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IMPROVE THE PROPERTIES OF POLYMER MATERIALS MODIFIED WITH METAL POLYPHOSPHATES AND REDUCE THEIR FLAMMABILITY

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Abstract- At the current, the demand for nanocomposites in the chemical industry produces most of them. Despite the small share of nanoparticles in the chemical industry, the demand for modifiers is growing every day. This is due to their high physical, mechanical and operational properties, resistance to aggressive media and their ability to be used over a wide temperature range. Therefore, it is more important to produce polymer materials on the basis of metal-containing compounds and apply them in practice. The aim of this work was to study the effect of complex improvement of the physical and mechanical properties of polyolefins, in particular, on the heat resistance and flammability of composites through the introduction of ammonium polyphosphate and metal phosphates into the polymer. For this purpose, Raman spectrometer analysis, Differential-thermal and thermogravimetric analysis and similar characterization methods were used. Studies have been conducted to determine the oxygen index and combustion time.Analyzes have shown that the addition of fillers helps to increase the fire resistance of the polymers. Improves the physico-mechanical properties of polyolefins.The composition of the ammonium polyphosphate-montmorillonite nanoparticle was found to increase the fire resistance of PP relative to ammonium polyphosphate and its mixture with montmorillonite microparticles.

Keywords - composites, nonocomposite, modification, deformation temperature under load, mechanical properties,burning time, oxygen index.

Introduction

Today, in industrialized countries, the main attention is paid to obtaining modified polymers. Zhang Zhenjiang., Sh. Mihan., K. Rainer., Abu Bakar., Ishak Z.A., A.Stec on the implementation and development of scientific research works in this field., Kozyrev Y., Jennifer R., Stdakova E.B., Yang Rongjie., Yi Deqi., Vaia R.A., Hudson S.D., Yang Y., Liu L.M., Zilg C., Taguet A., Cassagnaub P., Lopez-Cuestaa M. and other fundamental researches of the world were conducted. A lot of scientific

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and practical work in this field has also been carried out in the countries of the Commonwealth of Independent States.[1]. In particular, scientists of the Russian Federation A.A. Sersova, S.I. Marakulin, E.V. Yurtov, scientists of the Republic of Belarus A. Lesnikovich, A.F. Selevich, E.V. Hrushevich and others carried out effective fundamental research and they are currently improving. In our republic, many scientists are conducting their scientific and practical work on the modification of polymers. In particular, scientists such as Askarov M.A., Negmatov S.S., Abdurashidov T.R., Djalilov A.T., Turaev Kh.Kh. and Tojiev P.J make a great contribution to the creation of new modified polymers with their fundamental research. Today, research in the field of development of high-performance products that meet the needs of the times in all fields and the use of reactive active modifiers with new multifunctional effects, improving the quality of additives, anti-corrosion coatings and refractory materials and expanding these systems for the chemical industry of our republic is of great importance. One of today's requirements is to create environmentally friendly and safe polymer materials with improved physical and mechanical properties and reduced flammability, especially based on local raw materials.[2,3].

1. Experimental Part

91 grams of ammonium polyphosphate and 224.7 grams of cobalt (II) oxide were weighed, mixed and heated in a muffle furnace. The reaction was carried out for 1-6 hours. When the process was carried out at a temperature of 250-300°C, a pale reddish mass was formed. The resulting mixture was cooled to room temperature. The resulting compound was analyzed in a Fourier infrared spectrometer (in the range of 4000-600 cm-1) SHIMADZU. Infrared spectroscopy is presented in Fig 1.

