

Ultralow Melting Ammonium Polyphosphate Compounds

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Abstract—When low molecular weight ammonium polyphosphate interacts with polyethylene polyamine, thermoplastic polymers containing fractions with glass transition temperatures $T_{\text{glass}} \geq -95^\circ\text{C}$ are obtained. Their thermal and heat resistance, as well as moisture resistance, is measured at a humidity of 40–50%. The structure and chemical scheme for the formation of interaction products are proposed.

Keywords: ammonium polyphosphate, polyethylene–polyamine, thermoplastic polymers, low-temperature polyphosphates, glass transition temperature

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INTRODUCTION

Ammonium polyphosphates have a linear or weakly branched structure and belong to a wide class of phosphoric acid polymers, including metallic phosphates, widely used as high-temperature materials and serving as the base for phosphate ceramics [1–5].

Such polymers are nonflammable, lack harmful thermal degradation products, and are of interest not only in terms of use as binder composite materials but also as a thermoplastic component of mixtures with organic polymers [6–9].

The production of products of the interaction of ammonium polyphosphate with phosphoric acid, which have negative glass transition temperatures [10], stimulated the search for new compositions for the synthesis of low-melting hybrid polymers based on inorganic and organic oligomers. Such products could promote the dissolution of ammonium polyphosphate, as a fire retardant, in the organic polymer matrix, and could be used as polyphosphate plasticizers, as rigid-chain polymers.

The products of the interaction of ammonium polyphosphate oligomers with the degree of polymerization $n = 2–10$ (APP) and polyethylene polyamine with $n = 2–6$ (PEPA), containing nitrogen atoms capable of strong donor-acceptor interactions, served as the objects of research.

than 30%) (Roskhim, Russia). Thermal treatment of the samples was carried out by raising the temperature at a rate of $10^\circ\text{C}/\text{min}$ in a heating cabinet with internal ventilation and subsequent holding at the given temperature for 1 h. Thermomechanical analysis was carried out on a Netzsch-TMA 402/2/G device (Netzsch, Germany) at a load of 500 mN. A Netzsch-DSK Jupiter STA 449 F3 (Netzsch, Germany) was used for the thermogravimetric analysis. The rate of the change in temperature in both cases was $10^\circ\text{C}/\text{min}$. Thermal effects at low temperatures were determined using a DSC produced by Mettler (Switzerland) at a heating rate of $10^\circ\text{C}/\text{min}$ and the mass of the sample was 10–20 mg; disposable aluminum oxide cups with a volume of 40 μL were used in the measurements. The moisture absorption of the samples was determined at $T = 20^\circ\text{C}$ for 30 days at air humidity of 40–50%. The chemical composition of the products of the thermal destruction was determined using a SETSYS Evolution (SETARAM) thermobalance. Mass spectrometric analysis was performed using an OmniStar device (Pfeiffer) when the sample was heated at a rate of $10^\circ\text{C}/\text{min}$ in the range from 30 to 700°C in a flow of a 5% O_2 –He (20 mL/min) mixture. Spectral analysis was carried out using a Carry 50 Varian spectrophotometer. For mechanical testing, a tensile testing machine LRX plus produced by Lloyd Instruments (United Kingdom) was used.

EXPERIMENTAL

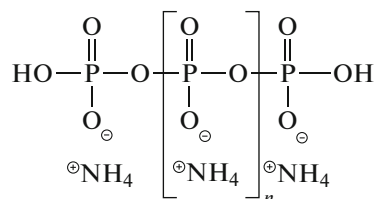
The starting compounds used were low molecular weight ammonium polyphosphate MACROPAK APP 3, polyethylenepolyamine (nitrogen content not less

RESULTS AND DISCUSSION

The choice of the objects of study was determined by the spatial structure of ammonium polyphosphate (degree of crystallinity 78%, $T_{\text{melt}} = 177^\circ\text{C}$) as a linear

oligomer with terminal hydroxyl groups, whose modification did not require breaking the intermolecular chemical bonds. Another component of the composition was polyethylene polyamine—a mixture of

short-chain imines with the number of monomer units $n = 2-6$ and terminal amino groups. Both components are soluble in water and form homogeneous solutions.



A thermal analysis of the starting compounds was carried out, which determined the temperature range at which there are no thermal transformations of the components of the mixtures, $T \leq 110^\circ\text{C}$, and the observed changes can only be explained by their interaction. It has been shown that at higher temperatures endothermic processes with significantly different temperature maximums are observed (Fig. 1).

