

## Improvement of Fire Resistance of Polymeric Materials at their Filling with Aluminosilicates

Oleksandr Blyznyuk<sup>1a</sup>, Alexey Vasilchenko<sup>2,b\*</sup>, Artem Ruban<sup>2c</sup>  
and Yuliia Bezuhla<sup>2d</sup>

<sup>1</sup>National Technical University «Kharkiv Polytechnic Institute», 2, Kyrpychova str., 61002, Kharkiv, Ukraine

<sup>2</sup>National University of Civil Defence of Ukraine, 94, Chernishevskya st., Kharkiv, Ukraine, 61023

<sup>a</sup>avb@kpi.kharkov.ua, <sup>b</sup>avas2006@ukr.net, <sup>c</sup>ruban\_artem1979@ukr.net, <sup>d</sup>bezuglaja@nuczu.edu.ua

**Keywords:** polymer composite material, zeolite, medium-density polyethylene, epoxy oligomer, oxygen index, aluminosilicate, fire resistance

**Abstract.** Effect of content of synthetic aluminosilicates in medium-density polyethylene on the fire hazard characteristics and mechanical properties of compositions is investigated. It has been shown that during decomposition of the filler with the release of water, its effectiveness depends not only on the endothermic effect of decomposition and the content of dehydration products, but also on the correspondence of temperature of the dehydration of the filler and the temperature of intensive decomposition of the polymer. Regardless of the type of fillers, an increase in their content in polymer composite material helps to reduce combustibility. It has been shown that compositions based on epoxy oligomers or medium-density polyethylene and synthetic zeolite have properties of self-extinguish and fairly high physical and mechanical characteristics. It is shown that epoxy polymer composite material with the content of inorganic fillers 40-70 wt.% can be used for sealing building structures and other products operating at elevated temperatures, as well as in a mode where the fire resistance and heat resistance of the sealing compound are decisive. A number of efficiency of flame-suppressing of fillers is presented. Formulations of compositions based on epoxy oligomers or medium-density polyethylene with synthetic zeolite having an optimal ratio of fire hazard and mechanical properties and not having toxic or carcinogenic effects when heated are recommended.

### 1 Introduction

Polymer materials are widely used in modern life. They are used in mechanical engineering, instrument making, construction and other industries as structural, finishing, heat-insulating materials, sealants, etc.

An important factor restraining the introduction of a variety of polymeric materials is their fire hazard due to combustibility and related processes. In technology the following characteristics of the fire hazard of materials and products made of them are determined: 1) combustibility, that is, the ability of the material to ignite, support and spread the combustion process; 2) fume evolution during combustion and flame exposure; 3) toxicity of gaseous combustion products and pyrolysis – decomposition of a substance under the influence of high temperatures; 4) fire resistance of the structure, that is, the ability to preserve the physical-mechanical (strength, stiffness) and functional properties of the product when exposed to flame. In turn, combustibility is a complex characteristic of a material or structure. It includes the following indicators: 1) temperature of ignition or self-ignition; 2) rate of burnout and spread of flame on the surface; 3) limit parameters characterizing the conditions under which a self-sustaining combustion process is possible, for example, the composition of the atmosphere (oxygen index) or temperature (temperature index). [1]

The problem of combustibility of polymers and polymer materials is a long-standing and constantly relevant. Polymeric materials are used in structures as sealants, thermal insulation, as part of fire-retardant materials, where their fire resistance is an important property [2, 3, 4].

Increasing fire resistance of polymer materials, reducing their combustibility, is always given special attention. All methods to reduce combustibility are based on the following principles: 1) change in the heat balance of the flame due to an increase in various kinds of heat loss; 2) reducing the heat flux from the flame to the polymer by creating protective layers, for example from the resulting coke; 3) decrease in the rate of gasification of the polymer; 4) change in the ratio of combustible and non-combustible decomposition products of the material in favor of non-combustible. Polymer materials with self-extinguishing properties can be obtained by introducing fire retardants and non-combustible fillers into their composition [5, 6]. The most common fire retardants are phosphorus compounds, antimony oxide and its organic derivatives, various halogen-containing substances. These fire retardants are entered both individually and in the form of synergistic mixtures, given their effect on the change in the complex of mechanical, dielectric and other properties.

A significant deterrent to the use of these fire retardants is the detection of their carcinogenic nature (both the products themselves and their decomposition products during combustion) [7]. Therefore, in our opinion, the use of various mineral fillers as fire retardants which devoid of the above disadvantages is more progressive.

