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Досліджено вплив на теплофізичні властивості композиційних матеріалів кополімеру етилену з вінілацетатом, які не підтримують горіння та наповнювачів-антипіренів. В якості наповнювачів-антипіренів досліджували тригідрати оксиду алюмінію, дигідрати оксиду магнію, гідромагнезити. Встановлено вплив типу, а також дисперсності наповнювачів-антипіренів, на теплофізичні властивості полімерних композицій (температури склування, температури плавлення та розкладу, ступінь кристалічності, питому теплоємність, енергію активації)

D-

Ключові слова: композиційні матеріали, вогнестійкість, кополімер етилену з вінілацетатом, наповнювачі-антипірени,теплофізичні властивості

Исследовано влияние на теплофизические свойства композиционных материалов сополимер этилена с винилацетатом, которые не поддерживают горения и наполнителей-антипиренов. В качестве наполнителей-антипиренов исследовали тригидрат оксида алюминия, дигидрат оксида магния, гидромагнезиты. Установлено влияние типа, а также дисперсности наполнителей-антипиренов, на теплофизические свойства полимерных композиций (температуры стеклования, температуры плавления и разложения, степень кристалличности, удельную теплоемкость, энергию активации)

Ключевые слова: композиционные материалы, огнестойкость, сополимер этилена с винилацетатом, наполнители-антипирены, теплофизические свойства

D-

1. Introduction

Polymeric composites are widely used in modern manufacturing of cable products [1]. Technical requirements for cable products have increased lately and, consequently, so has the need for development of new advanced materials, including polymeric composite materials that do not maintain combustion. Polyolefin composite materials that do not maintain combustion are very promising. This is due to the growing use of wires and cables for power industry, nuclear power industry, railway transportation, construction, etc. Requirements for fire safety of cable materials in these areas are considerably higher than for cables for general purposes. Insulation and shell materials must comply with the level of European standards. It is necessary to create special-purpose materials that meet specific operational needs, such as non-propagation of burning and absence of halogens in composition of the material, reduction of smoke and toxicity of combustion products.

Therefore, manufacturers of polymer composite materials are constantly faced with the question of selection of a filler that acts as a fire retardant. In the European market, one can observe the tendency of the accelerated growth in consumption of halogen-free cable compositions. The principle of creation of formulations of halogen-free cable tracks is based on an increase in oxygen index up to the value of 35–40. This is achieved by introduction of fire retardants – hydroxides of metals – to the basic polymer. Hydroxides of aluminum

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EFFECT OF FIRE RETARDANT FILLERS ON THERMOPHYSICAL PROPERTIES OF COMPOSITE MATERIALS OF ETHYLENE-VINYL ACETATE COPOLYMER

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Al(OH)₃ and magnesium Mg(OH)₂ of synthetic and natural origin, and hydromagnesites started to be used in industry.

Polymeric composite materials are exposed to thermal influence (of both elevated and low temperatures) during processing and operation. During combustion, due to endothermic reaction, they degrade to produce water, carbon oxides and oxides of metals.

That is why, research into dependence of thermal properties on the polymer composition, taking into account the chemical composition, dispersity and amount of fire retardant fillers, is an actual problem.

2. Literature review and problem statement

Literature analysis demonstrates that one of the ways of decreasing flammability of polymeric materials of polyolefins is introduction of fire retardant fillers to a polymer composition [2]. For this purpose, inorganic fire-retardant fillers are used. In the face of a real fire, PVC plastic compounds that are the elements of the cables, which have KI value of up to 40 units, are a source of emission of HCl gases and significant smoke pollution. That is why, in order to address the problems, associated with release of HCl and smoke pollution, the polymeric compositions, which that do not emit corrosion active gases and have a much lower level of smoke release, were created [3]. These materials not only increase fire resistance due to absorption of greater amount of heat, but also neutralize acidic gases, which results in lower smoke formation [4]. Polyolefins are normally used as a polymer base for these materials, and magnesium oxide trihydrates, aluminum oxide dihydrates and magnesites are used as fire retardants. This trend is the focus of a significant amount of research. Mechanical and fire-retardant properties of composite materials of EVA and aluminum oxide of trihydrate with different diameters of particles were explored, and a change in these properties depending on dispersity of a filler was determined [5]. Effectiveness of usage of calcium hydroxide in order to improve fire resistance of polyethylene of high density was shown [6]. Fire-resistant properties of composite materials, the base polymer of which is LDPE/EVA, were studied. Metal hydroxides (magnesium hydroxide and aluminum oxide trihydrate) were used as fire retardant fillers. Fire-resistant properties were estimated by horizontal combustion and oxygen index [7]. Using the methods of TGA/DSC, polymeric compositions with the use of magnesium dioxin as fire retardant were examined. Thermal capacity of these materials was determined [8]. The influence of magnesium hydroxide and nanoclay on inhibition of combustion of ethylene-vinyl acetate (EVA) copolymer was studied. The studies were carried out using the methods of determining of oxygen index and calorimetric methods of analysis. The results of the studies demonstrated effectiveness of replacement of magnesium hydroxide and aluminum hydroxide with 1-2 % nanoclay in EVA compositions [9].

