

PHYSICOMECHANICAL PROPERTIES OF COMPOSITES BASED ON THE MIXTURE OF POLYETHYLENES AND THE SYSTEM MULTI-FUNCTIONAL MODIFIER-FLAME RETARDANT

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Abstract. The article presents the results of a study of the effect of a flame retardant and a flame retardant-modifier system on flammability, ultimate tensile stress, elongation at break, melt flow index, and thermal stability of composite materials based on a mixture of high and low density polyethylene taken in a ratio of 50/50. Aluminum hydroxide was used as a flame retardant, and S-(carballyloxy)methyl-N,N-diethyldithiocarbamate was used as a multifunctional modifier. The studies were carried out with samples containing 10, 50 wt. % of aluminum hydroxide and 1, 3, 5 wt. % modifier. Tests have shown that the use of a modifier contributed not only to an improvement in physicomechanical properties, but also to an increase in the oxygen index of composites. The best fire resistance was obtained for a composite with a combination of HDPE / LDPE + 50 wt. % Al (OH)₃ + 3 wt. % modifier (LOI = 24.5).

Keywords: high density polyethylene, low density polyethylene, a mixture of polymers, aluminum hydroxide, flame retardant, modifier, oxygen index.

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1. Introduction

Every year, several million tons of polyolefins related to large-capacity polymers are manufactured and consumed in the world (Nwabunma, 2008). Polyolefins are widely used due to a variety of properties, ease of processing, relatively low cost, the possibility of modification by various methods, expanding the field of their practical application. Flammability of polymeric materials often contributes to limiting their use as building materials.

Therefore, reducing the combustibility of polymeric materials, including those based on polyolefins, is today an urgent task, which is achieved mainly by loading of flame retardants into the material. World consumption of flame retardants is more than 2.25 million tons per year (<https://www.flameretardants-online.com/flameretardants/market>), and their production growth trend is increasing. An analysis of the global market for the consumption of flame retardants designed to increase the fire resistance of polymers clearly shows an interest in the use of aluminum hydroxide. It is the most consumed flame retardant with a share of 38% (<https://www.flameretardants-online.com/flameretardants/market>). Its advantage is that it reduces the combustibility of polymeric materials, reduces smoke formation, along with this it is one of the cheapest, easily available, non-hygroscopic flame retardants. It is also important to note

that aluminum hydroxide and its decomposition products are non-toxic. The disadvantages of aluminum hydroxide as a flame retardant is that the effectiveness of aluminum hydroxide is directly proportional to its content in the polymer and therefore, to achieve good fire retardant properties in the material, its use in an amount of about 50-60 wt % is required. Such high levels of filling negatively affect the physicomechanical properties of the composites, which to some extent limits their practical use.

To improve the compatibility of the polymer and aluminum hydroxide, and to improve the physicomechanical properties of the composites based on them, various modifying additives were used (Zhang *et al.*, 2007; Hippi *et al.*, 2003). There is reason to believe that the loading of modifiers in the composition of homopolymers or their mixtures, on the one hand, will contribute to a multiple improvement in the melt flow index of the compositions, reduction of energy consumption during their processing into various types of products, and, on the other hand, will increase the compatibility of the components of the mixture. The aim of this study was to study the effect of aluminum hydroxide and the aluminum hydroxide-modifier system on the flammability and physicomechanical properties of composites based on a mixture of high and low density polyethylene polymers.

2. Experimental

2.1 Materials

As an object of research used industrial samples of high density polyethylene (HDPE) grade HD 52518, low density polyethylene (LDPE) grade 17703-01, filler-aluminum hydroxide (GOST 11841-76, RPC 631887, packaged by CJSC "VECTON"), modifier - S- (carballyoxy) methyl-N, N-diethyldithiocarbamate (In the tables, the abbreviation of the word modifier is marked as "M").

LDPE- density of 912 kg / m³, ultimate tensile stress of 10.3 MPa, elongation at break 250%.

