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MgAl-Layered Double Hydroxides: Synthesis, Characteristics, and Their Effects on Flame Retardant and Mechanical Properties of Casting Polyurethane

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Abstract—MgAl–layered double hydroxides with different molar ratios of cations were synthesized. The compound with a ratio of 2 : 1 was shown to exhibit better characteristics of thermal stability. The modification of polyurethane by using these hydroxides led to the improvement in the properties of composites: decrease by 47% in flame retardancy, and increase by 24.8 and 54.1% in tensile strength and Young's modulus, respectively.

Keywords: MgAl-layered double hydroxides, casting polyurethane, composites, flame retardant, mechanical properties

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INTRODUCTION

Nowadays, environmentally friendly and economical flame retardant materials used in different fields of industries have attracted more and more attention. In particular, layered double hydroxides (LDH) are considered as a new type of environmentally friendly flame retardants for polymers owing to their high flame retardancy and smoke suppression [1, 2]. Moreover, LDHs are also widely used as adsorbents [3–5], catalysts [6, 7], and fireproofing compounds and are used for the production of hybrid materials [8] because of their easily adjustable interlayer structure.

LDHs are well known as a group of layered materials with a general chemical formula of $[(M^{II})_{1-x}(M^{III})_x(OH)_2]^{x+}(A^{m-}_{x/m})\cdot nH_2O$. The layers consist of divalent (M^{II}) (Ca^{2+}, Mg^{2+}, Fe^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}) and trivalent (M^{III}) (Al^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, Ga^{3+}, ...) metal ions, while the interlayer region contains charge-balancing anions (CO_3^{2-}, NO_3^-, Cl^-, SO_4^{2-}, ...) and water molecules.

Polyurethane (PU) represents a class of synthesized polymers whose molecules contain urethane groups. They are widely applied owing to their high performance characteristics, like hardness, wear resistance, significant elasticity, and wide operating temperature range (from −40°C to +100°C) [9]. There is an abundance of products made from PU in a variety of shapes and sizes, so its area of application is quite huge. A significant number of polyurethane-based products are used in the furniture, automotive, construction, and aerospace industries. However, like most polymers, PU is flammable; therefore, to improve the flame retardancy, flame retardants are used as additives. Some types of halogen-free flame retardants, such as modified LDH [10], organophosphates compounds [11], graphene oxide (GO) [12], and polyhedral oligomeric silsesquioxane (POSS) [13], have become more and more attractive.

The change in the types of metal cations, their ratios, and interlayer anions leads to the formation of a large number of different types of LDH with different properties. In this work, MgAl–layered double hydroxides (MgAl–LDH) with different molar ratios of Mg^{2+} : Al^{3+} cations were synthesized by the coprecipitation method. Samples based on PU and LDH were fabricated using the hot-curing casting method with introduction of an in situ modifier. LDH samples were studied using X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry, and particle size distribution methods. Flame retardant and mechanical properties of composite materials were investigated.

EXPERIMENTAL

Synthesis of MgAl–LDH

The MgAl–LDHs precursors with different molar ratios of Mg^{2+} : Al^{3+} ((1 : 1), (2 : 1), (3 : 1), and (4 : 1)) were synthesized by the coprecipitation method [14]. The typical LDH synthesis procedure is described as follows. Magnesium and aluminum salts ($MgSO_4$ and $Al_2(SO_4)_3 \cdot 18H_2O$, respectively) were dissolved in distilled water at a temperature of 60 ± 5°C. Next, a 3 M NaOH solution was gradually added to the mixture to increase the pH value of the system to 10. The suspension was continuously stirred at the given temperature (60 ± 5°C) for 1 h and then was treated thermally in oven for 20 h to increase the crystallinity of LDH. The resulting precipitate was thoroughly washed from free sulfate ion and dried at 70°C for 24 h. Next, the LDH samples were milled to a size no larger than 0.25 mm.

Preparation of Polyurethane-Based Composites

Casting polyurethanes were synthesized by hot-curing casting of the mixture of pre-polymer SKU-PFL-100 based on polyether and toluene diisocyanate (TDI) and hardener MOCA (methylene-bis-orthochloroaniline) of urethane pre-polymer.

MgAl–LDH modifier and $Mg(OH)_2$ were introduced into the pre-polymer in situ during the synthesis process, when the initial components were in the liquid state, followed by curing in an open form at 100°C [15]. LDH with loading content of 1, 3, and 5 wt % and $Mg(OH)_2$ in the amount of 1 wt % were added to the pre-polymer, in which NCO reactive groups are present. These groups facilitate the reaction for polyurethane synthesis.