Fire resistance of ethylene-vinyl acetate copolymer, which was filled with metal hydroxides (aluminum oxide trihydrate and magnesium oxide dihydrates) and silicon dioxide, was studied. It was noted that silica provides an advantage if the amount and other properties of fillers promote formation of a protective mineral layer [10].

Possibility of using magnesium hydroxide, zinc borate and joint influence of polypropylene fiber as a combustion inhibitor were explored. Effectiveness of using zinc borate was shown. The use of magnesium hydroxide is ineffective. Thermal, mechanical and morphological properties were examined [11].

These studies show that the properties of polymeric compositions vary depending on the composition. During processing of polymeric compositions and during operation of cables, temperatures of melting, decomposition and energy of activation of processes are of great importance. However, many problems associated with creation of polymer compositions that do not maintain combustion still have been insufficiently studied. This is especially true of the influence of fire retardant fillers and polymer matrix on thermal properties.

3. The aim and objectives of the study

The aim of present research is to study the influence of the type and concentration of fire retardant fillers and the polymer matrix on thermal properties of composite materials with ethylene-vinyl acetate copolymer that does not maintain combustion. This will enable us to approach reasonably determining of the polymer type, amount, type and dispersity of a fire-retardant filler. This will also make it possible to quickly adjust composition formulation depending on available raw materials or on desired thermal properties of the final product.

To accomplish the set aim, the following tasks must be solved:

 to study dependence of temperatures of physical transformations (vitrification temperature, melting temperature), degree of crystallinity and specific thermal capacity on properties of ingredients of polymeric compositions;

 to establish the patterns of changes in temperature and energy activation during decomposition of polymer compositions on their formulation.

4. Materials and equipment for the study of thermophysical properties

We studied copolymers of ethylene-vinyl acetate (EVA), characteristics of which are shown in Table 1, as well as fire retardant fillers, such as aluminum oxide trihydrates, magnesium oxide dihydrates, mixture of magnesite and hydromagnesite. Characteristics of fire retardant fillers are shown in Table 2.

Table 1

EVA characteristics

Indicator	EVA 1	EVA 2
Density, kg/m ³	939	951
Indicator of melt fluidity, 2.16 kg, g/10 min	2.5	5
Content of vinyl acetate, %	18	28

Table 2

Characteristics of fire retardant fillers

Indicator	Al(OH) ₃		Mg(OH) ₂		Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O; Mg ₃ Ca(CO ₃) ₄
	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
$\begin{array}{l} \text{Mass fraction, \%:} \\ &-\text{Mg(OH)}_2 \\ &-\text{Al(OH)}_3 \\ &-\text{SiO}_2 \\ &-\text{Fe}_2\text{O}_3 \\ &-\text{Na}_2\text{O} \\ &-\text{CaO} \end{array}$	- >99.2 <0.05 <0.035 <0.6 -	- >99.5 <0.1 <0.03 <0.4 -	>93 - <0.05 <0.3 <0.05 -	>93.2 2.2±0.2 0.12±0.02 2.2±0.2	98.96 - 0.67 0.04 <0.05 -
Median diameter of particles, micron: – medium (D ₅₀) – max. (D ₉₈) – min. (D ₁₀)	1.5 3.6 0.5	3 18 1	3 20 1	3.7 12.5 1.1	1.4 8.35 1.02

The data, shown in Table 1, 2 were taken from the certificates of provider and are the results of input control of raw materials.