The mass spectrometric analysis of the products of the destruction of APP in the temperature range up to 110°C showed they were practically absent, while at higher temperatures the main gaseous products were water and ammonia (Fig. 2). This suggests that the first endothermic peak is related to the condensation of hydroxyl groups, and the following one with the formation of side OH groups with the release of ammonia.

The reaction products of APP and PEPA were obtained by mixing aqueous solutions at a weight ratio of APP/PEPA = 1/0.1–1.4 followed by heat treatment. It was noted that during mixing, the release of ammonia gas was observed, which did not occur when APP was mixed separately with the amine and with water.

The interaction products of APP and PEPA obtained at $T = 106^\circ\text{C}$, in the absence of thermal transformations of the components, were resinous heterogeneous mixtures, and when $T = 150^\circ\text{C}$, when the chemical activity of ammonium polyphosphate was observed, solid samples were obtained that were transparent in visible light.

The presence of chemically active hydroxyl groups of APP, whose interaction with each other was determined by the thermomechanical analysis of APP

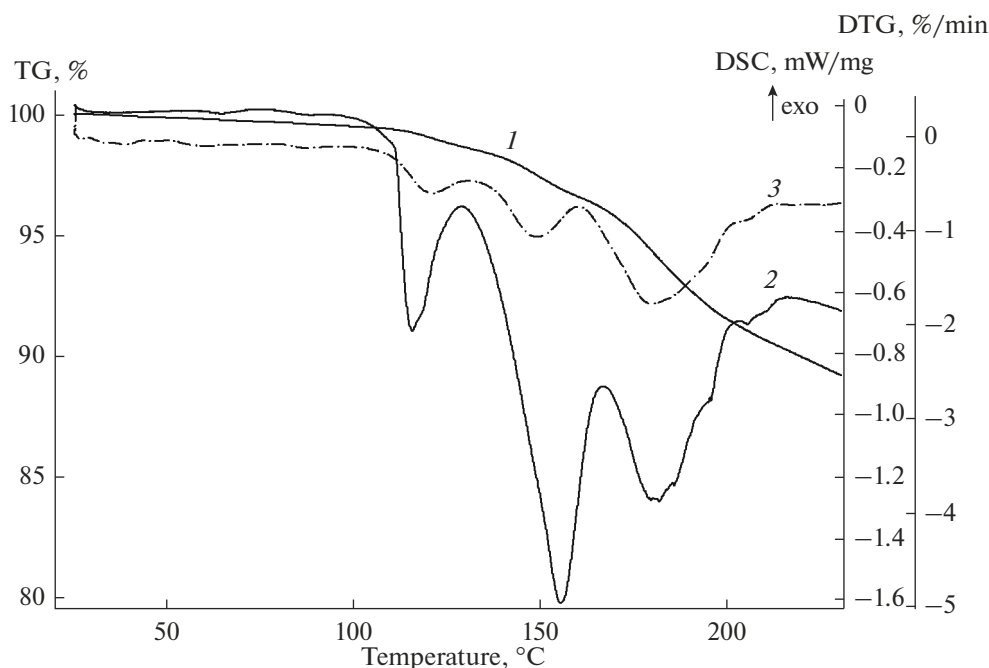


Fig. 1. Mass loss (1) and thermal effects (2) when heating ammonium polyphosphate (the dotted line represents the derivative of mass loss).

