Mechanical, thermal and morphological characteristics of poly(methyl methacrylate) (PMMA) nanocomposites reinforced with Cu-Cr layered double hydroxide

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Abstract
The current work deals with the influence of Cu-Cr layered double hydroxide (LDH) on the properties of PMMA nanocomposites. The Cu-Cr LDH was organically modified with sodium dodecyl sulfate (SDS) in order to obtain LDH layers more compatible with polymer chains. PMMA with various quantities of Cu-Cr LDH nanofiller (1-5 wt%) and 5 wt% of polystyrene-grafted maleic anhydride were first melted and extruded in a twin screw extruder and, finally, processed by injection moulding machine to prepare testing specimens. The nanocomposites were examined by X-Ray diffraction (XRD), transmission electron microscope (TEM) and submitted to thermogravimetric (TGA), tensile and hardness testing. The XRD analysis showed an exfoliated structure of the nanocomposites whereas TEM exhibited the intercalated morphology at higher LDH contents. The TGA results revealed that the thermal degradation temperature was enhanced by the incorporation of Cu-Cr LDH. When 50% of the initial sample weight is established as point of comparison, the decomposition temperature of the nanocomposites was increased about 26 - 32 $^\circ$C with respect to neat PMMA. From the mechanical analysis, it was also observed that PMMA nanocomposite with 1 wt% LDH presented higher tensile strength and hardness than neat PMMA.

1. Introduction

In the last two decade, polymer/inorganic hybrid systems have gained enormous attention both in research and industry due to their high mechanical strength, better dimensional stability, lower weight and improved thermal properties. These enhanced properties are primarily depending upon the distribution of nanofiller in the polymer matrix. PMMA is a hard, rigid, and transparent material, which is found useful in optical and electrical applications. However, PMMA applications are limited at elevated temperatures. Layered double hydroxides (LDH's), also known as an anionic clay or hydrotalcite, are an important class of layered crystals used as flame retardants, catalysts, adsorbents, stabilizers and ion-exchangers [1]. It resides of positively charged metal hydroxide sheets with anions situated between the layers to counter-balance the positive layer charges. The LDH structure is described with the ideal formulae: $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{n-}_{x/n}.mH_2O$, where M^{2+} represents divalent cations (Mg^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+},Ca^{2+}), M^{3+} represents trivalent cations (Al^{3+}, Fe^{3+}, Mn^{3+},

Cr^{3+}, Co^{3+}), A^{n-} represents inorganic or organic anions (Cl^-, NO_3^-, ClO_4^-, CO_3^{2-}, SO_4^{2-}), m represents the number of interlayer water and X(= M^{2+}/ (M^{2+} + M^{3+})) is the layer charge density of LDH.[3] The presence of hydroxyl groups makes the LDH hydrophilic. After modification with suitable organic molecules, LDHs are highly appropriate for making polymer nanocomposites with non-polar polymers. Three major approaches have been used for the preparation of polymer nanocomposites such as melt-intercalation, in-situ polymerization and solvent blending method.

Most of the research work have been focused on the polymer/ montmorillonite (MMT) nanocomposites, while the LDH based nanocomposites have much less studied because of the strong interlayer electrostatic interactions, small gallery space, and hydrophilic property of LDH [2-4]. Huskic et al. [5], synthesized PMMA/MMT nanocomposites by solution polymerization technique and the prepared nanocomposites exhibited an enhanced glass transition temperature (T_g) of about 4-9 °C over the neat PMMA. Wang et al. [6], reported that thermal stability of the nanocomposite was improved about 10, 21 and 29 °C over neat PMMA by the addition of kaolinite, LDH and MMT, respectively. Qiu et al. [7], reported that the thermal stability was improved by 19 °C for exfoliated polystyrene (PS)/Mg-Al LDH nanocomposites prepared by emulsion polymerization. Manzi-Nshuti et al. [8], observed that PMMA nanocomposites with Ca_3Al LDH presented better fire retardant behaviour compared to Ca_3Fe LDH based nanocomposites. Nyambo et al. [9], concluded that modified LDH exhibited enhanced thermal stability over MgAl-carbonate, MgAl-nitrate and calcined LDH based PMMA composites. Kim and Wilkie [10], observed the decreased of the peak heat release rate (PHRR) and enhanced thermal resistance in solution polymerized PMMA nanocomposites consisting of organoclay and triphenyl phosphate. Du et al. [11], demonstrated that the crystallization temperature was increased by 12°C in exfoliated Nylon-6/Mg-Al LDH nanocomposites. From the above literature review, it is observed that none of the earlier researcher had worked on PMMA nanocomposites using Cu-Cr LDH as nanofiller. Therefore, the aim of the present study was to investigate the influence of Cu-Cr LDH on the mechanical and thermal properties of PMMA nanocomposites by direct melt-intercalation method using PS-g-MA as a compatibilizer.

