

THE USE OF NOVEL BIOMATERIALS FOR AFFORDABLE PACKAGING

Karnik Tarverdi, and Kun Qi
Wolfson Centre for Material Processing
Brunel University London, UK

Abstract

The effects of the use of biomaterials for the development of novel packaging composites have been evaluated. An increase in the amount of treated fillers improved the dispersion of the particles and consequently led to an enhancement of the mechanical properties of the materials. The composites were melt-blended using co-rotating intermeshing twin screw extrusion technology and although there can be degradation of the organic additives during extrusion processing, it did not affect the dispersion of the novel biocomposites and the biofillers.

A range of techniques used to characterise these materials will be discussed, including morphology, differential scanning calorimetry, (DSC), Scanning electron microscopy (SEM), including experimental techniques like mechanical property evaluations.

Introduction

Non-food starch reclaimed from starch production industry is one of the low cost naturally occurring polymers, abundantly availability and a renewable resource and it also could be a pollutant if washed into waterways. The use of starch in the packaging area however has been limited due to its hydrophilic nature. There were many attempts to modify the hydrophilic property of starch. One of the most efficient methods is compounding of starch with other suitable polymer materials to produce more hydrophobic starch based materials.

This study is focused on improved packaging materials that will be biodegradable and recyclable and will reduce wastage by improving the storage stability and shelf life of food during transit between the producer and the urban consumer, reduce the level of adulteration via sealable and tamper-evident features, reduce urban solid waste from packaging going to landfill, and improve health and well being of the population by improved retention of nutritional quality and reducing risk of spoilage. To achieve these objectives, this paper will develop innovative bio-based hybrid polymer packaging films with selective humidity and permeability control and improved shelf-life performance with enhanced environmental characteristics. The packaging systems will be based on the incorporation and compatibilisation of presently under used agri-waste (certain starch from waste water treatment) at low costs into conventional and other bio-based polymers. The treatment of the agri-waste will

contribute to minimising significant waste issues with regard to starch being washed and processed for food and other uses.

Materials and Experimental Procedure

Materials

LDPE polymer used in this study was Dow film grade: 410E, which has a melt flow rate (MFR) of 2 g/10 min (190°C/2.16 kg). Glycerol, ACROS Organics was purchased from SigmaAldrich. DuPont™ Fusabond® functional polymers (maleic anhydride grafting) was used as compatibilizer to help bond together dissimilar polymers and starch.

Several reclaimed starch samples generated from waste during starch production were collected by partners in India, refined and supplied to the consortium from Hennock International Ltd, a partner in the project. For comparison a food grade tapioca starch with brand name NEWGRADE (Thai Wah Public Company Limited, Thailand) was also used.

The biodegradable polymers are from various sources. G-Polymer™, a degradable/water soluble PVOH from Nichigo. Ecoflex™, a biodegradable aliphatic-aromatic polyester PBAT from BASF. Supplied to by solutions4plastic a partner in the project. Bio-Flex® F1110 and F1130, biodegradable polymer-blend based on polylactic acid (PLA), copolyester and additives made by FKUR Kunststoff GmbH.

Sample Preparation

The selected different starches were dried at 80°C in an oven for 24 hours, and premixed with glycerol and polymer with different percentages. Compounding and processing was carried out using a co-rotating intermeshing 25 mm diameter twin screw extruder and the modular screws were assembled with a special design semi severe screw profile with a volatilisation zone three quarters downstream of the extruder length Figure 1.

The extrusion blending was carried out with barrel temperatures of 60°C, 120°C, 150°C, 140°C, 140°C, 140°C, 120°C, from the hopper to the die and a screw speed of 100-300 rpm. The Polymer/starch compound was extruded through a 6 mm die and pelletized.



Figure 1. 25mm twin screw extruder used for polymer/starch composite processing.

The polymer/starch compounds were dried at 80°C in an oven for 24 hours before subjecting the blend to continuous extrusion processing and film blowing.

Characterizations

Scanning Electron Microscopy (SEM)

The dehydrated starch samples were placed in a vacuum evaporator and covered with carbon tape and coated with gold using sputter coater for 30 seconds to obtain conductive samples for SEM. The samples were analyzed using a scanning electron microscope (Zeiss Supra 35VP instrument) at 12kV accelerating voltage.

Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis tests were carried out on the samples under nitrogen at 50 mL/min using TA Instruments (TGA500) to determine the thermal stability of the compounds. All the test samples were heated up to 600°C at a heating rate of 20°C/min. Evaluation was carried out using Universal Analysis 2000 V4.3.

