

PREPARATION AND STUDY OF MECHANICAL PROPERTIES OF POLYLACTIC ACID/STARCH OLEATES BLENDS

Jarmila Kebísková^{1*}, Iva Sroková¹, Vlasta Sasinková², Mária Chromčíková³

¹Faculty of Industrial Technologies, University of Alexander Dubček in Trenčín, I. Krasku 1809/34, 020 01 Púchov, Slovakia

²Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 38 Bratislava, Slovakia

³Vitrum Laugaricio – Joint Glass Centre of the Institute of Inorganic Chemistry SAS, University of Alexander Dubček in Trenčín, CHFPT STU and RONA, j.s.c., Študentská 2, 911 50 Trenčín, Slovakia

* Corresponding author E-mail address: jarmila.kebiskova@fpt.tnuni.sk

Received 16. 10. 2012; accepted in revised form 06. 12. 2012

Abstract

In presented work, the blends composed from pure polylactic acid (PLA) and starch oleates were examined. Starch oleates (SO) with different degree of substitution (DS) were prepared by esterification of native starch and oleoyl chloride in heterogeneous conditions (pyridine). These prepared starch esters were used in the function of additives for preparation of blends with PLA. The PLA/starch oleates blends (9:1) have been prepared and evaluated by using attenuated total reflectance (ATR) spectroscopy technique. Subsequently, their mechanical properties, such as storage modulus (E'), loss modulus (E'') and tan D were studied as a function of temperature by dynamic mechanical thermal analysis (DMTA). These blends containing 10 wt. % SO show satisfactory mechanical properties in comparison to pure PLA.

Keywords: starch oleates, PLA, blends, mechanical properties

1 Introduction

An increasing interest in the recycling and the use of biodegradable materials, together with improved thermo-mechanical properties of polymer blends has led to the use of polysaccharides as biodegradable filler. The greatest application of polysaccharides, especially starch, cellulose, xylans, galactomannan and their derivatives in the polymer field are as a component in various polymer formulations [1]. Starch and cellulose polymers derived from biofeedstocks are also finding use directly or as blends with other biobased and biodegradable polymer materials [2]. Starch is one of the most studied and promised raw materials for biodegradable plastics because of its natural abundance and low cost, otherwise, starch and its derivatives have better reactivity than the other biodegradable natural biopolymers, such as cellulose, chitin, etc. [3,4]. Natural starch is rarely used in the function of the additive itself, because is hydrophilic. The hydrophilic nature of starch is a major constraint that seriously limits the development of starch-based materials, in fact, their properties depend on the ambient humidity. To improve its properties must be physically and chemically modified. Chemical modification involves the introduction of functional groups into the starch molecule, using etherification and esterification or decomposition reactions. This is a useful alternative that allows to modify the structure and consequently the properties of natural starch [5].

Poly(lactic acid) (PLA), produced from renewable resources like corn, is one of the most important biodegradable polyester with good mechanical properties, high transparency and good processability. However, disadvantages such as brittleness, poor thermal stability, and high costs limit its applications in general use plastics such as industrial packaging and agricultural films. Therefore, it is necessary to modify PLA for commercial applications in order to improve its properties (to overcome the limitation of its inherent brittleness) and reduce its cost [4,6]. Many properties of PLA are comparable to those of polyethylene, polypropylene, polystyrene, and polyethylene terephthalate, such as stiffness, tensile strength, and gas permeability. However, PLA is more expensive than conventional petroleum polymers for disposable or short-term applications [7].

PLA and starch are good candidates for polymer blends, since both are biodegradable, made from renewable resources. Starch improves biodegradability, increases heat resistance and also reduces cost while PLA offers superior mechanical properties [2]. Starch has been used as filler in blends with PLA, but the mechanical properties of the blends decreased significantly with increased starch content [7]. The goal of blending completely degradable polyester (PLA) with low cost starch is to improve its cost competitiveness whilst maintaining other properties at an acceptable level [8].

