

Properties of Blends of Starch and Synthetic Polymers Containing Anhydride Groups

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SYNOPSIS

Corn starch was blended with styrene maleic anhydride copolymer (SMA), ethylene-propylene-*g*-maleic anhydride copolymer (EPMA), and corresponding nonfunctional polystyrene and ethylene propylene copolymers. The concentration of starch in the blend was varied between 50 and 80% by weight. The torque generated during blending is reported as a function of starch content, mixer speed, and mixing time. Torque increased with increasing starch content for starch/SMA blends; the reverse was true for starch/EPMA blends. The torque was higher for the blends of the anhydride functional polymers compared to the blends of corresponding nonfunctional polymers. Water absorption of the blends increased with an increase in the starch content. Starch/SMA blends made at higher mixer speed or time were more water sensitive. Blends containing EPMA absorbed less water than SMA blends containing the same weight fraction of starch. Tensile strengths of blends containing functional groups were superior compared to the blends made from nonfunctional polymers. When the starch contents increased from 60 to 70%, the tensile strength remained unchanged for SMA blend but increased for EPMA blend. All samples supported the growth of microorganisms, which increased with increasing starch content. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, much attention has been focused on the filling up of landfills by nondegradable materials such as plastics. This had led to legislation mandating recycling or development and use of alternative degradable materials. Several reviews are available¹⁻⁴ that deal with a wide range of possible biodegradable polymers from polyesters to polyhydroxy butyrate. Products from agricultural sources, such as starch or proteins, offer an attractive and cheap alternative in developing degradable materials. By itself, starch or protein is a poor choice as a replacement for any plastic. These are mostly water soluble, difficult to process, and brittle. In order to improve some of the properties, blending with hydrophobic polymers is necessary.

Starch is a mixture of amylose and amylopectin. Amylose and amylopectin are anhydrous D-glucose

polymers. Amylose is a linear polymer of molecular weight between one thousand and one million, made up of several hundred glucose units linked by α 1-4 glycosidic linkages. Amylopectin is a branched polymer of glucose units with α 1-6 glycosidic linkages at the branching points and α 1-4 glycosidic linkages in the linear region. The molecular weight of amylopectin can run into several millions. The structure of amylose and amylopectin is shown in Figure 1. Starch is not truly thermoplastic as most synthetic polymers. However, it can be melted and made to flow at high temperatures under pressure and shear. If the mechanical shear becomes too high then starch will degrade to form products with low molecular weight. Addition of water or other plasticizers enables starch to flow under milder conditions and reduces degradation considerably.

In principle, some of the properties of starch can be significantly improved by blending it with synthetic polymers. However, most of the synthetic polymers are immiscible with starch at the molecular level. This thermodynamic incompatibility often leads to poor performance of these blends. In order

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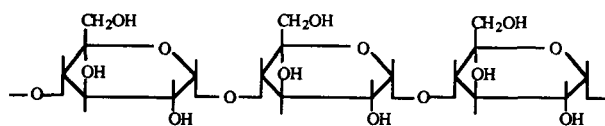


Figure 1 (a) Structure of amylose.

to overcome this drawback, graft copolymerization of vinyl monomer on the starch backbone is used to modify starch. Fanta and Bagley⁵ and Fanta⁶ have reviewed the synthesis and discussed some applications of starch graft copolymers. Grafting of synthetic polymer on starch is known to improve some of its properties. A review of the literature indicates that although the grafting of starch with synthetic polymer has been known for 30 years, very few processes have led to full-scale commercialization. Thus, the amount of starch being used in plastics is relatively small and accounts for a small fraction of the total plastics produced.

An alternative approach is to bring about some compatibility in starch and synthetic polymer by blending starch with polymers containing polar functional groups that can interact with starch. In recent years, several patents have been granted⁷⁻⁹ and the Novon division of the pharmaceutical giant Warner Lambert has build a 100 million pound annual production capacity to develop starch-based degradable plastics.

