, the XRD pattern of MgAl LDH shows a prominent peak at 2θ value of 10.27º, 20.66º, 35.2º and 61.51º, corresponds to miller indices (003), (006), (009) and (110) planes as reported earlier in literature**[22]**. Low 2θ peaks at equidistant positions shows that this MgAl LDH had a crystalline layered structure. The interlayer d-spacing is calculated by Bragg's equation which is 8.6 A° and average crystallize size is 5.5 nm, calculated by using Sheerer equation for (003) plane.

The diffraction peaks were symmetrical at low 2θ values, which indicate that the material was crystalline. As seen in **Fig 3(a-b)**, the SEM image of MgAl LDH, recorded at 1μm, had a layered structure with sharp but irregular edges. MgAlDS LDH showed the same patterns with slight surface changes due to sulphate functionality.

The EDX spectra of MgAl LDH shown in **Fig. 4**, indicates that atomic ratio of magnesium and aluminum is 1.94. In the XRD pattern of MgAlDS LDH the diffraction peak for (003) plane appears at lower 2θ value which confirmed the increase in d-spacing from 8.6Å to 12.39Å. By using sherrer equation on plane (003), the average crystalline size was 9.68 nm. SEM image (**Fig.3b**) shows that this was crystalline with irregular edges and EDX confirms the presence of sulphur in MgAlDS LDH.

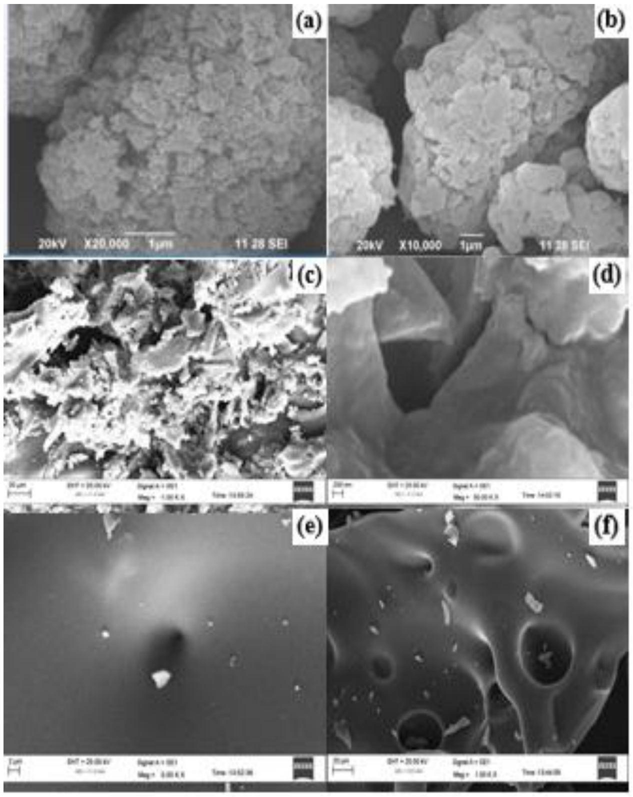

Fig.3(a-b)SEM image (1μm) of MgAl LDH and MgAl DS LDH respectively; **(c-d).** SEM image (200nm-20μm) of MgAl DS LDH and TXP blended UP-3 nano-composite.(**e-f**) The SEM image of Charred UP-2 and UP-3 LDH composites.

Characterization of Trixylenyl phosphate

Trixylenyl phosphate **(TXP)** was synthesized and obtained as colourless liquid as per the procedure reported in literature**[20]**. The IR spectra of Trixylenyl phosphate was observed in **Fig.5.** The FTIR spectra (S2) of Trixylenyl phosphate shows the characteristic bands due to phosphate ,C-H in aromatic ring and alkyl groups on the aromatic ring . Band at 1305.86cm^{-1}was due to P=O group present in phosphate of trixylenyl phosphate as reported in earlier literature**[23]**. Presence of band at 1191.09 cm^{-1} was due to P-O-C (phenyl). Methyl group on aromatic ring gives band at 2924.21cm^{-1}.C-H present on aromatic ring shows band around 3000 cm^{-1}. This FTIR spectra superimposes the standard spectra for TXP. This establises the formation of Trixylenyl phosphate.

