



Biodegradable boron-containing poly(lactic acid) for fertilizers with prolonged action

N.B. Svishcheva^{a,*}, S.A. Uspenskii^{a,b}, N.G. Sedush^a, P.A. Khaptakhanova^a, A.I. Kasatova^c, A.I. Buzin^a, P.V. Dmitryakov^{a,d}, M.S. Piskarev^a, A.I. Aleksandrov^a, S.Y. Taskaev^c

^a Enkolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 70, Profsoyuznaya Street, 117393 Moscow, Russia

^b R&D Center "Suisselle", CEI3, rue Galilée 6, 1400 Yverdon-les-Bains, Switzerland

^c Budker Institute of Nuclear Physics, Siberian Branch of Russian Academy of Sciences, 11 Lavrentieva, 630090 Novosibirsk, Russia

^d National Research Centre "Kurchatov Institute", 1 Akad. Kurchatova pl., Moscow 123182, Russia

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ABSTRACT

A new strategy for obtaining long-acting fertilizers in the process of joint polycondensation of lactic and boric acids is presented. The article shows the effect of boric acid or boric anhydride additives in an amount of 0.1–1% wt. on the synthesis and final properties of poly(lactic acid). With increase in the amount of boric acid or boric anhydride in poly(lactic acid), polymers show higher T_g and T_m at approximately equal molecular weights compared to poly(lactic acid) without additives. Comprehensive studies of the structure of the obtained compositions were carried out: theoretical calculations using method DFT (Becke-Lee-Yang-Parr) and experimental - proton NMR, IR spectroscopy and melt rheometry. It has been suggested that the addition of boric acid when heated promotes the formation of B-O-C bonds and the branching of lactic acid oligomer chains. The compositions and the dynamic of boric acid release by granules obtained from boron-containing poly(lactic acid) melts were studied using elemental analysis for aqueous systems. During 7 days of testing in aqueous medium, the granules lose from 16% to 72% of boric acid. This study can serve as further development of the use of low-molecular-weight poly(lactic acid) with different molecular weights in the design of long-acting fertilizers.

1. Introduction

Plants need boron for the formation of strong stems and rapid growth. Soil solution should contain boron for plants to use it [1]. The availability of boron for plants is affected by alkalinity, insufficient organic substances content in the soil, soil adsorption capacity, quantity and types of minerals in the soil, content of soil water and leaching. Therefore, boron deficiency is found all over the world in regions with frequent precipitation and alkaline soils. Boron can be introduced into soil in the form of sodium tetraborate (borax), colemanite, ulexite, kernite, datolite, hydroboracite, howlite, boron-containing frit, boron phosphate. Seem not very effective, plants absorbing only dissolved boric acid (BA) from the soil. At the same time, excessive use of boron containing granules can have the opposite effect: many plant species are sensitive to both deficiency and excess of boron in soil and water [2].

The use of slow-release nutrient mixtures can protect seedlings from overabundance of boron, and a fruiting plant from the lack of element in a later period. Recent studies describe slowly-released fertilizers based

on boric acid and its oligomers. For example, in paper [3] the authors propose to use borated cellulose fiber as fertilizer; in [4] carboxymethylcellulose and polyacrylamide hydrogels with the addition of calcium montmorillonite clay swelling in boric acid solutions are considered. Studies are known where boric acid is used as a modifying agent within of a complex fertilizer. For instance, in paper [5] a slow-release urea-based fertilizer was prepared using starch and polyvinyl alcohol crosslinked by boric acid. A few mixtures of polymers containing boric acid and its oligomers have also been studied: with polyethylene [6,7], polypropylene [8], polydimethylsiloxane [9]. The above mentioned polymers have long decomposition periods, their use as fertilizer components can create an additional burden on the environment – "plastic pollution".

Among the approaches to the creation of slow-release fertilizers [10, 11], the methods where biopolymers are used as a biodegradable carrier-substance have received the greatest development. Biodegradable polymers can release substances in a specified period of time and decompose themselves to form environmentally friendly products. The

* Corresponding author.

E-mail address: svishcheva_nb@ispm.ru (N.B. Svishcheva).

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use of such a technique is quite widespread: long-term release of both nutrients and herbicides, pest repellents and pesticides for full growing season is possible. Biodegradable polymers can serve both a shells of granules of nutrient mixtures and the carcass of mixed fertilizer.

Poly(lactide) can be a promising polymer in this direction. Currently, prolonged fertilizers with poly(lactide) (PL) and poly(lactic acid) (PLA) are being studied in the form of (i) "mixed fertilizer" of polymer composites filled with fertilizer [12–14] and (ii) fertilizer granules coated with polymer [15–17]. The fertilizer can be added to monomer, after which the composite is synthesized, or mixed with the finished polymer. In our work, boric acid (0.1–1%wt. BA)/boric anhydride (0.1–1%wt. BAA) are added to the monomer - lactic acid. Then the polycondensation reaction is carried out and PLA is synthesized. It is assumed that the resulting polymer with boron can be used as a granule shell or a mixed fertilizer framework in the production of complex macro fertilizers. During the vegetative period plants require a small amount of boron (~0.28–2.6 kg/ha [18–21]) and a large amount of macro fertilizers, for example, nitrogen and phosphorus (~50–180 kg/ha and ~48–90 kg/ha [22–25]). Therefore, a small amount of boron compounds present in the polymer is related to the fact that plants need only 0.3–4 mg/l of boron as fertilizer, while 5 mg/l of boron are already toxic [2,26].

The purpose of this work is to study the effect of boric acid and boric anhydride additives on the synthesis and final properties of PLA (thermophysical, molecular-mass characteristics, rheological properties of melts of boron-containing composites) which are essential for understanding the process of forming boron-containing PLA granules; to evaluate the general profile of boric acid release by granules in aqueous systems.