STUDY OF THE PROPERTIES OF THE OBTAINED MATERIALS

Powder X-ray Diffraction

The powder X-ray diffraction plots were recorded using a D8 Advance diffractometer (Bruker, Germany) in monochromatic CuK_α radiation (λ = 1.5406 Å) in the 2θ angle range from 5° to 70° in steps of 0.02° with a counting time per step of 0.2 s.

Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC)

The behavior of LDH samples during thermal decomposition was studied using a STA 449 F1 instrument (NETZSCH, Germany) in an argon atmosphere at a heating rate of 10°C/min in the temperature range from 35 to 700°C.

Particle Size Distribution

The size of particles was determined using a Microsizer 201 laser particle analyzer (BA Instruments). The results of analysis represent the dependence of the mass fraction of particles P (%) on their diameter D (μm).

Flame Retardant Properties

The test for flame retardant properties of PU and PU composites was carried out in accordance with GOST 27484 [16]; the time of exposure to the flame source was 30 s.

Hardness

The hardness of samples was measured by a Shore A hardness tester (Vostok-7, Russia) with digital indicator.

Density

The density of samples was determined by hydrostatic weighing method in accordance with GOST 15139 [17, 18]. The density (ρ, g/cm^3) was calculated by the following equation:

$$\rho = \frac{m_{dry}}{m_{dry} - m_{wet}}\rho_{liq},$$

where m_{dry} and m_{wet} are the mass of the sample weighted in air in the dry state and in liquid (ethanol), respectively, g; and ρ_{liq} is the density of the used liquid (ethanol), g/cm^3.

Elongation at Break and Tensile Strength

These tests were carried out using an Instron 5944 machine in accordance with GOST 11721 [19].

RESULTS AND DISCUSSION

Characteristics of MgAl–LDH

X-ray diffraction study of MgAl–LDH. A typical powder diffraction plot of MgAl–LDH is shown in Fig. 1. All peaks are indexed in hexagonal structure [20, 21].

According to XRD data, all of the synthesized MgAl–LDH samples in this work are in good agreement with the structure of LDH. In Fig. 1, all typical peaks of a hydrotalcite-like structure are indicated with sharp and intense reflections (003), (006), (012), (015), (110), and (113) [21, 22]. The position of the (003) reflection, which characterizes the layered structure of the material, depends on the size of hydrated anions and the electrostatic interaction strength of hydroxide layers with the counter anions. The value of lattice parameter a, which can be calculated from the position of the (110) reflection, depends

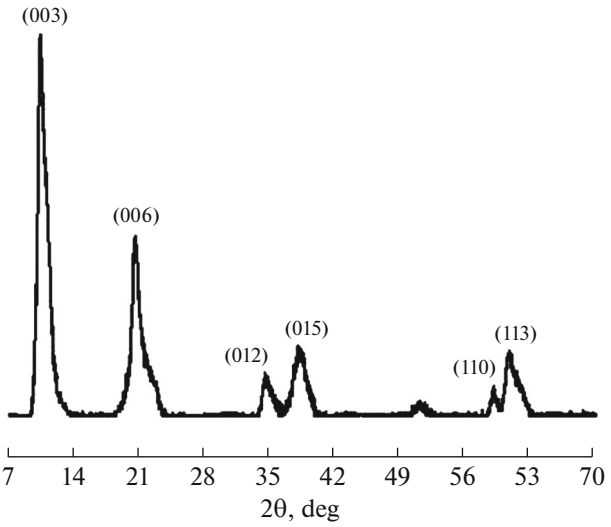

Fig. 1. XRD plot of MgAl–LDH.

on the radii of cations and, therefore, on the $M^{II} : M^{III}$ ratio in layers.

The lattice parameters *c* and *a* are calculated using the formulas from [21]: $c = 3d_{003}$ and $a = 2d_{110}$, respectively. The obtained results are given in Table 1.

It can be seen that lattice parameter *a* slightly increases with increasing proportion of Mg^{2+} ions in the $Mg^{2+} : Al^{3+}$ ratio, since Mg^{2+} has a larger ionic radius (0.72 Å) as compared to the ionic radius of Al^{3+} (0.53 Å) [23]. Moreover, a decrease in interplanar distance d_{003} from 0.87 to 0.85 nm is also observed, and consequently, there is a decrease in lattice parameter *c* from 2.60 to 2.56 nm, which is due to the different amount of interlayer anions and water molecules in various LDH samples.

The crystallite size (*D*, nm) of LDH samples was calculated using Scherrer formula [21]:

$$D = \frac{K\lambda}{\beta\cos\theta},$$

where *K* is the dimensionless Scherrer constant ($K = 0.9$); λ is the X-ray wavelength (λ = 0.154056 nm); β is the full width at half maximum, radians; and θ is the diffraction angle, radians.