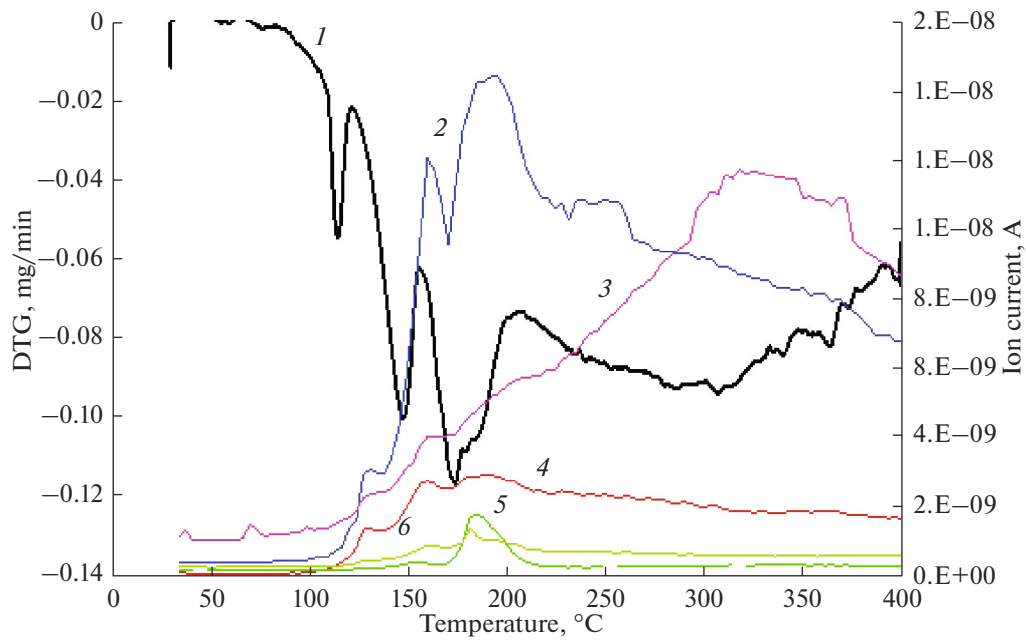


Fig. 2. Differential curve of APP mass loss (I) and current intensity at ion mass values corresponding to NH_3 (2), N_2O (3), NO (4), CO_2 (5), CO (6).

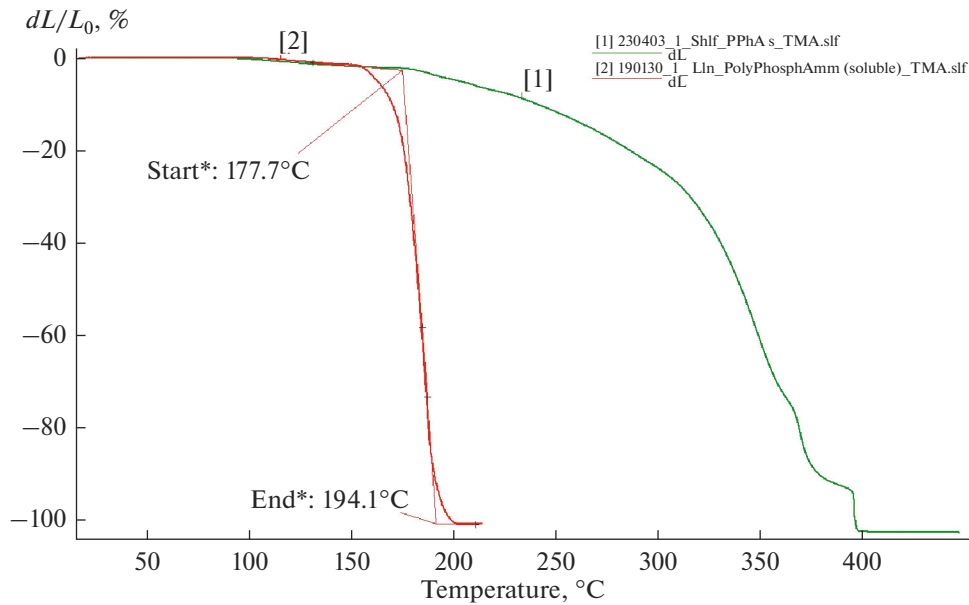


Fig. 3. Thermomechanical curves obtained before and after heat treatment of APP at 150°C , 1 h.

treated at 150°C for 1 h. A significant increase in the softening temperature (T_s) and melt flow temperature (T_{flow}), as well as in the values $T_s - T_{\text{flow}}$, correlated to the width of the molecular weight distribution of the polymer, was found (Fig. 3).

Based on the presence of hydroxyl groups in APP, it was assumed that when $T = 106^\circ\text{C}$, complexation of hydroxyl and amino groups should be observed, and

when $T = 150^\circ\text{C}$ polycondensation of the APP oligomer should take place.

