

POLYLACTIDE AND THERMOPLASTIC STARCH BLENDS PLASTICIZED WITH SILANE COMPOUNDS

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Introduction

Poly lactide (PLA), a biodegradable aliphatic polyester, is one of the most potential materials with great environmental benefits since it offers very low toxicity and high mechanical performance. However, a low glass transition temperature (about 60 °C) and relatively high brittleness limit its applications [1]. There are many ways of improving PLA toughness including copolymerization and melt blending with other more flexible commodity polymers such as linear low density polyethylene or rubbers, as well as plasticizers [2, 3]. Generally, an efficient plasticizer decreases the glass transition temperature (T_g) and melting point (T_m) of polymers [4].

Thermoplastic starch (TPS) is one of the well-known biopolymers and is often used in order to lower the cost of the final product and enhance the biodegradable characteristics of polymer composites [5]. Thus, melt compounding TPS with PLA is one of the most promising methods to solve PLA limitations [6]. Nevertheless, incompatibility between hydrophobic PLA and hydrophilic starch results in poor mechanical properties, due to inadequate interfacial interaction between these polymers. It has been previously suggested that the intensive interfacial interactions among hydrogen bonds of the anhydride groups of the maleated polylactide (MPLA) and the hydroxyl groups of the starch are responsible for the increase in tensile, flexural and impact properties of PLA and thermoplastic potato or corn starch blends [7].

The objective of this paper is to investigate the thermal, mechanical, rheological and morphological properties of silane nonreactive and reactive compounds toughened PLA/TPS blends in the presence of MPLA used as a compatibilizer.

Materials

Poly lactide polymer (PLA) 2003D, melt flow rate (MFR) of 6.9 g/10 min (ISO 1133) was provided by NatureWorks (USA). Maleated polylactide (MPLA) containing 0.68 wt.% of grafted maleic anhydride, MFR = 3.8 g/10 min (ISO 1133) was obtained according to the procedure published elsewhere [8] and used as a compatibilizer for PLA/TPS blends at the concentration of 10 wt.%.

Thermoplastic corn starch (TPS) was obtained by melt blending according to the procedure published elsewhere [9] and used as biodegradable additive. Corn starch standard with about 23 % of amylase, 11–13 % humidity and pH 6.5 was purchased from Cargill (Germany). The glycerol with 99.5 % purity was product of Rafineria Trzebinia (Poland).

Silicone rubbers, such as polydimethylsilane (POLSIL OM-2000, Chemical Plant Polish Silicones Ltd.), $\eta = 2000 + 500$ cP, $d = 0,97$ g/cm³ and polydimethylsiloxanol (Plastosil M-2000, Chemical Plant Polish Silicones Ltd.) containing 0.04 wt.% of reactive silanol groups, $\eta = 2000 + 500$ cP, $d = 0,97$ g/cm³.

Blends preparation

The various blends containing 1.5, 3 or 5 wt.% of nonreactive (NP) and reactive plasticizer (RP) were prepared through melt-compounding using a Berstorff twin-screw co-rotating extruder

(D = 25 mm, L/D = 33). Compounding was carried out using a screw speed of 150 rpm and also a temperature profile of 35°C/165°C/175°C/180°C/180°C/180°C/175°C/185°C/185°C and 200°C for the sequential heating zones, from the hopper to the die. Then, the material was cooled in water and pelletized.

Results and discussion

To investigate the effect of interfacial modification on the mechanical performance of the nonreactive and reactive silane compounds toughened PLA/MPLA/TPS (60/10/30) blends, the tensile stress-strain behavior was characterized (Fig. 1). Table 1 illustrates the influence of plasticizers on the tensile and flexural properties, as well as impact strength, HDT and melt flow rate (MFR) of PLA/MPLA/TPS blends. The addition of plasticizers caused a significant increase in an elongation at break, tensile and flexural strengths, as well as in impact strength. Simultaneously, the nonreactive plasticizer decreased tensile and flexural modulus. The opposite behavior was observed in the presence of reactive plasticizer indicating that the polydimethylsiloxanol is an efficient plasticizer for PLA/MPLA/TPS blends. It is well known that the degree of polymer crystallinity may significantly influence on the polymer mechanical properties, since it affects the extent of the intermolecular secondary bonding (Table 2). For crystalline regions wherein molecular chains are packed in an ordered arrangement, wide-ranging secondary bonding occurs between adjacent chain segments. These bonds lead to significant increase of polymer tensile modulus with growing degree of crystallinity.

