POLYPROPYLENE/STARCH BLENDS. STUDY OF THERMAL AND MORPHOLOGICAL PROPERTIES

MÓNICA A. PÉREZ R*, BERNABÉ L. RIVAS Q*, SADDYS RODRÍGUEZ-LLAMAZARES**.

*Polymer Department, Faculty of Chemistry Sciences, University of Concepción, Casilla 160-C, Concepción, Chile. Edmundo Larenas 129 Concepción- CHILE.

**Research Center of Advanced Polymers (CIPA), Conicyt-Regional R08C1002, Avda. Cordillera, Concepción, Chile

(Received: September 3, 2012 - Accepted: November 21, 2012)

SUMMARY

Polypropylene/starch blends were prepared using starch of different botanical source. The influence of starch type and starch content on thermal properties and morphology of polypropylene/starch blends was studied. Corn and potato starches were used as starch source. The starch content in the blends was 7 and 15 wt-%. Characterization of PP and PP/starch blends by (DSC), (TGA), and (SEM) was carried out to obtain information on miscibility among PP and starch. The starch domains exhibited characteristic voids be due to thermal degradation.

Two types of PP, PP₁ poly(propylene-co-ethylene), random copolymer, and PP₃ poly(propylene-co-ethylene), heterophasic copolymer were studied

Keywords: Polypropylene, starch, blends, characterization

INTRODUCTION

Blends are a mixture of two or more polymers obtained by melting or in solution. Its objective is the preparation of a material that possesses the combination of properties of their components, not compassable by separated. The development of a blend with an adequate behavior, especially with respect to their mechanical and physical properties, depends on the interfacial adhesion among the phases. A compatible blend is that in which the dispersed or minority phase is found homogeneously distributed in the matrix or majority phase and in which the adhesion among the same is strong. In this type of blends, a force applied is transmitted among the components of the phases (1).

Polypropylene (PP), a synthetic polymer is an economical material that offers a combination of outstanding physical, mechanical, thermal, chemical properties that are not found in any other thermoplastic polymer (2)

The great number of polyolefinic products has caused harmful consequences to the nature due to the low degradation rates reached by the traditional polyolefins, e.g. low-density polyethylene (LDPE) and isotactic polypropylene (iPP).

By this way, researchers have studied the incorporation of biodegradable polymers, such as the starch, to the traditional polyolefins, which is justified by the presence of hydrolyzable groups in the natural polymer that are able to induce the biodegradation of the polyolefins (3-5).

Ramis et al. (6) evaluated the biodegradability of iPP/starch blends under simulated soil and observed the materials decomposition under nitrogen and oxygen atmosphere, by different mechanisms of degradation. The biodegradation affected the starch but not the iPP matrix.

When dealing with starch-derivative materials, this last can present a thermoplastic characteristic (commonly called thermoplastic starch or TPS) when incorporating glycerin to it, acting as a plasticizer (7). Moreover, the use of glycerin, as described by Carvalho (7) can increase the fragmentation rate of the material (morphological structure), obtaining though materials with many different characteristics just by varying the amount of glycerin on the starch.

In general, it is said that in order to let the polyolefins more susceptible to degradation, some kind of modification is necessary, such as modifications on the crystallinity degree (8), chemical degradation and reduction on the molar mass of polymers to create short molecules that are capable of being absorbed by microorganisms (9).

The inclusion of such materials allows products traditionally produced from non-renewable and environmentally persistent petroleum-based materials, to be produced from materials made from renewable resources which may also provide a degree of degradability to the final product. Starch, in particular, has been used since the 1970s as a filler in plastics (10) and has recently been plasticized and extruded with traditional plastics (11) used as a baked foam for thin walled applications (12), and used as packaging foams (13). Dry granular starch and baked starch, which is pressed and molded, have limited processability and can be used in only a limited range of applications. Plasticized starch, however, is more versatile and can be blended with various polymeric materials for numerous applications.

