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PJBS

ISSN 1028-8880

**Pakistan
Journal of Biological Sciences**

ANSI*net*

Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Morphology-mechanical Property Relationship of Polypropylene/starch Blends

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Abstract: The influence of morphology on mechanical property of several polypropylene/starch (PP/starch) blends of varying compositions was studied. The blends prepared were at wt%PP/wt%starch of 97.5/2.5, 95/5, 92.5/7.7, 90/10, 87.5/12.5 and 85/15. The morphology of the blends observed, using scanning electron microscopy showed them to be immiscible blends with distinct polymer-starch domains at high starch volume fractions (85%PP/15%starch-87.5%PP/12.5%starch), which gradually showed the morphology of well dispersed miscible blends at lower starch volume fractions (97.5%PP/2.5%starch, 95%PP/5%starch, 92.5%PP/7.7%starch, 90%PP/10%starch). The starch domains exhibited characteristic voids which could be due to thermal degradation at the processing temperatures employed. The particle size of the starch domains increased with increase in volume fraction, probably due to the agglomeration and formation of aggregates of the starch granules. The mechanical properties of the blends and viscosity of the blends decrease with increase in starch volume fractions. The mechanical properties were explained using the blend morphologies at various volume fractions.

Key words: Polypropylene/starch, morphology-mechanical property

Introduction

The insertion of starch as a filler in particulate products as a method of producing biodegradable composites have been pioneered by Griffin (1991) and expanded by many others like, Gonsalves *et al.* (1991) Thieubad *et al.* (1997) and Bikiaris *et al.* (1999). Most of the work was focused on the relationship of composition and morphology to mechanical properties. The function of compatibilizers on the properties were also investigated (Bikiaris and Panayiotu, 1998; Prinos *et al.*, 1998 and Bikiaris *et al.*, 1999). Lately the work of Thakure *et al.* (1998) examined the use of starch acetate in influencing the morphology, thermomechanical properties and biodegradability of LDPE/starch blends.

The choice of starch is a natural one, since it is a crystalline polymer having physical and optical properties similar to polythene (PE) as well as being thermally stable up to 265°C. The problems associated with it are those, due to its hydrophilic nature, rendering poor adhesion and the degradation of properties during melt processing.

The addition of granular starch to polyolefins, particularly PE, follows the general trend of filler effects on polymer properties. Mechanical properties decrease as the starch content is increased and the maximum content of starch has been found to be acceptable only at compositions below 15%. In this work, the starch composition by weight (%) to the matrix was kept only to 12%.

In this work, the mechanical properties of starch /PP blends such as tensile strength, elongation at break as well as flow properties, measured as Melt Flow Index (MFI) were obtained and compared to morphology. The morphology was investigated by a general examination of features as well as the function of composition on granule particle size to properties. Griffin (1994) has reported that starch particle size has significant impact on mechanical properties, the smaller the particle size, the better the mechanical properties. In this context, maize and rice were the best options having particle sizes (mean particle sizes) of 14-5 μm .

Materials and Methods

Starch from tubers (mostly cassava) were obtained by commercial sources and was used in the as-received condition. It was however sun-dried for 24 hours and kept in a low temperature oven (90°C) for another 24 hours before

blending work commenced, dryness being a premium in keeping optimum mechanical properties. The polypropylene (PP) was obtained from Propylene Malaysia (Grade A GSE II) in the form of granules and were used without prior pre-treatment. The components were manually mixed prior to feeding into the hopper of an Amut single screw extruder (Model EA Subor) at a temperature of 200°C and a screw speed of 18rpm. These compositions were prepared in the ratio of (weight% starch/weight% PP): 2.5/97.5, 5/95, 7.5/92.5, 10/90, 12.5/87.5 and 15/85. The extrudate was then crushed using a Model RLL Plastics Crusher repeatedly to obtain a homogenous size, deemed sufficient through visual inspection. These were pressed in a hot press into plates of dimensions 3 mm x 150 mm x 150 mm at 170°C and 240kPa.

Samples for morphological examination and examination for fracture surfaces were obtained from the dumbbell specimens used in the evaluation of mechanical property. Specimens for morphological examination were sputter-coated with gold (Polaron Sputter Coater) and observed at 3 magnifications using a Phillips 30XL Scanning Electron Microscope. Samples for MFI were obtained from the granules and measured using a Zwick Melt Indexer with BS 720A as standard method. Mechanical testing was carried out on a Tensometric Universal Testing Machine at a crosshead speed of 1mm/min at 23°C using ASTM 638M as standard. Analysis of the mean particle size were effected manually, using a large number of particles i.e more than 40 at any one time.