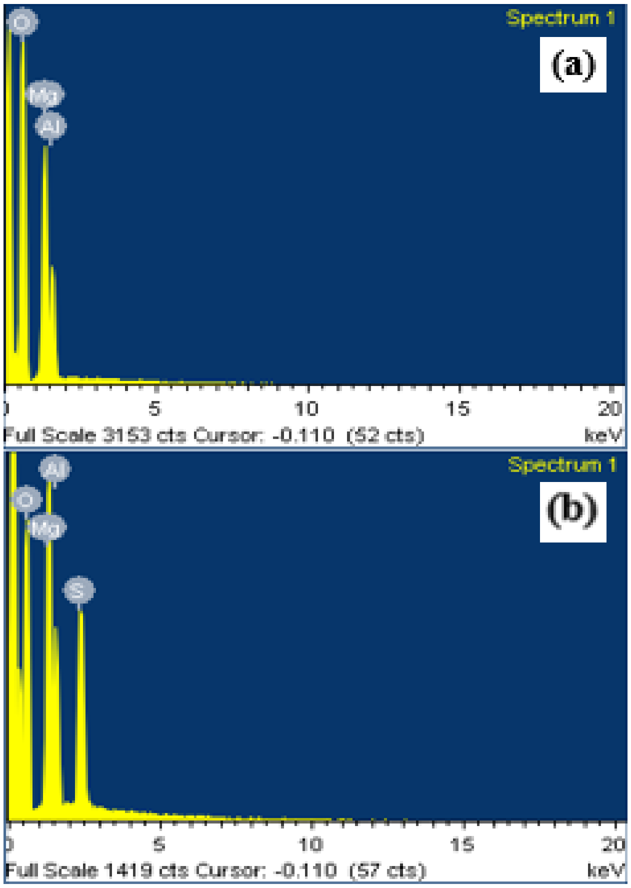

Fig. 4(a)EDX spectra of MgAl LDH **(b)** EDX spectra of MgAl DS LDH.

Characterization of unsaturated polyester resin nanocomposite containing MgAlDS LDH and TXP

Unsaturated polyester (UP) resin is mixed with TXP and MgAlDS LDH as per the compositions given in **Table-1.** The XRD pattern of UP-1 which contains only unsaturated polyester resin, accelerator and catalyst shows broad hump at 2θ (21º). In UP-3, nanocomposite containing 24% of TXP and 1% of MgAlDS LDH were present and XRD pattern showed that all low 2θ diffraction peaks had disappeared and only broad hump appeared due to unsaturated polyester at 2θ(21º). Similarly in case of UP-5, this contained only 2% of MgAlDS in unsaturated polyester resin and showed a broad diffraction hump at similar 2θ. This clearly suggests that MgAlDS LDH has exfoliated in the resin which was supported by SEM images in **Fig. 4(c-d),** of UP-3 which showed the uniform distribution of MgAlDS LDH within the nanocomposite.The disappearance of characteristics peaks of MgAlDS LDH in nanocomposites were due to the intercalation of bulky polymer chains in galleries of LDH.

Thermal stability

Thermal stability of unsaturated polyester resin nanocomposite was studied by Thermogravimetric analysis and their TGA curves were shown in **Fig. 6(a)** and their derivative were shown in **Fig. 6(b)**. Different temperatures were shown for 20%, 50% and 70% weight loss for different nanocomposites in **Table-2**. At 20% weight loss, UP-2 and UP-3 both have lower temperature than the UP-1 which was virgin unsaturated polyester resin composite without any additive. The nanocomposite UP-4 and UP-5 had higher temperature than UP-1 for 20% weight loss may be because of cooling effect due to water loss present in MgAlDS LDH and dehydration of metal hydroxide sheet present in MgAl LDH. At 50% weight loss, all nano-composites show more stability than UP-1. Up to 50% weight loss, UP-2 and UP-3 degrade at same temperature but on 70% weight loss, UP-3 has better Thermal stability than UP-2 as shown by better $\Delta T_{0.7}$ value.

The increase in thermal stability was due to the presence of MgAlDS LDH with TXP which act as endothermic heat sink by releasing water vapors present between the layers and formation of mixed metal oxide on decomposition and formation of phosphate derivatives which react with polymer fragments and form char which was catalyzed by the presence of metal oxides.

In **Fig. 6(b),** DTG shows that UP nano-composite decomposed in two stages. The mass loss rate in first stage was low in comparison to second mass loss rate peak. In first stage only cross linking chain of polystyrene was lost as CO, CO_2, Methane and ethylene and major mass loss in second stage is due to unsaturated polyester. UP-2 had maximum mass loss rate for first peak. The second mass loss peak shows maximum mass loss in case of UP-3 at -0.703 in comparison to UP-2 which had maximum mass loss rate of -0.76. This shows that there is the reduction of 8% in mass loss rate due to the presence 1% MgAlDS LDH which make protective layer on upper surface of nanocomposite to reduce the intensity of heat flux. At 600°C, UP-3 has more residue than UP-2.

