

Processing and Characterization of LDPE/Starch Products

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ABSTRACT: Low-density polyethylene/plastisized starch blends varying in starch content were processed by conventional extrusion, injection-molding, and film-blowing techniques. Polyethylene-*g*-maleic anhydride (PE-*g*-MA) was used as a compatibilizer. X-ray diffraction was used to investigate starch destructure during extrusion and on subsequent processing. The effect of starch content on the blends was evaluated by mechanical property measurement and scanning electron microscopy. Starch, except for being a biodegradable material, can also act as a reinforcing agent. The reinforcing effect of starch was only realized in injection-molded materials. Processing–structure–property relationships could explain this behavior. The present study also brought out the effect that the degree of molecular orientation existing in a polymeric matrix may have on the coupling performance of an adhesion promoter. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2548–2557, 2001

Key words: polyethylene; starch; extrusion; injection; film blowing

INTRODUCTION

Starch is an inexpensive natural biopolymer, which is totally biodegradable in a wide variety of environments. Different approaches have been adopted to use starch, in combination with other synthetic thermoplastic polymers, for the production of totally or partially biodegradable materials.^{1,2}

Natural starch exhibits a pronounced macromolecular structure, which is suitable for the production of bioplastics. However, prior to production of such materials, the structure of native starch should be suitably modified. This is necessary, because starch degradation starts at a temperature lower than its melting point, and thus native starch cannot be processed by conventional

plastics technology without any modification. During the modification process structure heterogeneity of native starch, brought about by the poor interpenetration of its macromolecules, is also eliminated, so as to convert it to an essentially homogeneous material suitable for thermoplastic processing.¹ The production of thermoplastic out of native starch involves the use of a plastifying agent, mainly glycols, which lower the melting point of starch, and melting of the mixture by the introduction of mechanical and heat energy. Today starch plastification is commonly carried out by extrusion in a temperature range of 120–220°C.³

The kind of native starch, moisture content, pressure, temperature, type and amount of plasticizer are significant factors influencing the conversion process. Thermoplastic starch with different properties can be prepared by altering one of these factors. Although starch in its native form can also be used for the preparation of blends

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with other synthetic thermoplastic polymers such as polyethylene, the finer dispersion of plasticized starch in the polymer matrix makes it more suitable.⁴ But even in this case the selection of a suitable phase mediator/compatibilizer, for increasing the homogeneity and interfacial adhesion of the starch/synthetic polymer blend, is also necessary.

Our preliminary studies to producing substantially biodegradable low-density polyethylene/starch products suggested that blends with increased mechanical properties could be prepared through reactive compatibilization with PE-*g*-MA copolymer.⁵ Compared with other compatibilizers such as ethylene-acrylic acid copolymer (EAA) and ethylene-vinyl acetate copolymer (EVA), polyethylene-*g*-maleic anhydride was found to be the most successful.⁴ The improvement in the mechanical properties of the blends was attributed to the fine dispersion of starch in the low-density polyethylene (LDPE) matrix caused by the use of PE-*g*-MA.⁶

The objective of this study was the production of LDPE/starch products by means of conventional plastic processing technology such as extrusion, injection molding, and film blowing and their characterization.

EXPERIMENTAL

Materials

The low-density polyethylene (LDPE), provided by Alcudia, was appropriate for packaging applications with a melt flow index of 2.16 g/10 min at 190°C. An ethylene-*g*-maleic anhydride (PE-*g*-MA) copolymer containing 0.9% maleic anhydride groups, as determined by titration with alcoholic solution of NaOH in toluene, was generously supplied by Du Pont under the trade name MB-226D. The native corn-starch containing 30 wt % amylose and 70 wt % amylopectin was supplied by Amylum (Greece). The moisture content of corn-starch powder, as estimated by thermogravimetric analysis (TGA), was 13 wt %.

Extrusion

Thermoplastically processable starch (TPS) was prepared in one step by extrusion processing with a Leistritz corotating, intermeshing twin-screw extruder, equipped with a modular type barrel,

heated by induction. As the most commonly used equipment for starch plastification today, it consisted of interchangeable screw elements to adjust conveying and mixing capacity. The screw configuration, suggested by U. Funke et al.,⁷ was adopted in this study. Glycerol was used as plastifying agent at a 20 wt % level,¹ and was continuously injected into the second zone of the extruder.

Starch extrusion was carried out at the following conditions: barrel temperature: 60/100/150/180/170/130/90°C; screw speed: 80 rpm. The venting port, located at the sixth zone, was kept open during processing, so as to allow moisture removal. The moisture content of extruded starch was 3.3 wt % as estimated by TGA.