HDPE- density of 963 kg / m³, ultimate tensile stress of 25.0 MPa, elongation at break of 500%.

Aluminum hydroxide Al(OH)₃— a colorless solid, insoluble in water, has amphoteric properties. Amorphous aluminum hydroxide has a variable composition Al₂O₃ · nH₂O. When heated above 180-200°C decomposes depending on the size of the particles.

S-(carballyoxy)methyl-N,N-diethyldithiocarbamate was synthesized in accordance with reference (Karimov, 2019). S-(carballyoxy)methyl-N,N-diethyldithiocarbamate- boiling point 160-162°C, $d_4^{20} = 1.1375$, $n_D^{20} = 1.5590$.

2.2 Preparation of composites

Composite materials based on a mixture of HDPE and LDPE in a ratio of 50/50, with different concentrations of aluminum hydroxide (10 and 50 wt. %) and a modifier (1, 3, 5 wt. %) were obtained by mixing the components on laboratory rollers at a temperature of 150°C for 8-10 minutes. Further, at a pressing temperature equal 170-180°C molded plates of which the respective samples were cut for testing.

2.3 Characterization of the composites

The limiting oxygen index (LOI) was determined on a MODUL FTA, STANTON REDGROFT (UK) device, in accordance with ASTM-2863 standards. The dimensions of the samples were 120 mm - 60 mm - 3.5 mm.

The thermal stability test was carried out using thermogravimetric analysis on a Q-1500 D derivatograph from the MOM company (Hungary) of the Paulik-Paulik-Erdey system. Weighed samples 100 mg, channel sensitivity TG-100, DTG-1mV, DTA-250 μ V, T / V -500/5, crucible Pt. Samples were taken on a derivative gas in a stream of air, heating rate 5° / min.

The melt flow index (MFI) of polymer materials was determined using a CEAST MF50 capillary rheometer (INSTRON, Italy). Measurements were carried out at a temperature of 190°C and 5 kg load according to ASTM D1238 standards.

Ultimate tensile stress (σ , MPa) and elongation at break (ϵ ,%) of the obtained compositions were determined in accordance with GOST 11262-80.

The particle size of aluminum hydroxide was determined using a Mastersizer 3000 laser analyzer (Malvern Instruments, England). The measuring range of the device is from 10 nm to 3500 microns. The particle size varied in the range of 0.675-144 μ m.

Infrared (IR) spectrum of the samples were recorded on an Agilent Cary 630 FTIR spectrometer, Agilent Technologies, ZnSe crystal. The range of wave numbers is 600-4000 cm^{-1} .

3. Results and Discussion

3.1. Physicomechanical properties

To achieve the required fire-resistant quality of composite materials, a high concentration of aluminum hydroxide is required. The addition of solid particles of aluminum hydroxide to thermoplastics contributes to the deterioration of the physicomechanical properties of composites (Nachtigall *et al.*, 2006; Farzad *et al.*, 2013; Su *et al.*, 2005). A comparative analysis of the test results (table 1) of the ultimate tensile stress and elongation at break of the HDPE / LDPE, HDPE / LDPE + 10% Al(OH)₃, HDPE / LDPE + 50% Al(OH)₃ composites confirms the existence of such a pattern.

As can be seen from table 1, the increase in the concentration of aluminum hydroxide to 50 wt % leads to a decrease in ultimate tensile stress by about 69%, and elongation at break by 33%. Such a sharp decrease in ultimate tensile stress and elongation is primarily associated with poor compatibility of the polymer matrix with Al(OH)₃.

The loading of a modifying additive contributes to some improvement in the value of these parameters, which clearly indicates the plasticizing role of the additive while increasing the compatibility of the reacting components. In all likelihood, when a polar modifier is loaded into the melt, the latter envelops Al(OH)₃ particles, as a result of which a thin modifier layer forms on its surface. The polymer macrochains interact with the monolayer of the modifier, focusing on the surface of Al(OH)₃ particles. As a result of this orientation, the polymer-particle adhesion bond increases, which ultimately affects the increase in ultimate tensile stress and elongation. However, with a further increase in the modifier concentration (over 3 wt %), a certain decrease in ultimate tensile stress is observed. This fact once again confirms our assumption about the

multifunctionality of the studied modifying additives: plasticizing effect and improving the compatibility of the studied components. It will be correct if the modifier used is considered as a plasticizer and compatibilizer of composite materials based on HDPE / LDPE, Al(OH)₃.