Differential Scanning Calorimeter (DSC)

DSC analyses were carried out using TA Instruments DSC Q1000. The test samples were dried under a vacuum at 120°C for 24 hours. The dried samples were encapsulated in aluminum pans and placed in the DSC cell. Initially, the samples were heated and kept at 200°C for 5 minutes to destroy their prior thermal history. Afterwards, the cooling scan test was recorded from 200°C to 20°C at rate of 10°C/min. The tests were carried out under nitrogen atmosphere.

Gas and Moisture Permeability Measurements

The Water vapor permeation rate (WVTR) of polymer and polymer/starch films were performed at 39.8°C and 90% HR by using Totalperm H₂O Permeability Test. Oxygen permeation (OTR) were tested by using PermTech Multiperm for O₂ Permeability Test.

Mechanical Properties Tests

Mechanical testing was carried out on a Zwick / Roell kind Zmart-PRO tensile testing machine with TestXpert III program. The tests were carried out in an air conditioned room at 23°C and a relative humidity of 43%. The specimens were cut from extruded and blown film samples. At least five specimens of each sample were measured following BS EN ISO 527-1:2012.

Results and Discussion

Starch preparation and Extrusion Modification

Scanning electron microscopy revealed the morphology of the starch granules. The granules of native tapioca starch have spherical shapes with truncated extremes and some oval shapes (Figure.2). Typical native tapioca starch has diameter range from 10 to 15 micrometers.

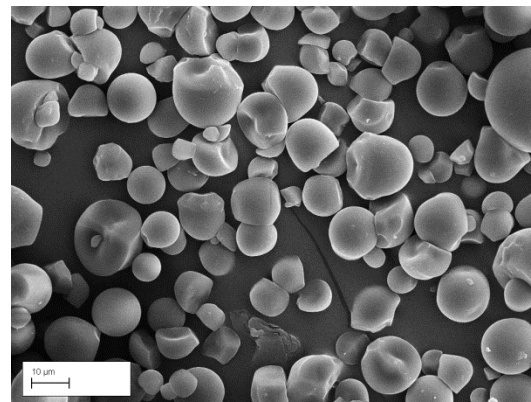


Figure 2. Morphology of tapioca starches SEM images.

The native starch consists of polydisperse anhydroglucose homopolymers in the form of amylose and amylopectin depending on the botanical origin of the starch. Amylose is a linear polymer with relatively lower molecular weight compared to the highly branched polymer amylopectin. The amylose content in native tapioca starch was of the region of 19.7% as reported by Herrero-Martinez [1], whereas amylose content in corn starch and wheat starch are well over 27%. Low amylose content means tapioca starch can be more suitably utilized as thermal plastic using extrusion compounding with the inclusion of flow promoters.

In our study, up to 50% (weight) starch has been compounded with LDPE and biodegradable polymers using extrusion processing. Trials have been carried show several facts affect the quality of Starch/polymer filaments produced through extrusion.

Starch/polymer formulations including glycerol as plasticizer resulting in good surface finish during film blowing exercise. Addition of processing aids like stearates can also improve surface finish.

Sharkskin and instability developed at surface of extruded filament when the amount of tapioca starch is increased. Addition of maleic anhydride as compatibilizer (LDPE-g-MAH, 10% based on Tapioca) can impart very good surface finish.

Temperature and moisture content of starch are critical. Moisture in the starch can cause foaming of extruded products even at very low extrusion temperatures.

Apart from blending of starch, polymer, and other additives, the extrusion processing with the appropriate screw profile will also help in dispersing and distributing the starch granules and effectively plasticizing the starch twith the help of the glycerol.

Polymer/starch film blowing extrusion

Polymer/starch compounds were processed using in house film blowing line for film blowing experiments (Figure 3). Some of the compounds failed to produce blown film due to various reasons. Mainly because low melt strength of polymer/starch compounds.

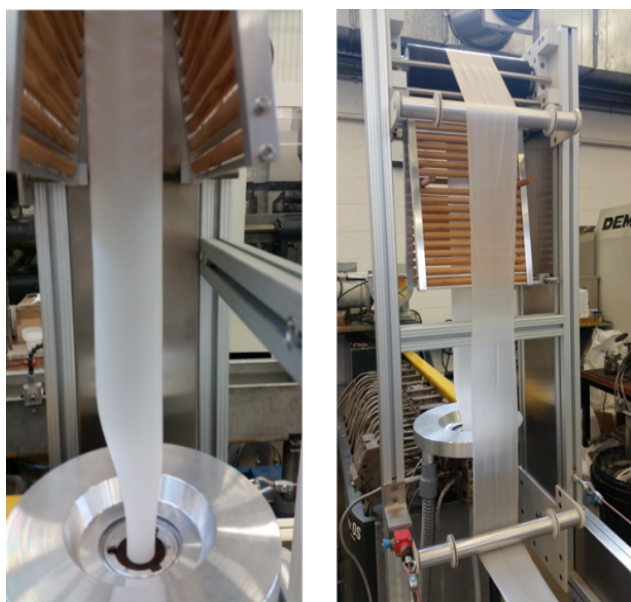


Figure 3. Film blowing trials for polymer/starch materials.