Results and Discussion

Mechanical properties: The results of the mechanical properties are shown in Table 1.

As expected, the mechanical properties showed a progressive degradation with increase in filler content. The actual values corresponded to values previously reported (circa 2-3 GPa) but was lower than that reported by Willet (1994), which reported the higher value of 15GPa in LDPE/granular starch fillers, and higher to that reported by Thakur *et al.* (1998) which reported values of 10 MPa at the lowest concentration of starch and around 6-7.5 MPa at the highest concentration of starch (30%). The higher values were attributed to the higher stiffness values of the filler used in Willet's work, who used corn-starch. In our work, the tensile strengths of

Table 1: Mechanical and flow properties of starch/PP blends

Weight % of starch	Ultimate tensile strength, σ_{max} / Mpa	Modulus/GPa	Elongation to break/mm	Granule size/ μ m (measured as mean diameter, d_p)	MFI values g/10 min
0.0	50.9	2.48	7.52	-	4.2
2.5	39.3	2.36	2.63	9.76	4.4
5.0	35.5	2.20	1.70	12.24	4.6
7.5	23.8	1.85	1.09	13.56	4.7
10.0	21.4	1.78	0.69	15.94	4.7
12.5	19.5	1.68	0.51	17.60	4.8
15.0	17.7	1.58	0.41	20.34	4.9

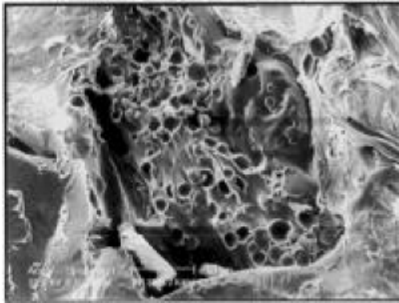


Fig. 1: A SEM micrograph of 85%PP/15%starch at 500X mag.

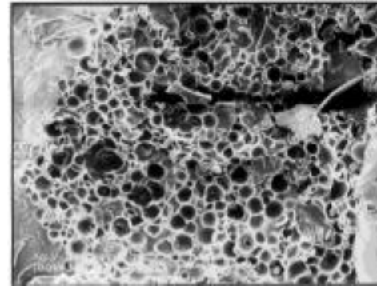


Fig. 4: A SEM micrograph of 90% PP/10% starch at 500X mag

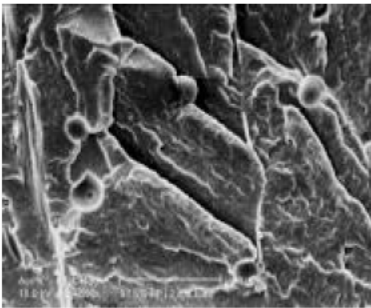


Fig. 2: A SEM micrograph of 97.5%PP/2.5% starch at a mag. of 500X

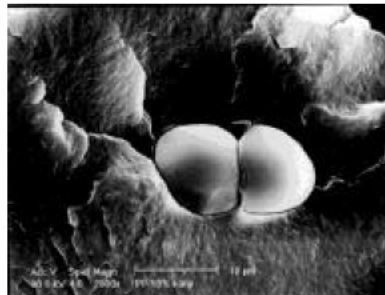


Fig. 5: A SEM micrograph of 90%PP/10% starch at 2K mag

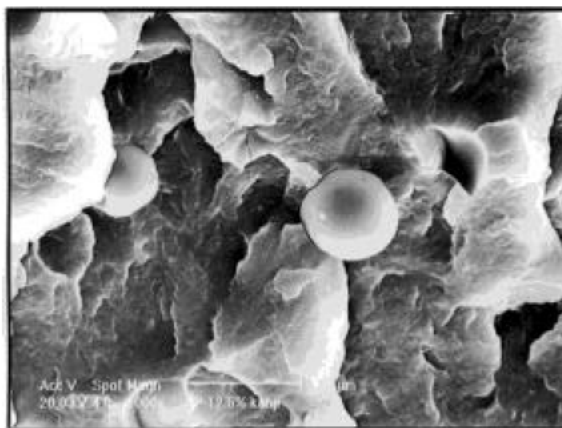


Fig. 3: A SEM micrograph of the 97.5%PP/2.5% starch at a mag of 2K showing a starch particle (in centre of the matrix) loosely adhered to the matrix, with a significant interface visible.

cassava though not measured, must be comparable to the PP used. The elongation to break decreased with increasing stiffness (as a function of the filler content) with the highest value at 100%PP. We can assume that with filler content, the matrix becomes increasingly stiff.

