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INFLUENCE OF EVA-g-PCL GRAFTED COPOLYMERS ON PHYSICAL PROPERTIES AND BIODEGRADATION

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ABSTRACT

Graft copolymers EVA-g-PCL as been synthesized by transesterification reaction between ethylene vinyl acetate (EVA) and poly(ε-caprolactone) (PCL), using titanium propoxide ($Ti(OPr)_4$) as catalyst. The extent of grafting reaction was estimated from the amount of copolymer extracted. Characterization of the copolymer formation was also performed using several analytical techniques, such as, scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). Biodegradability of the prepared materials was monitored. The results obtained show that blends of EVA and PCL with copolymer formation can be prepared by recative extrusion (REX) and that the biodegradability of EVA is enhanced.

INTRODUCTION

Synthetic polymers are more effective than the natural ones due to the best properties (as mechanical properties, UV resistance, etc.). Many attempts have been made to combinate the best properties of both in order to obtain biodegradable polymers with good performance. One of the most important polymers for the modification of EVA is PCL, because it can be degraded aerobically by a large number of microorganisms in various microbiological environments (Salomet al. 2006) and it is compatible with a variety of the polymers. Another important feature of PCL, from the polyesters family, is the potential for transesterification.

The extent of grafting reactions due to transesterification depends on the composition of the reaction mixture and on the reaction conditions. Transesterification reactions can be induced by using a catalyst. In this work, graft copolymers of EVA and PCL were synthesized by using PCL with different molar mass and $(Ti(OPr)_4$ as catalyst. The prepared materials were characterized by various techniques, such as, SEM, DSC and rheology.

EXPERIMENTAL

Materials

EVA with 28% (28 % of vinyl acetate (VA)) (M_n=7. 9 $kg.mol^{-1}$) from ARKEMA was used as a non-biodegrable polymer and PCL with two different molar mass (M_w = 10 $kg.mol^{-1}$ (PCL1) and M_w = 60 $kg.mol^{-1}$ (PCL2)) were used as a biodegradable polyesters. $Ti(OPr)_4$ was used as catalyst. The compositions of the materials prepared are shown in Table 1.

Compounding

Blends of EVAand PCL without and with catalyst were prepared in a Haake batch mixer equipped with two rotors running in a counter-rotating way. The rotor speed was 50 rpm and the set temperature was 160 ºC. Firstly, the dried components were pre-mixed and introduced together in the mixer. Blends, after 20 min of mixing the rotors were stopped and the total sample was removed.

Characterization

Scanning Electron Microscopy:

EVA/PCL blends were fractured in liquid nitrogen and then gold plating, the morphology was analysed using FEI QUANTA 400 scanning electron microscope.

Differential Scanning Calorimetry

Thermal properties of all samples were measured using PERKIN ELMER differential scanning calorimeter (DSC 7). Samples were heated from 30 ºC to 130 ºC at a heating rate of 10 ºC/min, cooled from 130ºC to room temperature at the same rate, under nitrogen flow.

Table 1. Samples Composition (wt.%)

Sample	EVA	PCL1	PCL2	$Ti(OPr)_4$
1	60,0	40.0	-	0,0
2	60,0	-	40,0	0,0
3	59,5	38.6	-	1,9
4	59,5	-	38,6	1,9

RESULTS AND DISCUSSION

From the morphology of the samples analysed by SEM (data not shown), it is possible to observe droplets of PCL in the EVA matrix, when blends are prepared without catalyst, being the adhesion between PCL/EVA not good. Nevertheless, the adhesion for PCL with higher molar mass is better than the one with lower After copolymer formation the morphology changes completely, it is not possible to detect two phases anymore. This is due to the effect of the copolymer at the interface, which acts as a compatibilizer.

DSC results are shown in figure 1. Due to the partial immiscibility between EVA (Tm = 83.3ºC) and PCL 10 $kg.mol^{-1}$ (Tm = 59.8ºC) and PCL 60 $kg.mol^{-1}$ (Tm = 59.4ºC), it would be expected that both polymers kept their thermal properties. However, in sample 1, the melting temperature of EVA changes slightly presenting a value around 58ºC and the melting temperature of EVA in sample 3 is 53.3ºC. The crystallinity degree also decreases from the former to the latter. This small difference could be related with some miscibility between EVA and PCL which is in according with SEM. The same trend was observed between sample 2 and 4. The decrease of crystallinity degree between physical blends and copolymers is related with the transesterification reactions, from which result covalent bonds between PCL and EVA chains leading to a lower regularity of the molecular structure. By SEM it is hard to identify two phases when transesterification reactions occurred.

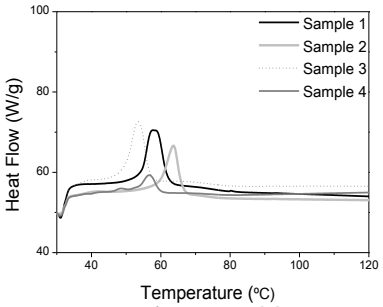

Figure 1. DSC

Biodegradability results indicate that EVA shows the lowest degree of biodegradability and PCL the highest, and the increase in biodegradability is enhanced for samples containing grafted copolymers.

CONCLUSIONS

The purpose of this work was to prepare biodegradable copolymers with a non-biodegradable (EVA) and biodegradable polymers (PCL) in order to obtain biodegradable copolymers. Morphological analysed of the prepared materials support grafting. The decrease of crystallinity degree of samples 3 and 4 is related to the lower regularity of the molecular structure. The biodegradability tests performed showed that all samples present an intermediate behaviour between EVA and PCL, where PCL shows a biodegradability around 99.8%. The results suggest that the presented method is an effective route to produce materials with a higher compatibility and consequently better properties, keeping its biodegradability.

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