2. Experiment

2.1. Materials

Analytically pure 88–92 % L-lactic acid, 99–100.5 % boric acid (PanReac AppliChem, Spain) and 98% boric anhydride (Sigma-Aldrich, USA) were used in the studies. All the other agents were analytical reagents.

2.2. Composite preparation

2.2.1. Synthesis of PLA and samples with boric acid and boric anhydride

Poly(lactic acid) was obtained by polycondensation of 15 g LA with a rotary vacuum evaporator in a thin layer at a temperature of 160–180 °C and a vacuum of 8–5 mbar for 13 h, PLA-BA and PLA-BAA composites were obtained by mixing LA, respectively, with pre-dried BA and BAA in a rotary vacuum evaporator flask and subsequent polycondensation according under the same conditions. The amount of BA and BAA in various composites was 0.1–3%wt.

2.2.2. A mixture of PLA and BA for comparison

A mixture of BA and PLA was prepared as a comparative material. To obtain it, 0.5 g of PLA and 0.5 g of BA were mixed in a mortar. The resulting mixture is designated as mix-PLABA.

2.2.3. Making of plates (granules) hydrolysis

The amount of boric acid in various composites wpc 0,32; 0,48; 0,64; 1; 1,5; 2% and 3% wt. of lactic acid. The composites were crushed, 0.2 g. portions were placed in 8 * 8 mm molds and melted at 150–155 °C for 5–10 min in the drying chamber without oxygen access. Then, the polymers were crystallized for 3 hot 120 °C and square plate (8 * 8 * 3 mm) were obtained. The plates were weighed and placed in ampoules with 10 ml phosphate buffer solution (pH = 7 ± 0.2); ampoules were

sealed and left at 8 °C in a dark place for time periods varying from 5 h to seven days. To increase the reliability of the experimental results, five parallel experiments were carried out. After that, the buffer solution was trained and an inductively coupled plasma atomic emission spectroscopy (ICP AES) analysis of the drain water was performed. When plotting the graph, average values were used. The fraction of the released boric acid was calculated by the ratio "y/x * 100%" where "x" is the initial content of boric acid in the plate, "y" is the amount of boric acid released into the aqueous medium during "t" (12–168 h.).

2.3. Characterization

The IR-spectra of the samples were taken on Bio-Rad (Digilab) FTS-40 spectrometer with attenuated total reflectance a device at the resolution of 4 cm⁻¹. Registration and processing of spectra was carried out using the Win-IR software package version 4 (Bio-Rad, Digilab Division). Samples for analysis were prepared in the form of finely ground powder.

The molecular weight (MW) and polydispersity (PDI) were determined using a highly efficient analytical chromatographic device with an automatic dispenser and fraction collector (Shimadzu, Japan) with a Phenogel - 15 kD column and a flow rate of 1 ml/min (40 °C, the columns are calibrated to polystyrene standards).

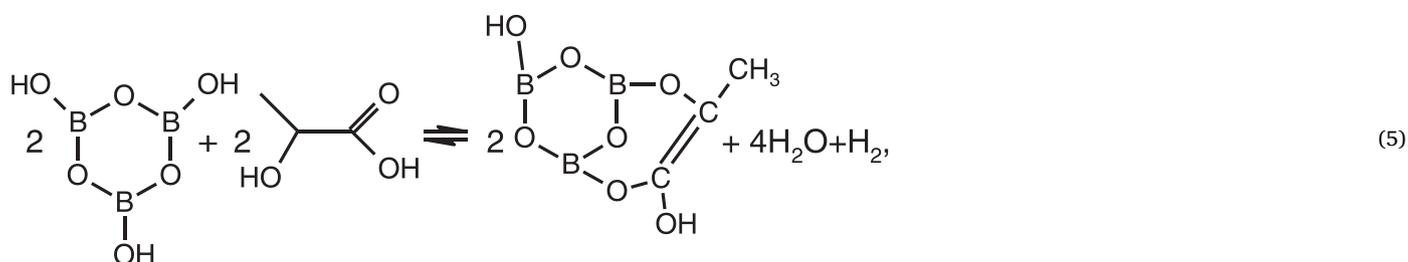
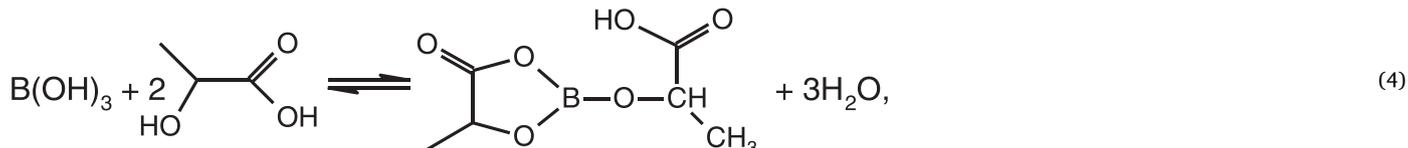
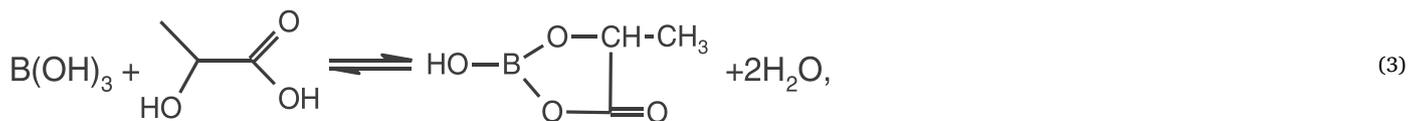
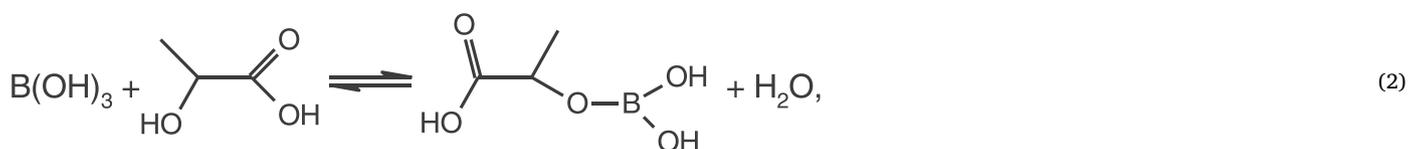
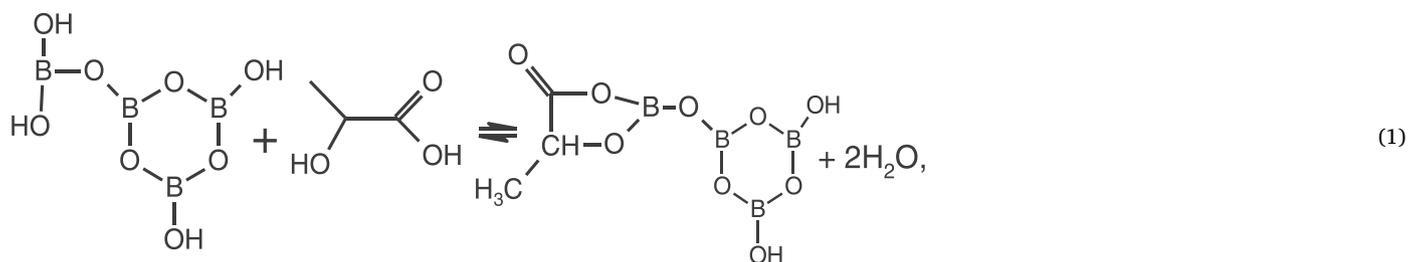
The actual proportion of boric acid and boric anhydride in the obtained compounds was determined using ICP AES on the "Shimadzu ICPE 9820" [27]. The distribution of boron in the polymer mass was considered earlier [28].