Mechanical properties generally were reported to increase favorably for the blends with the addition of compatibilizers, usually increasing the interfacial adhesion between domains or particles in the matrix (see for example Thiebad *et al.*, 1997, Thakur *et al.*, 1998, Bikiaris *et al.*, 1999) but not all compatibilizers seem to affect in this way. An example of this would be the use of ethylene-co-acrylic as a compatibilizer in LDPE/Granular starch blends (Willet, 1999). In the main, most researchers use LDPE as the main matrix in their work instead of PP, following the pioneering work of Griffin, so the results of our work were mostly compared to that.

Morphology: Griffin reported that SEM work on his LDPE/starch blends showed the starch granules to be encapsulated in the PE, matrix, rendering it unavailable for enzymatic digestion. The biodegradative action of these biopolymers were attributed to the degradation of the starch domains in the matrix when exposed to degradative agents

such as photooxidation, chemical degradation and such like rather than to enzymatic action. However in our work, we do not observe the starch granules to be encapsulated by the matrix. The granules appear to be in an open and accessible structure, loosely adhering to the matrix. We examined micrographs reported in Thakore's work and we found that the presentation of the starch granules were similar to our, i.e. in an open and accessible structure, in what we described as loosely residing in contact with the matrix. Hence compatibilization, if seen to be improving interfacial adhesion did not affect the mechanical properties much. More insight into the old theory of compatibilization and increase in interfacial adhesion would have to be made in this research. An examination of the blends investigated in this work (Fig. 1-5) showed the morphology to be starch granules, dispersed in the matrix with clearly demarcated domains of starch at higher starch content (Fig. 1). Dispersion of the starch is also a function of the starch content, showing higher dispersion at the lower content (Fig. 2).

An examination of the blend at the same composition clearly showed the starch granules to be loosely, adhered to the matrix, contributing to the decrease in mechanical properties. (Fig. 3)

We can therefore, infer that at lower starch content the particles are well dispersed granules throughout the matrix but at higher starch content the granules are grouped together in domains, in contrast to individual granules (Fig. 4). The starch granules may also be present as agglomerates as evidenced by SEM micrographs in Fig. 5. The improvement in mechanical properties evidently is not merely a matter of surface adhesion of filler-matrix but also one of particulate dispersion. This was the observation of Thakur *et al.* (1998) as well.

The granule size was found to increase with increasing filler content, again due to agglomeration of the particles. This contributed to the reduction in mechanical properties. This problem could be alleviated by reducing agglomeration through super-drying the starches (Griffin, 1977).

Melt Flow Index: The melt flow index (MFI), a measure of the inverse of its viscosity increased with increasing starch content, making the viscosity decrease. This is expected behaviour. Griffin (1994) advised keeping the starch content in the polyolefinic blends around 6% to maintain the consistency of the MFI values, but generally he observed that the addition of starch did not affect the MFI values drastically. In the blends studied the decrease in MFI was observed but did not depreciate significantly. However in Thakore's work using the starch and starch acetate, interesting results were reported; there was no significant change at filler content below 10% but thereafter till 20% was an exponential jump which did not vary until the maximum starch content of 30%. Presumably the starch acetate had this effect on the LDPE rather than just the starch. Griffin (1994) reported that in lieu of the insignificant effect of starch on the MFI values, the blends

could be processed without difficulty using conventional processing machines and indeed, work in our laboratories proved this (Azhari and Ahmad, 1999). Processing temperature rather than starch content affected the processability of the biodegradable polymers.

Much of the work on starch particulate fillers centres around starch/PE blends, following the pioneering work of Griffin working independently in Brunel University, Uxbridge. The work in this paper used PP instead of PE. However much of the general properties of the starch/PP blends were again confirmed in the starch/PP blends. The mechanical properties were found to decrease with increase in starch content. Morphological examination showed that, apart from the usual discussions on filler-matrix adhesion as contributing to the mechanical properties, an equally important aspect that needs to be further elucidated is the starch particulate size and dispersion. This will need a micron analysis of the mechanical properties and the factors contributing to that.

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