Starch is an abundant, naturally occurring polysaccharide that is obtained from various plant sources, such as corn, potato, rice, and cassava [14]. Starch is a semi-crystalline polymer comprised of glucose monomer units. its granular

form is comprised of linear amylose or branched amylopectin macromolecules with amylose content of ranging from 20-30% (see Scheme 1). Dry granular starch, by itself, cannot be processed like a plastic; however, it can be heated and blended with several different small polar molecules (water, glycerol) or polar oligomers (polyols), giving a thermoplastic material, generally called (PLS). This process, known as gelatinization, breaks up the granular structure of starch by disrupting hydrogen bonding between adjacent glucose molecules and essentially destroys its crystallinity [15].

Scheme 1. Starch structure

On the other hand, St. Pierre et al. (16) studied the mechanical properties of low density polyethylene (LDPE)/thermoplastic starch blends and of linear low density polyethylene (LLDPE)/thermoplastic starch. These compounds had better processability and mechanical properties than those with the untreated starch. Nevertheless, for high percentages of thermoplastic starch, there was a drastic reduction in the mechanical properties. Therefore, Matzinos et al. (17) studied the effect of incorporating low density polyethylene functionalized with maleic anhydride (LDPE-g-MAH) as a compatibilizer with 30% of natural corn starch, emphasizing that the biodegradation of the compatible blends was only slightly lower than that of the non compatible compounds

The aim of this study was to determine the morphological and thermal properties of PP/ starch blends, using starches of different botanical sources. The starch content in the blends ranged from 7 to 15 wt-%.

2. EXPERIMENTAL PART

2.1 Materials

PP₁ poly(propylene-co-ethylene); random copolymer (MFR 2,16 kg/230°C): 8.5 g/10 min, PP₃ (MFR 2,16 kg/230°C), poly(propylene-co-ethylene), heterophasic copolymer 12 g/10 min, from PETROQUIM S.A. Glycerine acquired Sigma-Aldrich.

The different types of starches: corn starch (CS) and potato starch (PS) were obtained Sigma-Aldrich.

2.2 Melt Processing

PP₁/ starch and PP₃/starch blends were obtained in a twin-screw co-rotating extruder (Haake H-25, model Rheomex PTW 16/25, L/D ¼ 25) operating at 80 rpm. The temperature conditions, 150 and 170°C for preparation and

processing of blends were chosen to minimize possible degradation of the organic modifier and the matrix.

The PP/starch blends were prepared as described in Table 1, using 7 and 15% wt CS and PS.

Table 1. Experimental conditions of PP/starch blends

Experimental conditions	PP ₁	PP ₃
Mixing temperature (°C)	150	180
Mixing time (min)	7	5
Mixing speed (rpm)	80	80
Glycerine concentration (% en mass)	2	2

From the prepared PP blends, the films were obtained by compression heating the polymer up to 190°C, maintaining for 2 min to obtain the complete melting of the pellets, and a pressure of 6 pounds was applied for 3 min.

1.3 PP/starch characterization

Differential scanning calorimetry (DSC) measurements were made on DSC Q200 TA Instrument. All measurements were carried out under nitrogen atmosphere. The samples were heated from 50 to 200°C at a heating and cooling rate of 5°C/min. The measurements were accomplished during the second heating and cooling cycle.

Thermogravimetric analyses were carried out on a T.A model QA-50 to obtain the inorganic and organic residue, and the clays' descomposition profile, and PP blends. The samples (10.0 mg in film form) were heated from 25 to 600°C at heating rate of 10°C/min under nitrogen flow.

The morphologies of the PP/starch blends were examined by JEOL-JSM 6380 LV scanning electron microscopy. The fractured surface of blends were coated with a gold film of ca. 50 nm and the images were taken at an accelerating potential of 20 kV.