The sizes of crystallites of samples are given in Table 2. It can be observed that the sizes of crystallites of LDH samples were changed in all directions upon varying the $Mg^{2+} : Al^{3+}$ ratios. The maximum crystallite sizes are 14.0 and 8.6 nm in the *a* and *c* direction, respectively, at the $Mg^{2+} : Al^{3+}$ ratio of 2 : 1.

Thermal analysis of MgAl–LDH. As a result of heating to 700°C, all LDH samples are characterized by three stages [14] with a total mass loss from 33.7 to 38.4% (Table 3). The first stage (up to 100°C) corresponds to the removal of physically adsorbed water. The second stage, which is located in the temperature range from 100 to 280°C, represents the removal of interlayer water and corresponds to the first endothermic peak with a mass loss from 10.7 to 13.7%. The third stage (from 280 to 700°C) corresponds to the mass loss of water produced by decomposition of hydroxides with the formation of metal oxides and the removal of CO_2 from interlayer anions. This stage represents a strong endothermic peak with a mass loss from 17.1 to 24.4%.

In addition, the first endothermic peak shifts to higher temperatures upon increasing the $Mg^{2+} : Al^{3+}$ ratio. This result may indicate an increase in strength of interaction of hydroxide layers with interlayer anions and water molecules. As shown in Fig. 2b, the maximum endothermic effect is observed at about 500°C for the sample with molar ratio of 2 : 1; consequently, at this ratio, the properties of flame retardant will be exhibited more effectively.

Subsequently, the LDH sample with the $Mg^{2+} : Al^{3+}$ molar ratio of 2 : 1 was used to prepare MgAl–LDH/PU composites, as well as to study their flame retardant and mechanical properties.

Table 1. Lattice parameters of MgAl–LDH samples with different ratios of $Mg^{2+} : Al^{3+}$

No.	$Mg^{2+} : Al^{3+}$ ratios	Lattice parameters, nm		
		a	*c*	d_{003}
1	1 : 1	0.30	2.60	0.87
2	2 : 1	0.30	2.58	0.86
3	3 : 1	0.31	2.58	0.86
4	4 : 1	0.31	2.56	0.85

Table 2. Sizes of crystallites of MgAl–LDH samples calculated using the Scherrer formula

$Mg^{2+} : Al^{3+}$ ratios	Size of crystallites (*D*) in the direction of	
	a, nm	*c*, nm
1 : 1	8.0	7.8
2 : 1	14.0	8.6
3 : 1	12.5	7.4
4 : 1	6.9	7.9

Table 3. Thermal analysis of MgAl–LDH samples

$Mg^{2+} : Al^{3+}$ ratios	Mass loss, %			
	total	up to 100°C	100–280°C	280–700°C
1 : 1	33.7	2.9	13.7	17.1
2 : 1	35.3	1.1	10.7	23.5
3 : 1	38.4	2.1	11.9	24.4
4 : 1	37.5	2.0	11.4	24.1

