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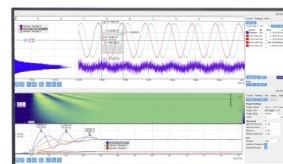
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Catalytic Degradation Study of Iron (Fe) Containing LDH-PP Composites

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Abstract. Layered double hydroxides (LDHs) have received increasing attention in recent years due to their multifunctional applications in different research fields. A comprehensive understanding of LDHs is important for their future applications as stabilizers and modifiers for polymeric materials. Although bi-metal and tri-metal LDHs were prepared successfully in recent years, the stabilizing or catalytic degradation actions in polymer composites need to be investigated further. This work highlights the synthesis of ternary metal LDHs using the urea hydrolysis method. Iron, (Fe) at two different concentrations, were substituted in MgAl LDHs. Polypropylene composites that include these LDH structures were prepared by melt mixing at three different concentrations. Their change in burning behavior was studied as indicator of degradation. X-ray powder diffraction (XRD) spectroscopy, energy-dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) were used to characterize the LDHs. Moreover, the flame retardant properties of the LDH-based polypropylene (PP) composites were studied by using limiting oxygen index (LOI) and UL94 (V and HB) testing, whereas the mechanical properties were studied using a universal testing machine (UTM).

INTRODUCTION

LDHs, known as hydrotalcite-like materials, are anionic clays containing divalent metal cations, trivalent metal cations and interlayer anions [1]. LDHs are very useful materials because of the many possibilities to alter their structure and properties. These include changes in the metallic and interlayer composition. The ease of synthesis, low cost and recyclable sources also make these materials promising for future research. There are different preparation methods available for the synthesis of LDHs, the most common being co-precipitation [2], urea hydrolysis [3], ion exchange and hydrothermal synthesis [4]. The preparation method and composition can hereby have a profound effect on the structural, chemical and photoelectric properties of the material [5, 6].

There are multiple types of bi-metallic combinations of LDHs with organic modification that are being used in different polymers for improving the material properties of composites [7]. MgAl-LDHs and modified MgAl-LDHs are the most common LDHs used in different polymers, mostly LDPE, PP and PVC. For many years, these LDHs have been used to improve the thermal, flame retardant and mechanical properties of polymer materials [8-12]. Multiple interesting and novel applications related to LDHs need to be investigated further, especially in the case of tri-metal LDHs. Previously it has been found that incorporation of a third metal into the layer structure can alter the properties of the LDHs such as optical properties, UV-Vis light absorption range and catalytic properties [13-15]. The interaction of transition metals with polymeric matrices is prone to catalyzing the degradation of polymers, especially polyolefins during processing [8]

Our group is working on different types of bi-metallic and tri-metallic LDHs and their modification; we have prepared different types of bi-metallic LDHs for applications in polymers and elastomers which have been used successfully previously. In this work Fe-containing tri-metal (MgFeAl) LDHs were prepared using urea hydrolysis and used in different amounts in PP with the aim to clarify the interaction between Fe ions in the LDH and the PP matrix. The flammability and mechanical properties of the PP composites serves as an indicator.

EXPERIMENTAL AND CHARACTERIZATION DETAILS

MgAl- and MgFeAl-LDHs were prepared using urea hydrolysis as discussed in our previous article [3]. Two types of MgFeAl-LDHs were prepared with 5 mol% and 10 mol% Fe substitution. Composites of PP with different amounts of LDH were prepared using a small scale extruder. The composition and details of the resulting composites are shown in Table 1. Chemically pure (CP) or analytical grade (AR) reactants were used for all experiments without further treatment. $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were purchased from ABCR. Urea was purchased from Sigma Aldrich and distilled water was used for all experiments. Polypropylene (PP)(HD120MO) was purchased from Borealis A/S Denmark. Polypropylene (PP) functionalized with maleic anhydride (SCONA TPPP 2112 FA) was provided by BYK additives & instrument Germany. All composites were processed at 190 °C and 100 rpm for 15 min.

X-ray diffraction measurements were performed on a Panalytical X'Pert PRO X-ray diffractometer in θ - θ configuration, equipped with Fe-filtered Co-K α radiation (1.789Å), an X'Celerator detector and variable divergence- and fixed receiving slits. Scanning electron microscopy (SEM) images were taken with a Zeiss Ultra Plus. Energy dispersive X-ray Spectroscopy (EDX) was done with a QUANTAX FlatQUAD from Bruker Nano GmbH. Thermogravimetric analysis (TGA) was performed with a heating rate of 10 °C/min using a TGA Q5000 from TA instruments in an inert nitrogen atmosphere in the temperature range of 25 °C - 1000 °C. The Limiting oxygen index (LOI) measurements were carried out by using an oxygen index meter (FTT, UK) following ASTM D2863-19. The UL94 V and UL94 HB testing were carried according to method provided previously to determine the burning rate of the composites [11]. Tensile tests were done with a Zwick 1456 (model 1456, Z010, Ulm Germany) with a crosshead speed of 50 mm min⁻¹ according to DIN EN ISO 527-2/1BA/50. The results were averaged over five measurements for each sample for the flammability investigation and tensile testing. All the specimens prepared for flammability and mechanical testing were injection molded under identical conditions.

