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Thermal characterization and sorption of Fe^{III} ion by ternary polylactide–poly-3-hydroxybutyrate–chitosan compositions

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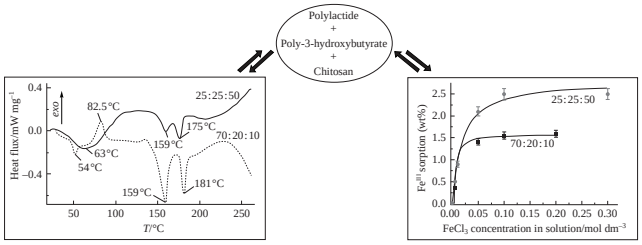
Thermal transitions have been determined for different ternary compositions of polylactide and poly-3-hydroxybutyrate with chitosan from their TGA and DSC data. The sorption capacity of the ternary mixtures for Fe^{III} ion has been evaluated using the Langmuir model and found to increase with the chitosan content.



Keywords: polylactide, poly-3-hydroxybutyrate, chitosan, iron, sorption, thermal properties, Langmuir equation.

Water pollution by heavy metal ions represents a serious ecological concern requiring both extensive preventive measures and significant costs.[1,2] Conventional methods of water treatment like precipitation or flocculation are of low efficiency and at present are substituted by membrane sorption technologies employing biodegradable polymeric compositions as innovative sorbents.[3] Therefore, there is a need for new selective sorbents with high productivity and a moderate cost.

Chitosan meets the above requirements being a selective, biocompatible and ecologically safe polysaccharide-type sorbent for use in industrial areas and biomedicine.[4] However, it has disadvantages resulting from swelling accompanied by deterioration of its mechanical properties.[5] In our works, the binary compositions of chitosan with reinforcing polyesters like polylactide (PLA) or poly-3-hydroxybutyrate (PHB) were proposed to improve the mechanical characteristics and adjust the hydrophilicity.[6,7]

The use of chitosan in the PLA–PHB compositions is advantageous for the following reasons. In spite of its natural origin, PLA is resistant to degradation and decomposes only in active media like compost or seawater, but it has relatively low cost, whereas fully biodegradable PHB is rather expensive. Thus, the presence of PHB allows one to enhance the degradability, while the presence of PLA decreases the cost of their mixture. The binary PLA–PHB compositions and their oil sorption properties were explored in our work.[8] The compositions of these two polymers with chitosan can represent a biodegradable material with promising mechanical parameters, high sorption capacity and potential application for removal of metal ions from wastewater.

In this work, we have characterized the ternary PLA–PHB–chitosan blends with an adjustable hydrophilicity as new eco-friendly sorbents for metal pollutants.† First, the thermal behavior of the triple systems was investigated‡ and then the sorption capacity evaluated for Fe^{III} as the most common metal species widespread in municipal and industrial wastewater.§

Figure 1 demonstrates the TGA and DSC curves for chitosan, PHB, PLA and their ternary compositions. The TGA data reveals that no weight loss occurs for the PHB and PLA homopolymers in the temperature range up to 200 °C, hence, these polymers can be considered thermostable. However, for chitosan a thermal transition at 50–75 °C accompanied by the weight loss of ~11% was recorded, the transition is clearly seen in the DSC curve as an endothermal maximum at 67 °C [Figure 1(*a*), curve *1′*]. The above transition originates from the destruction of hydrogen bonds, formed by water molecules and hydroxyl groups of the polymer, followed by water desorption from the sample. The DSC curves of PHB and PLA reveal several thermal transitions resulting solely from the changes in thermal capacity of the polymers. Easily crystallizing PHB demonstrates one endothermal melting peak at 177.0 °C and the specific enthalpy of melting ΔH_m = 99.2 J g^{-1}. The conversion of this value to degree of crystallinity by the standard formula $\alpha_c = \Delta H/\Delta H_0$ using the enthalpy of melting for a pure crystalline PHB ΔH_0 = 142 J g^{-1} affords a high crystallinity value for PHB equal to ~70%. For PLA, three thermal transitions are detected, which

† PLA (4043D, from NatureWorks, USA, mp 155 °C, transparency 2.1%, degree of crystallinity 37%), PHB (from Biomer, Germany, $M = 3 \times 10^5$ Da, mp 175 °C, degree of crystallinity 75%), chitosan (from Bioprogress, Russia, $M = 4.4 \times 10^5$ Da, degree of deacetylation 0.87), chloroform (from Chimmed, Russia, bp 61.15 °C, ρ = 1.489 g cm^{-3}) and $FeCl_3$ (from Fluka Chemie, Switzerland, mp 307.5 °C) were used. Films were obtained by evaporation from solutions of PLA and PHB in chloroform containing the chitosan powder.