It is known that in some cases, to significantly increase the heat resistance of the polymer composite material (PCM), even without the introduction of antipyretic additives into it, an increase in the content of inorganic dispersed fillers allows.

The influence of the chemical nature of powdered fillers and their content on the fire hazard of polymer composite material is not well understood. In this regard, it is of interest to study the influence of these factors on the combustibility, flammability and smoke generating ability of highly saturated polymer composite material based on epoxy oligomers or medium-density polyethylene.

## 2 The Study of Epoxy Compositions with Inorganic Fillers

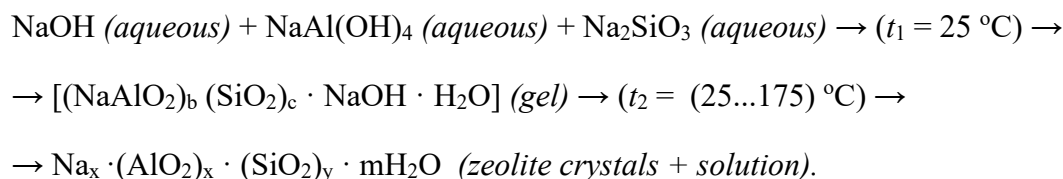
Polymer composite materials based on epoxy oligomers, containing up to 60 wt.% of fine inorganic fillers are widely used in various fields of technology (for example, as sealants). Clarification of the effect of these fillers on reducing the fire hazard of epoxy polymer composite materials will increase the reliability and safety of the structures in which they are used.

The introduction of inorganic fillers into polymer binders can reduce the polymer composite material fire hazard by reducing the content of combustible components and increasing the enthalpy of the polymer composite material gasification process, as well as by phlegmatizing the flame with dehydration products [5].

One of the poorly studied fillers of polymeric materials are aluminosilicates (zeolites) [8, 9], in particular synthetic aluminosilicate of the general formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 1.8\text{H}_2\text{O}$ .

The specified aluminosilicate in terms of a unit cell has the following chemical composition:  $\text{Na}_{12} | (\text{AlO}_2)_{12} (\text{SiO}_3)_{12} | \cdot 27\text{H}_2\text{O}$ .

Synthetic aluminosilicates are obtained from aqueous solutions of sodium aluminate, sodium silicate and sodium hydroxide according to the following scheme [10, 11]:



For the most part, aluminosilicates have a crystalline structure in the form of a three-dimensional skeleton containing cavities inside – the voids connected to each other and the outer space by a channel system. The inside volume of crystalline cavities can reach of 50 %. The porous skeleton of aluminosilicates carries a negative charge, which is compensated by cations of alkali and alkaline earth metals (Na, K, Ca, etc.). Cations penetrate intracrystalline cavities together with water

molecules. Particles of aluminosilicates have a size of 4...40  $\mu\text{m}$  and have high sorption ability [12, 13].

For the experiment, highly dispersed inorganic fillers with a particle size of 3...40  $\mu\text{m}$  were introduced into the composition of an epoxy resin based on Epoxy-520 (analogue of ED-20) with a hardener polyethylene polyamine:

- synthetic aluminosilicate (zeolite) of the general formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ;
- aluminum hydroxide,  $\text{Al}(\text{OH})_3$ ;
- magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ .

For polymer composite materials auto-ignition temperature ( $t_{ai}$ ), oxygen index (OI) and smoke generation coefficient ( $D_m$ ) in the smouldering and combustion mode were determined according to [14]. Thermal-oxidative stability of polymer composite materials was determined using a Paulik, Paulik and Erdei derivatograph. The heating rate of the samples was  $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ , a 100 mg sample.

Combustibility and smoke generating ability of polymer composite material based on Epoxy-520 epoxy oligomer with hardener polyethylene polyamine and with a filler content of 40 wt.% given in table. 1.

