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In Situ Compatibilization of Thermoplastic Starch and Poly(Butylene Adipate-co-terephtalate) by Reactive Melt Blending in Presence of Maleic Anhydride

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Thermoplastic pea starch (TPPS) and poly(butylene adipate-co-terephtalate) (PBAT) were melt blended using a Brabender mixer. In a first step, maleic anhydride was used as an esterification agent of starch or grafted to PBAT; in a subsequent operation functionalized TPPS and PBAT were blended to obtain a grafted copolymer. Results showed that the ultimate mechanical properties of the blends were, in both cases, improved by this addition of maleic anhydride, thanks to compatibilization effects.

1. Introduction

Starch is a very common biobased and biodegradable polymer. Raw, granular starch comes from a variety of sources, including corn, wheat, rice, potatoes or pea. Thermoplastic starch (TPS) is processed through extrusion and injection units. Unfortunately, there are some strict limitations to the development of starch-based products due to its poor mechanical properties and high sensitivity to moisture: pure starch is brittle and highly water sensitive. Many attempts have been made to overcome these drawbacks by combining starch with other polymers, thus in the meantime increasing the biodegradability and decreasing the cost of the latter.

This paper aims at investigating 50/50 w/w melt blends of TPPS (plasticized with 30 w% glycerol) with poly(butylene adipate-co-terephtalate) (PBAT), a biodegradable polyester. Since starch and hydrophobic polyesters are rather immiscible, simple mixing produces biphasic blends with poor interfacial properties. Several compatibilization strategies involving maleic anhydride (MA) were therefore investigated in order to promote higher compatibility of the two phases. MA-compatibilized blends were studied by tensile testing and microscope observation.

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2. Experimental

2.1 Materials

Commercial-grade PBAT Ecoflex SBX7025 was purchased from BASF. The unmodified granular pea starch NASTAR, with high amylose content, was supplied by Cosucra. The moisture content of the starch was 11% (w/w). Glycerol from VWR was used as platicizer. Maleic anhydride 99 % was purchased from Sigma and 2,5-dimethyl-2,5-di(T-butylperoxy)hexane (Luperox 101) from Arkema.

2.2 Processing

MA-grafted PBAT (MPBAT) was prepared in a Brabender internal mixer according to procedure 1 (table 1) by adding MA to 50 g of PBAT after 2 min. In some cases, Luperox was added as an initiator for the grafting reaction (procedure 2, MA after 5 min, Luperox after 7 min).

TPPS was prepared by hand mixing native starch with glycerol (70/30 wt%) prior to proceeding to the plasticization in the mixer following procedure 3. Maleated starch (MTPPS) was prepared a similar way, MA being added during the hand mixing step.

Binary blends of (M)TPPS with (M)PBAT were prepared by melt blending 30 g of each component following procedure 4, (M)PBAT being added after 4 min mixing of (M)TPPS alone. Blends compositions are reported in Table 2.

Table 1: Mixing procedures in Brabender

Procedure (n°)	Temp (°C)	Step 1 (rpm, min)	Step 2 (rpm, min)	Step 3 (rpm, min)
1	130	50, 3	100, 10	
2	130	30, 5	40, 2	60, 10
3	110	50, 2	100, 10	
4	130	30, 5	100, 10	

Table 2: TPPS-PBAT blends 50-50 (wt%) prepared according to procedure n°4

Sample	MA (wt% of TPPS)	MA (wt% of PBAT)	Luperox (wt% of PBAT)
TPPS-PBAT			
TPPS-MPBAT-1		1	
TPPS-MPBAT-L1		1	1.2
TPPS-MPBAT-L2		2.5	1.2
TPPS-MPBAT-L3		5	1.2
MTPPS-PBAT-1	0.4		
MTPPS-PBAT-2	0.7		
MTPPS-PBAT-3	1.4		
MTPPS-PBAT-4	5.6		

2.3 Characterization and Analysis

Tensile test bars (1*3*25.4 mm) were cut into compression moulded (150 °C, 130 bar, 3 min) sheets. Tensile tests were performed on a Hounsfield H10 KT with a 100 N load cell at 19 °C and at a crosshead speed of 10 mm/min.

An environmental scanning electron microscope Philips XL20 with tungsten filament was used to observe the morphology of the samples at 20 kV. The samples were submerged in liquid nitrogen to fracture them with a pestle in a mortar. They were then mounted on gold stubs.