2 Experimental procedure

2.1 Preparation of PMMA/LDHs nanocomposites

The detailed procedure for preparation of Cu-Cr LDH was reported elsewhere [12]. Prior to melt intercalation, PMMA pellets and LDHs were dried in a vacuum oven at 80 °C and 65 °C for 12 h, respectively. PMMA nanocomposites containing different loading (1-5 wt.%) of LDH's were prepared by melt intercalation technique in a counter rotating twin screw extruder Model-ZV-20 HI TORQUE from Specifiq Engineering and Automats, Vadodara, India. In a typical experiment, PMMA, LDHs and PS-g-MA compatibilizer were fed into the extruder and the obtained extrudate quenched in water at room temperature. Subsequently, the extrudate was cut into pellets and then dried before being injection moulded at 180-250 °C in a Model-180 High Pressure machine from JSW, Japan) to make specimens for mechanical testing. Hereafter, the nanocomposites prepared using 1, 3 and 5 wt.% Cu-Cr LDH is referred as PMMA-1, PMMA-3% and PMMA-5, respectively. Neat PMMA sample was also prepared by a similar method without compatibilizer and LDH.

2.2 Characterization of PMMA/LDH nanocomposites

X-ray diffraction (XRD) profile of nanoclay and various PMMA nanocomposite samples was done under air at room temperature using AXS D8 ADVANCE Fully Automatic Powder X-ray Diffractometer (Bruker) equipped with a Cu-Kα radiation (λ = 0.15406 nm) and Ni filter. The patterns were recorded for 2θ in the range 1° - 50° using a scan speed of 0.05° sec^{-1}. The transmission electron microscopy (TEM) images of PMMA nanocomposites were obtained on a JOEL JEM-2100

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transmission electron micro analyzer with an accelerating voltage of 200 KV. Thermo gravimetric analysis (Mettler Toledo Instrument) was performed under a nitrogen atmosphere at a heating rate of 10°C/min. For DSC measurement, nanocomposites samples were heated at the rate of 10 °C/min in the temperature range of 25-250 °C under nitrogen atmosphere. The tensile and flexural tests were carried out according to ASTM D638 and D790, respectively, by using an INSTRON (M 3382, UK) universal testing machine. The tensile properties were determined at a cross-head speed of 5 mm/min on 165.1×19.0×3.0 mm samples. Three point bending tests were performed to determine the flexural properties at a cross-head speed of 1.42 mm/min cross-head speed on rectangular bar specimens having 127×12.7×3 mm. The hardness (Shore D) values were determined according to ASTM D2240 by carrying out 15 readings on each sample to calculate the average value. The flammability test was performed according to ASTM D 635 method.

3. Results and Discussion

3.1 XRD Analysis

XRD is an efficient technique to analyze the morphology of nanocomposites that can be classified accordingly to the dispersion of nanoparticles present in the polymer matrix into three main types, namely: immiscible, intercalated and exfoliated. In case of immiscible nanocomposite, polymer chains are incapable of penetrating within the interlayer gap of the nanoparticle. When the polymer chains are able to penetrate within the gallery space of nanomaterial without changing its ordered structure, the nanocomposite is termed as intercalated. For an exfoliated structure, polymer chain penetration within the gallery space is extensive and the ordered structure of the nanomaterial is violated. In an exfoliated system, nanoparticle dispersion in the polymer matrix is considered excellent and due to the disordered orientation of the nanomaterial, this type of composite is also known as delaminated system [8]. The basal-spacing is calculated from 2θ values corresponding to peak location in the XRD graph using Bragg's law: $n\lambda = 2d\sin\theta$, where λ represents the X-ray wavelength ($\lambda=1.5406$Å) and $n = 1$.