During certain processing conditions bubble may collapse and air escapes through the bubble due to the presence of solid hard un-dispersed particles, this can take

place with some of the reclaimed tapioca starch compounds. Refining the reclaimed tapioca to remove the hade particles is particularly important for successfully film production.

Compounds with plasticizer or compatibilizer have very good bubble stability and drawing down ability and thus better possibility of successfully film production.

Thermal analysis of polymer plays an important role in the practice of film blowing. Take PBAT for example. TGA demonstrate a two-step degradation for PBAT, and thermal stability levels up to 350C (Figure 4) DSC results show PBAT melting temperature 120 °C (Figure 5) but a very low crystallization temperature 38°C which presents problems for the film blowing process.

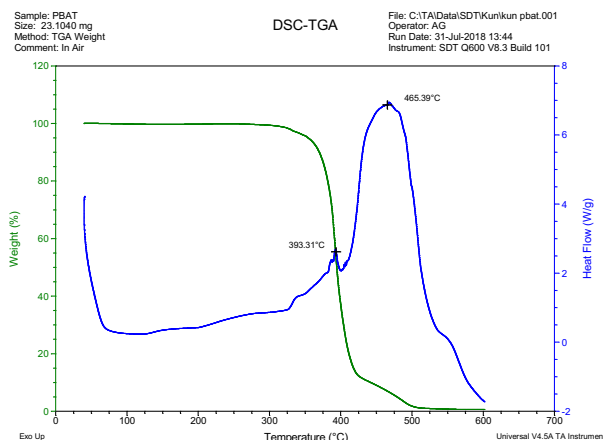


Figure 4. TGA measurement of PSAT.

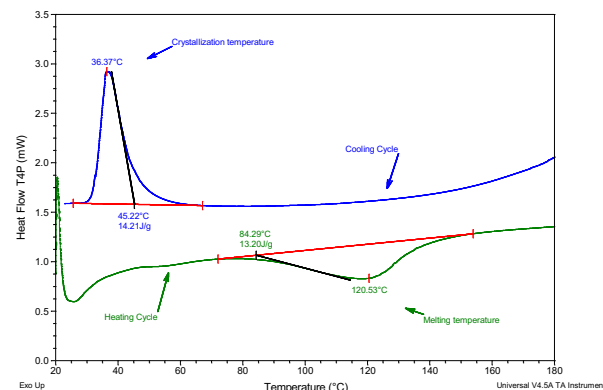


Figure 5. DSC Measurement of Ecoflex™ (PBAT).

Compounding starch with PBAT accelerated crystallization of PBAT. DSC results (Figure 6) show by adding starch to PBAT crystallization temperature increased from 38°C to 75°C which improved the film blowing process ability.

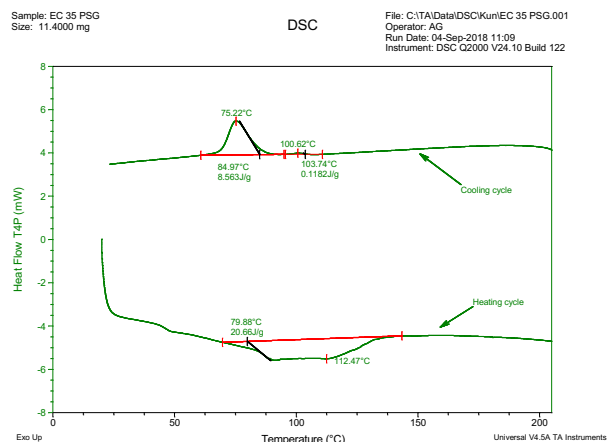


Figure 6. DSC Measurement of EC35TSG (PBAT + 35% Starch + Glycerol).

14 different samples of India waste/recycled starch sample were evaluated. These samples demonstrated different properties in terms of appearance color and odor. Some sample with visible fiber which affect film blow experiments. Six of these starch samples were selected to compound with LDPE and subjected to film blow process. They were sample Nos 1, 7, 8, 9, 12, and 13. As demonstrated in Table 1 and Figure 7.