2 Experimental

Materials

The polylactic acid (PLA) was obtained from VÚCHV, Inc. (SVIT, Slovakia). Native starch was supplied from Spolana, Inc. (Neratovice, Czech Republic) and for experiments it was dried at 105 °C for 1 h. The oleoyl chloride and dichloromethane were purchased from Aldrich Chemie (Steinheim, Germany). The pyridine and the ethanol were of standard purity, supplied by the AFT Ltd. (Bratislava, Slovakia).

Esterification of starch

The esterification of starch with oleoyl chloride was carried out in an analogous way by method used for the modification of native starch with octanoyl chloride [9]. Starch oleates (SO) with different degree of substitution (DS) have been prepared by esterification of starch with oleoyl chloride in pyridine at constant weight ratio 1:3 and at temperature 105 °C with reaction time 6 and 3 h., respectively. It has been reported in Table 1.

The two methods of heating were used for esterification: classical heating and microwave heating (MW), which was used for shortening of reaction time from hours to minutes. Microwave device stood for the microwave oven which is normally used in households but this oven was suitably modified for the experimental conditions.

Table 1 Esterification of starch with oleoyl chloride (1:3) in pyridine at 105 °C and DS

Starch oleate (SO)	Reaction time (h,min)	Degree of substitution (DS)
SO1005	6 h	1.85
SO1006	3 h	1.30
SO1009*	2.5 min	2.67

Preparation of PLA/SO blends (9:1)

PLA/SO blends were prepared as follows: 0.1 g of the starch oleate was dissolved in 10 ml of dichloromethane (CH₂Cl₂) under stirring for 24 h at room temperature in a beaker with a lid. Then 0.9 g PLA was added to the mixture and stirred at room temperature until the PLA was dissolved. Prepared mixture of PLA/SO was spilt on Petri dish (diameter 9.5 cm) and then the mixture was let to be evaporated spontaneously in the dark place for 24 h.

For comparison purposes was also prepared standard from pure PLA as follows: 1 g PLA was dissolved in 10 ml of dichloromethane (CH₂Cl₂) by stirring at room temperature in a beaker with a lid. Then the prepared mixture of PLA was spilt on Petri dish (diameter 9.5 cm) and then the mixture was let to be evaporated spontaneously in the dark place for 24 h.

Characterizations

The ATR spectra were measured on a NICOLET 6700 spectrometer by ATR technique. For each spectrum 128 consecutive scans with 4 cm⁻¹ resolution was averaged. Company: SHIMADZU Corporation, Kyoto, Japan.

Dynamic mechanical thermal analysis (DMTA) was carried out on a TMA Q400 EM, TA instrument. DMTA was used for comparison of the stress and strain signals and resolution of the strain into the in-phase (storage) and out-of-phase (loss) components, from which storage or elastic (E') and loss (E'') moduli as well as tan D = E''/E' were obtained as a function of temperature. The range of temperature of measurements was from 40 to 75 °C. The used standard heating rate was 3 °C/min, under a periodic load between 0.08 and 0.06 N at frequency of 0.5 Hz. Test samples, which were used for evaluation of mechanical properties had dimensions (W x T x L = 4.5 x 0.2 x 16 in mm). A drop in storage modulus and a peak in tan D were used as indicators of a glass transition.

3 Results

ATR measurements

The compatibility of the polymer blends was also characterized by ATR spectroscopy. For compatible polymer blends, the ATR spectrum band would considerably deviate or be obviously shifted (band frequency shifting, along with peak style asymmetrically widening), compared to that of the single polymer component. However, for the completely incompatible polymer blends, the characteristic absorption spectrum would overlap perfectly, compared to the single polymer component [9,10].