Otey et al.¹⁰⁻¹² blended starch with poly(ethylene-co-acrylic acid) (EAA). Their objective was to use these blends to produce films that would display properties of conventional plastic films. The authors suggested the formation of hydrogen bonds between the carboxylic group in EAA and the hydroxyl group in starch. Increasing the level of starch decreased the percentage elongation of the film and increased the diffusion rate of water. The authors also reported⁹ that low density polyethylene (LDPE) could be substituted for EAA up to a level of 40% without adversely affecting the physical properties of the blends.

Willet⁹ used starch, copolymers of an olefin, and optionally, a poly(mono)olefin or poly-(mixed)olefin to make blends that were injection molded or film blown into commercial articles. Increase in the starch percentage adversely affected the physical properties of the blends.

Yet another economical and commercially viable approach is to form graft or block copolymers *in situ* during the blend preparation by using polymers containing reactive functional groups. The blending is performed under the conditions that promote the reaction. This method is commonly known as "reactive blending." Small amounts of block or graft copolymers formed during the blending process, due to reaction between the two components, are generally enough to stabilize the morphology and improve the properties of the blend. Reactive blending is known to improve the compatibility and interfacial adhesion of two immiscible polymers. This technique has been extremely popular in generating polymer blends in the synthetic polymer industry.¹³ Synthetic polymers having functional groups such as carboxylic acid, anhydride, epoxy, urethane, or oxazoline, can react with the hydroxyl or carboxyl group (in modified starch) to form a blend with stable morphology.

Jane et al.⁸ in their patent used starch, oxidized polyethylene, and LDPE to produce film. According to these authors, the carboxy and ketone groups of oxidized polyethylene react with the hydroxyl groups on the starch to form bonds. They also report that as the percentage of starch in the blend is increased, the tensile strength and the percentage elongation decreases.

The reactivity of the functional groups is an important parameter in reactive blending. Most of the blends are commercially prepared in an extruder. The functional groups should react to form the required concentration of graft or block copolymers in the short residence times typical of extrusion processes. From this point of view a cyclic anhydride group may react more quickly than the carboxylic

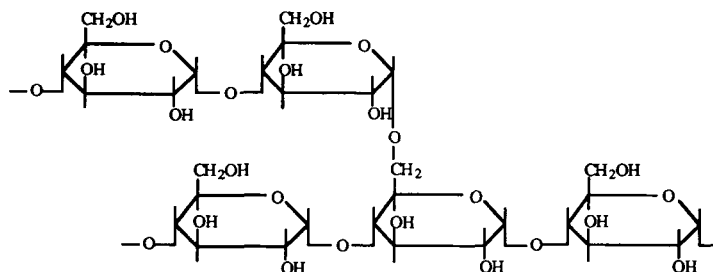


Figure 1 (b) Structure of amylopectin.

group because of its higher reactivity. Unlike carboxylic groups, reaction of anhydride with hydroxyl to form an ester is not an equilibrium reaction and no water is produced during the reaction. Anhydride functionality can be incorporated into a polymer by copolymerization or grafting of anhydrides like maleic anhydride. Maleic anhydride can be grafted with relative ease onto many polymers at normal melt processing temperatures.¹³

Although studies involving reactive blending of starch with anhydride functional polymer are unavailable, there are indications that the anhydride compounds improve the properties of composites made from cellulosic fillers. Pholman¹⁴ reported on the improved bonding between cellulose fibers using anhydrides. Maldas and Kokta¹⁵ used anhydride functionalized polystyrene to improve the compatibility and adhesion with cellulosic fibers (wood chips and pulp). They reported that the properties of the composites varied with the concentration of maleic anhydride, type of wood used, and pulping technique. Maleated high density polyethylene (HDPE) improved the tensile strength of composites containing wood flour with increasing concentration of filler.¹⁶

Detailed and systematic study of starch-based polymers is scarce. In this article, we present the results of preliminary findings on the blends of starch and synthetic polymers containing anhydride functional groups. The objective of this study was to blend starch at concentrations between 50 and 80% weight with styrene maleic anhydride (SMA) or ethylene-propylene-*g*-maleic anhydride (EPMA). The torque during mixing, water absorption, tensile strength, and mold growth on the samples as a function of starch concentration is reported and discussed.