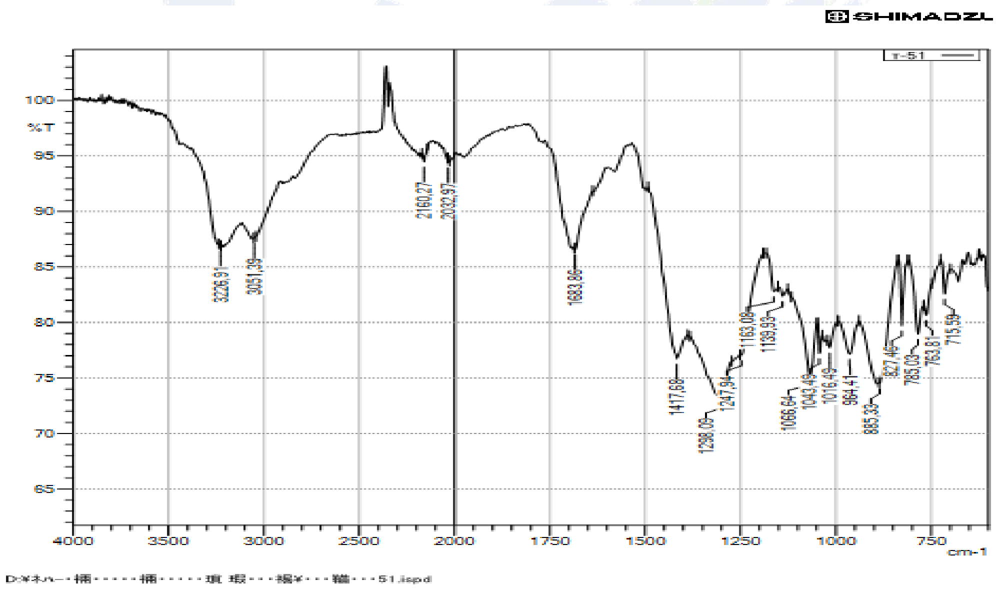

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Fig. 1 IR-spectrum of the resulting ammonium cobalt polyphosphate

According to the results of IR analysis, ammonium cobalt polyphosphate has the valence vibration of P=O in the 1247.94 cm-1 area, the vibration related to P-O-P in the 896.90 cm-1 area, the vibration frequencies related to the NH4+ ion in the 1417.68 cm-1 area, and -O-P- appears in the 785.03 cm-1 area belonging to the group. It can be seen that it exists in the area 715.59 belonging to the -Co-O- group in cobalt oxide.

From the IR-spectrum analysis of the reaction product and ammonia release during the reaction, it can be suggested that the process proceeded on the basis of the following reaction equation:

$$3(NH_4PO_3)_n + CoO \rightarrow (NH_4Co(PO_3)_3)_n + 2NH_3 + H_2O$$

Ammonium cobalt polyphosphate was formed as a result of the reaction.[4,5].

2.1. Differential-thermal and thermogravimetric analysis

The thermal stability of the synthesized complex was analyzed by differential-thermal and thermogravimetric methods on the Japanese SHIMADZU-DTG 60 device. 3.46 mg of the complex compound crystal was taken for analysis and the process was carried out at a temperature of up to 600°C. It was studied by automatic recording of the derivatogram in the derivatograph at a speed of 10 degrees/min, T-900, TG-200, DTA - 1/10, and DTG - 1/10 galvanometer sensitivity (Fig. 2).

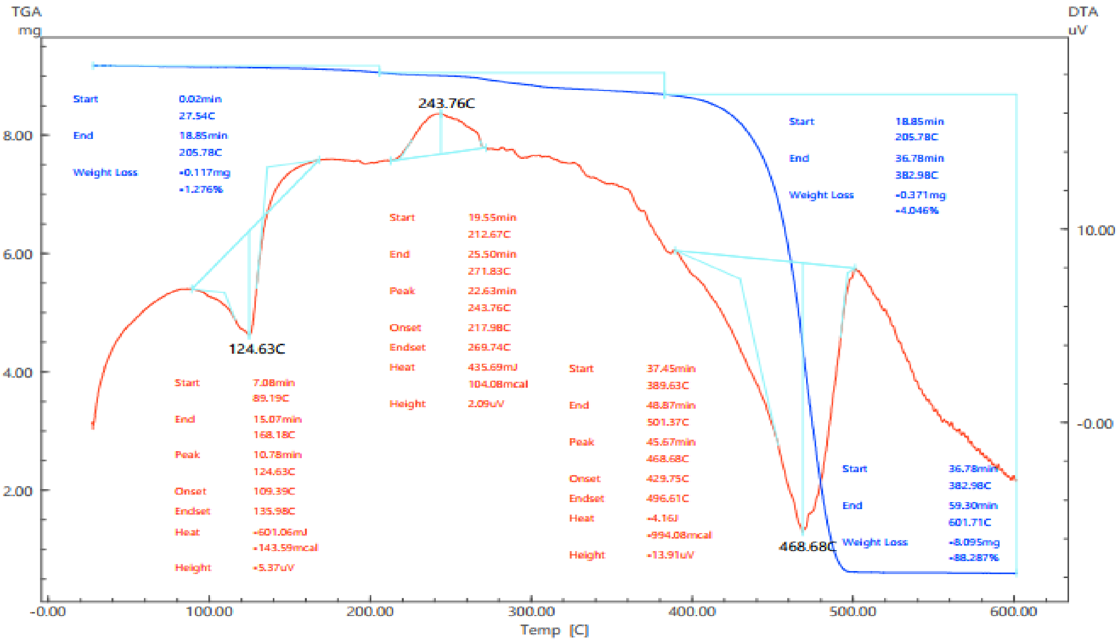

Fig. 2 Thermogravimetric (TGA) and differential thermal (DTA) analysis of NH4Co(PO3)3 complex