Flammability properties

The Flammability properties of unsaturated polyester nano-composites are analyzed by UL-94 standard which is a qualitative method for testing flammability. Horizontal Burning method shows rate of burning per minute of polymer composite.

These observations show that addition of MgAl LDH in UP-5 has reduced the burning rate by 2.32 mm/min in comparison to virgin polymer UP-1(S3(a-b)). In case of UP-2, UP-3 and UP-4 polymer nanocomposites, flame extinguishes before reaching 25 mm mark. These all samples are categorized in HB rating.

Morphology of charred unsaturated polyester nanocomposite

In order to understand the relation between the Thermal and flame retardant properties of polymer nanocomposite and micro structure of char which stops the flow of volatiles and act as insulating barrier to stop or reduce the heat reaching to polymer surface. Polymer nanocomposites were charred in muffle furnace at 600°C for 5 min. In **Fig. 3(e-f)**,the SEM image of upper layer of UP-2 andUP-3nano-composites were homogeneous without any pin holes but UP-3 had more hard and compact layer which protect the lower portion of nanocomposite more efficiently and stops the escape of flammable volatile matter. The uniform distribution of MgAl DS LDH layers in UP, containing TXP, was responsible for reduction in mass loss rate seen in UP-3.

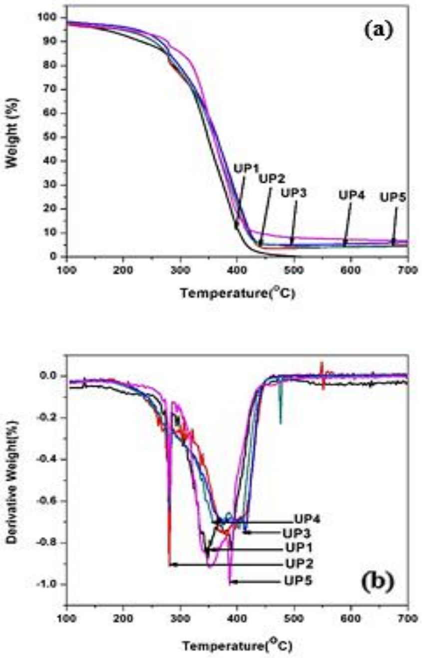

Fig. 6(a) TG spectra of UP-LDH composites **6(b).** DTG spectra of UP-LDH composites.

Table 2.TGA and DTG data of UP nano-composite of different compositions.

Sample I.D.	$T_{0.2}$ °C	$T_{0.5}$ °C	$\Delta T_{0.7}$ °C	$\Delta T_{0.2}$ °C	$\Delta T_{0.5}$ °C	$\Delta T_{0.7}$ °C	Residue (600^{0}C) %	Peak-1	Peak-2
UP-1	286.0	348.8	374.4	-	-	-	3.27	-0.873	-0.876
UP-2	283.5	363.8	391.4	-2.5	15	15	4.31	-0.91	-0.76
UP-3	283.5	363.8	393.9	-2.5	15	17.5	5.43	-0.64	-0.703
UP-4	291.1	358.8	386.5	5.1	10	10.1	4.1	-0.61	-0.71
UP-5	321.1	358.9	383.8	35.1	10.1	7.4	7.2	-0.52	-0.91

Conclusion

The nano-composite of unsaturated polyester containing TXP and MgAlDS LDH were prepared. The XRD study of these nano-composite revels that MgAlDS LDH had exfoliated in the polymer matrix as diffraction peaks of MgAl LDH have disappeared. TGA study has shown that nano-composite containing 1% of MgAlDS LDH along with TXP had better thermal stability than the nano-composite containing TXP only. Due to the exfoliated layers of MgAlDS LDH there was reduction of 8% in mass loss rate in case ofnano-composite UP-3 in comparison to nano-composite UP-2 containing only TXP. High residue in nano-composite UP-3 suggests that MgAlDS LDH has catalyzed the charring process. Flammability studies shows that MgAlDS LDH had flame retardant effect as shown by nanocomposite UP-4 low rate of horizontal burning. Three samples of nanocomposites i.e. UP-2, UP-3 and UP-4 have good flame retardancy and extinguishes before reaching 25mm mark. Morphology of charred nanocomposite revels that SEM image of both UP-2 and UP-3 are smooth, homogeneous and have no pin holes.

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Supporting information

Supporting informations are available from VBRI Press.

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