EXPERIMENTAL

Materials

Industrial corn starch (SMP 1100) was obtained from Cargill Inc. Styrene maleic anhydride copolymer (Dylark 232) was obtained from Arco Chemicals. This grade of SMA contains about 8% maleic anhydride. EPMA (VA1801) was obtained from Exxon Chemicals and contains approximately 0.8% maleic anhydride.

Blend Preparation

Blends were prepared in a batch mixer as well as continuously in an extruder. The batch mixer was

equipped with roller blades (C. W. Brabender Instruments Inc., South Hackensack, NJ) and connected to a variable speed motor through a torque meter. Starch, SMA, and EPMA were dried in a vacuum oven at 100°C overnight. The required quantities of the starch and synthetic polymer were hand mixed in a plastic beaker and introduced into the mixer preheated to 180°C. For starch/SMA experiments, the amount of starch in the blend was 50, 60, 70, or 80% by weight. For starch/EPMA experiments, the amount of starch in the blend was 60, 70, or 80% by weight. For each composition, the mixer speed was set at 50, 100, or 200 revolutions per minute (rpm) and mixing time was 10, 20, or 30 min. During the blending process, the torque and melt temperature were recorded continuously and stored in a microcomputer (IBM PC/AT). At the end of the desired mixing time, the mixer was quickly dismantled and the material removed with the help of a spatula.

The extruder, used in the blending, was a laboratory scale twin screw with corotating screws (Haake Instruments, Paramus, NJ). The barrel length to diameter ratio was 20 : 1 and the extruder was divided into three zones for temperature control. The materials were extruded through a capillary die. For this set of experiments, the moisture content of the starch was 10% to enhance processability. Only blends containing 60 and 70% starch were made in the extruder. At higher starch content (80%) the pressures and torque exceeded the manufacturers safety limit, thus, shutting down operation. For starch/SMA experiments, the extruder had a venting screw. The first zone temperature was set at 120°C, the second at 165°C, and the third at 180°C. The die temperature was set at 180°C. Extrusion was carried out at a screw speed of 63 rpm. The resultant extrudate was in the form of a rope and had a smooth texture. For starch/EPMA experiments, the extruder had a mixing screw with no venting section. The first zone temperature was set at 80°C, the second at 150°C, and the third at 180°C. The die temperature was set at 80°C. Extrusion was carried out at a screw speed of 72 rpm. The resultant extrudate was in the form of a flexible rope. The minimum residence time for both cases was approximately 45 s.

Molding

The extruded and batch mixed samples were molded for water absorption and tensile studies. For water absorption, thin strips of samples (60 × 10 × 2 mm) were compression molded. For tensile strength, the

dimensions of the samples were as outlined in the ASTM test method D-638. The platens of the press were heated to 190°C for SMA blends and 180°C for EPMA blends. The mold cavity was filled with the material and covered with the top plate and placed between the two platens of the press. After 5 min, the platens were slowly pressed together until the force was 10 T. Pressure was applied for a period of 10 min, after which the platens were cooled to 50°C, the pressure relaxed, and the mold removed from the press.

Water Absorption

The molded strips of the blends were weighed and immersed in water. The samples were then removed at specified intervals, gently blotted with tissue paper to remove the excess water on the surface, and the weight recorded. This process was repeated at several time intervals.

Tensile Strength

Tensile testing was done on an Instron Universal testing machine according to the procedure outlined in ASTM test method D-638.