The spectrophotometric measurements of the absorption of aqueous solutions of APP and APP/PEPA in the visible light region showed a shift of the absorption maximum to the long wavelength region by 21.8 nm (Fig. 4, Table 1), explained by the formation of complexes of phosphate and amino

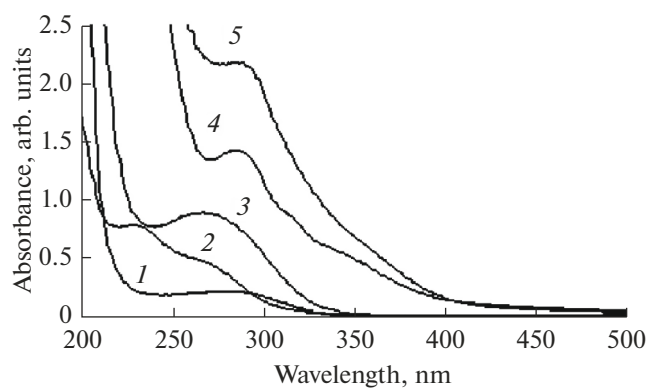


Fig. 4. Absorption spectra of aqueous solutions of APP, PEPA, phosphoric acid and their mixtures. PEPA (1), phosphoric acid (2), APP (3), phosphoric acid/PEPA (4), APP/PEPA (5).

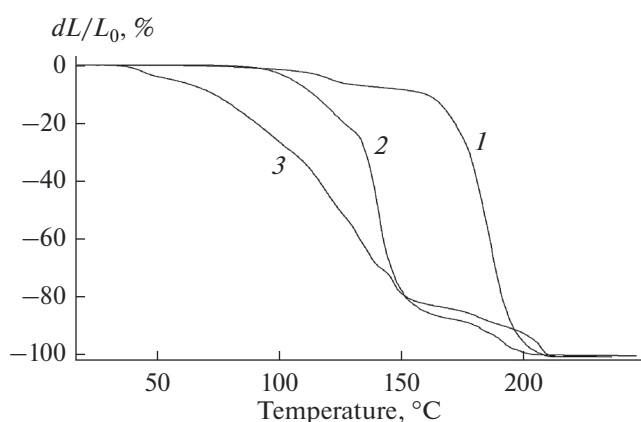


Fig. 5. Thermomechanical properties of APP (1) and reaction products of APP/PEPA mixtures = 1/0.1 wt (2) and APP/PEPA = 1/0.2 wt (3) (150°C, 1 h).

Table 1. Spectrophotometric data of aqueous solutions

Compound	Maximum absorption wavelength, nm
APP	267.0
PEPA	281.9
Phosphorus acid	228.9
APP/PEPA	288.8
Phosphorus acid/PEPA	285.0

Table 2. Glass transition temperatures of APP/PEPA compositions = 1/0.2 wt

Synthesis temperature, °C	Glass transition temperature, °C
106	-95
150	-15

groups, whose interaction energy can reach 13.6–26.1 kcal/mol for various amines [11].

In order to confirm the nature of the formed complexes, the absorption maximums of APP/PEPA and phosphoric acid/PEPA solutions were compared, which showed that their values practically coincided, which can be considered as the same nature of the formed complexes.

The influence of the PEPA concentration on the properties of the interaction products was studied by considering the dependence of the thermomechanical properties obtained at 150°C, under conditions where both processes are observed: complexation and polycondensation.

It has been shown that as the PEPA content increases the softening temperature (T_s) of the resulting products shifts to the region of low temperatures (Fig. 5).

In addition, fractions with low glass transition temperatures were found in the obtained samples (Figs. 6a, 6b), whose values are determined by the synthesis temperature (Table 2).

It should be noted that the formation of complexes inhibits the polycondensation process, which was previously noted for the example of compositions of boric acid with *n*-phenylenediamine [12] and imidazole [13].

The synthesis conditions affect not only the glass transition temperature of the amorphous phase but also the softening and fluidity temperature of the high-temperature fraction (Fig. 7).

The observed T_{glass} amorphous phase of the interaction products during mild heat treatment, in conditions where there are no chemical transformations of the components, is the smallest, while T_s and T_{flow} of the samples obtained at higher temperatures grow.

The increase in T_s and T_{flow} is a consequence of the interaction of phosphate groups with each other, both terminal and side groups, formed during the release of ammonia when the aqueous solutions of the components are mixed. The molar ratio of APP/PEPA at a content of 20 wt % is 1/1.

Using the example of the composition APP/PEPA = 1/0.3 wt % (150°C, 1 h), it is shown that during the synthesis the structure of phosphate changes, which follows from the disappearance of one of the endothermic peaks, probably related to the formation of hydroxyl groups. In this case, the total heat of the endothermic reaction drops from -408.0 J/g for APP to -139.3 J/g for the reaction product of the APP/PEPA mixture = 1/0.3 wt (150°C, 1 h) (Fig. 8).