Table 1. Physicomechanical properties of composites based on HDPE / LDPE + Al(OH)₃ and HDPE / LDPE + Al(OH)₃ + modifier

N _o	Composite composition wt %	Ultimate tensile stress MPa	Elongation at break %	MFI, g /10 min
1	HDPE/LDPE	22.2	60	3.9
2	HDPE/LDPE +10 Al(OH) ₃	18.7	30	2.7
3	HDPE/LDPE +10Al(OH) ₃ +1M	19.1	40	3.0
4	HDPE/LDPE +10Al(OH) ₃ +3M	17.7	50	3.4
5	HDPE/LDPE +50Al(OH) ₃	15.4	20	1.6
6	HDPE/LDPE +50Al(OH) ₃ +3M	16.4	20	2.2
7	HDPE/LDPE +50Al(OH) ₃ +5M	14.2	20	2.6

M- modifier; The mixture of HDPE / LDPE were taken in a ratio of 50/50

3.2. Melt flow index

A comparative analysis of the melt flow indices of the studied composites shows that the high filling of the HDPE / LDPE mixture with aluminum hydroxide reduces its fluidity due to the limited mobility of macromolecular chains. Adding a modifier to the HDPE / LDPE + Al(OH)₃ mixture increases the MFI of the samples not only at low aluminum hydroxide concentrations (10%), but also at 50% Al(OH)₃ content. The reason for the increase in the MFI and the elongation at break of the samples indicates that the modifier promotes intra- and interpackage plasticization of polymers. This is the state of polymers, when some of the S-(carballyoxy)methyl-N, N-diethyldithiocarbamate molecules are able to integrate into the crystalline phase of the supramolecular structure of the polymers during crystal growth, and the other is forced out and accumulates in the intersferolithic amorphous space. In this space, the modifier plays the role of an external lubricant agent, as a result of which, at a lower value of the applied force, an unhindered process of drawing out packs of through macrochains under uniaxial tension proceeds.

3.3. Limiting oxygen index (LOI)

To compare the flammability of HDPE / LDPE + Al(OH)₃ and HDPE / LDPE + Al(OH)₃ + modifier, the method of determining the oxygen index was used. The oxygen index characterizes the minimum volumetric percentage of oxygen in the oxygen-nitrogen mixture at which candle-like burning of composite materials under test conditions is possible (Chulieieva, 2017). The oxygen index value is used in the development of polymer compositions with reduced flammability and the control of the flammability of polymeric materials. The experimental method was to find the minimum concentration of oxygen in the flow of the oxygen-nitrogen mixture, in which there is independent burning of a vertically located sample, ignited from above.

As can be seen from Fig. 1, the minimum oxygen concentration required to ignite the materials increased for all samples relative to the initial HDPE / LDPE mixture (LOI = 17.0). The results show that an increase in the concentration of aluminum hydroxide in the composite HDPE / LDPE + Al(OH)₃ up to 50 wt % leads to an increase in LOI to 23.6. An increase in the oxygen index indicates a decrease in the flammability of the studied composites. This is explained by the fact that at high temperatures, aluminum hydroxide decomposes with the release of water vapor; the decomposition reaction is endothermic, which leads to cooling of the substrate to temperatures below the flash point. The escaping water vapor displaces oxygen from the pyrolysis region and reduces the burning rate, and helps to dilute combustible gases. Along with this, alumina obtained during decomposition catalyzes coke formation processes and forms a protective layer on the surface of a flammable polymer (Beltrán-Ramírez *et al.*, 2014).