3. RESULTS AND DISCUSSION

3.1.1. PP₁ blends characterization for DSC

The figure 1 shows the DSC thermograms of neat PP₁ and PP₁/CS blend, and Figure 2 shows pure PP₁ and PP₁/PS blend. The peak around 150°C, corresponds to melting temperature of PP₁ in both thermograms.

Figure 1: DSC thermograms for pure PP₁ compared with PP₁/CS blend.

The peak above 400°C in pure PP₁ and PP/CS (see Figure 1), and PP/PS in figure 2 blend is due to the decomposition of PP₁ and PP₁/CS and PP/PS blend, respectively. In both figures, the thermograms show the presence of an additional melting peak around 300-350°C. This peak is not present in pure PP₁. It is due to the presence of an amylose content as well as corn and potato starches increase in the blend. This increase of amylose content that produce greater dispersion of CS and PS in PP₁ increases the miscibility, as showed by Simmons et al (18).

Figure 2: DSC thermograms for pure PP₁ compared with PP₁/PS blend.

The peak between 300-350°C is clearly observed with 7% corn starch (CS) (see figure 1) instead with a 7% potato starch (PS) is not, it is due the content is higher in amylose corn starch (~29%) compared to potato starch (~21%) (19).

3.1.2. PP₃ blends characterization for DSC

The Figure 3 shows the DSC thermograms of pure PP₃ and PP₃/CS blend, and Figure 4 shows pure PP₃ and PP₃/PS. The peak ~ at 170°C corresponds to melting temperature of PP₃ (see Figures 3 and 4).

Figure 3: DSC thermograms for pure PP₃ compared with PP₃/CS blend.

Figure 3 shows at ~450°C the decomposition temperature of neat PP₃ and PP₃/CS blends. The thermograms show the presence of an additional melting peak which occurred at 300-350°C. This peak, which was not present in pure PP₃, is due to the presence of amylose. The peak intensity between 300-350°C increases with the amylose content, and increases the miscibility of blend.

Figure 4: DSC thermograms for neat PP₃ compared with PP₃/PS blend

Figure 4 shows between 300-350°C an additional melting peak. This peak was not present in pure PP₃, is due to the presence of amylose content. In this case, with 15% CS is not yet clearly see the peak corresponding to amylose, probably due to the potato starch amylose has a lower concentration (~21 wt%)

3.1.3. PP₁ and PP₃ blends characterization for TGA.

Figure 5 shows decomposition profile of PP₁ and PP₁/CS blend. Thermal stability decreases in the presence of a mixture compared with neat PP

Figure 5. TGA curves of PP₁ and PP₁/CS blend

The decomposition temperatures decrease with increasing the starch content of the blends

Table 2 shows the T_{5%} (temperature at which 5% of weight loss occurs) and T_{50%} (temperature at which 50% of weight loss occurs) for PP₁ and PP₃ and their blends, respectively.

Table 2. Thermal properties of PP/starch blends.

Sample	T _{5%}	T _{50%}
PP ₁	334	408
PP ₁ /7% CS	317	406
PP ₁ /15% CS	311	397
PP ₁ /7% PS	320	404
PP ₁ /15% PS	317	396
PP ₃	336	410
PP ₃ /7% CS	317	403
PP ₃ /15% CS	314	394
PP ₃ /7% PS	334	407
PP ₃ /15% PS	322	392

Table 2 shows that the initial decomposition temperature (T_{5%}) of PP₁ is 334 °C. In the blends PP₁/7%CS and PP₁/15%CS initial decomposition temperatures decrease with the increase of corn starch in the blend. This effect is due to amylose content

The same occurs when T_{50%} decomposition temperature decreases by increasing the starch content in the blend. The increase of amylose content that produces greater dispersion de CS and PS in PP increases the miscibility (19).