The XRD trend of Cu-Cr LDH nanoparticle, PMMA and PMMA/Cu-Cr LDH nanocomposites for different particle loadings are shown in Figure 1. The basal spacing (d_{003}) of Cu-Cr LDH is 2.90 nm, which corresponds to a (003) peak situated at 2θ value of 3.09°. For neat PMMA, the diffraction peak is appeared at 2θ value of 13.34° and the large broad is originated due to amorphous nature of PMMA matrix. In the PMMA nanocomposites containing various loadings (1-5 wt.%) of Cu-Cr LDH, the main diffraction peak (003) corresponding to LDH disappeared (see Figure 1). Wang et al.,[13] also stated similar kind of pattern for PMMA/Mg-Al LDH nanocomposites. In order to confirm these facts, morphologic analysis needed to be carried out by TEM.
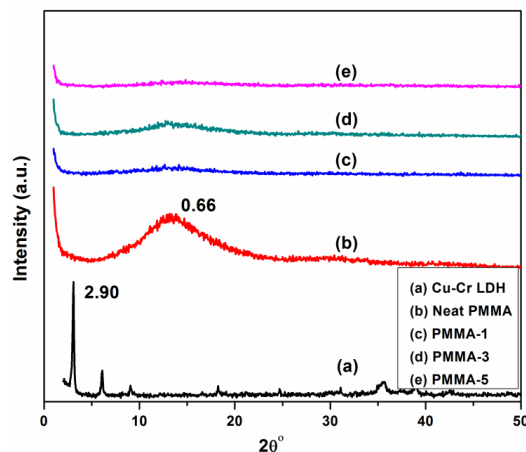

Figure 1. XRD patterns of PMMA/Cu-Cr LDH nanocomposites

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3.2 TEM Analysis

TEM micrographs are utilized to further validate the results obtained from XRD analysis. Figure 2 shows the micrographs of different PMMA/Cu-Cr LDH nanocomposites. They evidently illustrates the lamellar structure of Cu-Cr LDH, which is exfoliated by the PMMA macromolecular chain; the lines of the layers are well shown using the aero marks and the exfoliated Cu-Cr LDH sheets are dispersed in the PMMA matrix, being consistent with the XRD results presented in Figure 1. The modified Cu-Cr LDH platelets might be broken into smaller ones when they are exfoliated during the extrusion probably due to the occurrence of layer breakage. In Figure 2(b), it is observed that as the loading increases, the nanocomposites having 4-5 parallel layers of LDH layers, which leads to intercalated structures. At 5 wt.% loading, it is clearly seen that the Cu-Cr LDH layers are dispersed in lamellar form and randomly distributed in polymer matrix [see, Figure 2(c)].
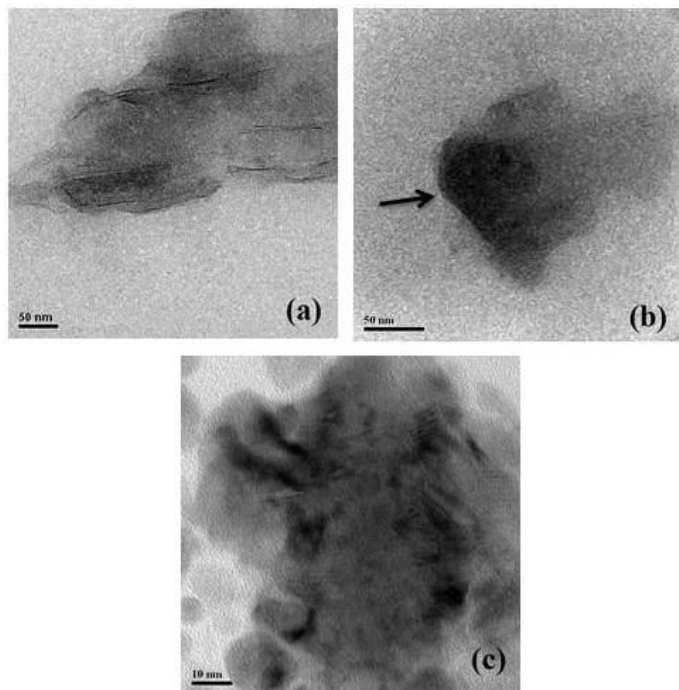