Thermal stability of PLABA/PLABAA composites was determined using the thermal analyzer Mettler TG50 at a heating rate of 10 °C/min in a nitrogen atmosphere (200 ml/min) from room temperature to 500 °C. The thermophysical properties were studied using the differential scanning calorimeter (DSC) PerkinElmer DSC7 when heated at a rate of 20 °C/min in a nitrogen environment (20 ml/min). The samples were heated above the melting point to remove the thermal background and cooled at a rate of 20 °C/min. In this paper the results of the second heating are presented.

Rheological measurements were carried out on the rheometer MCR-92 (Anton Paar) using RheoCompass software. Viscosity curves were obtained in the rotational mode on a plane-plane system (diameter 50 mm and a gap of 1 mm) in a range of shear rates of 0.01–1000 s⁻¹. Before each rheological test, the temperature of the lower plate was reduced to room temperature, then the material to be tested was applied to the lower plate. The material was melted at 150 °C, kept for 5 min to remove the thermal background of the sample. After that rheological measurements were carried out at 148 °C. The isothermal test (oscillating mode) was carried out at the same temperature and gap. Shear rates, shear strain were kept constant by 10 rad/s (1.6 s⁻¹) and 10 % respectively.

3. Results and discussion

A forms esters and complexes with a wide range of mono-, di- and polyhydroxyl compounds (some properties of BA are indicated in the appendix, paragraph 1). These borate esters are formed and dissociate spontaneously in dynamic pH-dependent equilibrium with fast kinetics. PLA also contains a hydroxyl group. While BA is introduced into the reaction mixture, various compounds of boric and lactic acids can be formed. The reaction between oligomers is possible under these conditions for the hydroxyl groups of lactic acid, the presence of a cation being required through the formation of chelate complexes with the participation of a carboxyl group [29]. Thus, the following reactions can occur in a mixture of BA + LA (depending on the concentration of these reagents in water or in melt):



Quantum chemical calculations of some compounds of boric and lactic acids using the method DFT (Becke-Lee-Yang-Parr (B3LYP)) with the LanL2DZ basis [30–32] in the GAUSSIAN 98 W program [33] were carried out. Optimal structures of compounds were obtained (Fig. 1) and the energies for the molecules were determined: $E(\text{BH}_3\text{O}_3) = -252.469$ a.e.; $E(\text{H}_2\text{O}) = -76.413$ a.e.; $E(\text{H}_2) = -1.174$ a.e.; $E(\text{C}_3\text{H}_6\text{O}_3) = -343.56$ a.e.; $E(\text{B}_3\text{O}_3(\text{OH})_3) = E(\text{B}_3\text{H}_3\text{O}_6) = -528.104$ a.e.; $E(\text{B}_4\text{O}_4(\text{OH})_4) = -704.164$ a.e.; $E(\text{B}_3\text{C}_3\text{H}_5\text{O}_7) = -718.712$ a.e.; $E(\text{B}_4\text{C}_3\text{H}_6\text{O}_9) = -894.863$ a.e.; $E(\text{BC}_3\text{H}_7\text{O}_5) = -519.606$ a.e.; $E(\text{BC}_3\text{H}_5\text{O}_4) = -443.167$ a.e.; $E(\text{BC}_6\text{H}_9\text{O}_6) = -710.308$ a.e. Based on the data on the total energies of these molecules (1 a.e.=27.21 eV, 1 eV = 23.06 kcal/mol), the enthalpy calculations of reactions (1) – (5) were carried out. With the introduction of BA or BAA, modification of

some part of the growing PLA chain may occur. The calculation of the enthalpy of reactions (1) – (5) showed that during the interaction of boric acid and lactic acid, both heat absorption and release can occur. Therefore, the resulting compounds can cause branching, as well as destruction (from local overheating in the reaction mass). Consequently, if the reaction of BA with LA is possible, then both linear and cyclic products are formed. In addition, BA may not react with LA, but act as a crystallization center or a catalyst [34] or a water-removing agent. However, it is not known how long boric esters of lactic acid can exist in the reaction medium or in the final product of the reaction and how resistant these esters are to the influence of external factors.