Experimental samples EVA polymeric compositions with different percentage of fire retardant filler of 40, 45, 50, 55, 60 % by weight within each composition were made by rolling method at temperature of (170 ± 5) °C within (7-10) min. Rollers have friction of 1.5.

EVA and fire-retardant fillers were weighed on the scales with accuracy of up to 0.001 g and were sequentially loaded on the rollers. Temperature of the operating roll-

er was (170 ± 5) °C. Temperature of the cold roller was (165 ± 5) °C. Samples were rolled for 3 minutes on the gap of 0.4–0.5 mm. Then the gap was adjusted up to 2 mm. In the process of rolling, they periodically were undercut not less than 2 times per minute. Over the last minute, the rolling was without undercuts.

The samples were conditioned at temperature of (20±2) $^\circ C$ not less than for 24 hours.

A series of experiments on the study of phase transitions, processes of thermooxidation destruction was carried out using only the device of thermogravimetric analysis and differential scanning calorimetry TGA/DSC 1/1100 SF and DSC of METTLER TOLEDO company at heating rate of 10 degrees/min and 50 degrees/min.

Kinetic characteristics, decomposition temperature and activation energy were studied using the device of thermogravimetric analysis and differential scanning calorimetry TGA/DSC 1/1100 SF of METTLER TOLEDO company at temperature from 20 °C to 650 °C at heating rate (β) of 50 °C/min, 75 °C/min or 100 °C/min.

Differential scanning calorimetry is based on the known Boersm principle, or the principle of thermal flow, according to which thermal flows of the sample and of control measuring are compared.

TGA/DSC 1 is a highly sensitive measuring instrument for thermogravimetric analysis (TGA). The main element of TGA/DSC 1 is the measuring cell, which consists of a furnace and scales. In addition to the weight of the sample, which is measured using the built-in highly sensitive scales, TGA/DSC 1 provides temperature measurement of the sample. Together with value of resistance temperature, these values are the basis for thermogravimetric analysis of the sample. In addition, TGA/DSC 1 allows measuring the thermal flow signal, by which it provides the use of a differential scanning calorimetry (DSC). Sample temperature and heat flux signal are determined by sensors' indicators of temperature, which is measured directly using the thermocouple, which is installed in the holder of the crucible.

Heat flux is calculated by DTA signal, which is the difference between the temperature of the sample and the value of temperature, assigned in the temperature program. The module transmits the measurement value to the software that calculates the values of heat flow from formulas:

$$\phi = E_{(T)}SDTA, \quad SDTA = T_s - T_{set},$$

where φ is the thermal flux, $E_{(T)}$ is the calorimetric sensitivity; T_s is the measured temperature of the sample, T_{set} is the value of temperature, assigned by temperature program [12].

Kinetic calculations were conducted using the model of free kinetics [13]. The model of free kinetics is based on dependence of temperature and transformation degree. Each transformation gives calculation value of energy activation. The reaction rate at a fixed value of transformation degree depends only on temperature. Temperature function of Arrhenius is used [14].

For calculation, analysis of three dynamic temperature curves for each polymer composition was used.

Processing of kinetic experiments was based on theoretical equation of S. Vyazovkin:

$$\frac{d\alpha}{dt} = k e^{-E/RT} f(\alpha)$$

where $\frac{d\alpha}{dt}$ is the reaction rate, s⁻¹; *k* is the constant of rate; *E* is the activation energy, J/mol; *R* is the universal gas constant, J/(mol×K); *T* is the temperature, K; α is the transformation degree, %.

The results were processed and the diagrams were plotted using the software Microsoft Office Excel 2007.

Adequacy of regression equation was verified by examining statistical significance of determination coefficient R^2 by F-criterion, determined from formula [15]:

$$F_{p} = \frac{R^{2}}{1 - R^{2}} \times \frac{n - m - 1}{m},$$

where n is the number of observations; m is the number of factors in the regression equation.