TABLE 1. Experimental data of Polypropylene (PP) composites with different ratios of MgAl, MgFeAl-5 and MgFeAl-10 LDHs

LDHs	Amount of LDHs (wt %)	PP+TPPP (wt %)
-	0	100
MgAl-0	2.5, 5 and 7.5	97.5, 95 and 92.5
MgFeAl-5	2.5 ,5 and 7.5	97.5, 95 and 92.5
MgFeAl-10	2.5 ,5 and 7.5	97.5, 95 and 92.5

RESULTS AND DISCUSSION

All the LDHs were characterized by XRD, SEM, EDX and TGA, the results of which are shown in our previous article [5]. The flammability was determined using limiting oxygen index (LOI) and UL94 testing. LOI and UL94 testing provide information about fire retardancy and burning behavior of polymeric composites. The LOI and burning rate of pure PP and PP composites with different LDHs (MgAl-0, MgFeAl-5 and MgFeAl-10) and with different loading levels (2.5%, 5% and 7.5%) are shown in Fig. 1(a, b). In all PP composites, the LOI increased compared to pure PP as can be seen in Fig. 1(a). The flame was propagated vertically during the LOI test and flame propagation took place through the surface to the core of PP composites. Notably, the formation of char was increased in the case of PP filled with LDH as compared to pure PP. Pure PP burned like a candle with continuous melt dripping until the whole sample burned. The LDH-based PP composites showed different burn-behavior. Three regions were identified on the burning surface. The skin layer of the PP composites consisted of char followed by a

melt layer supported on a solid layer. As the concentrations of LDH in the composites used in this study were not high enough to form a thick char layer, the difference in LOI is small. Francis Costa *et al.* used MgAl-LDHs up to 20 wt.-% in polyethylene (PE) and the LOI only increased from 18 to 22 % [11].

The UL94 burning test was performed with two methods (UL94 V (vertical burning) and UL94 HB (horizontal burning)) and the burning rate results are shown in Fig. 1(b). MgFeAl-5 based PP composites burned faster than pure PP and MgFeAl-10 based composites as can be seen in Fig. 1(b). The increase in the burning rate might be a result of the availability of free Fe on the edges of the MgFeAl-LDH structure. As the loading of LDHs was increased, the burning rate decreased. This is attributable to the higher energy consumption to keep the sample burning and more water being available to be released from the LDH structures. As the loading level of LDH was increased, the amount of char increased, leading to a hindrance in burning that can be validated by the changes in burn rate shown in Fig. 1(b).

UL94 HB testing showed that all composites started to burn after they had been subjected to the flame for 10 s after which they burned completely up to the clamp holder in the chamber. The higher loading of LDH changed the melt viscosity of composites and the dripping behavior. UL94 HB showed that at a lower loading of MgFeAl-5, the burning rate enhanced. This is probably because of the catalyzing effect of Fe. The viscosity of the composites at lower loadings was also not high enough to hold the burned particles and char. Therefore, dripping of the samples provided new material for fast burning.