Table 1. Film blowing feasibility of blends of LDPE with selected starch samples.

Starch	Formulation (weight)			Film blowing easy 1-5 difficult	Colour light 1-----dark 5	Odour light 1-----strong 5
	starch	LDPE	Glycerol			
Food Grade	30	70	13	1	1	1
No 01	33	67	14	5	3	4
No 07	33	67	14	4	3	4
No 08	30	70	13	1	5	5
No 09	33	67	14	1	1	1
No12	30	70	13	4	4	5
No 13	33	67	14	1	2	2



Figure 7. Blown film sample from blends of polymer with reclaimed starches.

Blends of LDPE with starch No 8, No 9, and No 13 (blends code 3008G, 3309G, and 3313G) had better

bubble stability and stable film drawing properties which were as good as the control LDPE with film (blend code 30TSG), resulting in very stable film production. For blends of LDPE with starch No 1, No 7, and No 12 (blends code 3301G, 3307G, and 3012G) bubble were not stable; the bubble collapsed and broke through by the presence of solid hard particles, therefore continuously film blow were not achievable.

Properties of Polymer/starch Film

Gas and moisture permeability measurements are shown in Table 2. The water vapor permeation rate (WVTR) results demonstrate that there is little increase of water vapor with starch content but it is still within the normal levels [2 and 3]. The oxygen permeation rate (OTR) also very for different polymers and starch..

Table 2. Water vapor and O2 permeability testing results of selective film samples.

Film samples	WVTR g/m2/24h	OTR cm2/m2.24h
LDPE+30% Tapioca Starch	9.9	1685
LDPE+30% Reclaimed Tapioca Starch	14	860
PBAT+35% Tapioca Starch	1873	617
PVOH water soluble	460	0.044

Mechanical properties of the starch based polymer films were determined as the tensile strength and elongation at break (Figures 8 and 9). It is obvious that the mechanical properties of the films depend significantly on the polymer used. Pure PVOH has the highest tensile strength but it is very weak in terms of elongation at break. Pure PBAT has a high tensile strength as well as good elongation at break.

It was also demonstrated that the PBAT/starch (35% starch) film has mechanical properties comparable to pure LDPE film. LDPE with reclaimed starch (formulation 3008G) has the comparable mechanical properties with that of pristine starch (30TSG).

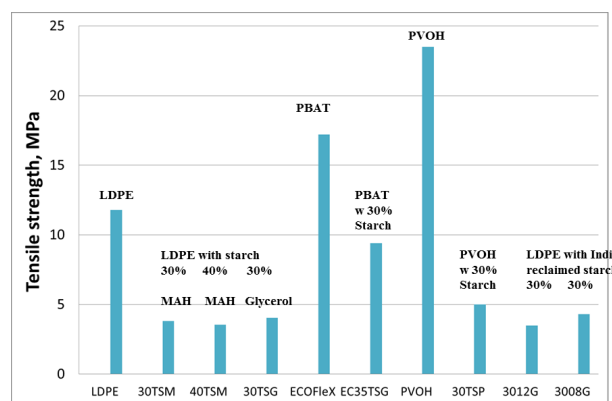


Figure 8. Tensile strength of selected blown film samples.

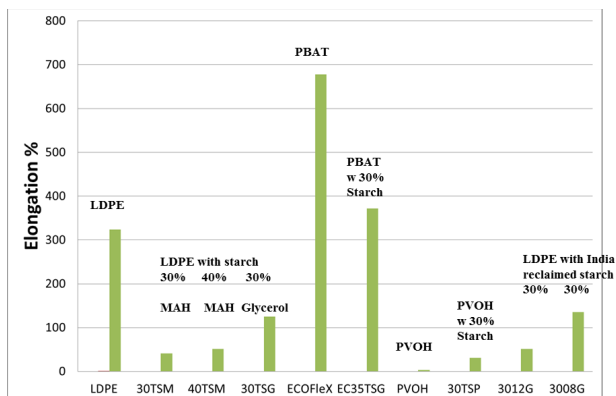


Figure 9. Strain at break of selected blown film samples.

Conclusions

Reclaimed tapioca starch from India was compounded with LDPE; blown films of up to 30% starch were successfully carried out. Utilization of the recycled tapioca starch will bring down the cost of film and make the product more affordable for many countries where the biodegradable polymers are too expensive to use for packaging.

Fully bio-degradable PBAT (Ecoflex) and PBAT/starch films were prepared using in house lab extrusion processing and film blowing equipment. The PBAT/starch (35% starch) film with mechanical properties comparable to pure LDPE film.

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