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The analysis of the thermogravimetric curve of the synthesized complex shows that the TGA curve mainly takes place in the temperature range of 2 mass losses. The 1st mass loss range is 18.85 – 205.78 °C, the 2nd range is 59.30 - 601.71 °C, the 1st mass loss is 0.117 mg, i.e. 1.276% of water vapor and CO2 gas escape, the main amount of mass loss 2 was 8,035 mg, that is, 88.287% mass reduction due to the destruction of the compound was observed. At the same time, an endothermic effect was observed at 124.630C and 468.68 0C in the DTA graph.

2. Results and Discussion

The resulting new compounds were processed as fillers for polymers. A 3% PP blend was produced in an extruder in the form of 0.25 mm granules. The tests were carried out on a universal tensile testing machine (SHIMADZU SORL 34472) with shovel-shaped specimens measuring 50x6x4 mm according to GOST 14236-81 at a deformation rate of 50 mm/min.

During the research on the physical and mechanical properties of PP filled with new polyphosphates, the following table shows that the number of elasticity, impact resistance, mechanical deformation, and heat resistance have increased.

Table-1.

Physico-mechanical properties of PP filled with modified metal polyphosphates

Indicators	Standards	PP	PP+ 3% $NH_4Co(PO_3)_3$
Modulus of elasticity in bending is MPa	ISO 178	1100	1380
Elongation %	ISO 527-2	100	100
Tensile strength, MPa	ASTM D638	24	25
According to Izod	ISO 180/1A	6,5	6,8
Shock tolerance,	ISO 180/1A	3	3,2
Forging tolerance on izod kDj/m2,+23°C	ISO 75-2	45	48
According to Izod	ASTM D955	1,2	1,05
Shock tolerance,	The thickness of the sample is 1.6 mm	45	≤50

In the analysis of the above results we can see that the introduction of metal phosphates increased the physico-mechanical properties of polymers, in particular the

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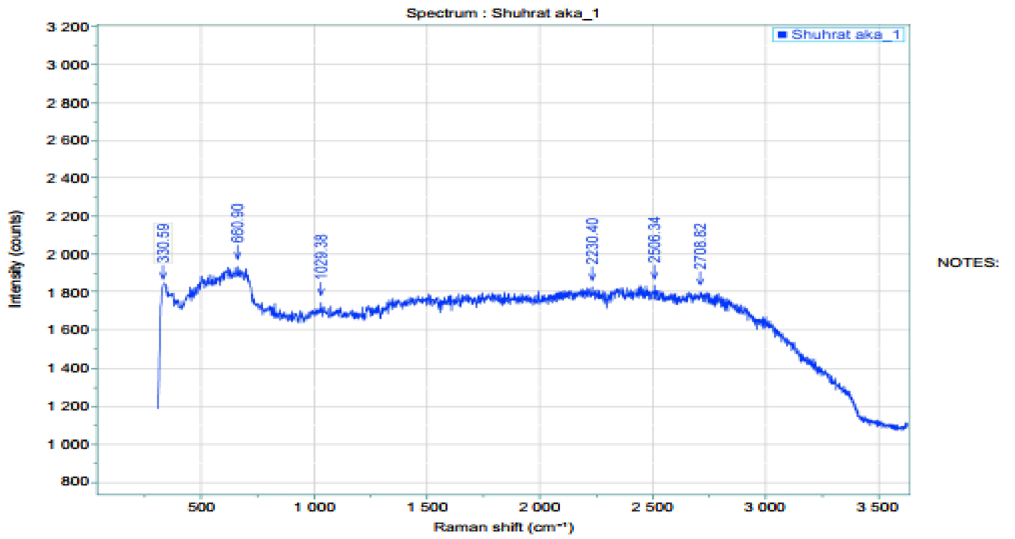
modulus of elasticity from 1100 MPa to 1380 MPa, bending temperature under load 45-50 oC and tensile strength from 24 MPa to 25 MPa [6,7].