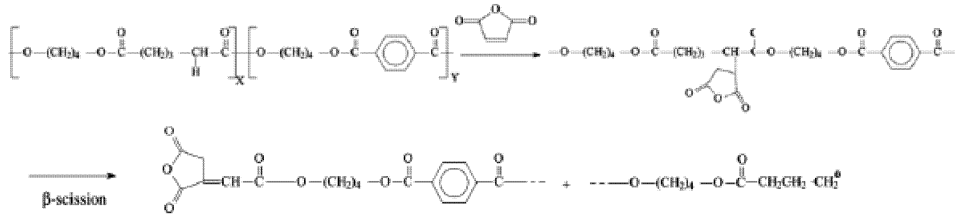
3. Results and Discussion

3.1 Reactions

MA grafting onto PBAT was performed to produce functional groups which can react with starch hydroxyl groups to form covalent bonds thus improving the interfacial adhesion between the dispersed starch and the continuous polyester phase. The free radical initiated maleation mechanism is illustrated in Scheme 1. In some cases Luperox was used as free radical initiator.

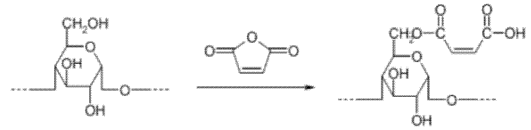
Size Exclusion Chromatography showed a decrease of PBAT molecular weight, indicating chain scission reactions most likely due to β-scission (Scheme 1) taking place along the polymer backbone during the reaction, as reported by Carlson et al. (1998).

Scheme 1: Mechanism of maleic anhydride grafting onto PBAT



In situ chemical modification of TPPS by MA was accomplished in an attempt to produce reactive carboxylic acid groups onto the starch backbone (Scheme 2), which is the most preferential position according to Raquez et al. (2008a).

Scheme 2: Esterification reaction of starch with MA occurring at the C6 position



TPPS-g-PBAT graft copolymers could be obtained during melt blending through transesterification reactions (acidolysis of PBAT chains by the acid moieties of MTPPS), as reported by Raquez et al. (2008b). Conversely, PBAT-g-TPPS would be obtained through esterification reactions between MA moities of MPBAT and hydroxyl functions of TPPS (Nabar et al., 2005).

3.2 Mechanical Properties

Figure 1 illustrates tensile properties of the different blends prepared, in comparison to pure PBAT and TPPS (very high *vs* very poor elongation at break respectively).

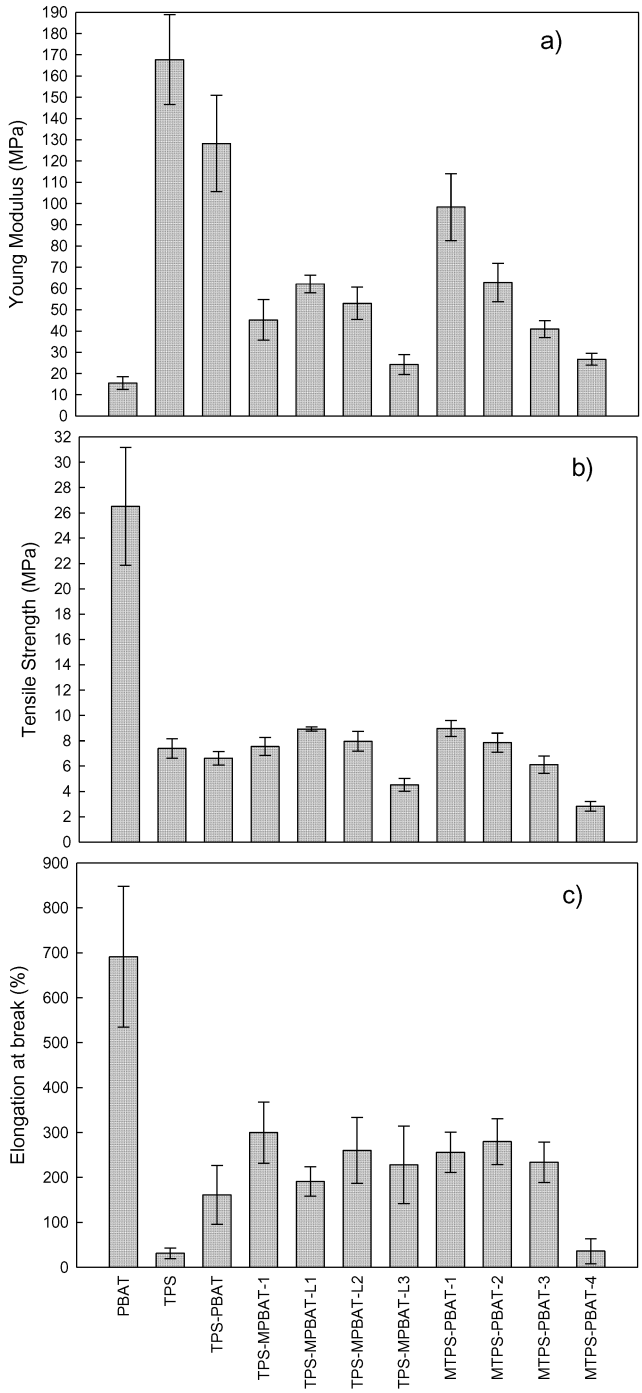


Figure 1: Tensile properties of TPPS-PBAT (50-50) blends a) Young modulus, b) Tensile Strength and c) Elongation at break