5. Results of research into thermophysical properties of polymeric compositions

Thermophysical properties of polymeric compositions, which are filled with aluminum oxide trihydrates, magnesium oxide dihydrates, and hydromagnesites were estimated by the method of differential scanning calorimetry. The composition of fillers in the compositions was changed from 40 % by weight to 60 % by weight.

Temperatures of phase transitions were determined according to characteristic points of description of physical phenomena on the DSC diagrams. Examples of DSC diagrams are shown in Fig. 1–3.



Fig. 1. DSC diagram. Melting temperature: 1 - EVA 1; 2 - EVA 2



Fig. 2. DSC diagram. Vitrification temperature: 1 - EVA 1; 2 - EVA 2

Beginning of melting effect (Fig. 1) or vitrification effect (Fig. 2) were determined as the point of intersection of the baseline with the diagram before phase transition. The end of effects was determined as the point of intersection of the base lines with the diagram after phase transition and the tangent of the curve, which was drawn to the deflection point.





Crystallinity degree (C) (Fig. 3) is calculated from formula:

$$C = \frac{\Delta H}{\Delta H_{100 \%}} \cdot 100 \%,$$

where *C* is the crystallinity of material, %; ΔH is the experimental melting heat, J/g; ΔH_{100} % is the melting heat of material of 100% crystallinity, J/g.

Specific thermal capacity is calculated from formula:

$$\Delta C_p = \frac{\dot{H}}{\beta \cdot m},$$

where ΔC_p is the specific thermal capacity J/g·K; β is the heating rate, K/min; *m* is the weight, g; \dot{H} is the enthalpy, J/mol (is determined as the shortest distance from two horizontal line, drawn through the points of the beginning and the end of the effect.

In accordance with the obtained values, we plotted the diagrams of melting temperature, vitrification temperature, crystallinity degree and specific thermal capacity of polymeric compositions on their composition. Results are shown in Fig. 4-10.



Fig. 4. Dependence of thermophysical characteristics of polymer compositions based on EVA 1 (diagram 1, 3, 5) and EVA 2 (diagram 2, 4, 6) on content of fire retardant filler of sample No. 1

Temperature of decomposition of polymeric compositions was determined using DSC diagrams, plotted with the use of device TGA/DSC 1/1100 SF (temperature increase rate is 50 $^{\circ}$ C/min).



Fig. 5. Dependence of the thermophysical characteristics of polymeric compositions based on EVA 1 (diagram 1, 3, 5) and EVA 2 (diagram 2, 4, 6) on content of fire retardant filler of sample No. 2



Fig. 6. Dependence of thermophysical characteristics of polymeric compositions based on EVA 1 (diagram 1, 3, 5) and EVA 2 (diagram 2, 4, 6) on content of fire retardant filler of sample No. 3



Fig. 7. Dependence of thermophysical characteristics of polymeric compositions based on EVA 1 (diagram 1, 3, 5) and EVA 2 (diagram 2, 4, 6) on content of fire retardant filler of sample No. 4



Fig. 8. Dependence of thermophysical characteristics of polymeric compositions based on EVA 1 (diagram 1, 3, 5) and EVA 2 (diagram 2, 4, 6) on content of fire retardant filler of sample No. 5



Fig. 9. Dependence of specific thermal capacity of polymeric compositions based on EVA 1 on content of fire retardant fillers of samples No. 1 - No. 5



Fig. 10. Dependence of specific thermal capacity of polymeric compositions based on EVA 2 on content of fire retardant fillers of samples No. 1 - No. 5

Temperatures of the beginning and ending of decomposition were determined as points of intersection of the baseline with the diagram before and after decomposition of polymer compositions and the tangent to the diagram, which was drawn to the point of inflection (Fig. 11). Using the obtained data, the diagrams of dependences of temperatures of the beginning and the ending of decomposition as a result of endothermal reactions depending on their composition were plotted. The results are shown in Fig. 12, 13.





Studies of kinetic characteristics of decomposition process of polymeric compositions that do not maintain combustion cause great interest. Using DSC research, we obtain graphic data of activation energy E_a on transformation degree (Fig. 14) and plot the diagrams of dependence of activation energy on degree of filling of polymeric compositions (Fig. 15, 16).



