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Mendeleev Commun., 2015, **25**, 361–363

Mendeleev Communications

Mechanical and thermophysical properties of biodegradable polylactide compositions with ethyl cellulose and chitosan containing poly(ethylene glycol)

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DOI: 10.1016/j.mencom.2015.09.015

The compositions of chitosan and ethyl cellulose with polylactide were obtained by the blending of components under shear deformation conditions in a Brabender mixer, and the influence of low-molecular-weight poly(ethylene glycol) on the mechanical and thermophysical properties of the blends was estimated.

Biodegradable polymers from renewable sources are of considerable current interest in the context of solving environmental problems.[1–3] Among these polymers, polylactide (PLA) produced by the polymerization of lactic acid from agricultural waste fermentation is most frequently utilized. Along with biodegradability, PLA has high mechanical characteristics, good transparency and processability. To improve the properties of PLA, its blends with synthetic polymers, such as poly(butylene carbonate),[4] poly(ethylene octene),[5] poly(ε-caprolactone),[6] poly(propylene carbonate),[7] and natural polymers (poly-3-hydroxybutyrate,[8] poly-3-hydroxybutyrate-co-4-hydroxyvaleriate,[9] hyaluronic acid[10] and chitosan[11,12]) are usually produced.

In this work, we obtained biodegradable polymer compositions based on PLA and polysaccharide derivatives (chitosan and ethyl cellulose) from renewable resources in order to impart new properties to the materials and to extend their areas of application. The films prepared from the compositions of PLA and chitosan are more water resistant than the films of pure chitosan, and they retain antimicrobial activity to improve their performance as packaging materials for agriculture. The compositions based on thermoplastic ethyl cellulose and PLA have improved mechanical characteristics, and they can be used in the preparation of various articles by molding techniques.

The compositions of chitosan and ethyl cellulose with PLA were obtained by an ecologically pure method using the solid-phase blending of components under shear deformation conditions in a Brabender mixer.

Tables 1 and 2 summarize the results of the mechanical tests of films obtained by hot pressing at 160 °C. The introduction of 30 wt% ethyl cellulose does almost not change the elastic modulus (E), whereas the addition of 70 wt% ethyl cellulose significantly decreased E. For the chitosan–PLA composition, E slightly increased since chitosan is a more rigid polymer than ethyl cellulose (Table 2). The introduction of 70 wt% ethyl cellulose led to decrease in the ultimate tensile strength σ_b by a factor of about 6 (in comparison with pure PLA); the effect observed may be explained by the poor compatibility of these polymers. For compositions containing 30 wt% ethyl cellulose or chitosan, this parameter diminished insignificantly, as compared to PLA. At the same time, the addition of ethyl cellulose and chitosan to PLA leads to a substantial decrease in the elongation at break ε_b. Thus, the change of mechanical characteristics of the polysaccharide blends with PLA depends on both the blend composition and the polysaccharide nature.

Table 1 Effect of the composition of blends based on ethyl cellulose and PLA on their mechanical characteristics.

Blend composition	Component ratio (wt%)	E/MPa	σ_b/MPa	ε_b (%)
PLA	–	2625±65	52±1.0	4.7±0.05
Ethyl cellulose–PLA	70 : 30	1650±96	8.7±0.6	0.9±0.09
Ethyl cellulose–PLA	30 : 70	2620±90	32.7±1.0	1.9±0.15
Ethyl cellulose–PLA–PEG	30 : 60 : 10	1500±74	12.9±0.4	1.8±0.13
	20 : 60 : 20	252±17	4.9±0.2	20.1±1.60

Table 2 Effect of the composition of blends based on chitosan and PLA on their mechanical characteristics.

Blend composition	Component ratio (wt%)	E/MPa	σ_b/MPa	ε_b (%)
PLA	–	2625±65	52±1.0	4.7±0.05
Chitosan–PLA	30 : 70	3110±90	45.5±2.2	2.5±0.21
Chitosan–PLA–PEG	30 : 60 : 10	1370±61	17.6±0.3	3.2±0.23
	20 : 60 : 20	106±11	8.9±0.1	57.5±2.00
	21 : 52 : 27	181±28	3.6±0.05	29.5±2.20

Poly(ethylene glycol) (PEG) is a widely used plasticizer for PLA.[13–18] The addition of PEG improves the brittleness, rigidity, hydrophilicity, flexibility and impact strength of PLA.