Suppose that acids form two types of compounds among themselves: unstable, which break down when water or oxygen enters the system,

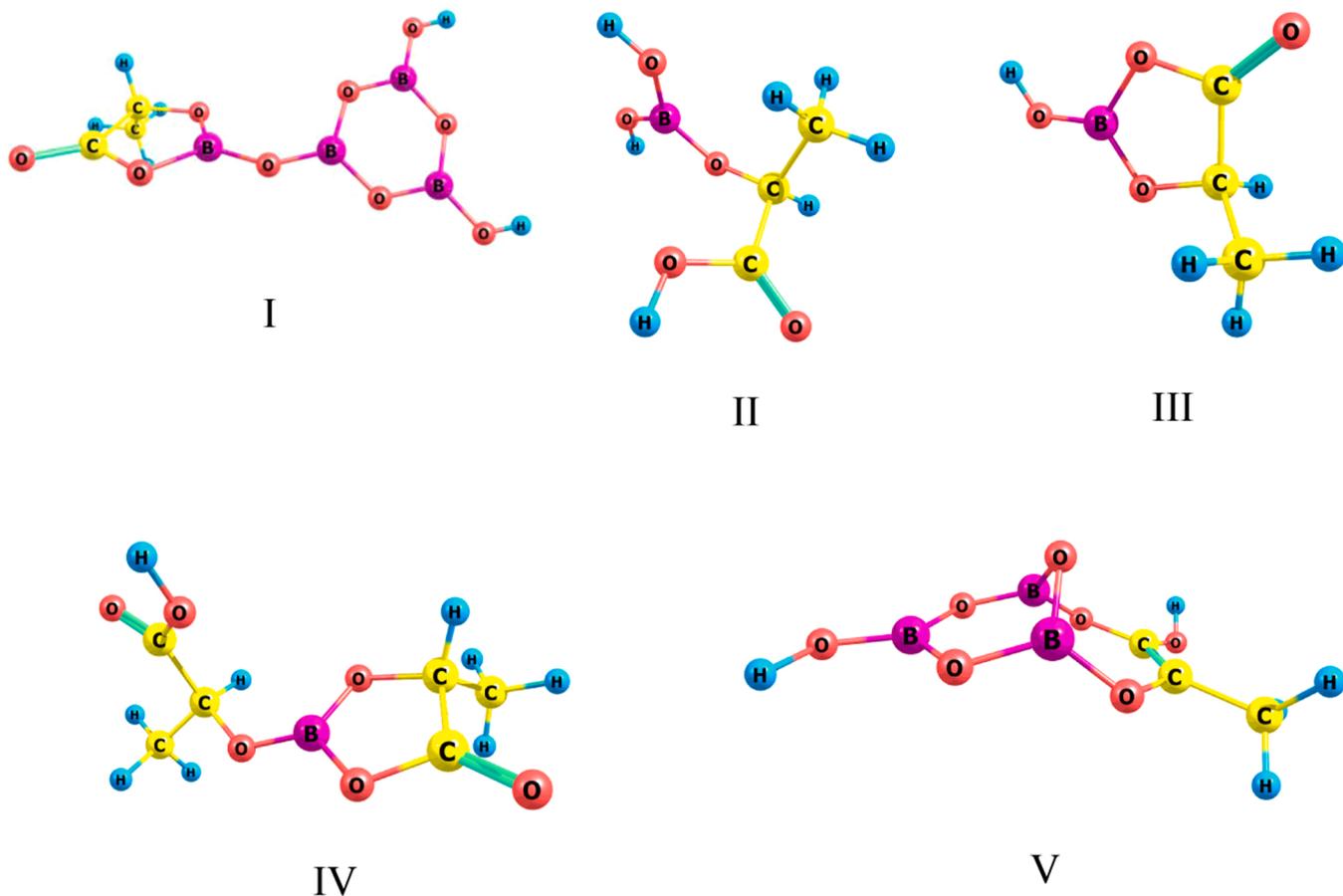


Fig. 1. Theoretically existing compounds of boric and lactic acids.