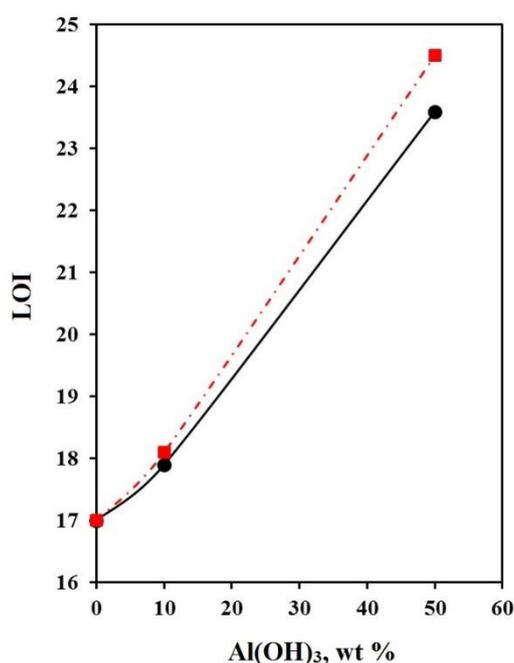


Figure 1. The dependence of the LOI from the concentration of Al(OH)₃ (wt %) in the composites: ●– HDPE / LDPE + Al(OH)₃, ■– HDPE / LDPE + Al(OH)₃ + 3% modifier

The best result (LOI = 24.5) among the studied composites was obtained for a sample with a combination of HDPE / LDPE + 50% Al(OH)₃ + 3% modifier. This is approximately 1 more than the LOI of the HDPE / LDPE + 50% Al(OH)₃ composite. It should be noted that the LOI (18.1) of the HDPE / LDPE + 10% Al(OH)₃ + 3% modifier composite is also higher than the LOI (17.9) of the HDPE / LDPE + 10% Al(OH)₃. This shows that the modifier- S-(carballyoxy)methyl-N,N-diethyldithiocarbamate used by us is multifunctional, since it improves not only the physicomechanical properties and compatibility of the components of the mixture of composites based on HDPE / LDPE + Al(OH)₃, but also increases their fire resistance. This can be explained by the fact that the nitrogen element is part of this modifier, and as it is known, many of its compounds have established themselves as a good flame retardant and are among the primary or main combustion retardants.

Considering the fact that the oxygen content in the atmosphere is 21%, then, when the LOI of the composite is lower than 21%, this material supports combustion in air

(John, 2019). In the case when the LOI value is more than 21%, the material does not burn in air, as this requires a higher oxygen concentration. Based on this, the above composites with HDPE / LDPE + 50% Al(OH)₃ and HDPE / LDPE + 50% Al(OH)₃ + 3% modifier composition, having a LOI value of more than 21%, can be attributed to the group of hardly flammable materials, not supporting combustion in an air atmosphere.

3.4. Thermogravimetric analysis

The method of thermogravimetric analysis was used to study the comparative characteristics of compositions based on a mixture of HDPE / LDPE with various concentrations of aluminum hydroxide with and without a modifier. The thermal stability of the composites was evaluated at temperatures T₁₀, T₂₀, T₅₀ at which the samples lost 10, 20, 50 % of weight, respectively.

Fig. 2 shows the curves of the dependence of the mass change on the temperature of the samples. Analysis of the curves shows that aluminum hydroxide (Figure 2 a-1, b-1) undergoes an endothermic dehydration reaction in the temperature range 205–280°C, leaving aluminum oxide as a residue due to decomposition and evolution of water vapor with a total mass loss of 36%.

As can be seen from Fig. 2 (a-2), the mixture of high and low density polyethylene decomposes completely. It was found that, in comparison with the initial HDPE / LDPE mixture, thermal decomposition of compositions with a high concentration (50%) of aluminum hydroxide proceeds in two stages (Figure 2 a-5, a-6) and the thermogravimetric (TG) curves of these composites occupy an intermediate place between TG curves of HDPE / LDPE and Al(OH)₃.