Melt compounding of TPS with LDPE was carried out in a laboratory-scale Haake conical twin-screw extruder (TW 100), at the following conditions: temperature profile: 160/180/180/180°C; screw speed: 80 rpm. For LDPE/TPS blends, five different levels of TPS were used, namely, 10, 20, 30, 40, and 50 wt %. PE-*g*-MA was used as compatibilizer at a 10 wt % level based upon TPS, in accord with previous studies suggesting that this amount of compatibilizer results in blends with optimum properties.⁶

Injection Molding

LDPE/TPS pellets obtained by extrusion processing were transformed into ASTM D638, Type dog-bone specimens, approximately 3 mm thick, using a 25-ton Arburg Allrounder 221E/150R injection-molding machine. The experimental molding conditions were: temperature profile: 170/180/190°C; injection pressure: 60 bar, mold temperature: 20°C. The conditions used for the production of LDPE specimens were: temperature profile: 200/210/220°C; injection pressure: 60 bar, mold temperature: 20°C.

Film Blowing

Pelletized LDPE/TPS extrudates were transformed into films, having an average thickness of 50 microns, using a three-zone Tacke extruder equipped with a blowing head. The temperature profile was: 140/170/170/140°C.

X-ray Diffraction

The modification of the physical structure of native starch with extrusion was studied by X-ray

diffraction. A Bragg-Brentario diffractometer, Siemens D500, equipped with a secondary monochromator, employing Cu K α radiation was used. The spectrum was recorded over the range of 2θ angle, 5–65°.

Mechanical Properties

Tensile strength, modulus and elongation at break were measured on an Instron mechanical tester, model 1122 according to ASTM D638 method. The crosshead speed was 5 mm/min. Six measurements were conducted for each sample, and the results were averaged to obtain a mean value.

Izod impact measurements were performed on a Tinius Olsen instrument according to ASTM D256. Six measurements were conducted.

Prior to mechanical measurements, the samples were conditioned at $50 \pm 5\%$ relative humidity for 48 h at ambient temperature, in a closed chamber containing a saturated Ca(NO₃)₂ · 4H₂O solution in distilled water (ASTM E-104).

Scanning Electron Microscopy (SEM)

Specimens were fractured after freezing in liquid nitrogen and the exposed surfaces either treated with HCl acid (1 N) for removing the starch component or untreated were observed with a scanning electron microscope (JEOL, JSM-840A). Film surfaces were also examined. All surfaces were coated with gold to avoid charging under the electron beam.

RESULTS AND DISCUSSION

X-ray Diffraction Pattern Change of Starch with Extrusion Processing

Starch is a polymeric mixture of primarily linear (amylose) and branched (amylopectin) α -D-(1–4) glucan molecules. Amylose molecules have a molecular weight of 0.1–1 million, while the amylopectin molecules have molecular weights as high as 10–1000 million. Small amounts of noncarbohydrate constituents such as lipids, phosphorous, and proteins are also present in starch.⁸ Native corn starch is present in semicrystalline granules of approximately 5–25 μ m in diameter, being mostly polyhedral in shape and characterized by almost perfect left-handed, six-fold double helices.⁹

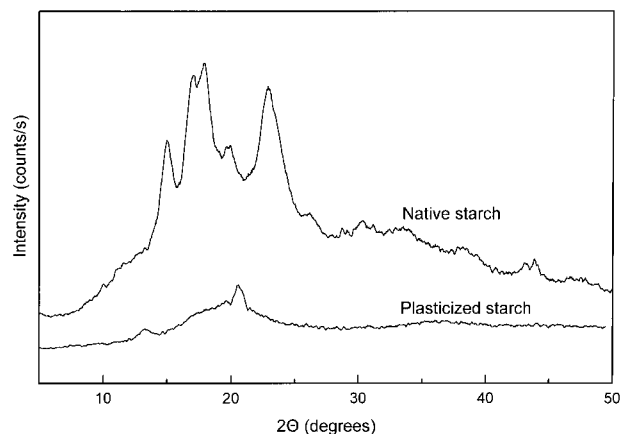


Figure 1 X-ray patterns of native and plasticized starch.

During extrusion granular starch is progressively compressed and transformed into a dense, solid, and compact material.¹⁰ Shearing of the molten granules destroys their organized structure, and crystalline, granular starch is converted to a dispersed, essentially amorphous, homogeneous material. The X-ray diffraction patterns of the native and plasticized starch are presented at Figure 1.