‡ Thermophysical characteristics and thermal stability of the starting polymers and their blends were obtained by TGA and DSC using a DSC 204 F1 Phoenix calorimeter (Netzsch, Germany) at a heating rate of 10 °C min^{-1} with samples weight ~10 mg and the accuracy of measurements 0.1 °C.

§ The content of Fe^{III} ions sorbed on the polymer films from 0.05, 0.1 and 0.3 M $FeCl_3$ solutions was determined using an ARL PERFORM'X X-ray Fluorescence spectrometer (Thermo Fisher Scientific, USA).

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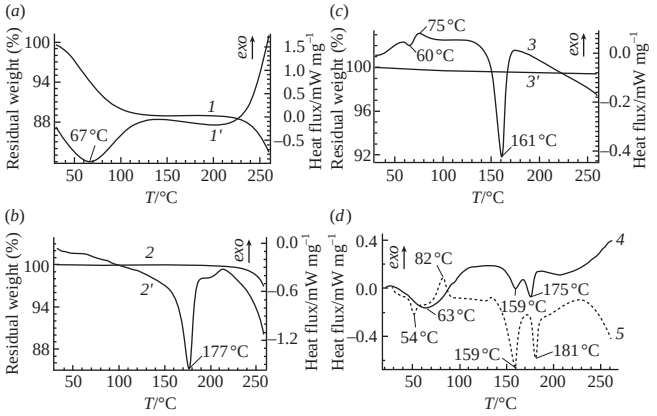

Figure 1 Thermal analysis data for the starting polymers and their blends: (*a*) the chitosan (*1*) TGA and (*1′*) DSC curves; (*b*) the PHB (*2*) TGA and (*2′*) DSC curves; (*c*) the PLA (*3*) TGA and (*3′*) DSC curves; (*d*) the DSC curves for ternary PLA–PHB–chitosan compositions of (*4*) 25 : 25 : 50 and (*5*) 70 : 20 : 10 weight ratios, respectively.

is typical of polyesters.[9] A peak at 60.0 °C is due to relaxation transition from a glassy to rubber-like state. It is customary to assign the subsequent exothermal maximum at 75.4 °C to the cold crystallization temperature T_{cc}. Note that the corresponding calculation of the crystallinity value using the enthalpy of melting for 100% crystalline PLA equal to 96 J g^{-1}, to account for the contribution of the cold crystallization, reveals $\alpha_c \sim 28\%$, which is lower than that for PHB.[6,10]

The thermal transition data for chitosan, PLA, PHB, the binary blends of PLA–chitosan, PHB–chitosan and PLA–PHB as well as the two ternary PLA–PHB–chitosan blends of different composition are collected in Table 1. On addition of chitosan to PHB, melting temperature of the latter is shifted from 177.0 °C to 168.0 °C. Moreover, a low-temperature peak of melting arises at 153.0 °C, which indicates a bimodal distribution of crystallites both by size and by the degree of structure perfection. A decline in the quality of the crystalline phase of PHB is accompanied by a sharp decrease in its degree of crystallinity from 70 to 22 wt%. Note that for PLA upon mixing with chitosan, the melting peak is shifted slightly, the enthalpy of melting (28.5 and 27.4 J g^{-1}, respectively) and, hence, crystallinity (~28%) are retained. The weight loss due to water desorption from chitosan remains significant with the higher value for PLA–chitosan compared with PHB–chitosan.

The thermal transitions presented in the DSC curve of a PLA–PHB–chitosan (70 : 20 : 10) ternary system having the maximum PLA content are of somewhat different character. Here, all the above mentioned transitions except the glass transition appear and are essentially shifted in temperature. Like for binary systems, a sharp drop in the crystallinity of both polyesters is observed upon mixing with chitosan. At the components ratio of 25 : 25 : 50, *i.e.*, in the excess of chitosan, actually no shift of the melting endotherm maxima is observed compared with the former ternary system, and these maxima are related to the ones of the PHB–chitosan binary blend described above (see Table 1). Therefore, in the melting region PHB with higher crystallinity conceals the corresponding thermal transition of PLA with lower crystallinity and thus prevents its appearance in the DSC curves.

Sorption of toxic metals like Cu^{II}, Pb^{II}, Cd^{II}, *etc.*, by chitosan is typically described using single-parameter models like the Langmuir or Freundlich ones due to the simple mathematical processing of adsorption equations and an unambiguous concept of the nature of sorption centers, including the hydroxyl groups of chitosan.[11,12] It is known that in neutral aqueous solutions polyvalent Fe^{III} ions are immobilized on chitosan *via* complexation with its functional groups.