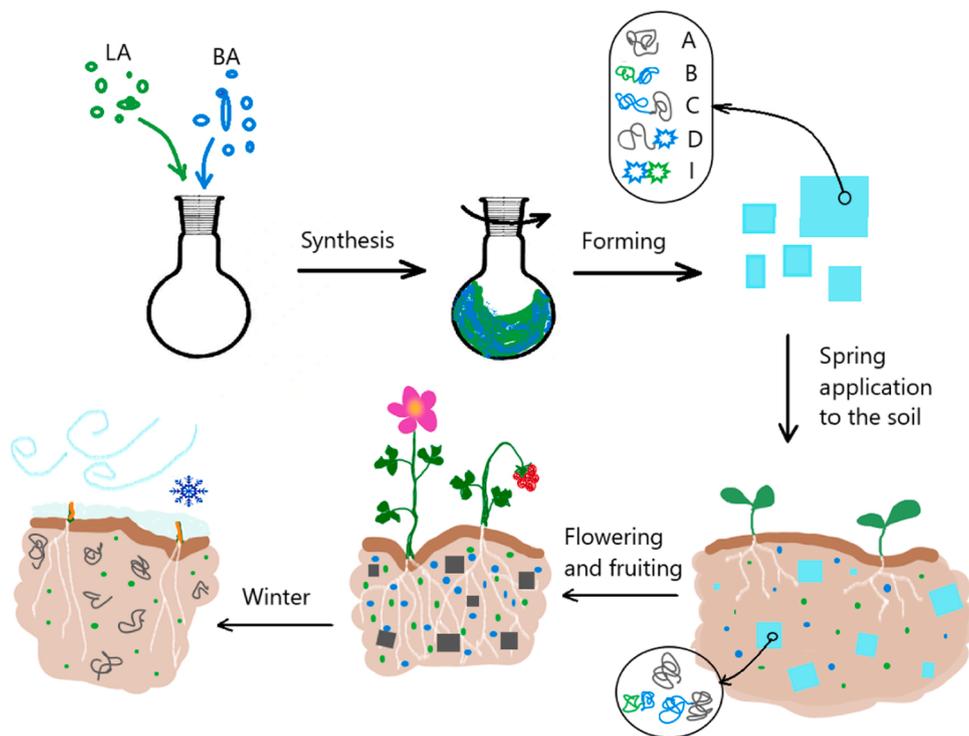


Fig. 2. The action scheme of prolonged action fertilizer.

and relatively stable, which break down in a humid environment for a long time. The scheme of obtaining fertilizers from boron-containing PLA and their application will look like as in Fig. 2. Lactic acid together with boric acid are loaded into a flask, PLA synthesis is carried out and granules are formed. The granules may contain PLA's molecules (Fig. 2, A), stable esters of lactic and boric acids (Fig. 2, B), stable crosslinked or branched PLA (Fig. 2, C), unstable crosslinked or branched PLA (Fig. 2, D), unstable esters of lactic and boric acids (Fig. 2, E), monomers. During the spring use of fertilizers the granules release LA and BA which come from the remnants of monomers and unstable compounds that gradually collapsed. During the flowering period and until the end of fruiting, all remaining polymer chains are destroyed, except for cross-linked and high molecular weight chains. The latter lose molecular weight during this period. This ensures the gradual release of both BA and LA. With the onset of winter, only the LA and the remnants of PLA chains (useful for plants [35]) remain in the soil.

To test the assumption of the existence of BA-LA bonds in the product, the IR spectra of PLA, PLABA1 and a mixture containing 50 % PLA and 50 % BA were obtained. FTIR spectra are shown in Fig. 3. All spectra have characteristic bands of PLA: at 3000, 2950 cm^{-1} attributed to asymmetric and symmetrical valence vibrations of CH_3 ; 1747 cm^{-1} due to the $\text{C}=\text{O}$ stretching band; 1453, 1383 attributed to asymmetric and symmetrical deformation vibrations of CH_3 ; 1359 cm^{-1} deformation

plane vibrations of CH + deformation symmetric vibrations CH_3 ; 1266 cm^{-1} deformation vibrations CH + valence vibrations $\text{C}-\text{O}-\text{C}$; 1183 cm^{-1} valence asymmetric vibrations $\text{C}-\text{O}-\text{C}$ + planar pendulum asymmetric vibrations CH_3 ; 1128 cm^{-1} planar pendulum asymmetric vibrations CH_3 ; 1083 cm^{-1} valence symmetric vibrations $\text{C}-\text{O}-\text{C}$; 1043 cm^{-1} valence vibrations $\text{C}-\text{CH}_3$; 870 valence vibrations $\text{C}-\text{COO}$; 755 cm^{-1} deformation vibrations $\text{C}=\text{O}$; 694 skeletal oscillations $\text{C}=\text{O}$. The following bands correspond to BA: 548 cm^{-1} deformation plane oscillations $\text{O}-\text{B}-\text{O}$; 643 cm^{-1} $\gamma([\text{BO}_3]-\text{O}) + \gamma(\text{O}-\text{H})$, out-of-plane OH deformation mode + $\delta(\text{B}-\text{O})$; 798 cm^{-1} deformation out-of-plane vibrations $-\text{B}-\text{O}$ + torsional deformation vibration $\text{O}-\text{H}$; 2520 cm^{-1} valence vibrations of internal water; 3200 cm^{-1} valence vibrations of water adsorbed on the BA surface [36–38]. The spectrum of the mixture demonstrates the presence of characteristic bands of boric acid. On the PLABA1 spectrum, the bands correspond to PLA bands. That is, according to the above spectra, the addition of boric acid does not affect the chemical structure of poly(lactic acid). Perhaps the amount of boric acid in PLABA1 is not enough for this type of analysis.

As known, BA is volatile, and BAA turns into BA in the presence of water. This means that the absence of BA/BAA in the products of LA polycondensation is possible. Therefore, with the help of ICP AES, the boron content was determined in all the samples studied. The BA/BAA content in the samples is less than BA/BAA were added to the reaction mass. This can be explained by the entrainment of boric acid (or its esters) with water vapor during the reaction. Also, MW and PDI were determined with the help of a highly efficient analytical chromatographic device with an automatic dispenser and fraction collector. Data on labeling, MW, PDI, boron's content in the samples under study is presented in Table 1. The presence of boron was confirmed in all analyzed samples. PDI is wide, which is typical for polycondensation reactions. In addition, we calculated the MW of the samples using ^1H NMR. The spectra were similar to the spectrum of pure PLA (see supplementary, point 2). The absence of the boron-related proton signals can be caused by a very low content of boron in the samples.