In the differential thermal analysis (DTA) curves of the HDPE / LDPE composite, two melting points were observed at 95°C and more expressive at 120°C (Fig. 2 b-2).

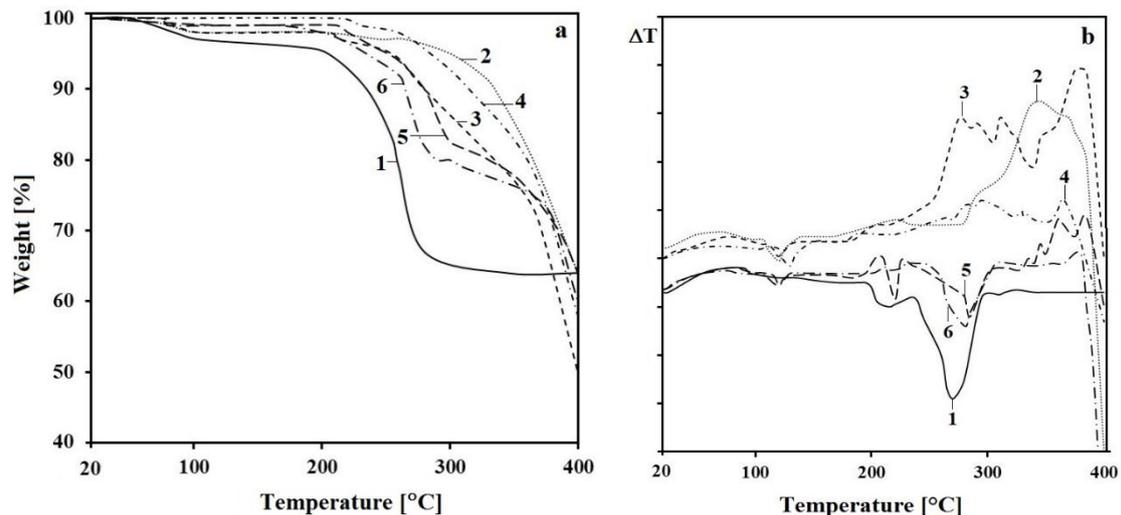


Figure 2. TG (a) and DTA (b) curves of composites: 1-Al(OH)₃, 2-HDPE / LDPE, 3-HDPE / LDPE + 10% Al(OH)₃, 4-HDPE / LDPE + 10% Al(OH)₃ + 3% modifier, 5-HDPE / LDPE + 50% Al(OH)₃, 6-HDPE / LDPE + 50% Al(OH)₃ + 5% modifier

The presence of not only one but several peaks on the DTA curve in the melting region can be explained by the difference in the melting points of HDPE and LDPE, the

existence of crystallites of varying degrees of perfection in polymers, as well as the polymorphism of the polymer, i.e., its ability to exist in several crystalline modifications. For DTA curves of the HDPE / LDPE mixture, the largest number of peaks corresponding to exothermic processes (crystallization, oxidation) were observed. In the HDPE / LDPE + 10% Al(OH)₃ composites compared to HDPE / LDPE composition, the number of peaks corresponding to endothermic processes (destruction, melting) were increased (Fig. 2b). And this is quite natural because, as mentioned above, aluminum hydroxide undergoes an endothermic dehydration reaction. All these data are reflected in table 2. As can be seen from table 2, the temperatures T₁₀, T₂₀, T₅₀ of the HDPE / LDPE mixture are higher than for composites containing aluminum hydroxide. A comparative analysis of the parameters of mass residues (%) of the composites corresponding to 400°C shows that the values of these parameters for HDPE / LDPE and HDPE / LDPE + 50% Al(OH)₃ composites are equal. The results of the analysis can be explained by the fact that aluminum hydroxide has a relatively low thermal stability, which, up to a certain temperature, leads to an increase in the rate of weight loss. After the initial degradation as a result of thermal decomposition, volatile gases are formed, fragments accompanied by a decrease in the rate of weight loss.