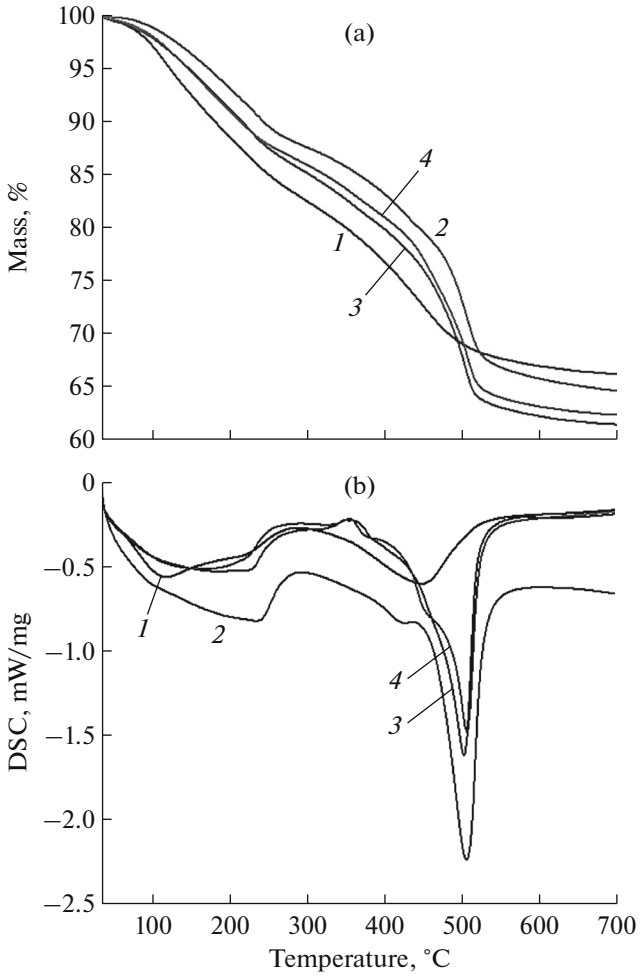

Fig. 2. TGA (a) and DSC (b) plots of MgAl–LDH with different ratios Mg^{2+} : Al^{3+}: (*1*) (1 : 1); (*2*) (2 : 1); (*3*) (3 : 1); (*4*) (4 : 1).

Particle size distribution of MgAl–LDH powder. The particle size distribution of MgAl–LDH with molar ratio of 2 : 1 is shown in Fig. 3. From the histogram, it can be seen that particles are distributed in a wide range of size, which indicates that they are polydispersed (or poorly assorted) with the values of P_{50} and P_{90} of 11.7 and 24.6 μm, respectively.

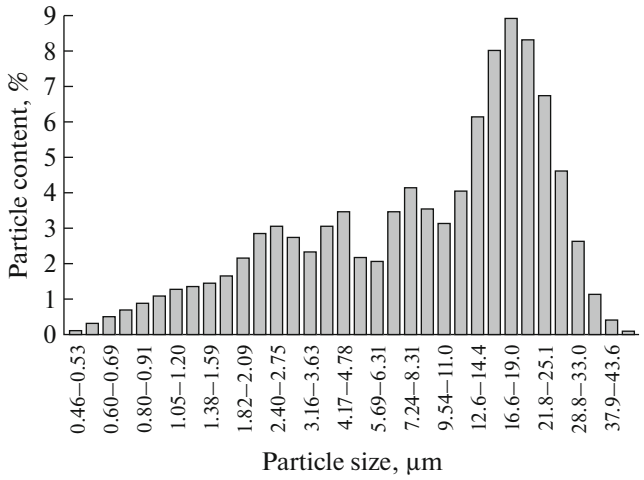

Fig. 3. Particle size distribution of MgAl–LDH (2 : 1).

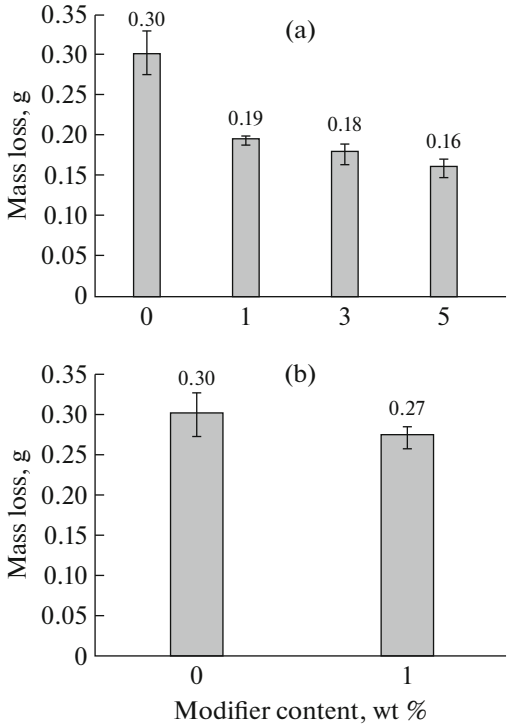

Fig. 4. Mass loss during combustion of PU and composites MgAl–LDH/PU (a) and $Mg(OH)_2$/PU (b).

CHARACTERISTICS OF PU AND MgAl–LDH/PU COMPOSITES

Flame Retardancy

Flame retardant tests of PU and MgAl–LDH/PU and $Mg(OH)_2$/PU composites were conducted in accordance with GOST 27484-87. MgAl–LDH with ion ratio of 2 : 1 and loading content of 1, 3, and 5 wt % and $Mg(OH)_2$ in the amount of 1 wt % were used as flame retardants. Test results are presented in Fig. 4.