The unprocessed corn-starch gives the well-known A-type spectrum.⁹ When extruded with glycerin, a significant reduction in crystallinity is observed and a fully transparent material is produced. The formation of a new structure can be also deduced by the appearance of new peaks, the most obvious located at $\sim 13.5^\circ$ and $\sim 20.5^\circ$ 2θ angle. This structure has been attributed to a complex formation between the amylose and the lipid fraction of starch, probably as a helical form of six and/or seven glucose residues per turn.¹¹ These two small peaks indicate that a very small amount of crystallinity still exists in the material. It is obvious that a fully amorphous material may be produced if the thermoplastic material was extruded for a second time. But in this case, a significant deterioration/reduction of the molecular weight could take place, which might reduce the properties of the thermoplastic starch.

During the compounding, injection-molding or film-blowing steps plasticized starch is subjected to additional thermomechanical treatment, and thus further destruction of its crystalline fraction would be expected. So, the diffraction scans for LDPE/TPS blends were also examined. A typical diffraction pattern of LDPE/TPS blends after the

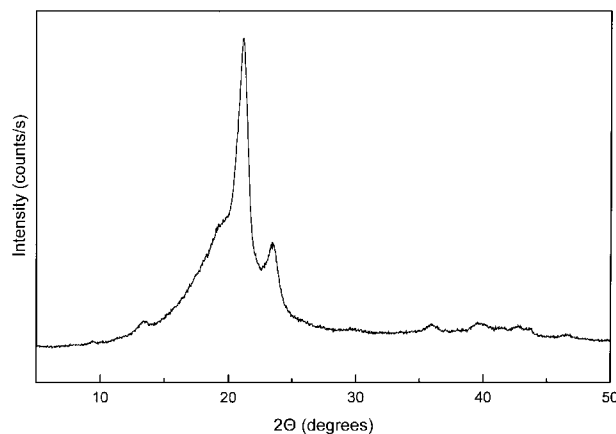


Figure 2 Typical X-ray pattern of LDPE/TPS blends (30 wt % TPS content).

compounding step is represented in Figure 2. The sharp peaks at 21.3° and 23.8° 2θ angle are the well-known 110 and 200 reflections from the crystalline domains of polyethylene, while the peak at $\sim 13.5^\circ$ and the shoulder at $\sim 20^\circ$ 2θ are reflections corresponding to the starch crystalline structures.¹² Figure 3 shows that the peak, at $\sim 13.5^\circ$, obtained from the LDPE/TPS blend, appears clearly to be blunter than that obtained from plasticized starch, suggesting that further destruction of crystallinity can occur during subsequent processing.

Blend Morphology

In polymer blends, it is essential to study the morphology of the final product because most of its properties, especially its mechanical properties, depend on it. In most cases, the major component of the blend forms the continuous phase, whereas the minor component is the dispersed phase. However, as the volume fraction of the minor component increases, at a certain value, depending on the nature of the polymers (interfacial tension, viscosities) and the processing conditions, continuity of both polymer phases can be obtained.¹³ Thus, in the LDPE/TPS blends, for low starch content, starch is expected to be the dispersed phase.

Another parameter affecting the morphology and properties of polymeric blends is the use of a compatibilizer. Preliminary studies⁶ showed that a finer and a more uniform dispersion of starch in the LDPE matrix can be achieved in blends compatibilized with the PE-g-MA copolymer. Polyeth-

ylene cannot react with starch, and does not exhibit any compatibility with it. The hydrophilic nature of starch, owing to its hydroxyl groups, adversely affects the miscibility and adhesion to hydrophobic thermoplastic matrix, and as a result, LDPE/TPS blends exhibit inferior mechanical properties. The excellent performance of PE-g-MA as a compatibilizer could be attributed to the following two factors: (a) the ability of the maleic anhydride groups to react with the hydroxyls of starch to form ester linkages; the formation of hydrogen bonding between the hydroxyls and the carboxylic acids resulting from the hydrolysis of the anhydride,^{6,14} and (b) the great compatibility of the grafted polyethylene (PE) chains of the compatibilizer with the main PE phase.

Considering the viscosities of the two components, starch exhibits a lower viscosity compared to LDPE, being about 20 times lower as deduced from the melt flow index at 190°C .⁶ In general, higher matrix viscosity is associated with finer dispersion of the minor phase component.¹⁵ However, in the absence of a compatibilizer, the morphology generated by rheological parameters may be unstable and coarsening can occur.¹⁵ Thus, the use of a compatibilizer is considered necessary.