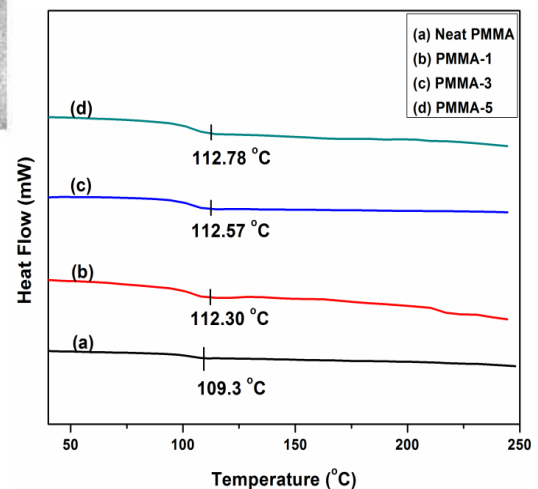**Figure 2. TEM images of (a) PMMA-1, (b) PMMA-3, and (c) PMMA-5**

Figure 3. DSC curves of PMMA/ Cu-Cr LDH nanocomposites

3.3 DSC Analysis

DSC thermograms (Figure 3) display the second order transition, which is related to the glass transition temperature (T_g) of the pristine PMMA. The T_g of PMMA, PMMA-1, PMMA-3 and PMMA-5 nanocomposites were found to be 109.3, 112.3, 112.5 and 112.5 ^{o}C, respectively. This demonstrates that nanocomposites exhibit around 3 ^{o}C higher glass temperature than neat PMMA. It is also noticed that higher loading of nanofiller does not have substantial influence on the mobility of PMMA chains. The increasing of the T_g of PMMA/Co-Al LDH nanocomposites is due to confined movement of PMMA chains within LDH gallery space [14]. The polymeric intercalation within the LDH layer restricts the movement of the polymer chain which in turn affects the overall T_g of the nanocomposite sample. In some cases, when only one end of polymeric chain remains constrained due to intercalation, its restricted immobility can have its effect on the T_g increasing of outer polymeric chains. In the work of Kuila et al.,[15] around 2 ^{o}C growing in T_g was observed for PMMA/graphene nanocomposites with 0.1 wt.% graphene loading.

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3.4 Thermogravimetric Analysis

Figure 4(a) represents the TGA graphs of neat PMMA and their corresponding nanocomposites. From the TGA curves, it is clear that thermal stability of the PMMA nanocomposites is higher than pure polymer, which is confirmed by shifting of the TGA curve of the nanocomposite samples towards right of the TGA curve of PMMA. When 50% weight loss is considered as a point of comparison, the degradation temperature of neat PMMA, PMMA-1, PMMA-3 and PMMA-5 nanocomposite is noticed to be 371.1, 397.9, 403.6 and 397.6 ^{o}C, respectively. The results show that PMMA nanocomposites exhibited a degradation temperature 26-32 ^{o}C higher than that of neat PMMA in the presence of LDH. This enhancement could be explained by the barrier effect of LDH lamellar layers, which delayed the emission of the produced degradation of gases and transmission of heat therefore, resulted in the improvement in the thermal stability of the nanocomposites. The increase in the midpoint temperature denotes the delayed degradation of PMMA/LDH nanocomposites. The results are in good agreement with the reported results of Qiu et al. [16] on the thermal degradation of PS/Zn-Al LDH nanocomposites.