Table 1. The effect of dispersed inorganic fillers on the fire hazard characteristics of epoxy PCM

Epoxy polymer material	Auto-ignition temperature, $t_{ai}$ [ $^\circ\text{C}$ ]	Oxygen index, OI [vol.%]	Smoke generation coefficient, $D_m$ [ $\text{m}^2 \cdot \text{kg}^{-1}$ ]	
			pyrolysis mode	combustion mode
Unfilled	440	18.6	1407	810
Filled with synthetic aluminosilicate (zeolite)	510	20.0	627	480
Filled with $\text{Al}(\text{OH})_3$	503	21.9	706	310
Filled with $\text{Mg}(\text{OH})_2$	487	22.0	660	320

The nature of effect of the fillers content in polymer composite material on their fire resistance can be traced by the change in oxygen index in Fig. 1. The introduction of the studied dispersed fillers in polymer composite material begins affect the increase in fire resistance at their content of 20-25 wt.%. With a degree of filling up to 50 wt.% the chemical nature of the studied fillers has a negligible effect on the parameters characterizing the polymer composite material combustion process (OI is 20-22 % by volume,  $t_{ai} = 487...570 \text{ }^\circ\text{C}$ ).

A noticeable increase in the oxygen index in epoxy resin compositions with  $\text{Al}(\text{OH})_3$ ,  $\text{Mg}(\text{OH})_2$  fillers and synthetic zeolite is observed, starting with a filler concentration of about 55 wt.%.

The effectiveness of the filler depends on whether it decomposes with the release of water or not. All investigated fillers decompose with the release of water [15]. Therefore, the effectiveness of their action depends not only on the endothermic effect of decomposition and the content of dehydration products, but also on the correspondence of the temperature of the filler dehydration and the temperature of intensive decomposition of the polymer. Differential thermal analysis method (DTA) determined the temperature of the maximum decomposition rate:

- for zeolite –  $380 \text{ }^\circ\text{C}$ ;
- for  $\text{Al}(\text{OH})_3$  –  $306 \text{ }^\circ\text{C}$ ;
- for  $\text{Mg}(\text{OH})_2$  –  $360 \text{ }^\circ\text{C}$ .

In the smouldering mode, the smoke generation coefficient of the studied materials is higher than in the flame combustion mode, which is apparently associated with the catalytic effect of fillers on the decomposition of the polymer binder. Regardless of the type of fillers, an increase in their content in polymer composite material helps to reduce combustibility. For example, with a filler content of 60-70 wt.% the degree of benignity of the samples on the scale of the Shramm-Tsebrowsky [16] is:

- for zeolite – 4;
- for  $\text{Al}(\text{OH})_3$  – 3;
- for  $\text{Mg}(\text{OH})_2$  – 3.

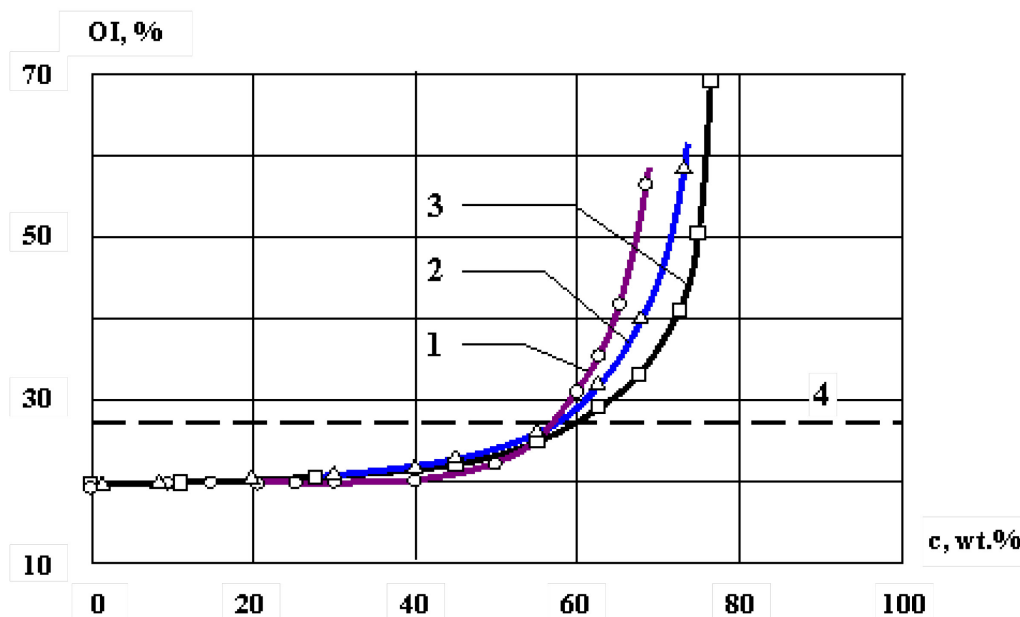


Fig. 1. The dependence of the oxygen index of the cured epoxy compositions on the filler concentration: 1 – zeolite; 2 –  $\text{Mg}(\text{OH})_2$ ; 3 –  $\text{Al}(\text{OH})_3$ ; 4 – boundary of self-extinction in the atmosphere (OI = 27 %).