Figure 2(*a*) demonstrates an equilibrium sorption of Fe^{III} ions by the PLA–PHB–chitosan ternary systems as determined using X-ray fluorescence. These isotherms represent ones of the Langmuir type:

$$C_{Fe} = C^0_{Fe} K_L C_{eq}/(1 + K_L C_{eq}), \quad (1)$$

where C_{Fe} is the amount of Fe^{III} ions adsorbed per unit weight of adsorbent at the equilibrium in mg g^{-1}, C_{eq} is the equilibrium concentration of the solute in mol dm^{-3}, C^0_{Fe} is the maximum adsorption capacity and K_L represents a Langmuir constant determined by the binding energy of functional groups of a polymeric adsorbent.

According to the model proposed, equation (1) can be brought to equation (2) suitable for graphic representation and calculation of the adsorption parameters C^0_{Fe} and K_L:

$$1/C_{Fe} = 1/C^0_{Fe} + 1/(C^0_{Fe} K_L C_{eq}). \quad (2)$$

Figure 2(*b*) demonstrates the Langmuir adsorption in the coordinates of equation (2). A good correlation between the adsorption model and the experimental results confirms the validity of the chosen model, with quadratic correlation coefficients R^2 being 0.9976 and 0.9285 for the linear regressions *1* and *2*, respectively. The calculation results are given in Table 2 to compare adsorption capacities of the systems explored.

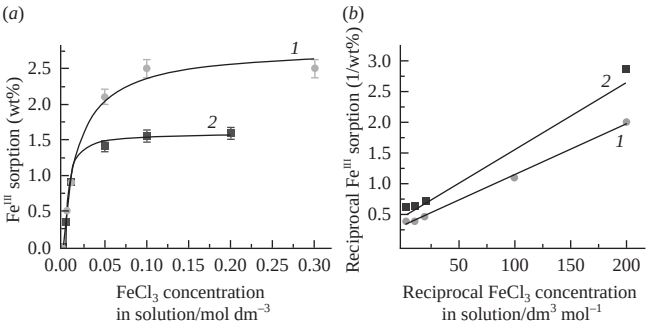

Figure 2 (*a*) Fe^{III} sorption isotherms for the PLA–PHB–chitosan compositions with (*1*) 25 : 25 : 50 and (*2*) 70 : 20 : 10 weight ratios; (*b*) the same isotherms in reciprocal coordinates corresponding to the Langmuir model.

Table 1 Thermal characteristics of chitosan, PLA, PHB as well as their binary and ternary compositions. For the transition designations, see the text.

Biopolymer	Endothermic peak of water desorption/°C	Weight loss of water desorption (%)	T_g/°C	T_{cc}/°C	T_m/°C	ΔH_m/J g^{-1}
Chitosan	~67	11.0	–	–	–	–
PLA	–	–	60.0	75.4	161.0	28.5
PHB	–	–	–	–	177.0	99.2
PLA–chitosan 50 : 50 wt	~63	8.8	–	–	160.0	27.4
PHB–chitosan 50 : 50 wt	~65	4.2	–	–	153.0 and 168.0	29.9
PLA–PHB–chitosan 25 : 25 : 50 wt	~63	6.0	–	–	159.0 and 175.0	21.3
PLA–PHB–chitosan 70 : 20 : 10 wt	~54	–	–	82.5	159.0 and 181.0	21.6

Table 2 Parameters C^0_{Fe} and K_L calculated for Fe^{III} adsorption by PLA–PHB–chitosan compositions.

PLA–PHB–chitosan weight ratio	$(K_L C^0_{Fe})^{-1}$/ mol dm^{-3}	C^0_{Fe} (wt%)	K_L/cm^3 mol^{-1}
70 : 20 : 10	$(8.20 \pm 0.17) \times 10^{-3}$	2.19 ± 0.84	$(5.57 \pm 0.11) \times 10^{-2}$
25 : 25 : 50	$(10.61 \pm 0.24) \times 10^{-3}$	3.05 ± 0.21	$(3.09 \pm 0.08) \times 10^{-2}$

It follows from data in Table 2 that an increase in the chitosan content in the ternary systems enhances their adsorption capacity by ~40%, whereas the adsorption constant reflecting the affinity of the hydroxyl groups of chitosan to Fe^{III} ions decreases approximately by half. The elevation of Fe^{III} ions sorption is determined by hydrophilization of the blends due to an increase in the content of hydroxyl groups. However, in an aqueous system this leads to a higher water sorption and, hence, to competition between water molecules and hydrated Fe^{III} ions for the hydroxyl adsorption centers, which supposedly results in a slight reduction of the Langmuir equilibrium adsorption constant.

In summary, thermal transitions have been determined for new biodegradable ternary PLA–PHB–chitosan blends from their TGA and DSC data as well as sorption capacity of the blends for Fe^{III} ions widespread in industrial wastewater has been evaluated using the Langmuir model. The chitosan-based composites can be successfully employed as new ecologically pure adsorbents.

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