The maximum degradation temperature (T_{max}) value of different nanocomposites is also demonstrated in Figure 4(b). The T_{max} value for neat PMMA, PMMA-1, PMMA-3 and PMMA-5 is found to be 373.6, 400.6, 407.8 and 399.5 ^{o}C, respectively. This confirms further that the addition of LDH into PMMA matrix increases the thermal stability of the nanocomposites.
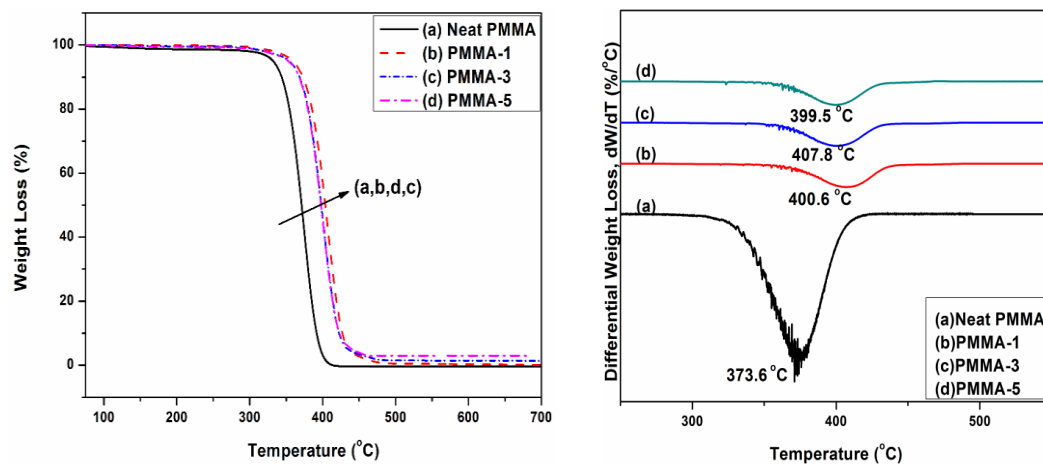

Figure 4: (a) TGA and (b) DTG curve of neat PMMA, PMMA-1, PMMA-3 and PMMA-5 nanocomposites

3.5 Tensile Properties

The tensile strength and modulus obtained on the neat PMMA and their corresponding nanocomposites are shown in Figure 5. The PMMA-1 nanocomposite reveals the highest tensile strength of 69 MPa as compared to PMMA-3 (68 MPa), PMMA-5 (60 MPa) and neat PMMA (58 MPa). This reduction occurred on the nanocomposites might be due to the agglomeration of Cu-Cr LDH in the polymeric matrix. The enhanced property demonstrated by PMMA-1 nanocomposite is due to strong bonding between Cu-Cr LDH and polymer matrix. An increase in the LDH loading beyond 1 wt.% leads to the gradual reduction of tensile strength values. This behaviour is owing to the poor dispersion of LDH in the polymer matrix at a higher concentration. Around 42% enhancement in the tensile strength was also noticed for EVA/Mg-Al LDH nanocomposite with 1 wt.% loading over pristine EVA [17].

The tensile modulus of PMMA nanocomposites are also depicted in Figure 5. It may be observed that there is a slight decrease of tensile modulus in PMMA/Cu-Cr LDH nanocomposites. Although the tensile modulus is considered to be directly related to the reinforcement content in polymers

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nanocomposites, it was reported that intercalated morphology has little contribution to it [18]. Hence, more intercalated structures migth occurred due to the increase of nanofiller loading, which reduces the tensile modulus of PMMA nanocomposites. Eng et al. [19], found a similar effects in tensile properties at 1 wt.% filler loading for PLA/PCL/clay nanocomposites.
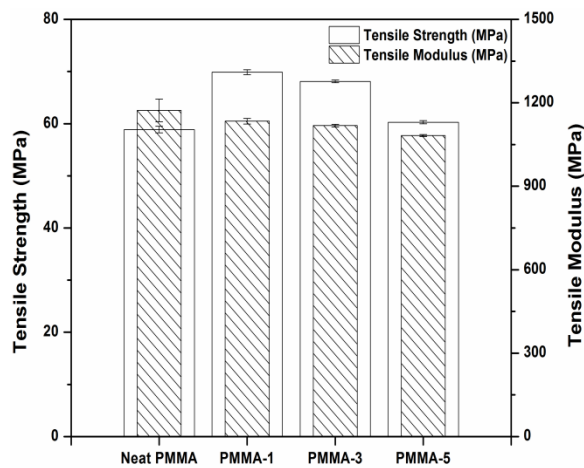

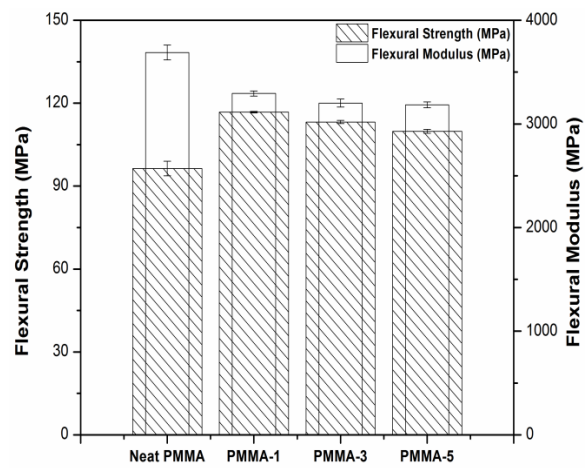**Figure 5. Tensile properties of PMMA/Cu-Cr LDH nanocomposites**