It could be concluded from these results that the addition of MA leaded to products that exhibit, when compared to simple TPPS/PBAT blends, higher ultimate properties (both tensile strength and elongation at break). However, it seems that too high amounts of MA (TPPS-MPBAT-L3 or MTPPS-PBAT-4) leaded to a drop in these properties. The higher level of ultimate properties could be attributed to the efficiency of the compatibilization strategies, since covalent bonding between the continuous and dispersed phases was likely to prevent debonding under high strain. It is interesting to note that both strategies seemed to be of equal efficiency, whatever the component MA was first added to. Besides, the observed drop of the properties for high MA contents was likely to be due to a competition between compatibilization and chain scission effects (chain scission was indeed shown in the preparation of MPBAT). Even if ultimate properties were enhanced in both cases, it had to be noticed that Young's modulus of the compatibilized blends was slightly lower than that of the binary simple blend. This difference was most likely to be due to the very same chain scission reactions. In the case of TPPS/MPBAT blends, this modulus loss was higher since chain scissions occured mostly in the continuous PBAT phase. The chain scission influence was lower in MTPS/PBAT blends, especially for low levels of MA, since chain scissions in the dispersed phase had less influence on low deformation properties. Taking all these observations and conclusions into account, it appeared that the blend that exhibits the best properties would be MTPPS-PBAT-1. Finally, there was no strong evidence from these mechanical results that the use of a radical initiator (Luperox) in the preparation of MPBAT had a real influence.

3.3 Morphology

SEM observation (see Figures 2 and 3) confirmed the postulated compatibilization effect of MA on TPPS/PBAT blends. The granular structure of the dispersed TPPS phase was highly visible in the binary uncompatibilized blend, whereas the distinction between the two phases was hard to make in the other blends. Here again, the added value of Luperox was not that obvious.

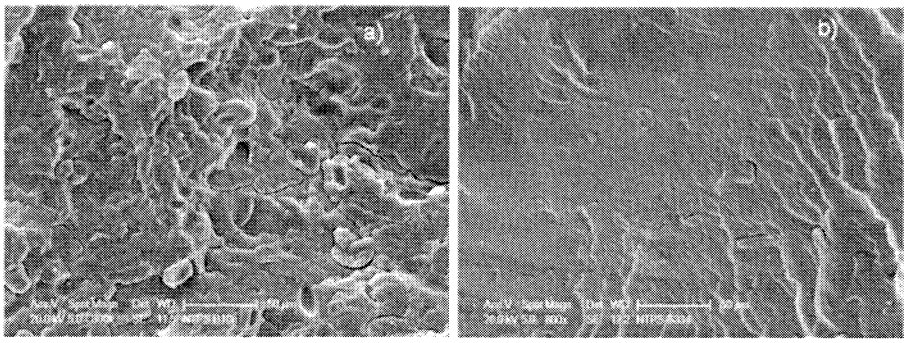


Figure 2: SEM observation of cryofractured surface of a) TPPS-PBAT and b) TPPS-MPBAT-1 melt-blends

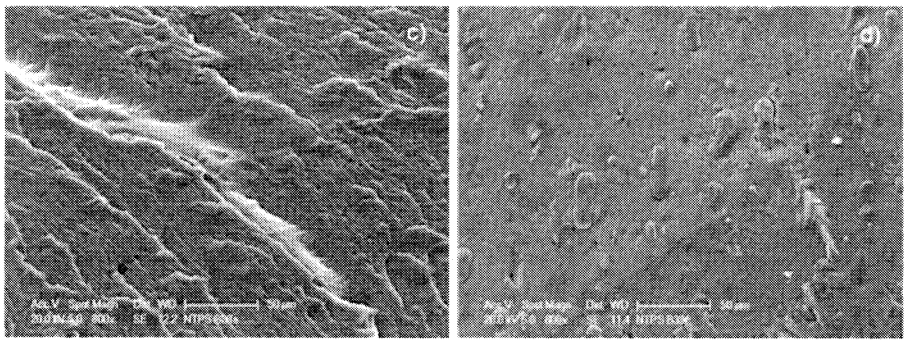


Figure 3: SEM observation of cryofractured surface of c) TPPS-MPBAT-L1 and d) MTPPS-PBAT-2 melt-blends

4. Conclusion

This work showed that the addition of maleic anhydride to TPPS/PBAT blends led to an improvement of the ultimate mechanical properties of these. This was attributed to reactive compatibilization between MTPPS and PBAT or TPPS and MPBAT, which was confirmed by SEM morphology observations. It was surprisingly observed that both compatibilization strategies were of equal efficiency. However, competitive chain scission reactions could occur in both phases, thus leading to a decrease of Young's modulus. It was shown that this side-effect was minimized when MA was first added to the dispersed TPPS phase, especially for low levels of MA.

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