According to the sum of the indicators, studied fillers can be arranged in the following order by the efficiency of flame suppression action:

$$\text{zeolite} > \text{Mg}(\text{OH})_2 > \text{Al}(\text{OH})_3 .$$

### 3 The Study of Compositions Based on Medium-Density Polyethylene with Inorganic Fillers

The introduction of flame retardants in the composition of polyethylene also helps to increase the fire and heat resistance of the resulting compositions [17, 18].

In the article effect of finely dispersed inorganic fillers on the thermal and mechanical properties of polyethylene compositions was studied. To do this, in a two-screw laboratory mixer at a temperature of 160...190 °C, highly dispersed synthetic aluminosilicate with a particle size of 3...40  $\mu\text{m}$  was mixed with medium-density polyethylene (MDP) Marlex® HMN TR-935-HMN TR-935G in the proportions presented in tab. 2. Samples for testing were made by the pressing method according to the regimes in accordance with DSTU EN ISO 527-2:2018 [19]. Samples with  $\text{Al}(\text{OH})_3$  and  $\text{Mg}(\text{OH})_2$  fillers were prepared using the same procedure.

The fire hazard properties of the samples of compositions were studied by the method of fire tube according to DSTU EN ISO 4589-3:2018 [14], the oxygen index was determined according to DSTU-N B EN 1991-1-2:2010 [20], and the mechanical properties were studied according to DSTU EN ISO 527-2:2018 [19]. The research results are presented in tab. 2 and in Fig. 2.

Analysis of data in table 2 shows that the proposed compositions based on medium-density polyethylene and synthetic zeolite are self-extinguish and have sufficiently high physical and mechanical characteristics. The tensile breaking stress remains almost unchanged, but the stiffness increases.

Table 2. The properties of the compositions of MDP and synthetic aluminosilicate

Composition number	Synthetic aluminosilicate concentration, [ wt.% ]	Time before burning, [ s ]	Self-extinction time, [ s ]	Weight loss during combustion, [ wt.% ]	Tensile stress, $\sigma_p$ , [ MPa ]	Elongation at break $\epsilon_p$ , [ % ]
1	0	Burns	-	-	29	870
2	10	198	18	26	30	137
3	15	240	7	8-10	28	130
4	20	280	7	7-8	29	125
5	25	405	6	6-7	28.5	110

When synthetic aluminosilicate is introduced into medium-density polyethylene, the time before the onset of ignition increases with an increase in its concentration in the polymer from 198 s to 405 s. When a sample is removed from the burner flame, its combustion ceases after 6-18 s, depending on the composition. Moreover, the own burning time decreases with increasing content of synthetic aluminosilicate. Meanwhile, in well-known compositions based on polyethylene, self-extinguish is achieved at a high (up to 25 wt.%) content of an antipyretic mixture (chloroparaffin + antimony trioxide) [17]. Therefore, in comparison with the existing ones, the studied compositions based on medium-density polyethylene and synthetic aluminosilicate have increased self-extinguish and the absence of expensive and toxic flame retardants in the composition. In terms of their physical and mechanical properties, the studied compositions are not inferior to the known ones.

In the graph of Fig. 2 shows that the introduction of the studied dispersed fillers in the composition of medium-density polyethylene begins to influence the increase in fire resistance with their content of 30-40 wt.%. But a significant increasing in the oxygen index in medium-density polyethylene compositions with  $\text{Al}(\text{OH})_3$ ,  $\text{Mg}(\text{OH})_2$  fillers and synthetic zeolite is observed, starting only from a concentration of about 65 wt.%.