3.1. Raman spectrometer analysis. A Raman spectroscopy study was conducted to determine the binding of synthesized ammonium polyphosphate compounds with polymer molecules, the movement of molecules in the process of modification, and the vibration modes of molecules in solid bodies.

This research was carried out in the Raman spectrometer in the laboratory of Termiz State University, and the results can be seen in Figure 3 below.



Date	16.12.2023 1...	Acq. time (s)	1	Accumulations	1	Laser (nm)	785
Spectro (cm-¹)		Hole		Slit		Grating	685
ND Filter		Objective		ICS correction	Off	Range (cm-¹)	

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16.12.2023 15:36 3/3

Fig. 3 Raman spectroscopy of PP/NH4Co(PO3)3

According to the analysis of the Roman spectrum, the molecule of the vibrational modes with strong sharp peaks of the spectra: C H of bending (1029.38 cm−1) or the presence of metals in C H (660 cm−1) and (330.59 cm−1) of external bending, polymer molecules of synthesized polyphosphate ammonium compounds with metal binders indicates that it is connected.[7].

3.2. X-ray diffraction analyses. Compositions of synthesized additives with polymers were analyzed based on X-ray diffraction. Diffraction patterns were recorded on an XRD-6100 X-ray diffractometer (Shimadzu, Japan) with computer control. CuKa radiation (β-filter, Ni 1.54178; current mode and tube voltage 30 mA and 40 kV, respectively) and constant detector rotation speed (step 0.02 deg.), 4 deg/min (ω/2nd

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scheme) and scanning angle from 4 to 80 oC. Scan Range: 5.0000-70.0000 (deg) Scan Mode: Continuous Scan Speed: 2.0000 (deg/min) Sampling Interval: 0.0500 (deg) Settling Time: 1.50 (sec). X-ray diffraction patterns of the studied composites were obtained by RFA. (Figure 4)

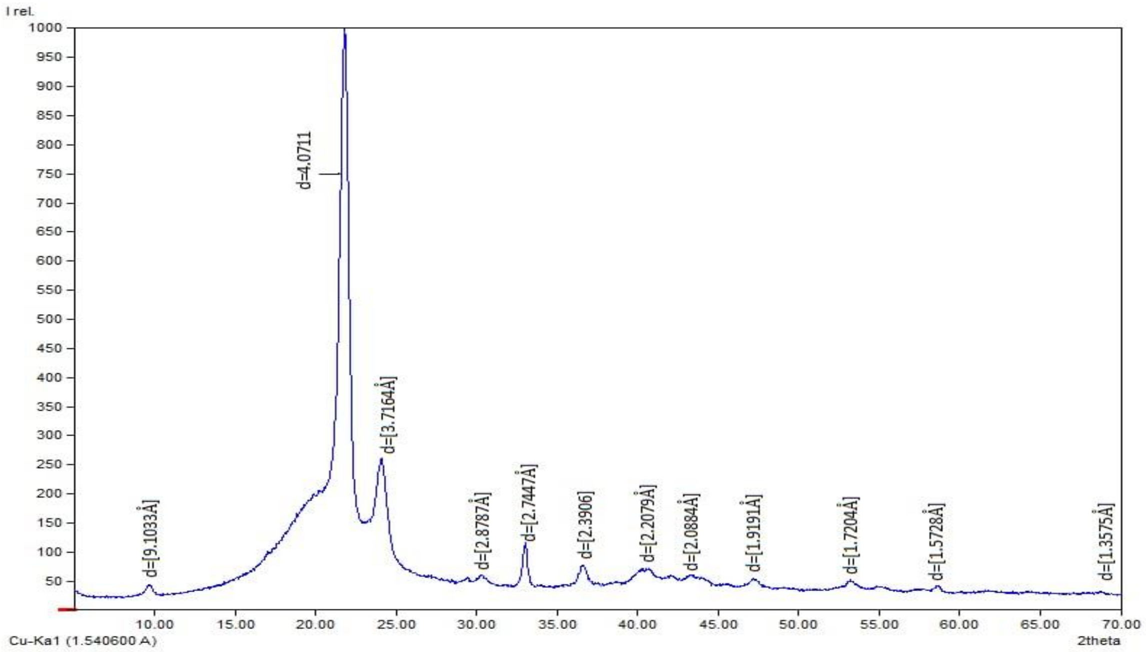

Figure 4- a) Appearance of PP + 3% NH4Co(PO3)3 in X-ray phase spectra

When studying the diffraction spectra of composites that differ according to the type of filler, the greater the interlayer distance of the fillers added externally to the polypropylene-based composite, the higher the degree of delamination of the layered additive[8].