The presence of boric compounds can affect the thermal behavior of PLA. We have performed thermogravimetric (TG) and calorimetric analyses of all samples; the curves are shown in Figs. 4, 5. For defining the effect of the amount of BA and BAA on the thermal stability of the PLA we determined the temperature of 5 % weight loss of the samples and the mass of the residues at 500 °C. Other important thermal characteristics are glass transition temperature (T_g) and melting point (T_m). The values of the temperatures of a beginning of destruction, T_g , T_m , are given in Table 2. With the addition of boric acid/anhydride, the temperature of 5 % weight loss increases, with the exception of PLABA1. However, the more boric additives are introduced, the faster the polymer loses mass with increasing temperature (Fig. 4).

As we can see, the melting point is approximately the same for PLA and samples with low content of boric acid/anhydride (Fig. 5, Table 2). The melting point increases with the addition of 1% wt. BA or BAA. Also, when boric compounds are introduced, the T_g of the studied samples increases. The glass transition temperature depends on many factors. The presence of a residual amount of solvents, monomers, plasticizers

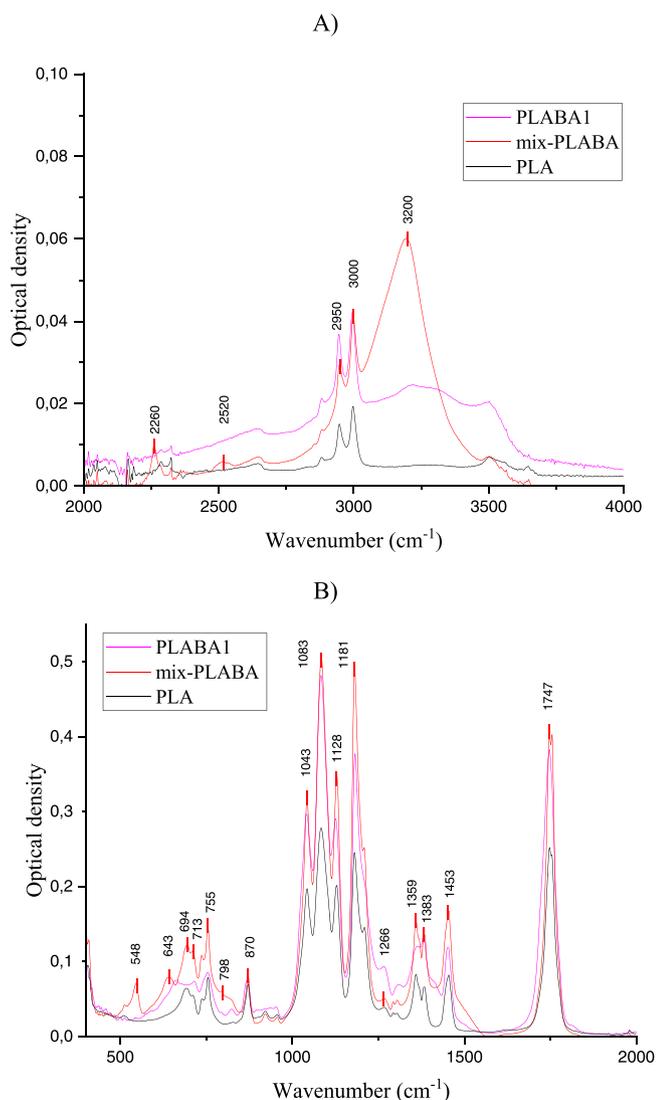


Fig. 3. IR spectra of mix- PLABA (red), PLABA1(purple), PLA(black) in the range A) 2000–4000 cm^{-1} ; B) 400–2000 cm^{-1} .

Table 1
Normalization of samples.

Designation	Added BA/BAA, % wt.	Molecular weight M_n , Da	DPI	MW from proton NMR spectra, Da	Actual BA/BAA content, % wt.
PLA	0	2300	2.44	2000	–
PLABA0,1	0,1	1500	2.87	2000	0,06
PLABA0,5	0,5	2100	2.55	1700	0,67
PLABA1	1	2300	2.61	1800	0,93
PLABAA0,1	0,1	2100	2.54	1800	0,07
PLABAA0,5	0,5	2400	2.75	2000	0,28
PLABAA1	1	2500	2.66	1800	0,29

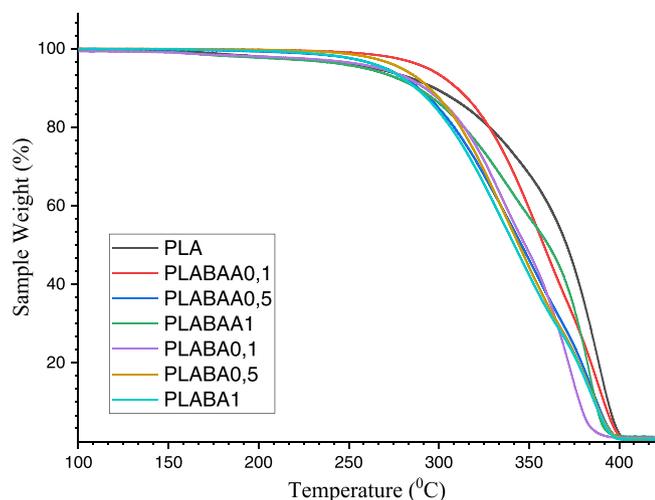


Fig. 4. TG curves of the studied samples.