The introduction of 10 wt% PEG with $M = 600$ leads to a slight change in the elongation at break of blends, while the addition of 20 wt% PEG results in a significant increase in ε_b, especially for compositions containing chitosan. Thus, the elongation of the chitosan–PLA–PEG (20 : 60 : 20 wt%) ternary composition grew up to 57.5%, as compared to the chitosan–PLA binary composition with the elongation at break of 2.5% (Table 2). However, a further increase in the PEG content up to 27 wt% leads to a decrease in ε_b to 29.5% due to the phase separation of the components.

Note that the majority of publications were focused on the influence of high-molecular-weight PEGs on the thermophysical behavior of PLA, whereas the plasticizing effect of low-molecular-weight PEG is poorly understood. For example, the plasticization of PLA by PEG$_{200}$ was studied[19] and the influence of five PEGs on the crystallization and impact properties of PLA was examined.[20]

We studied the thermal behavior of PLA in the presence of low-molecular-weight PEGs (M_w = 600, 1000 and 3000) by DSC.

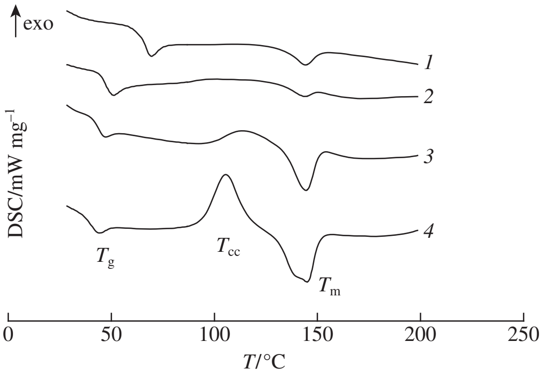

Figure 1 DSC curves of (*1*) PLA and PLA–PEG$_{600}$ compositions obtained in air at component ratios of (*2*) 95 : 5, (*3*) 93 : 7 and (*4*) 90 : 10 wt%.

Figure 1 shows the DSC thermograms of PLA and its compositions with PEG$_{600}$ at different plasticizer contents. Compared to T_g of pure PLA (69.3 °C), the T_g of blends diminishes with the increase in PEG$_{600}$ content to 44.1 °C in the presence of 10 wt% PEG. This behavior can be explained by a gain in the segmental mobility of PLA with the number of plasticizer molecules leading to the enhancement of PLA molecular mobility. The cold crystallization of both PLA and its blend containing 5 wt% PEG$_{600}$ was not observed, but it appeared with increase in the PEG content. Moreover, the cold crystallization temperature T_{cc} of PLA decreased as the PEG content increased, that was most probably caused by a growing number of crystallization centers. The T_m of PLA–PEG$_{600}$ blends only weakly depends on their composition.

Table 3 summarizes the determined values of T_g and the crystallization and melting temperatures (T_{cc} and T_m) of the initial PLA and PLA plasticized by PEGs of different molecular weights. For PEGs of different molecular weights, the T_g and T_{cc} of PLA–PEG blends decreased with rise in the PEG content. The melting temperature weakly depends on the blend composition, but the heat of melting rises with the PEG content. This can be explained by an increase in the crystallinity of the composition.

The molecular weight of PEG affects the thermal properties of PLA–PEG blends. Thus, the lower the molecular weight of PEG, the lower the T_g of PLA–PEG compositions; this is especially evident from a comparison of PLA–PEG$_{600}$ blends with PLA–PEG$_{1000}$ and PLA–PEG$_{3000}$ blends (Table 3).

Figure 2 demonstrates the thermograms of PLA compositions containing 7 wt% PEGs of different molecular weights. The heats of cold crystallization grow with decrease in the molecular weight of PEG. This is explained by an increase in the number of PEG molecules, which act as crystallization centers for PLA, with decrease in the molecular weight of PEG. On the other hand, the interaction of PEG terminal hydroxyl groups with PLA in a Brabender mixer under shear deformation conditions cannot be excluded. In this case, the lower the molecular weight of PEG, the greater the amount of hydroxyl groups capable of reacting with PLA and the higher the heat effect of reaction. The possibility of some chemical reactions in polymers under these conditions was demonstrated previously.[20–22] Nevertheless, this problem demands its further investigation and the possibility of reaction between PEG and PLA should be proved by other physicochemical methods.