Figure 1 depicts the ATR spectra of PLA/starch oleates blends (9:1) and pure PLA in region 2700-3100 cm⁻¹. There are no significant differences observed in the spectra of the blends with PLA (e. g. peak shifts) in comparison to the spectrum for pure PLA. Only few changes may be observed in these spectra, especially in

some peak intensities. The strong bands at 2851 cm^{-1} and 2924 cm^{-1} , can be assigned to the methyl/methylene groups of starch oleates in the blends with PLA. In comparison to PLA, the given ATR spectra of the blends showed differences and therefore it can be concluded that prepared blends are compatible.

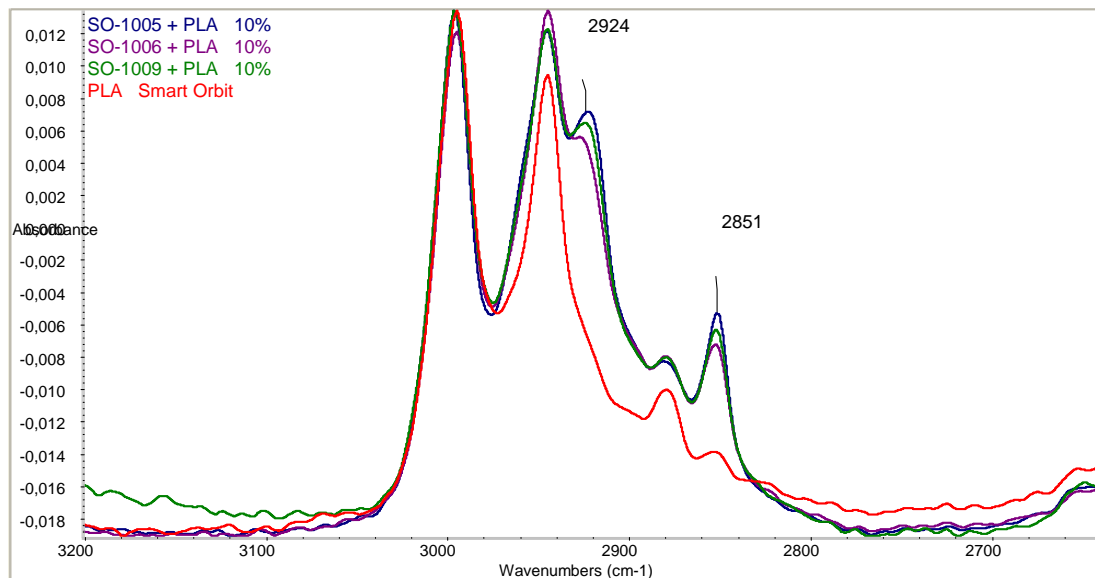


Fig. 1 ATR spectra of PLA/starch oleates blends (9:1) and PLA

Mechanical properties

DMTA method is a very useful technique for study of the viscoelastic response of the polymers as well as their composites in a wide range of temperatures. Using DMTA method was determined the storage modulus (E'), loss modulus (E'') and $\tan D$ of PLA/starch oleates blends and pure PLA as a function on temperature. The DMTA data, i.e. the storage modulus (E'), loss modulus (E'') and $\tan D$ of selected polymer blends as well as pure PLA are shown in Figs 2, 3 and 4, respectively.

The behaviour of storage modulus E' for selected PLA/starch oleates blends and pure PLA is shown in Fig. 2. As can be seen that storage modulus E' of unmodified PLA and PLA/SO blends shows various behavior. The selected PLA/SO blends showed slightly decreased storage modulus E' from cca 200 MPa up to 100 MPa at the temperature $\sim 50\text{ }^{\circ}\text{C}$ and then the storage modulus E' increased rapidly to the maximum temperature at $\sim 55\text{ }^{\circ}\text{C}$ for both derivatives with maximum $\sim 400\text{ MPa}$ for derivate (SO1009) with $\text{DS} = 2.67$ and $\sim 200\text{ MPa}$ for derivate (SO1006) with $\text{DS} = 1.3$ and then it decreased again to zero MPa at the temperature about $70\text{ }^{\circ}\text{C}$ to the modulus of initial PLA.