In Figure 4, the SEM images of injection-molded LDPE/TPS specimens are presented. Starch particles, in blends with up to 30 wt % starch content, could be effectively removed during the fracture of the specimens leaving cavities in the matrix, while in blends with 40 and 50 wt % starch content, HCl acid treatment was a req-

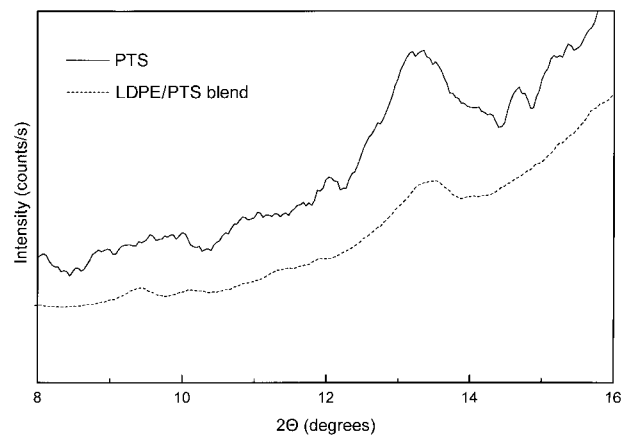


Figure 3 Comparison of the $\sim 13.5^\circ$ starch reflection from plasticized starch and LDPE/TPS blend (30 wt % TPS content).