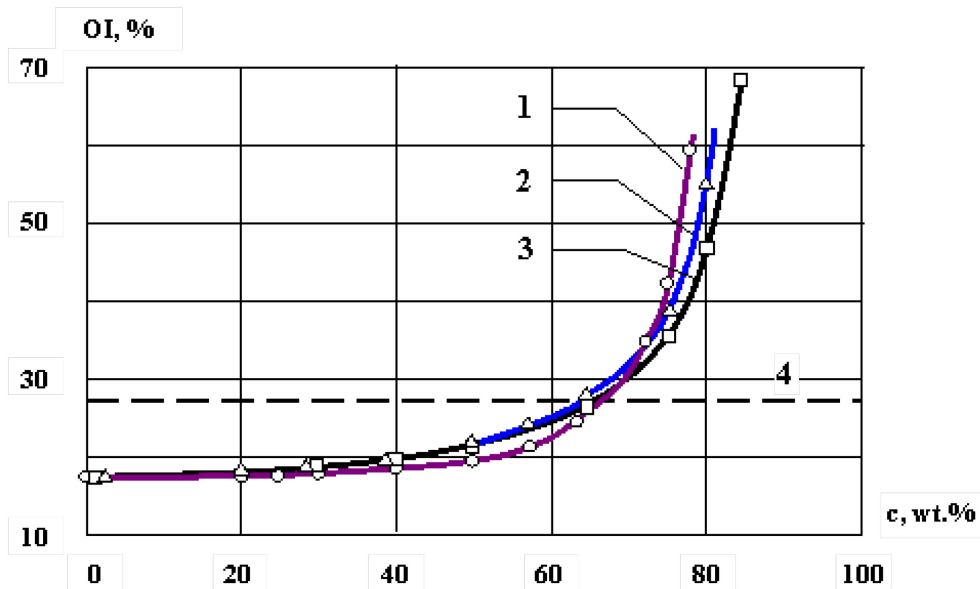


Fig. 2. The dependence of the oxygen index of the cured MDP compositions on the filler concentration: 1 – zeolite; 2 –  $\text{Mg}(\text{OH})_2$ ; 3 –  $\text{Al}(\text{OH})_3$ ; 4 – boundary of self-extinction in the atmosphere (OI = 27 %).

The decrease in combustibility significantly depends on the ratio of heat loss on decomposition of the filler and all other heat losses from the flame, which are always the higher, the greater the total heat of combustion of the polymer. With the introduction of fillers that decompose with the absorption of heat (in our case, water is split off); heat is consumed both for heating the filler and

for decomposing the filler and heating the resulting water [21]. Therefore, introduction into the composition of polyethylene or epoxy resin fillers  $\text{Al}(\text{OH})_3$ ,  $\text{Mg}(\text{OH})_2$  and synthetic zeolite up to 60 wt.% (see Fig. 1 and Fig. 2) does not lead to a significant increase of oxygen index (OI increases from 17.5 % to 25-26 %).

The oxygen index of the material, which can be used in various fields, for example, in construction, meeting the requirements of standards for combustibility, is adopted OI = 27 % (in Fig. 1 and Fig. 2 is indicated by a dashed line) [1].

Therefore, it can be expected (see Fig. 1) that polymer composite materials based on epoxy resin can exhibit self-extinction properties at a filler content of at least: zeolite – 55 wt.%,  $\text{Mg}(\text{OH})_2$  – 55 wt.%,  $\text{Al}(\text{OH})_3$  – 60 wt.%.

Similarly, polymer composite materials based on medium-density polyethylene can have the property of self-extinguish when the content of zeolite,  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  fillers is at least 65 wt.% (see Fig. 2).

#### 4 Conclusion

Thus, the studies showed that introduction of finely dispersed aluminosilicate into the polymer composite material based on epoxy resin or medium-density polyethylene leads to a decrease in the combustibility of polymer composite material, with a slight increase in stiffness.

The availability of this filler allows you to recommend it at a concentration of 55-60 wt.% in epoxy polymer composite material for sealing building structures and other products operating at elevated temperatures, as well as in a mode where the fire resistance and heat resistance of the sealing compound are decisive.

Studies have also shown that the studied compositions based on medium-density polyethylene and synthetic zeolite have self-extinguish and fairly high physical and mechanical characteristics. This allows us to recommend compositions based on medium-density polyethylene with a concentration of finely divided aluminosilicate 65-70 wt.% for use in the construction, cable, instrument-making and other industries.