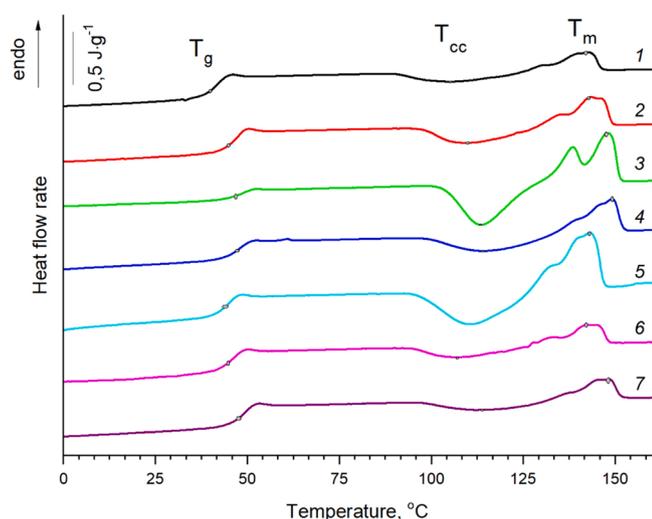


Fig. 5. DSC thermograms of the studied samples: PLA (1), PLABAA0,1 (2), PLABAA0,5(3), PLABAA1 (4), PLABA0,1 (5), PLABA0,5(6), PLABA1 (7).

reduces T_g . At the same time the limitations of polymer chain mobility associated with crosslinking or crystallinity increase T_g . In this work, the T_g increases, while the IR spectra do not confirm the formation of BA-LA bonds. It can be assumed that crosslinking or branching of the polymer doesn't occur, or the number of crosslinking/branching nodes is small.

The reason for the change in the thermal characteristics of the modified polylactic acid can be established using rheometry, because the melt flow of linear, branched and crosslinked polymers are different. As shown in Fig. 6, PLA's melts and modified samples exhibit viscoelastic behavior. At low shear rate with an increase in the amount of additives, the viscosity of polymers also increases, whereas at high shear rate polymers with 0.5–1% additives have the lowest viscosity. The molecular weights of samples with boric compounds are less than with poly

(lactic acid) and increase with the addition of boric compounds. However, the viscosity of boron-containing samples is greater than the viscosity of pure poly(lactic acid). A drastic increase in the viscosity of the composite melt indirectly supports that PLA chains start branching due to the presence of boric oxides. The entanglement as a result of branching may explain the increase in melt viscosities when an additive is introduced.

Additionally, an isothermal oscillating test was carried out ($T=148\text{ °C}$, the test time is 10 min, shear rates is constant - 10 rad/s (1.6 s^{-1}), shear strain is constant - 10 %). The viscosities in Figs. 6 and 7 are different. This is due to the fact that the samples passed the isothermal test after other rheology tests (after more than 5 h of measurement of complex viscosity not given in the article). One of the difficulties in measuring the viscoelastic behavior of PLA is the low thermostability of the polymer, which results in degradation during rheological measurement in the melt [39]. Despite these difficulties, it was found that the complex viscosity of the samples gradually increases in time, except for the viscosity of PLA, PLABA0.1 (Fig. 7). May branching can occur during the melting of polymers, but it not known if it exists room temperature. The authors of the work [40] observed a similar rheological picture, studying the steady shear rheological behavior of pure PLA and a series of intercalated PLA/organically modified layered silicate nanocomposites. Shear viscosity of the layered silicate nanocomposites at a fixed shear rate it increases monotonically with increasing modified fillers content [39–41]. In the case of layered silicate nanocomposites, the nanocomposites exhibited strong rheopecty behavior shear-induced structural change involved a process with an extremely long relaxation time. In the case of boric compounds and poly(lactic acid) exhibited also rheopecty behavior. Specific type of interaction between boric compounds and poly(lactic acid) will be studied by us in future.

The main direction of application of PLA-BA polycondensates is the compensation of boric insufficiency in soil. For this reason, an important characteristic is the behavior of PLA-BA in humid environment. To study it, plates of approximately the same mass were mold from the melts in to the same shapes and under the same conditions, after that their mass loss in water was studied. In our article [28], we reported the gradual destruction of the plates over time when exposed to water, but the amount of boric acid released in this process was not established. In the present study, we conducted an ICP AES analysis of drain water after 12–168 h hydrolysis of the plates obtained by polycondensation of lactic acid with different amounts of boric acid (0,48; 0,64; 1; 1,5; 3 % from the weight of the reaction mass). It was found that the more boric acid is in the plate, the faster it releases the microfertilizer (Fig. 8). However, the release of boric acid occurs gradually and not simultaneously. ICP AES analysis of the plates "before" and "after" hydrolysis confirmed that boric acid is present in the plates after 168 h (Table 3). It can be seen that in plates with initially low content of boric acid the release of the micro fertilizer is slower. For example, before hydrolysis the plate contains 0.44 % wt. BA (0.48% wt. BA was added to the reaction mass), then after hydrolysis 0.33 % wt. BA. At the same time the plate with 1.54 % wt. BA (3 % wt. BA was added to the reaction mass) content 0.65 % wt. BA after hydrolysis. Consequently, in future it will be possible to regulate the rate of boric acid release from plant to plant by varying the concentration of boric acid in the polymer.

Table 2

Thermal characteristics of the samples.

	PLA	PLABA0,1	PLABA0,5	PLABA1	PLABAA0,1	PLABAA0,5	PLABAA1
Temperature of 5 % mass loss, °C	264	265	279	270	294	270	259
Residue at 500 °C, % wt.	0,42	0,73	0,36	0,34	0,26	0,31	1,04
Glass transition temperature T_g , °C	40	44	45	48	45	47	47
Cold crystallization T_{cc} , °C	105	110	107	114	110	113	114
Melting point T_m , °C	142	143	142	148	143	147	149
Enthalpy of melting ΔH_m , J/g	5,7	17,2	6,1	5,8	8,6	15,2	8,9