Fig. 12. Dependence of temperature of the beginning of decomposition of polymeric compositions based on EVA 1 on fire retardant fillers of sample No. 1 - No. 5







Fig. 14. Dependence of activation energy on transformation degree for EVA 1



Fig. 15. Dependence of activation energy of decomposition process of polymeric compositions based on EVA 1 on content of fire retardant fillers No. 1 – No. 5

Activation energy of thermal-oxidizing destruction of ceteris paribus is the measure of resistance of a polymer composition to the influence of elevated temperatures. As you can see from the results of this research, its increase is associated with an increase in degree of filling of polymeric compositions.



Fig. 16. Dependence of activation energy of decomposition process of polymeric compositions based on EVA 2 on content of fire retardant fillers of samples No. 1 – No. 5

6. Discussion of results of research into thermophysical properties of polymer compositions

The study of phase transition temperatures (vitrification temperature, melting temperature), as well as crystallinity degree and specific thermal capacity of polymeric compositions was conducted using the DSC method. Dependence of these indicators on properties and the number of ingredients of polymeric compositions shows (Fig. 4–8) that melting temperature and vitrification temperature grow with an increase in content of fire retardant fillers of all samples.

It should be noted that melting temperature of polymer samples based on EVA 1 grows more efficiently than in the case of EVA 2. Indicator of melt fluidity of EVA 1 is 2.5 and content of vinyl-acetate equals to 18. Vitrification temperature, on the contrary, increases more effectively in case of using compositions based on EVA 2. Indicator of melt fluidity of EVA 2 is 5.0 and content of vinyl acetate is equal to 28. However, these indicators change not so significantly with a change in the composition of fire retardant fillers. An increase or decrease in temperatures of melting and vitrification are mostly influenced by the polymer matrix.

Crystallinity degree decreases at an increase in percentage of filling of polymer compositions. Especially sharp decrease in crystallinity degree is observed in the compositions based on EVA 2. During maximal filling (60 % by weight), crystallinity degree is almost the same both for compositions based on EVA 2 and compositions based on EVA 1.

Specific thermal capacity of all polymeric compositions (Fig. 9, 10) increases at an increase in degree of filling. However, larger values are observed during the use of EVA 2 as the polymer matrix. At the same time, during the use of EVA 1 as polymer matrix, this indicator has the highest values during the use of aluminum oxide trihydrate, sample No. 1, the lowest values are characteristic for hydromagnesite, sample No. 5.

If we compare this indicator for polymeric compositions with fire retardant fillers of different dispersity, we observe that specific thermal capacity is larger for polymeric compositions with fire retardant fillers, which have smaller average diameter of particles. Aluminum oxide trihydrate, sample No. 1, has an average diameter of particles of 1.5 μ m compared with sample No.2, which has an average diameter of particles of 3.0 μ m. Magnesium oxide dihydrate, sample No. 3, has an average diameter of particles of 3.0 μ m compared with sample 4, an average diameter of particles of which is 3.7 μ m.

In case of using EVA 2 as the polymer matrix, the highest value of specific thermal capacity is characteristic for polymeric compositions, in which fire-retardant filler is magnesium oxide dihydrate, sample 4, an average diameter of particles of which is 3.7 microns. Polymer composition comprising aluminum oxide trihydrate has a higher value with an average diameter of particles of 1.5 microns. The lowest value of specific thermal capacity is characteristic for polymeric compositions with the use of hydromagnesites as fire retardant fillers. We obtained the data that indicate a difference in processes of structure formation of polymer compositions in case of using ingredients that differ in chemical structure and properties. This is caused by the following factors: a decrease of molecular mobility in external superficial layers around particles of the filler, specific features of structure formation of polymer compositions with different fillers.

It should be noted that important parameters during operation of compositions include initial decomposition temperature, because it characterizes the initial stage of destruction during combustion.

Analysis of DSC curves (Fig. 11) makes it possible to discover exothermal effects in the temperature range from 240 $^{\circ}$ C to 460 $^{\circ}$ C for polymeric compositions with different content of ingredients.

Analysis of the results shows that temperature of the beginning of decomposition in the case of using polymeric compositions based on EVA 1 is higher. In addition, these indicators have higher values for polymeric compositions with the use of magnesium oxides dihydrates and hydromagnesites. If you consider dependence of temperature of the beginning of decomposition of polymeric compositions depending on dispersity of fire retardant fillers, higher values were obtained for sample No. 4 of magnesium oxide dihydrate and sample No. 2 of aluminum oxide trihydrate, i.e. with a larger average diameter of particles.