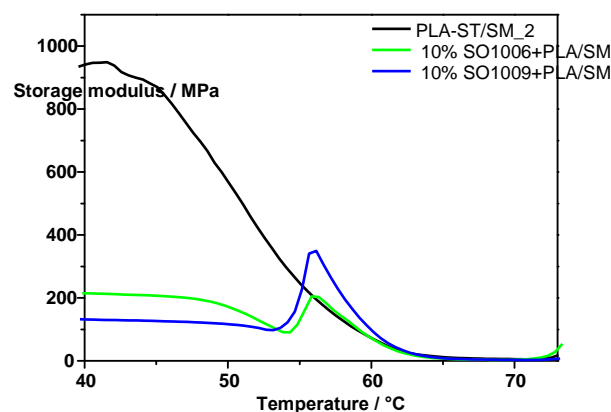


Fig. 2 Dependence of storage modulus E' of selected polymer blends and PLA on temperature

The storage modulus E' is an important parameter for rigid materials. Storage modulus or dynamical modulus characterizes behaviour of materials as a reversible component of complex modulus after low oscillation strain or stress. The dependence of storage modulus E' is influenced by the presence of starch oleates in a blends with

PLA. Storage modulus of starch oleates was lowered at temperature 45-50 °C and it means that SO have positive effect. This modulus characterizes the stiffness of PLA/polysaccharide blends and it is lower than PLA.

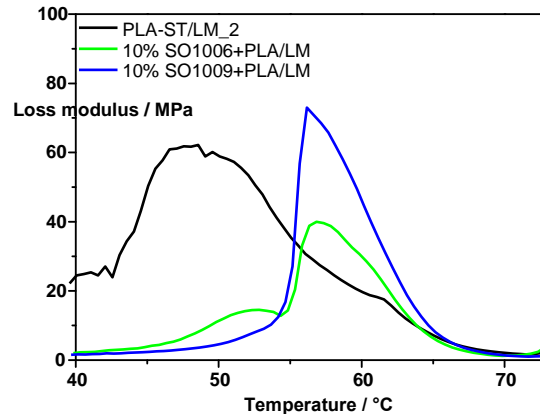


Fig. 3 Dependence of loss modulus E'' of selected polymer blends and PLA on temperature

Fig. 3 presents the dependence of the loss modulus E'' of selected polymer blends and PLA on temperature and as can be seen, the dependence of the loss modulus E'' is affected by the presence of starch oleates in a mixture with PLA. Although there was the low addition of additives (10 wt. %) in a mixture of PLA, the loss modulus of the PLA/SO blends was increased together with temperature and DS of starch oleates in the blends and due to this fact there was the influence on the dependence of $\tan D$ on the temperature.

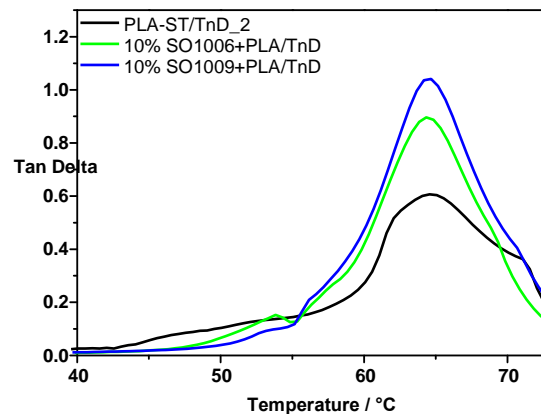


Fig. 4 Dependence of $\tan D$ of selected polymer blends and PLA on temperature

The $\tan D$ of selected PLA/starch oleates blends and PLA (9:1) is shown in Fig. 4. From the dependence $\tan D = f(\text{temperature})$ can be evaluated the temperature of glass transition (T_g) of polymer blends [11]. From the diagram for the pure PLA and PLA/SO blends it can be concluded that these blends have T_g in the range 60-65 °C and it is also confirmed by literature [12].

4 Conclusion

Starch oleates (SO) with different degree of substitution (DS) were prepared and used in the function of additives for preparation of polysaccharide blends with PLA.