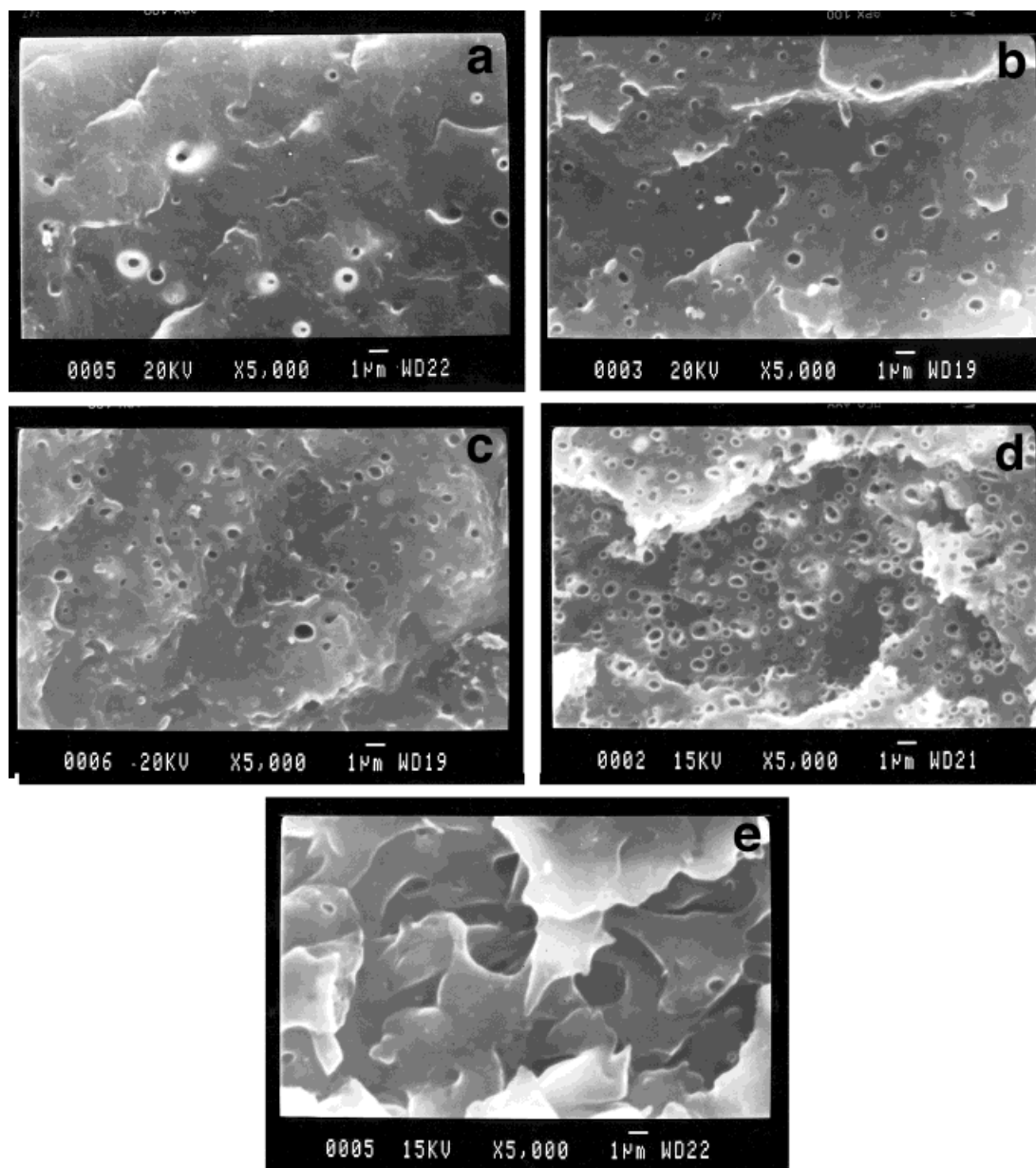


Figure 4 SEMs of LDPE/TPS injection specimens with (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %, and (e) 50 wt % TPS content.

uisite for removing the starch phase and make possible the examination of the samples under microscope. Looking at the micrographs, it is clear that in blends with starch content up to 40 wt %, as indicated by the presence of cavities, the dispersed phase consists of plasticized starch, while at 50 wt % starch content, a cocontinuous structure is formed.

Blends containing up to 40 wt % starch exhibited a similar morphology. Starch droplet-like

particles not larger than $\sim 1\text{--}1.5\ \mu\text{m}$ are homogeneously dispersed throughout the polymeric matrix. However, at 40 wt % content, although the starch droplets are still well dispersed within the polymeric matrix, they apparently show a tendency to form clusters and, as implied by the presence of elongated cavities, droplet coalescence probably started taking place. At 50 wt % content, the coalescence process was apparently further intensified, under the experimental con-

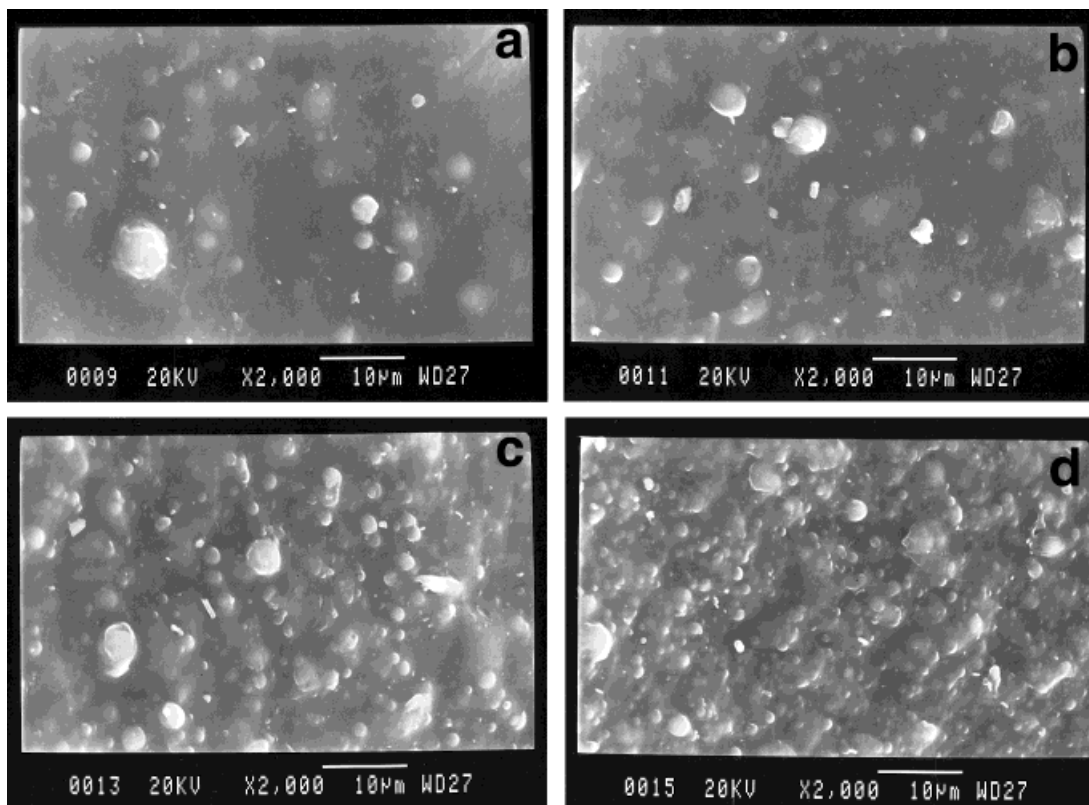


Figure 5 SEMs of LDPE/TPS films with (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, and (d) 40 wt % TPS content.

ditions used, resulting in a fully cocontinuous structure.