The next stage of the study was to determine the influence of the ingredients of polymeric compositions on activation energy of thermal destruction of polymeric compositions. Activation energy is a supersensitive parameter of the measure of resistance of polymer compositions to thermo-oxidizing degradation.

Calculation of activation energy was carried out using the model of free kinetics.

Research results (Fig. 14, 15) show that activation energy increases with an increase in content of fire retardant fillers in polymeric compositions.

Among polymeric compositions based on EVA 1, the polymer composition with fire retardant filler in sample No. 5 – hydromagnesite, has the highest value of activation energy of the beginning of decomposition, samples No. 1 and No. 2 of aluminum oxide trihydrate have the lowest value, samples No. 3 and No. 4 of magnesium oxide dihydrate are in the middle.

For polymeric compositions based on EVA 2, a similar tendency as for polymeric compositions with fire retardant fillers in samples No. 5 and No. 1, is observed. Polymer composition with fire retardant fillers of samples No. 2 – No. 4 have medium values.

Thus, an increase in the value of activation energy of the beginning of decomposition of polymeric compositions indicates slowing down of molecular mobility in the system.

The obtained results can be explained by different physical-chemical, thermo-chemical properties of the components of polymeric compositions. Thermal properties of the studied compositions are greatly influenced by formation of supermolecular structure of the derived compositions. This is evidenced by results of the studies of phase transformations, crystallinity degree and specific thermal capacity. Results of the research allow developing technologies of obtaining polymer compositions with controllable characteristics of flame propagation.

The benefits of this research include the study of thermophysical properties of polymer composite materials that do not maintain combustion, using high-precision modern methods. Obtained results give comparative evaluation of thermophysical properties when using ingredients of polymeric compositions with different physical-chemical properties. Development of the study may be nanostructural modification of polymeric compositions.

7. Conclusions

1. Temperatures of physical transformations (temperatures of vitrification, melting and decomposition) of polymer compositions that do not maintain combustion depend on the properties of ethylene-vinyl acetate copolymer. EVA 1 has lower values of the indicator of melt fluidity and content of vinyl-acetate than EVA 2. Melting point increases more effectively for polymeric compositions based on EVA 1 during an increase in content of fire retardant fillers. Vitrification temperature, on the contrary, increases more effectively for polymeric compositions based on EVA 2 at the increased content of fire retardant fillers. Crystallinity degree decreases and specific thermal capacity increases at the increased content of fire retardant fillers in the polymer composition.

2. The use of fire retardant fillers of different composition and dispersity affects the value of temperature of the beginning of decomposition and activation energy of the beginning of decomposition of polymeric compositions. It was found that temperature of the beginning of decomposition has the largest value for polymeric compositions based on EVA 1, with lower fluidity indicator, as well as in the case of usage of magnesium oxide dihydrates and hydromagnesites as fire retardant fillers. At the same time, it was found that temperature of the beginning of decomposition increases when using fire retardant fillers with a larger average diameter of particles (3 µm for aluminum oxide trihydrates and 3.7 µm for magnesium oxide dihydrate). Activation energy of the beginning of decomposition of polymeric compositions increases at increased content of fire-retardant fillers. This is especially noticeable while using hydromagnesites. Activation energy of the beginning of decomposition of polymeric compositions increases from 60 kJ/mol to 270 kJ/mol for polymeric compositions based on EVA 1 and from 100 kJ/mol to 200 kJ/mol for polymeric compositions based on EVA 2. Aluminum oxide trihydrates and magnesium oxide dihydrates make less influence on an increase in activation energy than hydromagnesites. A change in the values of activation energy was recorded at the level from 60 kJ/mol to 140 kJ/mol for polymeric compositions based on EVA 1 and from 100 kJ/mol to 140 kJ/mol for polymeric compositions based on EVA 2. Thus, the studies demonstrated the possibility of regulation of thermophysical properties of polymer compositions EVA and fire-retardant fillers of different qualitative composition that do not maintain combustion.

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