Subsequently, the mechanical properties of the selected PLA/starch esters blends were evaluated by DMA method. The following conclusions have been drawn from this work:

- DS of starch oleates were 1.3 -2.67;
- the increase of storage modulus E' together with DS of starch oleates in the blends;
- starch oleates in a blends with PLA had a positive effect on the stiffness of blends;
- the relatively low content of additives (10 wt. %) in blends with PLA influenced the dependence of the loss modulus E'' as well as the value of $\tan D$;
- from the dependence of $\tan D$ on temperature were evaluated temperature of glass transition (T_g) at 60-65 °C of prepared selected blends;

- the PLA/starch oleates blends show satisfactory mechanical properties in comparison to pure PLA. This means that relatively low amounts of starch esters (10 wt. %) can be tolerated in blends with PLA to obtain blends with acceptable mechanical properties.

Acknowledgements

This work has been supported by VEGA grant No. 2/0062/09

References

- [1] HEYDE, M.: *Ecological considerations of the use and production of biosynthetic and synthetic biodegradable polymers*. Polymer Degradation and Stability 59, 1998, pp. 3-6.
- [2] JANG, W. Y., SHIN, B. Y., LEE, T. J., NARAYAN, R.: *Thermal Properties and Morphology of Biodegradable PLA/Starch Compatibilized Blends*. J. Ind. Eng. Chem., Vol. 13, No. 3, 2007, pp. 457-464.
- [3] MA, X., CHANG, P. R., YU, J.: *Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites*. Carbohydrate Polymer, 72, 2008, pp. 369-375
- [4] LIU, X., ZHAO, N., YANG, K., WANG, Y., ZHENG, CH., LI, S., ZHANG, Z.: *Preparation of Poly(lactic acid)/Etherified Starch Composites*. Iranian Polymer Journal, Vol. 17, Nr. 12, 2008, pp. 947-952.
- [5] LOPEZ, O. V., GARCIA, M. A., ZARITZKY, N. E.: *Film forming capacity of chemically modified corn starches*. Carbohydrate Polymer, 73, 2008, pp. 573- 581.
- [6] LEE, J., MCCARTHY, S.: *Biodegradable Poly(lactic acid) Blends with Chemically Modified Polyhydroxyoctanoate Through Chain Extension*. J Polym Environ 17, 2009, pp. 240-247.
- [7] KE, T., SUN, X. S.: *Starch, Poly(lactic acid), Poly(vinyl alcohol), Blends*. Journal of Polymers and the Environment. Vol. 11, No. 1, 2003, pp. 7-14.
- [8] LU, D. R., XIAO, C. M., XU, S. J.: *Starch-based completely biodegradable polymer materials*. eXPRESS Polymer Letters, Vol. 3, Nr. 6, 2009, pp. 366-375.
- [9] ABURTO, J., THIEBAUD, S., ALRIC, I., BORREDON, E., BIKIARIS, D., PRINOS, J., PANAYIOTOU, C.: *Properties of octanoated starch and its blends with polyethylene*. Carbohydrate Polymer 34, 1997, pp. 101-112.
- [10] PEI-XI, W., LIU-CHENG, Z.: *Polymer Blending Industry*, 52, 2002, pp. 245.
- [11] POLANSKÝ, R., KOLÁROVÁ, L.: *Analýza teplotních závislostí dielektrických parametrů s ohledem na možnosti určení teploty skelného přechodu T_g*. In : Zborník Medzinárodná konferencia „Diagnostika 07“, séria 3, Ed. V. Mentlík, Západočeská univerzita Plzeň, 2007, ISBN 978-80-7043-557-1.
- [12] ČERNOSKOVÁ, E., et al.: *High-temperature dynamic thermomechanical analysis of NBS 711 glassy fiber*, 2005, [cit. 2007-03-23] dostupné na: www.sciencedirect.com.

Review: Eugen Jóna
Anna Prnová