Comparison of the size of the granules existing in native starch (5 to 25 μm in diameter⁹) with that of the particles present in the blends it clearly shows that at the present conditions, starch granules underwent complete melting and, as suggested by the X-ray diffraction data, extensive deconstructurization as well. So, it would appear that the sufficient starch plasticization achieved, the effective compatibilization performance of PE-*g*-MA and the selection of suitable processing conditions can account for the fine dispersion of the starch component within the polymeric matrix observed in this study. This fine dispersion and the small particle size of TPS in the LDPE matrix is the reason that LDPE/TPS blends have better mechanical properties from LDPE/native corn starch blends.

The highest starch content in the films produced was 40 wt %. Blends with 50 wt % starch content could not be transformed into films without processing problems. It is believed that the

remaining water in the plasticized starch, whose content in the blend increases with increasing starch content, is probably associated with the difficulties encountered.

SEMs of blown films containing up to 40 wt % starch are shown at Figure 5. All films exhibited a similar morphology, with the starch droplet-like particles being homogeneously dispersed throughout the polymeric matrix. The average size of the particles appears to be of ~ 1.0 – $5 \mu\text{m}$ in diameter, although smaller and larger particles of ~ 1 and $5 \mu\text{m}$, respectively, can also be seen. It is also worth noting that the size of starch particles in the films is larger than that in the injection-molded specimens. As mentioned earlier, the type of morphology, formed during processing, does not only depend on the nature of the polymers, their volume, and the type or amount of compatibilizer used, but on the processing conditions as well.¹³ Because the same blends containing the same amount of PE-*g*-MA were used for the preparation of the films and injection specimens, it would appear that the observed difference is

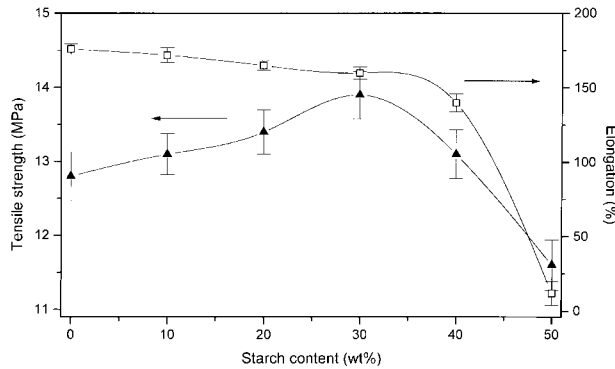


Figure 6 Variation of the tensile strength and elongation at break of LDPE/TPS injection specimens with TPS content.

related to the processing conditions existing at the two different processes.

The last step of the injection-molding process is the cooling of the specimens in the mold, initially under high pressure being decreased as cooling proceeds, while in the blowing process the films, as get drawn by the nip rolls of the machine, are cooled by means of air under relatively low pressures. In the latter process the temperature of the blowing head was 140°C, and the temperature of the film had to be kept above 60–70°C. Under these conditions the remaining water and the glycerol existing in TPS could possibly evaporate leading in starch particle swelling (as in foaming) or another reason may be the release of stresses (as in die swelling).

Mechanical Properties

The variation of the tensile strength and elongation at break of starch/LDPE injection-molded specimens with the starch content is shown in Figure 6. The tensile strength increased with increasing starch content, passed through a maximum at 30 wt % content, and fell significantly thereafter. The elongation at break decreased with increasing starch content. The change was progressive up to 30 wt %, more significant at 40 wt %, and became especially significant for blends with 50 wt % starch content, actually reflecting the change in the tensile strength of the material. The Young modulus increased with increasing starch content (Fig. 7), its change mirroring the change of the other two parameters, i.e., tensile strength and elongation at break.

Both natural and plasticized starches are especially strong and stiff materials.¹ The plasticized starch prepared in this study by injection molding, exhibited a tensile strength value of 18.5 MPa, modulus of 2 GPa, and elongation at break of 0.8%. Comparing these values with those measured for polyethylene, 12.8 MPa, 162.7 MPa, and 176% respectively, it is apparent that in composite materials made of the two components, under certain conditions, starch would act as reinforcement.