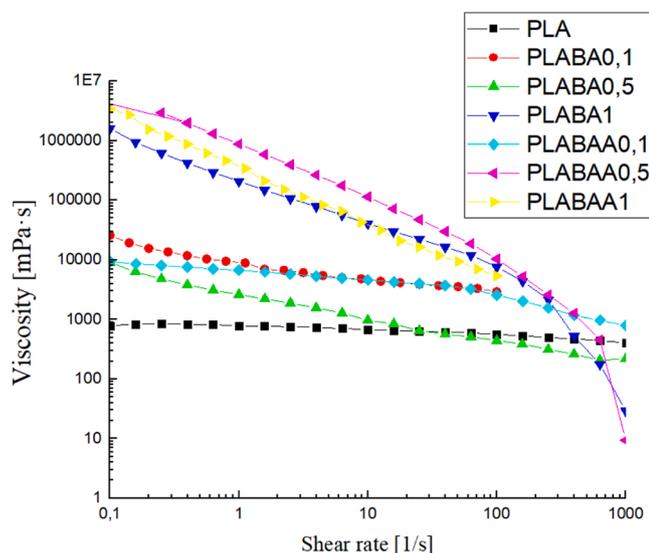


Fig. 6. Dependence of the dynamic viscosity of the studied samples on the rotation speed of the measuring system at 148 °C.

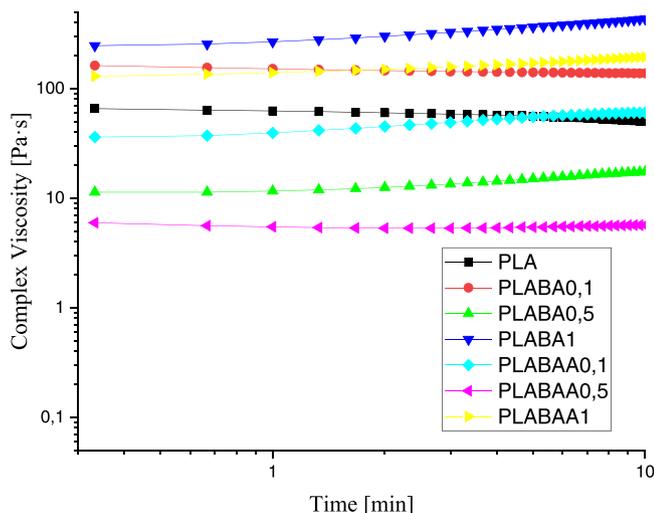


Fig. 7. Isothermal test (148 °C, shear rates 10 rad/s): change in viscosity of samples in time.

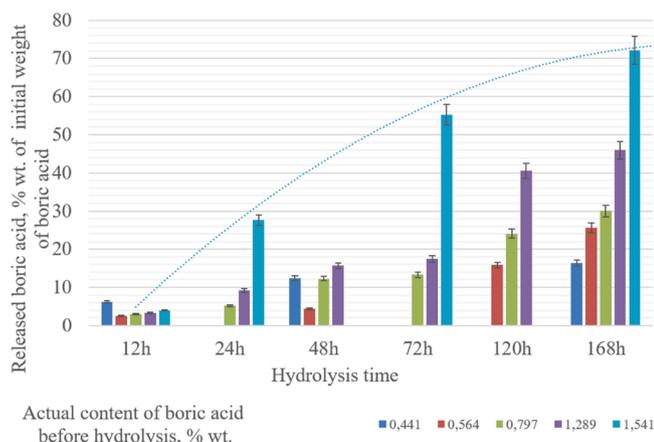


Fig. 8. Release of boric acid from plates into water over time.

Table 3

Boric acid content in plates of modified poly(lactic acid) according to ICP AES analysis.

Mass fraction of boric acid introduced into lactic acid before polycondensation, %	Actual amount of boric acid in the plate, % wt.	Amount of boric acid in the plate after 168 h hydrolysis, % wt.
0,48	0,44	0,33
0,64	0,56	0,46
1	0,8	0,57
1,5	1,29	0,54
3	1,54	0,65

4. Conclusions

The current study shows that an increase in the amount of BA and BAA affects the thermal and rheological characteristics of boron-containing PLA. It has been suggested that the addition of boric acid contributes to the branching of PLA chains. The time of existence of bonds between boron oxide and LA molecules in this case is not known: branched chains may not exist in the polycondensation product, arising only when heated, which will be the subject of our studies. It is assumed that the polymers synthesized from lactic acid with the addition of boric oxides will become the framework of mixtures fertilizers or shells of macro fertilizers of prolonged action. Such fertilizers will release both macro fertilizer and boric acid during the vegetation period. Therefore, we additionally studied the release of boric acid from granules (plates) molded from melts of modified polymers. It has been shown that boric acid is released into water in a controlled manner and not at the same time. Within 7 days, poly(lactic acid) containing 0.44–1.5 % wt. boric acid releases 16–72 % of the boric acid, respectively. On average, the release rate is 1.5–10 % of the boric acid present per day. Obviously, to increase the duration and decrease the rate of release of boric acid, it is necessary to use poly(lactic acid) of a higher molecular weight - presumably about 30 kDa. The production of PLA-BA composites as a result of the common polycondensation reaction of lactic and boric acids to will help to reduce the cost of fertilizer. Given the importance of these findings, we believe our strategy can serve further development of utilizing low molecular weight poly(lactic acid) in the creation of controlled-availability fertilizers, which will contribute to the establishment of next-generation smart fertilizer.

CRediT authorship contribution statement

Svishcheva N.B.: Methodology, Investigation, Formal analysis, Writing – original draft, Visualization. **Uspenskii S.A.:** Project administration, Conceptualization. **Sedush N.G.:** Supervision. **Khaptakhanova P.A.:** Critical review. **Kasatova A.I.:** Inductively coupled plasma atomic emission spectroscopy. **Buzin A.I.:** Differential scanning calorimetry. **Dmitryakov P.V.:** Thermogravimetric analysis. **Piskarev M.S.:** Rheological measurements. **Aleksandrov A.I.:** Quantum chemical calculations. **Taskaev S.Y.:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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