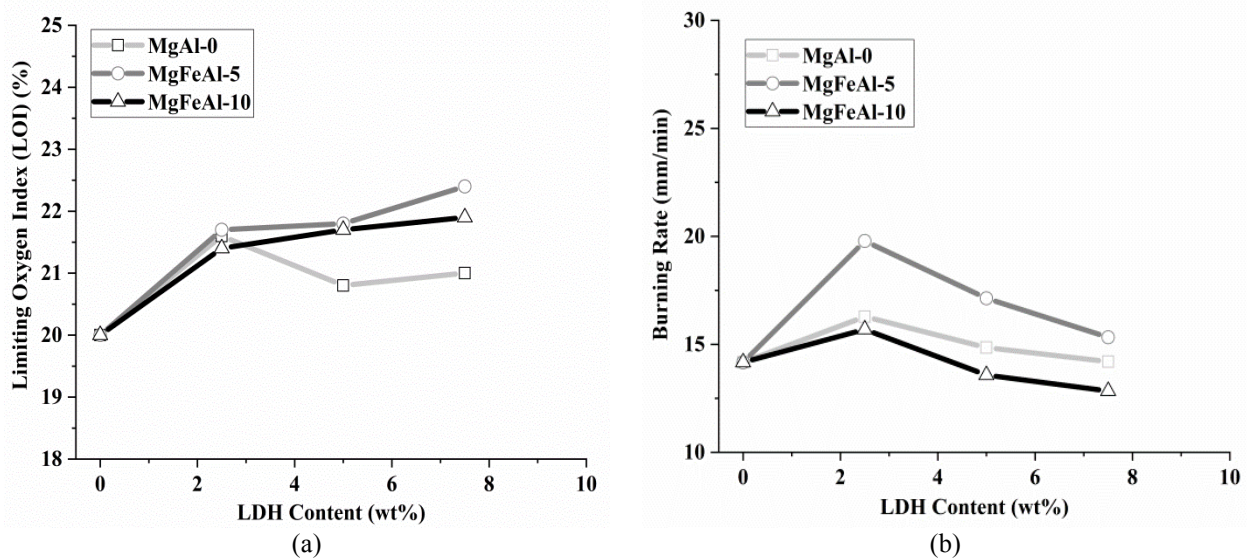


FIGURE 1. (a) Limiting oxygen index (LOI) of different LDHs based PP composites at different loading of LDHs, (b) Burning rate of different LDHs based PP composites at different loading of LDHs

The tensile strength and Young's modulus of pure PP and PP composites with different LDHs (MgAl-0, MgFeAl-5 and MgFeAl-10) and with different loading levels (2.5%, 5% and 7.5%) are shown in Fig. 2(a, b). Because of degradation during melt processing, the tensile strength decreased as the amount of LDH was increased (Fig. 2 (a)). The modulus of composites increased steadily as the loading of MgAl-0 and MgFeAl-5 increased. In case of MgFeAl-10 the results indicate that Fe-content in the LDHs seems to have a limited effect on the Young's modulus unless present at high substitutions and loading. It is possible that this observation is a result of the influence of Fe on the formation of the LDH platelets used in this study [2, 3] and can be explained by the Halpin-Tsai model. The flammability study and mechanical properties indicate a degradation of the PP composites during processing. Samples prepared with MgFeAl show - especially with higher loading - a reduced performance in mechanical testing and burning rate as well as a contradictorily increase in LOI due to the presence of Fe.

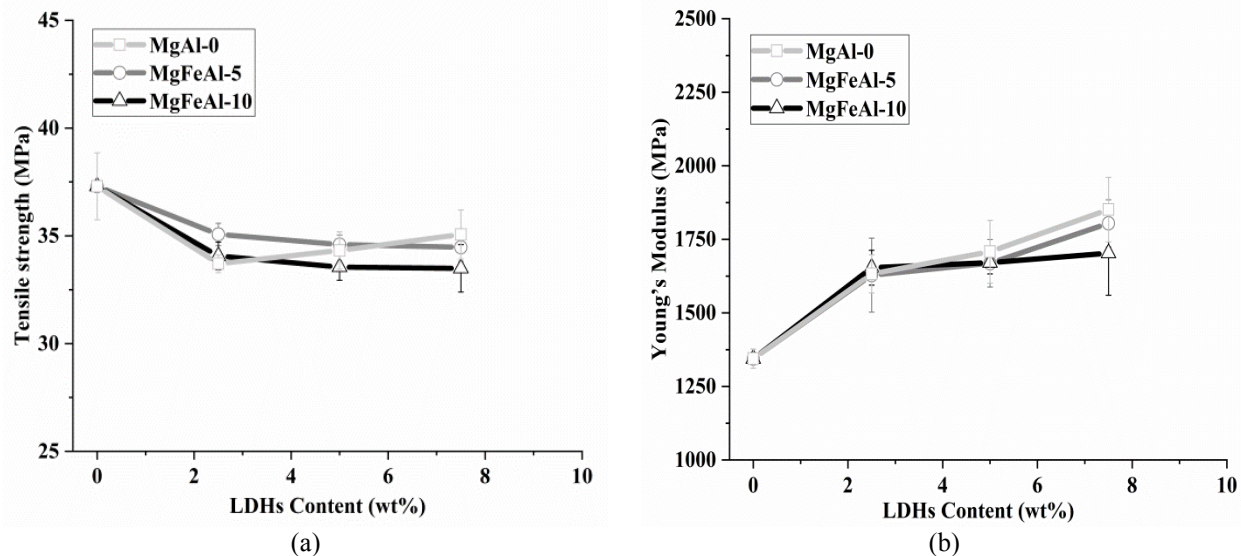


FIGURE 2. (a) Tensile strength of different LDHs-based composites at different loading of LDHs, (b) Tensile modulus of different LDHs based composites at different loading of LDHs

CONCLUSION

The effect of Fe-containing MgAl-LDH loading in PP composites on the thermal degradation of PP has rarely been studied previously in terms of degradation. The flammability study showed the catalyzing effect of Fe by enhancing the burning rate of MgFeAl-LDH-based PP composites, while increasing the LOI value at the same time. A reason for that change in behavior might be found in the presence of Fe in the composites, leading to enhanced degradation during processing and faster char formation while burning. The decrease in the mechanical properties of MgFeAl- in comparison to MgAl-LDH-based PP composites indicates a slightly enhanced catalytic degradation during melt processing. Further, the different growing behaviors of the LDH structures with and without Fe lead to different reinforcement effects as indicated by Young's modulus. To better understand the mechanisms behind these results, further investigation is necessary.

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