Mechanical tensile tests were carried out on samples of the APP/PEPA composition = 1/0.3 (120°C, 1 h) ($T_s = 62.5^\circ\text{C}$) at a stretching speed of 1 and 10 mm/min (Fig. 9, Table 3).

The possibility of the practical use of the obtained compounds makes it necessary to determine the products of their thermal destruction. The analysis showed

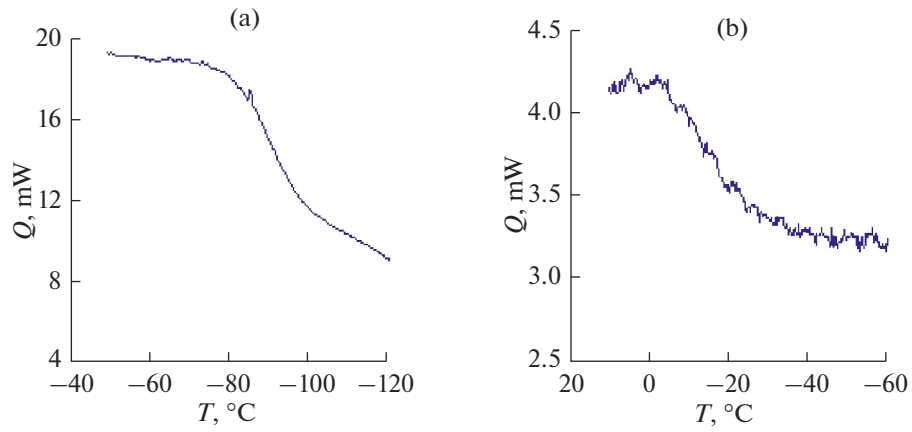


Fig. 6. DSC—curves of low-temperature fractions of interaction products of APP/PEPA compositions = 1/0.2 wt (106°C, 1 h) (a) and APP/PEPA = 1/0.2 wt (150°C, 1 h) (b).

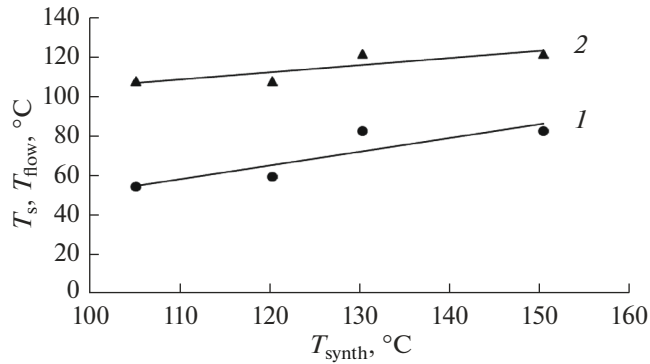


Fig. 7. Temperature dependence T_s (1) and T_{flow} (2) compositions APP/PEPA = 1/0.3 wt.