Table 3 Characteristic temperatures of PLA and PLA–PEG compositions.

Blend composition	Component ratio (wt%)	T_g/°C	T_{cc}/°C	T_m/°C	H_m/J g^{-1}
PLA	–	69.3	–	144.4	4.5
PLA–PEG$_{600}$	95 : 5	50.7	–	144.2	1.8
	93 : 7	46.8	113.5	145.0	12.7
	90 : 10	44.1	105.4	145.5	18.6
PLA–PEG$_{1000}$	95 : 5	52.1	–	143.9	4.1
	93 : 7	49.3	121.5	144.8	6.4
	90 : 10	46.0	105.9	145.9	21.6
PLA–PEG$_{3000}$	95 : 5	52.1	–	143.6	4.7
	93 : 7	49.1	120.5	144.9	11.6
	90 : 10	44.8	110.3	143.1	19.8

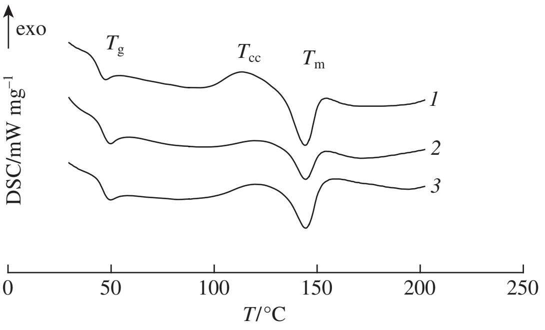

Figure 2 DSC curves of (*1*) PLA–PEG$_{600}$, (*2*) PLA–PEG$_{1000}$ and (*3*) PLA–PEG$_{3000}$ (93 : 7 wt%) compositions obtained in air.

Figure 3 shows the DSC curves of binary polysaccharide–PLA and ternary polysaccharide–PLA–PEG$_{600}$ compositions. The peaks of cold crystallization are absent on the DSC curves of binary chitosan–PLA and ethyl cellulose–PLA compositions, *i.e.*, the crystallization of PLA does not occur in the presence of polysaccharides (Figure 3, curves *1*). However, the addition of PEG leads to the appearance of a peak of cold crystallization for chitosan–PLA–PEG$_{600}$ and ethyl cellulose–PLA–PEG$_{600}$ compositions (Figure 3, curves *2*). At the same time, a decrease in T_g is observed for the binary compositions as compared with the initial PLA (Figure 3).

Thus, the presence of a polysaccharide as a third component does not hinder the plasticizing effect of PEG on PLA.

This work was supported by the Russian Foundation for Basic Research (project no. 13-03-12070-ofi_m).

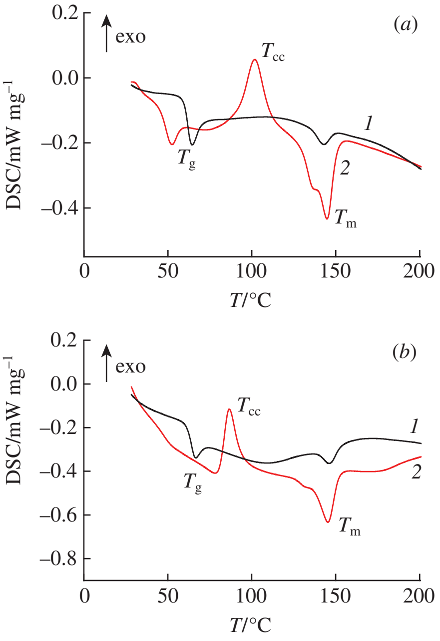

Figure 3 DSC curves of binary and ternary compositions obtained in air: (*a*) (*1*) ethyl cellulose–PLA (30 : 70 wt%) and (*2*) ethyl cellulose–PLA–PEG$_{600}$ (30 : 60 : 10 wt%); (*b*) (*1*) chitosan–PLA (30 : 70 wt%) and (*2*) chitosan–PLA–PEG$_{600}$ (30 : 60 : 10 wt%).

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Received: 15th January 2015; Com. 15/4544