As can be expected, MFR of the blends increased as a function of plasticizer. However, the higher values were obtained for the blends with reactive plasticizer. Moreover, nonreactive plasticizer decreased HDT. Based on the mentioned above results it can be supposed that using of reactive plasticizer can improve intermolecular interactions among the blend components through the reactive =SiOH groups.

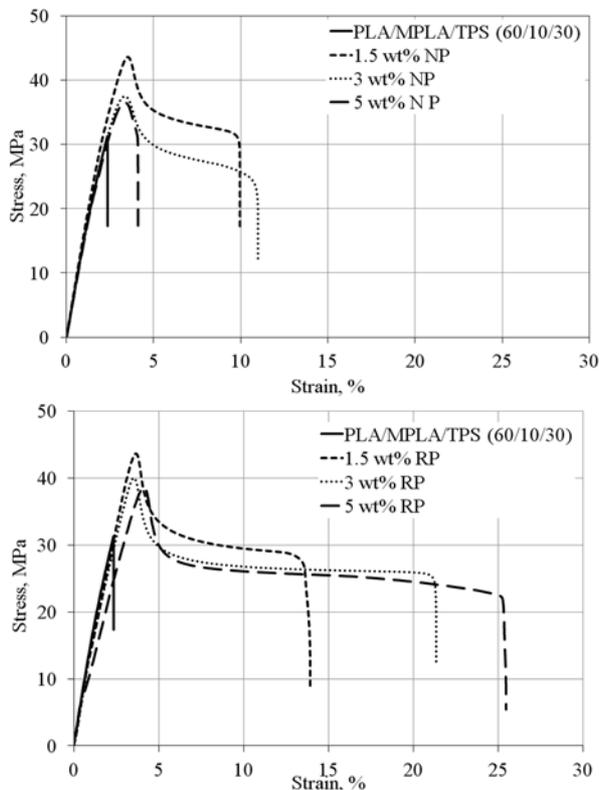


Fig. 1. Stress-strain curves for PLA/MPLA/TPS (60/10/30) blends with nonreactive (a) and reactive plasticizers (b)

Table 1

Mechanical and rheological properties of plasticized PLA/MPLA/TPS blends

Property	PLA/MPLA/TPS 60/10/30	Nonreactive plasticizer, wt%			Reactive plasticizer, wt%		
		1.5	3	5	1.5	3	5
Elongation at break, %	2.4±0,3	9.8±0,8	11.0±0,4	3.9±0,7	13.9±0,9	22.2±0,6	25.7±0,2
Tensile strength, MPa	33 ±1	43±1	38±1	37±1	44±1	41±1	39±1
Tensile modulus, MPa	3264 ±64	3090±32	3085±47	2862±37	3534±68	3452±60	3374±43
Flexural strength, MPa	53±2	64±2	60±3	53 ±1	64±2	62 ±1	58 ±1
Flexural modulus, MPa	2658±67	2350±25	2319±57	2220±48	2937±29	2717±61	2676±28
Impact strength, kJ/m ²	1.2±0.2	1.7±0.4	1.9 ±0.4	2.0±0.5	1.5±0.4	3.0±0.7	2,5±1.1
HDT, °C	54	52	52	52	54	54	54
MFR (210 °C; 2.16 kg), g/10 min	34.5	31.5	31.7	41.5	28.6	52.3	60.4

Table 2

Thermal properties of plasticized PLA/MPLA/TPS blends

Property	PLA/MPLA/TPS 60/10/30	Nonreactive plasticizer, wt%			Reactive plasticizer, wt%		
		1.5	3	5	1.5	3	5
Crystallinity, %	14.6	14.4	11.0	12.6	13.7	19.0	17.7