Thus, the experimental results confirm the proposed mechanism of the flame retardant properties of aluminum hydroxide. As water is released, alumina forms a protective layer that prevents oxygen contact with the polymer, as a result of which the decomposition of the polymer slows down.

Table 2. Some parameters of thermal degradation of composites based on HDPE / LDPE + Al(OH)₃ and HDPE / LDPE + Al(OH)₃ + modifier

№	Composite composition, wt %	T ₁₀ , °C	T ₂₀ , °C	T ₅₀ , °C	Residue at 400°C
1	HDPE/LDPE	340	370	410	64%
2	HDPE/LDPE +10 Al(OH) ₃	280	335	400	50%
3	HDPE/LDPE +10Al(OH) ₃ +1M	300	350	390	55%
4	HDPE/LDPE +10Al(OH) ₃ +3M	310	360	405	57%
5	HDPE/LDPE +50Al(OH) ₃	280	335	415	64%
6	HDPE/LDPE +50Al(OH) ₃ +5M	265	290	410	60%

M- modifier; The mixture of HDPE / LDPE were taken in a ratio of 50/50

3.5. Infrared spectroscopy (IR)

The following absorption bands were observed in the IR spectrum of the initial aluminum hydroxide (Fig. 3 (a)): stretching vibrations of the –OH bond (free groups O–H 3614 cm⁻¹; inside and intermolecular H-bonds 3516, 3427, 3365 cm⁻¹), O–H vibrations of interlayer hydroxyls bound by a strong H-bond between aluminum hydroxide packets (2001-2322 cm⁻¹), bending vibrations of OH hydroxide groups (1012, 966, cm⁻¹), Al–O bond vibrations (732, 664 cm⁻¹).

The following absorption bands were observed in the IR spectrum of the initial HDPE / LDPE mixture (Figure 3 (b)): antisymmetric stretching vibrations of C–H bonds of the CH₂ group, (2914cm⁻¹), symmetric stretching vibrations of C–H bonds of the CH₂ group (2847cm⁻¹), the bending vibration of C–H bonds of the CH₂ group (1461

cm^{-1}), a small absorption band at 1376 cm^{-1} (symmetric bending vibration), which is a methyl group in highly branched LDPE (Junga *et al.*, 2018), the bending vibration of C–H bonds CH_2 groups (718 cm^{-1}).