As shown, the stratification of the layered additive depends on the time of mixing the components and the viscosity of the liquid of the mixture. In the table, we can see the result of the PE diffraction pattern under the crystalline or amorphous structure of the polymer material obtained in the X-ray analyzer. It allows you to measure the size, shape, and internal structure of the material.[9,10].

Table -2.

Results of the diffraction pattern of polypropylene filled with modified metal polyphosphates

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T/r	2theta- scanning angle	d- Interplanar distance	I-Peak Intensity	FWHM- integral width of reflexes
1	9,87	9,1033	335,07	0,4500
2	21,80	4,0711	341,86	0,7000
3	24,08	3,7164	994,76	0,9500
4	30,33	2,8787	597,84	0,7000
5	33,02	2,7447	853,71	0,3000

According to the results of X-ray spatial analysis, it was found that the size of particles in all composite materials is in the nanoscale.

The development of modern nanotechnologies in the field of polymer materials always requires in-depth knowledge of the internal structure of micro- and nano-sized materials and their physical properties.

Although there are several ways to solve these problems, a new technique - the scanning atomic force microscope - helps to achieve greater precision. By effectively using traditional methods, we can achieve excellent results. One effective way to solve these problems is atomic force microscopy.

Analysis Samples of the "Mifil" brand ultrafiltration membrane at the Institute of Polymer Physics were scanned with a SmartSPM-1000 atomic force microscope.

Figure 5 shows the polypropylene surface filled with ammonium Co polyphosphate (3D view). As can be seen

from the above results, the surface roughness of pure polypropylene is 100 nm, and the roughness of the polypropylene filled with +3% cobalt polyphosphate is 49.6 nm. From the 2D image, we can see that there is also a 1.16 nm

spherical metal (cobalt) particle and small spherical particles.

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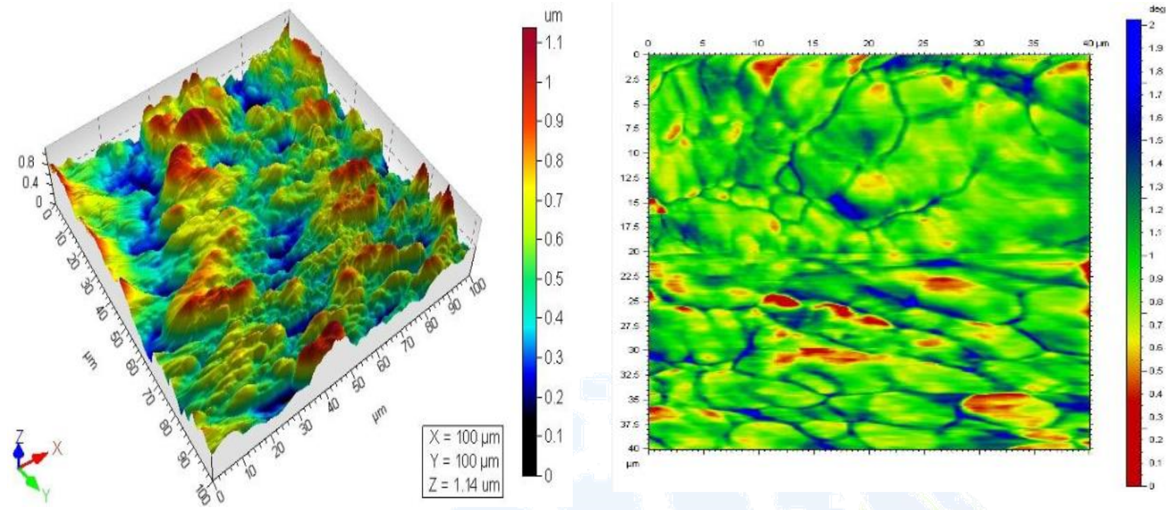

A) B)

Figure 5. ACM image of polypropylene surface filled with modified polyphosphate compounds: A) - three-dimensional image B) - two-dimensional image.