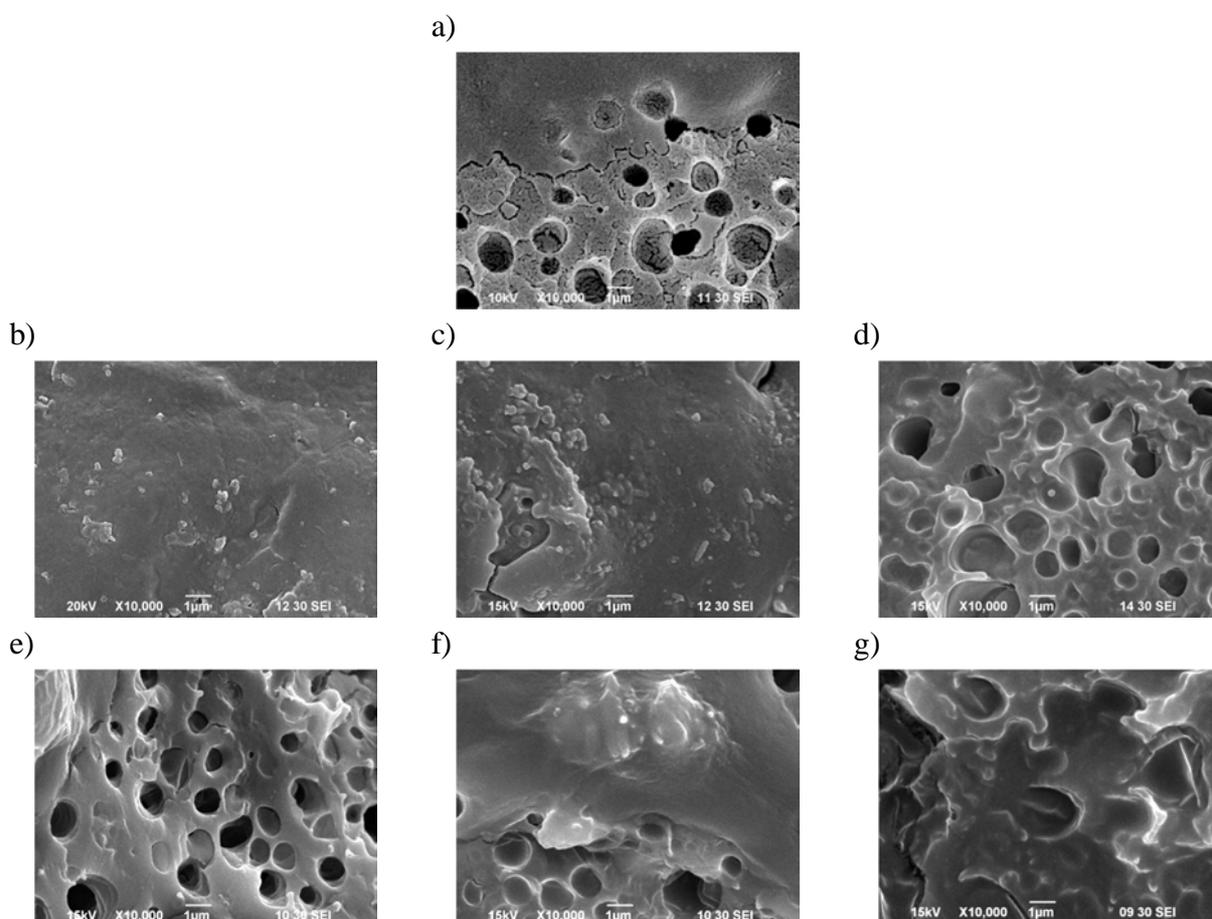


Fig. 2. SEM images of PLA/MPLA/TPS (60/10/30) blends: (a) without plasticizer, (b) 1.5 wt% NP, (c) 1.5 wt% RP, (d) 3 wt% NP, (e) 3 wt% RP, (f) 5 wt% NP, (g) 5 wt% RP

It is well known for polymer blends that the morphology control of the respective phases is a key factor in achieving the desired material properties. In fact, the apparent morphology can be easily observed using a scanning electron microscope. Figure 2 shows cross-sectional images of the various PLA/MPLA/TPS blends differing in plasticizer type and content. As expected, the PLA and thermoplastic starch blend in the presence of compatibilizer (MPLA) shows individual grains of starch forming dispersed phase in PLA matrix. The phase morphology of these samples can be depicted as continuous and porous. The addition of plasticizer results in less porous structure with increasing its content, suggesting improved toughness.

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