During the flammability test, it was established that samples based on casting polyurethane are not subject to prolonged burning after removing from the flame source, but the formation of dripping drops and soot was observed. The mass loss of samples induced by the exposure to the flame source decreases from 0.30 to 0.16 g with increase in the amount of MgAl–LDH introduced into PU (Fig. 4a). For example, adding 5 wt % of MgAl–LDH into polymer matrix leads to 47% reduction in mass loss as compared to this value of pure PU. From Fig. 4b, it is clear that the application of 1 wt % of $Mg(OH)_2$ in PU leads to a decrease by 10% (from 0.30 to 0.27 g) in mass loss of

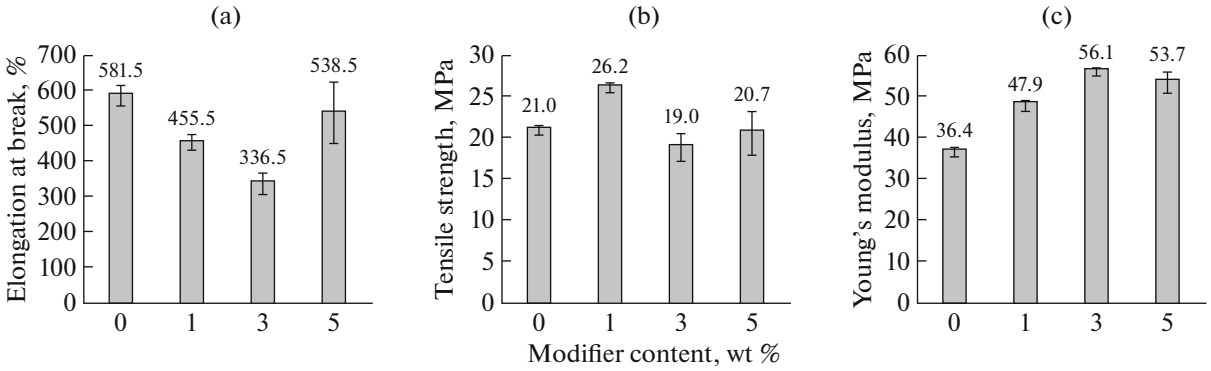

Fig. 5. Mechanical properties of PU and MgAl–LDH/PU composite: (a) elongation at break, %; (b) tensile strength, MPa; (c) Young's modulus, MPa.

samples during combustion, while using MgAl–LDH with the same amount leads to a decrease by 36.7% (from 0.30 to 0.19 g). Therefore, MgAl–LDH has a significantly higher effect on the flame retardancy in PU-based composites compared to $Mg(OH)_2$.

Mechanical Properties of PU and MgAl–LDH/PU Composites

The mechanical characteristics of PU and MgAl–LDH/PU composites, such as density, Shore A hardness, elongation at break, and tensile strength, were determined (Table 4, Fig. 5). Young's modulus (E, $N/mm^2 = MPa$) was also calculated using the following formula [24]:

$$E = \frac{P/A}{dL/L} = \frac{P}{A}\frac{L}{dL},$$

where P is the force exerted on an object under tension, N; L is the original length of the object, mm; A is the actual cross-sectional area over which the action of the force is distributed, mm^2; and dL is the change in length of the object under deformation, mm.

Pure PU showed a density of 1.13 g/cm^3 and Shore A hardness of 91.3. Modification of PU by adding MgAl–LDH (up to 5 wt %) to the polymer matrix led to no change in density, but an increase in Shore A hardness to 95.5 (by 4.6%). The tensile strength increases from 21.0 to 26.2 MPa (by 24.8%) by the incorporation of PU with 1 wt % of modifier. A further increase in modifier loading content to 3–5 wt % leads to a decrease in strength of the composite to values characteristic of unmodified polyurethane (~21 MPa). In this case, Young's modulus is increased from 36.4 to 56.1 MPa (by 54.1%). The maximum value of Young's modulus is observed at loading content of MgAl–LDH of 3 wt %.

Table 4. Mechanical characteristic of PU and MgAl–LDH/PU composite

Loading content of MgAl–LDH, wt %	Shore A hardness
0	91.3 ± 0.5
1	95.5 ± 0.2
3	95.6 ± 0.4
5	95.4 ± 0.1

As a result of the incorporation with modifier particles, the supramolecular structure of polymer matrix is transformed, as described in [25], which leads to a change in the physical and mechanical characteristics of MgAl–LDH/PU composites.

CONCLUSIONS

MgAl–layered double hydroxides (MgAl–LDH) with different Mg^{2+} : Al^{3+} molar ratios from 1 : 1 to 4 : 1 were synthesized by the coprecipitation method. It is established that MgAl–LDH with molar ratio of 2 : 1 shows the best thermal stability among all studied LDH molar ratios in this work. In situ modification of polyurethane using MgAl–LDH powder with the loading content up to 5 wt % was carried out. Changes in the properties of composites were observed: a decrease of 47% in flame retardancy (evaluated by mass loss during combustion), increase of 24.8% in tensile strength, and increase of 54.1% in Young's modulus.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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