The increase in the tensile strength of blends with 10, 20, and 30 wt % starch to 13.1, 13.4, and 13.9 MPa, respectively, compared to 12.8 MPa for polyethylene, can apparently be attributed to the reinforcing effect of the starch component. It would appear that the morphology obtained allows the successful stress-transfer from the weaker polymeric matrix to the stronger and stiffer starch particles resulting in a material with increased mechanical properties. For the blend with 40 wt % starch content the tensile strength (13.1 MPa) is still higher from that of LDPE, but in the case of the 50 wt % starch content, the tensile strength of the blend decreases to 11.6 MPa. Thus, the starch component at 50 wt % content not only cannot act as reinforcement, but in the contrary, weakens the polymeric matrix. This decrease in the tensile strength is also associated with a significant decrease in elongation at break from 176% for polyethylene to 12% for the blend. So, although a stiffer material is produced as suggested by the increased modulus (Fig. 7), its strength cannot be realized, because it fails at low elongation.

Looking at the fracture images of the untreated surfaces in Figure 4(a), (b), and (c), broken starch

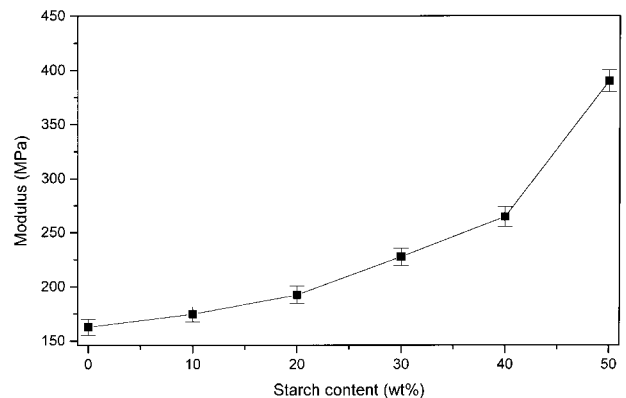


Figure 7 Variation of the modulus of LDPE/TPS injection specimens with TPS content.

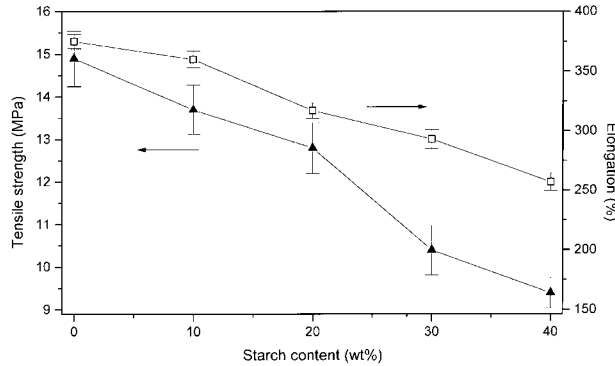


Figure 8 Variation of the tensile strength and elongation at break of LDPE/TPS films with TPS content.

particles cannot be seen, implying that failure takes place at the weak particle/matrix interface. So, when starch is incorporated into the polymeric matrix an interface of weakness is also introduced. At this interface cracks can be formed when the material is subjected to a certain stress.

Existence of phase cocontinuity in blends containing 50 wt % starch it also provides the material with a weak, continuous interface, and it would appear that crack propagation by means of this interface could probably account for the failure of the material at low elongation (12%).

However, if the starch phase exhibits a continuous character in blends containing 50 wt % starch, then it can be safely anticipated that the onset of continuation is related with lower starch concentrations. Such considerations and the microscopic evidence suggesting starch particle clustering in the blends containing 40 wt % starch could also explain the failure mechanism of the material. It seems that cracks can bridge only over limited areas of material, where starch particles cluster, and so failure occurs at much higher elongation (140%) than that (12%) of the blend with 50 wt % starch. However, the tensile strength of this material, 13.1 MPa, is still higher than that of polyethylene, 12.8 MPa.

The existence of starch particle clustering and phase cocontinuity in blends containing 40 and 50 wt % starch, respectively, also had a significant effect on the impact strength of the material. Polyethylene is an extremely tough material, and its impact strength cannot be recorded, unlike with starch, which is a very brittle material. Starch incorporation, as expected, causes matrix embrittlement, because tough matrix is replaced with a brittle material. However, blend specimens

containing up to 40 wt % starch did not break in a manner that their impact strength could be recorded according to ASTM D256. As starch content increased the distance of fracture increased being quite longer for the 40 wt % blend (approximately 1/3 of the distance between the vertex of the notch and the opposite side). The impact strength of the blend containing 50 wt % starch could be recorded at the value of 92.6 J/m (complete break). Thus, it would appear that starch content and the developed morphology control also the impact strength of the material.