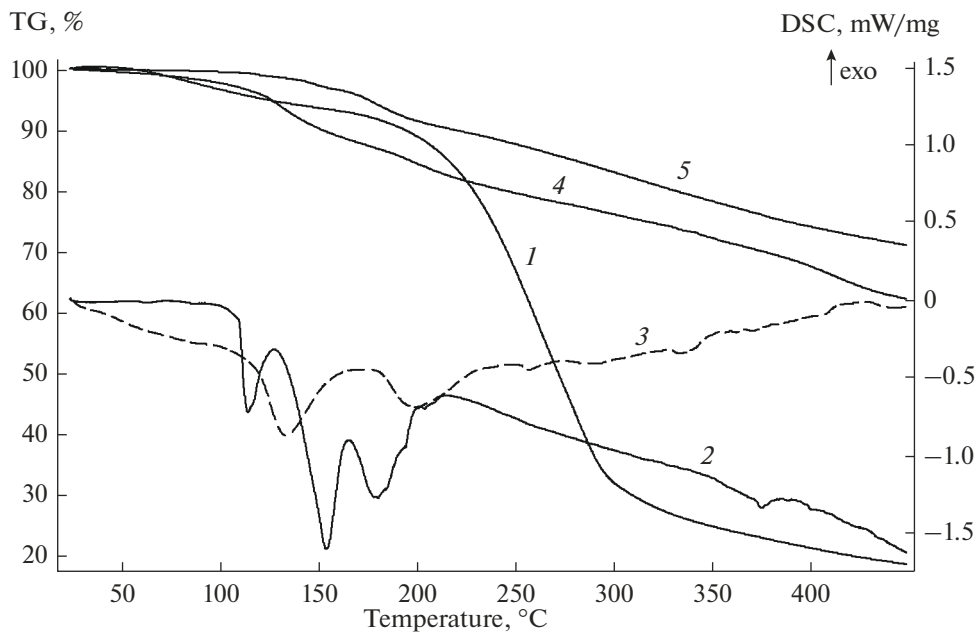


Fig. 8. Weight loss of APP, PEPA, and APP/PEPA mixture. DSC PEPA (1), DSC APP (2), DSC APP/PEPA = 1/0.3 wt (150°C, 1 h) (3), APP/PEPA = 1/0.3 wt (150°C, 1 h) (4), APP (5).

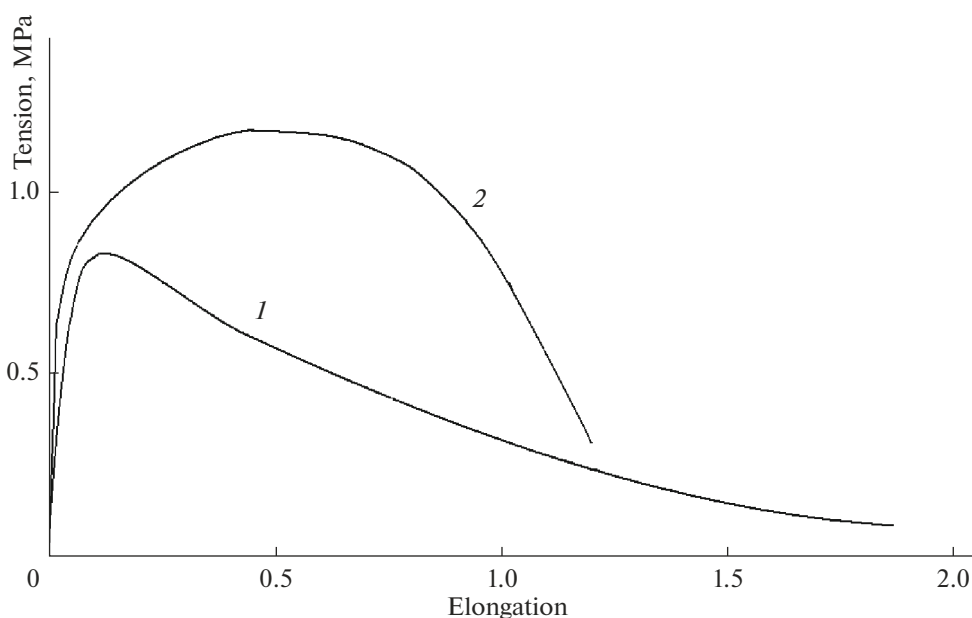


Fig. 9. Tensile diagram of composition APP/0.3 wt PEPA (120°C, 1 h) at different deformation rates, (1) 1, (2) 10 mm/min.

Table 3. Elastic characteristics when stretching the composition APP/PEPA = 1/0.3 wt (120°C, 1 h)

Deformation rate, mm/min	Maximum stress, MPa	Modulus of elasticity, MPa	Relative elongation at maximum stress, %
1	0.8	30	12
10	1.2	100	50

that the main compounds released at $T < 500^{\circ}\text{C}$ are ammonia and water. In the products of the destruction products, CO, CO₂, and NO, whose total content is less than 3 wt %, are also observed.

CONCLUSIONS

Based on the data obtained, we can conclude that when ammonium polyphosphate interacts with polyethylene polyamine, the formation of thermoplastic polycomplexes with a branched structure with low glass transition and softening temperatures is observed.

The chemical scheme of the observed transformations can be explained by several processes [14, 15]: the formation of $-\text{P}-\text{OH}$ groups of APP with the release of ammonia upon interaction with water and thermal exposure, polycondensation of APP in phosphate groups accompanied by an increase in the molecular weight of polymers, the formation of APP/PEPA polycomplexes, and the depolymerization of APP in the presence of protons of water molecules [16, 17].

The expected structure of the resulting compounds consists of weakly branched polycomplexes of ammo-

nium polyphosphate and polyethylene polyamine of various molecular weights.

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CONFLICT OF INTEREST

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

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