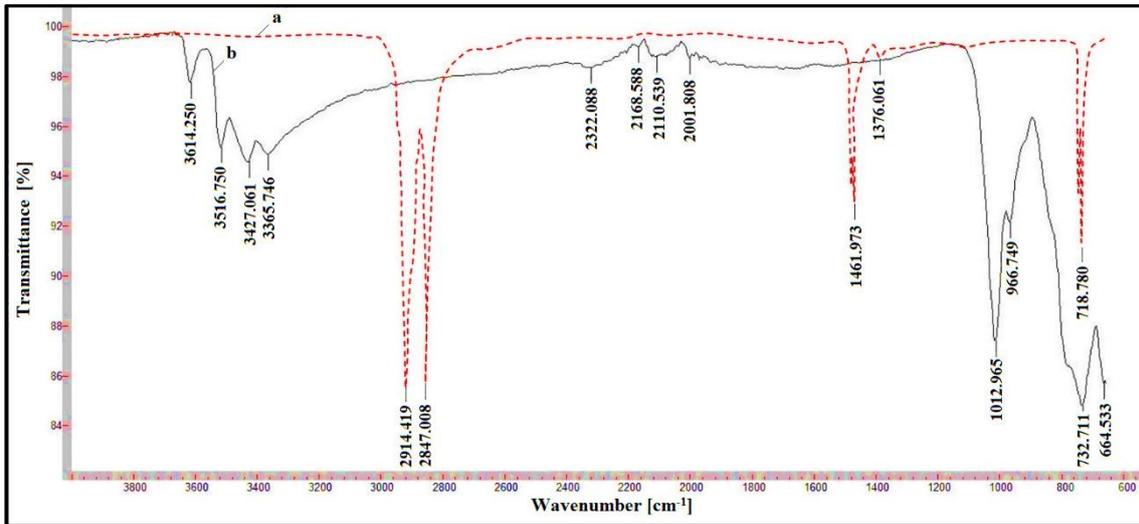


Figure 3. IR spectrum of (a)- HDPE / LDPE, (b)-Al (OH)₃

From Fig. 4a illustrating the IR spectrum of the HDPE / LDPE + 50% Al(OH)₃ composite, it is clearly seen that the 2001-2322 cm^{-1} bands of the H-bonds of the interlayer hydroxyl disappeared. This can be explained by the fact that during the mixing of the components of the mixture on the rollers or during pressing at a temperature of 170-180°C, this bond breaks.

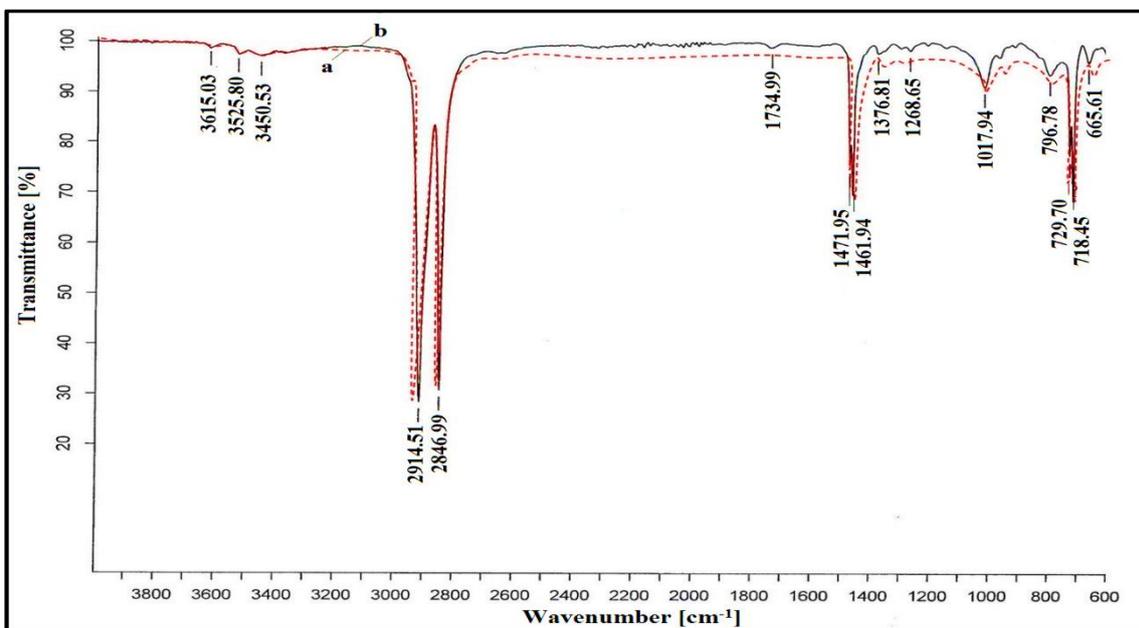


Figure 4. IR spectrum of (a)-HDPE / LDPE + 50% Al (OH)₃,
(b)- HDPE / LDPE + 50% Al (OH)₃ + 5% modifier

A comparative analysis of the IR spectrum of HDPE / LDPE + 50% Al(OH)₃ and HDPE / LDPE + 50% Al(OH)₃ + 5% modifier shows that almost all absorption bands overlap. In other words, there are no absorption bands corresponding to the modifier. This can be explained by the fact that the amount of modifier in the composition of the composite is negligible.

4. Conclusion

Thus, based on the foregoing, it can be stated that the loading of a modifier in the composition of HDPE / LDPE + Al(OH)₃, along with improving the physicomechanical properties, increases the oxygen index of the composites. The modifier improves the compatibility of the components of the mixture, has a relatively high thermal stability (within 255°C), which allows the processing of composites at relatively high temperature conditions, up to 255°C.

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