The variation of the tensile strength, elongation at break, and modulus of LDPE/TPS films with the starch content is shown in Figures 8 and 9. The tensile strength and elongation at break decreased (Fig. 8), while the modulus increased (Fig. 9) with increasing starch content. Unlike with the injection-molded specimens, the tensile strength of films decreased at all starch levels. A similar behavior was also observed with cast LL-DPE/starch films.¹⁶ Their decreasing strength with increasing starch content was attributed to the poor interfacial adhesion of the two components. Thus, an interesting question rising is how stress-transfer, from the weaker polymeric matrix to stiffer and stronger starch particles, can take place in injection-molded specimens, while does not in films.

But the effect of the two shaping processes, i.e., film blowing and injection molding, on the structure of the produced material is different.^{17,18} A biaxial molecular orientation is imparted into the materials produced by the film-blowing process, with the two axes of orientation being the axial direction due to the drawing of the tube and the circumferential

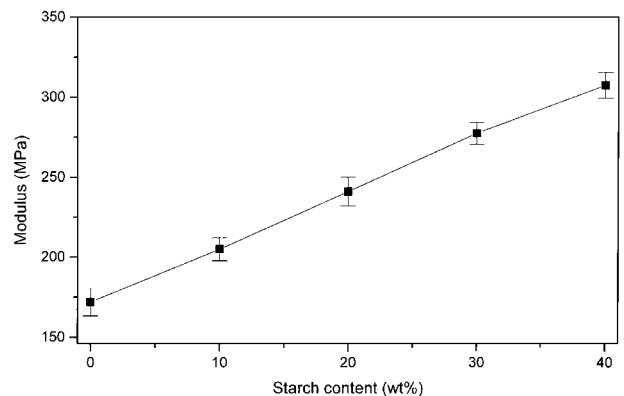


Figure 9 Variation of the modulus of LDPE/TPS films with TPS content.

direction due to the air pressure existing inside the tube. For the injection-molded materials the fountain flow mechanism has been suggested by Tadmor.¹⁷ According to this mechanism, a higher degree of orientation exists in the material at the mold wall than at the interior of the material.

Considering the coupling mechanism of the PE-g-MA copolymer, which is based on the ability of the anhydride groups to react with the hydroxyls of starch and the compatibility of the grafted and main phase PE chains, it is possible that the coupling efficiency of PE-g-MA may be influenced by the structure of the main PE phase. For instance, it can be assumed that the degree of entanglement achieved between the grafted and main phase PE chains, in a manner analogous to that postulated by the interpenetration theory,^{19,20,21} i.e., the formation of a pseudointerpenetrating polymer network through solubility and interdiffusion, could be influenced by the degree of molecular orientation existing in the main phase. It would be probable that the higher the degree of molecular orientation, the lower the extent of chain entanglement and the associated intermechanical locking. A higher degree of chain entanglement apparently makes more effective the transfer of stresses from the matrix to starch particles. Also, if stresses can also be transferred from the polymeric matrix to starch particles by means of simply intermechanical locking, even without the presence of an adhesion promoter, this mechanism would be more effective in the case of injection-molded materials in which less molecular orientation exists. Such considerations may explain how stress-transfer can be more effective in injection-molded materials.

Looking at the morphology developed in the films and injection-molded specimens, the only apparent difference observed is that the size of starch particles is larger in the films than in injection-molded specimens. Thus, the size of flaws, i.e., the weak starch/matrix interface introduced in the films, is also larger. Matrix weakening due to the presence of larger flaws maybe the reason related to the decrease of film properties with increasing starch content.

CONCLUSIONS

The effect of thermoplastic starch on the mechanical properties of LDPE/TPS materials was found to depend not only on starch content and the

developed morphology, but on the employed shaping process as well. TPS containing 20 wt % glycerol, under the experimental conditions used, could act as a reinforcing agent in injection-molded materials but not in films. It appears that the degree of molecular orientation imparted in the LDPE polymer matrix by the two shaping techniques is probably related with this behavior.

Starch size particle can also have an effect. In injection-molded specimens containing up to 40 wt % TPS there was a fine dispersion of the starch particles in the LDPE matrix with a mean size less than 1.5 μm . The higher tensile strength and modulus values of TPS compared with those of LDPE had as a result the increase of values of both parameters in the blends with up to 40 wt % TPS, but not in that with 50 wt %. The destruction of the fine starch particle dispersion and the formation of a continuous phase can explain this behavior. In the case of blown films, the mean TPS particle size was higher compared to that of the injection-molded specimens, and this could possibly account for the decrease in the tensile strength with increasing TPS content.

Finally, it can be said that LDPE/TPS injection-molded products containing up to 50 wt % TPS can be prepared without any problem. In the case of blown films, a 50 wt % TPS content appears to cause processing problems. The higher water content that this specific blend contains is probably related with these problems.

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