#### References

- [1] Al.AI. Berlin Gorenje polimerov i polimernye materialy ponizhennoy goryuchesti, Sorovskiy obrazovatelnyy zhurnal. 9 (1996) 57-63 [in Russian].
- [2] A. Vasilchenko, Y. Otrosh, N. Adamenko, E. Doronin, A. Kovaliov, Feature of fire resistance calculation of steel designs with intumescent coating, MATEC Web of Conferences 230 (2018) 02036.
- [3] V.F. Kablov, O.M. Novopoltseva, V.G. Kochetkov et al., Elastomer Heat-Shielding Materials Containing Aluminosilicate Microspheres, Russ. Engin. Res. 37 (2017) 1059–1061.
- [4] S. Nie, S. Qi, M. He et al., Synergistic effects of zeolites on a novel intumescent flame-retardant low-density polyethylene (LDPE) system, J Therm Anal Calorim. 114 (2013) 581–587.
- [5] Yu.A. Mihaylin, Teplo-, termo- i ognestoykost polimernyih materialov, NOT Sankt-Peterburg, 2011 [in Russian].
- [6] M. Zhi, Q. Liu, H. Chen, X. Chen, S. Feng, Y. He, Thermal Stability and Flame Retardancy Properties of Epoxy Resin Modified with Functionalized Graphene Oxide Containing Phosphorus and Silicon Elements, ACS Omega. 4(6) (2019) 10975-10984.
- [7] L. Li, X. Shao, Z. Zhao, X. Liu, L. Jiang, K. Huang, S. Zhao, Synergistic Fire Hazard Effect of a Multifunctional Flame Retardant in Building Insulation Expandable Polystyrene through a Simple Surface-Coating Method, ACS Omega. 5(1) (2020) 799-807.

- 
- [8] Mingzhe Dong, Xiaoyu Gu, Sheng Zhang, Hongfei Li, Peng, Jiang Effects of Acidic Sites in HA Zeolite on the Fire Performance of Polystyrene Composite, *Ind. Eng. Chem. Res.*, 52(26) (2013) 9145-9154.
- [9] J.P. Hos, P.G. McCormick, L.T. Byrne, Investigation of a synthetic aluminosilicate inorganic polymer, *Journal of Materials Science*. 37 (2002) 2311–2316..
- [10] D. Brek, *Tseolitovyie molekulyarnyie sita*, Mir, 1976 [in Russian].
- [11] I.D. Kashcheev, K.G. Zemlyanoi, K.O. Stepanova, Possibility of Preparing Aluminosilicate Fillers Based on Kaolin and Technogenic Materials, *Refractories and Industrial Ceramics*. 58(5) (2018) 566-572.
- [12] P.A. Sitnikov, A.V. Kuchin, A.G. Belykh et al. Preparation of epoxy composite material containing natural aluminosilicate filler, *Polym. Sci. Ser. D* 4 (2011) 281–283.
- [13] Yang Zhao, Dietmar Drummer, Influence of Filler Content and Filler Size on the Curing Kinetics of an Epoxy Resin, *Polymers*. 11(11), (2019) 1797.
- [14] DSTU EN ISO 4589-3:2018 (EN ISO 4589-3:2017, IDT; ISO 4589-3:2017, IDT) *Plastmasi. Vyznachennya harakteristik gorinnya za kisnevym indeksom. Chastina 3. Viprobuвання za pidvischenoyi temperaturi* [in Ukrainian].
- [15] Edward D. Weil, Sergei Levchik, A Review of Current Flame Retardant Systems for Epoxy Resins, *Journal of Fire Sciences*. 22(1) (2004) 25-40.
- [16] Alex A. Lyapkov, Nelly M. Rovkina, *Producing polymers by the polymerization techniques* Editor: prof., M.S. Usubov, Publisher of Tomsk Polytechnic University, 2015.
- [17] A.S. Panshin i dr., Vliyanie antipirenov na goryuchest polietilena, *Plasticheskie massyi*. 1 (1974) 40-43 [in Russian].
- [18] Tiurlina Siregar, Bambang Ari Wahjoedi, Sentani Natural Zeolite as a Filler for Polyethylene Composite, *International Journal of Scientific and Research Publications*. 5(1) (2015) 2250-3153.
- [19] DSTU EN ISO 527-2:2018, *Plastmasi. Vyznachennya vlastivostey pid chas roztyaguvannya. Chastina 2. Umovi viprobuvannya dlya plastmas, vigotovlenih metodom formuvannya ta ekstruziyi* (EN ISO 527-2:2012, IDT; ISO 527-2:2012, IDT) [in Ukrainian].
- [20] DSTU B N EN 1991-1-2:2010 *Diyi na konstruktsiyi. Chastina 1-2. Zagalnl diyi. Diyi na konstruktsiyi pid chas pozhezhI* (EN 1991-1-2:2002, IDT) [in Ukrainian].
- [21] B. Samujło, Effects of the flame retardant and lubricant types on fire retardancy effectiveness of medium density polyethylene, *Polimery-Warsaw*. 49(3) (2004) 191-194.