Figure 6. Flexural properties of PMMA/Cu-Cr LDH nanocomposites

3.6 Flexural Properties

The influence of Cu-Cr LDH on the flexural properties of PMMA nanocomposites is exhibited in Figure 6. The neat PMMA reveals flexural strength of 96 MPa. The PMMA-1, PMMA-3 and PMMA-5 nanocomposites demonstrate flexural strength of 116, 113 and 109 MPa, respectively. The flexural strength of PMMA nanocomposites display a maximum value at 1 wt.% loading of LDH when compared to other nanocomposites and neat PMMA. It is apparent that the flexural strength of the nanocomposites is higher than that of neat PMMA. The enhancement of flexural strength may be due to the improved adhesion between the LDH nanofiller and polymer matrix since PS-g-MA compatibilizer acts as a bridge between them. However, flexural strength reduces when the LDH concentration increases beyond 1 wt.%. The other factors, degree of intercalation/exfoliation, dispersion and orientation of LDH layers in the direction of flow play a crucial role in determining the flexural properties of the nanocomposites [20]. It is also observed that the flexural modulus is decreased as the loading of LDH increases in the PMMA nanocomposites (Figure 6). One of the main reasons is that the density of LDH material is higher than the nanoclay as a result has lower surface area. Apart from density, other factors such as filler-filler interaction, polymer-filler interaction and dispersion of nanofiller also influence the results of flexural modulus. More research is needed in this region since no literature has found for the reduction on modulus.

3.7 Hardness

The Shore D hardness was measured on the pristine PMMA and their nanocomposites according to ASTM D2240. The mean values of Shore D hardness obtained were 58, 81, 84 and 88 for neat PMMA, PMMA-1, PMMA-3 and PMMA-5 respectively, showing that the hardness increased with the increasing of LDH concentration in the PMMA matrix. This allows to conclude that the LDH layer limits the indentation and enhances the hardness of the polymer nanocomposites compared to neat PMMA. The PMMA-5 nanocomposite demonstrates the highest Shore D hardness value, which is 51% higher than that of neat PMMA.

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3.8 Flammability Test

The flammability analysis of PMMA/Cu-Cr LDH nanocomposites was performed to analyze the effect of Cu-Cr LDH on PMMA. The rate of burning for neat PMMA, PMMA-1, PMMA-3 and PMMA-5 was found to be 65, 37, 35 and 33 mm/min, which evidenced that PMMA nanocomposites presented higher flame retardancy than the neat PMMA. This demontrates that Cu-Cr LDH has considerable influence on the burning characteristics of PMMA, problably because the quantity of char formation was increased with the rise in LDH concentration whereas the heat release decreases. It is also found that intercalated structures are more effective as the path is intervened by LDH platelet structures. According to Xu et al., [21] the layered double hydroxides have lost their hydroxyl groups and interlayer anions and transformed into oxides of mixed metal that can induce carbonizing of the nanocomposite surface. The charred layer can act as a shielding hinder surface and slow down the volatilization rate of polymer.

4. Conclusions

The PMMA nanocomposites containing of Cu-Cr LDH has been successfully prepared by melt-intercalation blending. The XRD analysis exhibited that all the nanocomposites were exfoliated structure while TEM micrographs validated that intercalated morphology was noticed at higher loading of LDH. The T_g was increased about 3°C with the addition of Cu-Cr LDH, however, no improvement was observed with further increasing the loading of LDH beyond 1 wt.%. The TGA analysis also promoted that thermal degradation enhanced by 26-32 ^{o}C at 50% weight loss. The tensile and flexural was found to be maximum at 1 wt.% LDH loading and it was increased by 18 and 21%, respectively. The fire retardancy and hardness were maximum at 5 wt.% loading, which were enhanced by 49 and 51%, respectively compared to neat PMMA.

Acknowledgments

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