B) S)

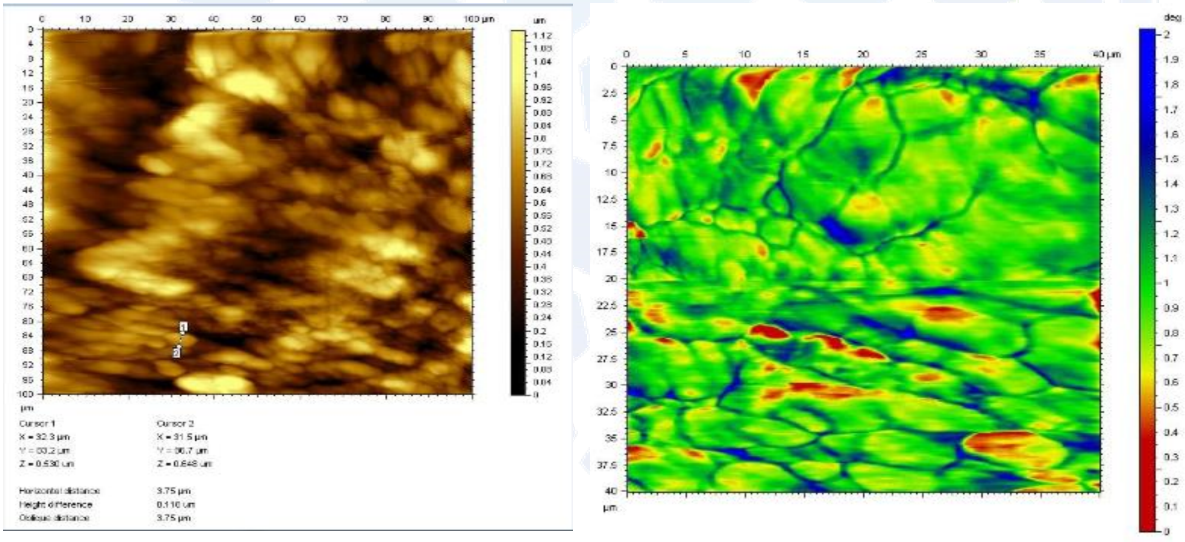

Fig. 6. AKM image of the surface of polypropylene filled with Co polyphosphate: A) - volume image (3D view) B) - phase S) - two-dimensional view (topography)

Thus, it can be said that the modification of the polymer surface with metal particles leads to an increase in the roughness of its surface. As shown in Figure A, the change of phase movement indicates the presence of two phases on the surface of the

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polymer and the work in the polymer composite material where the polymer macromolecules form a mechanical mixture with the metal particles [11,12].

In order to study the fire resistance properties of composite materials filled with new metal-containing polyphosphate compounds, the oxygen indicator parameters of the polymer were studied using test experiments.

In the course of practical experiments, it was proved that the average value of the oxygen index of polymer composite materials filled with metal polyphosphates is equal to 41. In particular, as a result of the inclusion of filler metal polyphosphates in the composition of polymers, the burning time decreased from 239 0C to 124 0C, and the oxygen index increased from 19 to 24%, respectively, compared to the original PP. (Table 3).[13,14].

Table -3.

Effect of composite materials filled with modified metal polyphosphates on heat resistance and flammability

Composite composition	Burning time, s	Mass loss during combustion in air, %	Oxygen index, %	Initial destruction temperature, °C	Coke residue at 600 °C, %	Heat resistance according to Vica, °C
PP	239	50	19	294	17	130
PP+ 3% MeF	124	27	24	302	34	135

As a result of filling polymers with metal-containing polyphosphates, their burning time slows down by two times compared to the original polymer, and mass loss during combustion in air is relatively reduced. A positive change in flammability indicators when metal phosphates are included in the composition of all polymers confirms that the resulting composite materials are difficult to burn.

The addition of a metal-bound ammonium polyphosphate compound to the polymer increases the thermal stability of the composite and shifts the decomposition onset

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temperature to a higher temperature range. As can be seen from the table below, reinforcement of PP with metal polyphosphates leads to an increase in the temperature of the onset of crystallization and the temperature of the onset of liquefaction of composites.[15,16]

4. Conclusion

Ammonium polyphosphate in the high temperature range, we can see that the introduction of metal phosphates increased the physico-mechanical properties of polymers, in particular, the modulus of elasticity from 1100 MPa to 1380 MPa, bending temperature of 45-50 oC under load and tensile strength. 24 MPa to 25 MPa.

In particular, as a result of the inclusion of filler metal polyphosphates in the composition of polymers, the burning time decreased from 239 0C to 124 0C, and the oxygen index increased from 19 to 24%.

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Conflicts of Interest

Conflicts of Interest: None.

- We hereby confirm that all the Figures and Tables in the manuscript are ours.

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