In the case of PP₃ T_{5%} and T_{50%}, the decomposition temperature decreases by less than PP₁ with increased starch content in the blends. This is probably due to the structure of PP₁ and PP₃, PP₁ poly(propylene-co-ethylene); random copolymer and PP₃ poly(propylene-co-ethylene), heterophasic copolymer

3.1.4. PP₃ blends characterization by SEM.

Figure 6 A), B), C), and d) show the SEM microphotography for PP₃, PP₃/7%CS, PP₃/15%CS. Micron scale phase separation was determined by an examination of blend with SEM. The CS does not undergo complete melting and remain dispersed in the continuous PP₃. The distribution is significantly higher in 15% CS. Due to the fact that de CS content is the highest compared with other blends

Figure 6: SEM images of PP₃ blends. A: PP₃, B: PP₃/7%CS, C: PP₃/15% CS

4. CONCLUSIONS

From the thermodegradative studies of the PP/CS and PP/PS blends, it can be concluded that the CS and PS content induces a retardant effect on the degradative process of the PP, since it increases the initial decomposition temperature of the blend, acting like an anti-oxidant agent.

The presence of an amylose content as well as corn and potato starches increase in the blend. This increase of amylose content produced a greater dispersion of CS and PS in PP₁ increases the miscibility. It was corroborated by DSC, TGA, and SEM

PP/CS blends have lower decomposition temperatures of PP/PS because corn starch has a higher content of amylose than that potato starch.

ACKNOWLEDGEMENTS

The authors thank the DIUC project (Grant No D05110383), CIPA (Centro de Investigación de Polímeros Avanzados). The commercial polypropylene samples provided by PETROQUIM S.A., Chile.

REFERENCES

1. R. Mani, J. Tang, M. Bhattacharya, Macromol. Rapid Commun, 19, 283 (1998).
2. M. Pérez, B. Rivas, S. Rodríguez, A. Maldonado, C. Venegas, J. Chil. Chem. Soc., 55, 4, 440 (2010).
3. D. Zuchowska; D. Hlavatá; R. Steller; W. Adamiak; W. Meissner Polym. Degrad. Stab. 64, 339, (1999).
4. P. Shah; S. Bandopadhyay; J. R. Bellare Polym. Degrad. Stab. 47, 165, (1995).
5. D. Zuchowska; R. Steller; W. Meissner Polym. Degrad. Stab. 60, 471, (1995)
6. X. Ramis; A. Cadenato; J. M. Salla; J. M. Moranco; A. Vallés; L. Contat; A. Ribes Polym. Degrad. Stab. 86, 483, (2004)
7. C. L. Carvalho, Master Thesis, Universidade São Francisco, (2005).
8. H. A. A. El-Rehim Photobiol. A: Chem. 163, 547, (2004).
9. D. Bikiaris Polym. Degrad. Stab. 57, 313, (1997).
10. Griffin, G.J.L., British Patent 1,586, 344, in British Patent. (1973).
11. Bikiaris, D. and C. Panayiotou. J. Appl. Polym. Sci, 70(8), 1503, (1998)
12. Shogren, R.L., et al., Polymer, 39(25), 6649, (1998)

13. . Fang, Q. and M.A. Hanna, *Industrial Crops and Products*, 13(3), 219, (2001)
14. Eliasson, A.-C., ed. *Starch in food: Structure, function and applications*. Woodhead Publishing. 384, (2004).
15. Shogren, R.L., Effect of moisture and various plasticizers on the mechanical properties of extruded starch, in *Biodegradable Polymers and Packaging*, Editors. Technomic Publication. p. 141-150. (1993)
16. St. Pierre, N., Favis, B.D. Ramsay, J.A., Vergoogt, H. *Polymer*, 38: 647-656, (1997)
17. Matzinos, P., Bikiaris, D., Kokkou, S., Panayiotou C. *J. Appl. Polym. Sci.*, 79: 2548, (2001)
18. Simmons S., Thomas L.E, *J. Appl. Polym. Sci.*, 58, 2259 (1995).
19. Hernández M, Torruco Juan, Chel Luis, Betancur David. *Cienc. Tecnol. Aliment*, 28, 718 (2008).