Biodegradation

Degradation was determined by ASTM test method D-1924. ASTM-D 1924 describes a method to evaluate the resistance of polymeric materials to fungi. Polymer samples were placed in sterile petri dishes containing solidified nutrient salt agar. A mixed fungus spore solution was prepared from spores of *Aspergillus niger*, *Penicillium funiculosum*, *Chaetomium globosum*, *Trichoderma sp* and *Pullularia pullulans* as described by the ASTM method. The samples were then inoculated with the spore suspension and the covered petri dishes were sealed with a paraffin film. The only carbon source for the growth of the fungi was from the samples. The fungus growth was followed by visual observations.

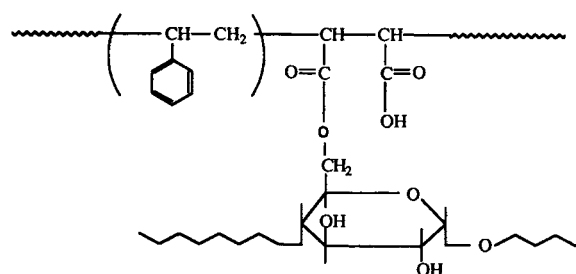


Figure 2(a) Structure of reacted starch/SMA blend.

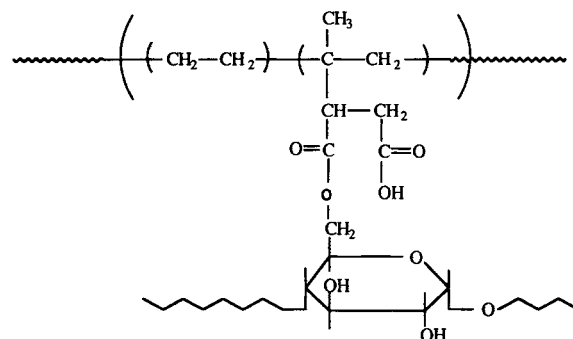


Figure 2(b) Structure of reacted starch/EPMA blend.

RESULTS AND DISCUSSION

During the reactive blending of SMA or EPMA with starch, the anhydride groups of the polymer can react with the hydroxyls of the starch to form ester linkages. The carboxylic groups, arising from the hydrolyzed anhydride, can also form hydrogen bonding with the hydroxyl groups. The possible reaction product of SMA/starch and EPMA/starch are shown in Figure 2.

The starch/SMA and starch/EPMA blends were made at various starch contents ranging between 50 and 80%. Blends of a general purpose grade of polystyrene and EP containing no functional groups, were also made at 60% starch content for comparison purpose. The starch/SMA blends were rigid, whereas the starch/EPMA blends were flexible and tough. At starch contents of 80% or higher, the blends made in the mixer appeared powdery due to large amount of unmelted starch. Blends containing higher amounts of starch (> 70%) and made at higher mixer speeds (> 100 rpm) or mixing time (> 20 min) appeared discolored, due to degradation and burning of starch. Blends containing 80% or more starch could not be made in the extruder, due to higher viscosity and pressures, which led to the shut down of the extruder (safety feature). It should be noted that the blend formulations in either the mixer or the extruder did not contain any lubricant or processing aids. Addition of such agents in the formulation may enable us to use the extrusion blending process for compositions with 80% or more starch.

Mixing Torque and Temperature

Typically, during blending in a batch mixer, as the polymers are introduced into the mixer, the temperature first decreases and then increases rapidly to the set temperature of the mixer. During this duration, the polymer starts to melt, forming a viscous

mass and hence, the torque starts to increase. As the temperature increases due to the external and viscous heating, the polymer completely melts. This leads to a decrease in the torque that then either remains unchanged for the remainder of the experiment or may vary, due to reaction and/or degradation of polymers. Data collected for mixer speed of 50 rpm is used for the following discussion.

The torque data, for starch/SMA blends measured from the batch mixer, is shown in Figure 3. During the first 2–4 min, the material is not homogenous and is still undergoing the process of melting and dispersion; hence, the later part of the data is considered for comparison. The torque increased with the increasing amount of starch in the blend. This was due to the increasing contribution of starch, which has a much higher viscosity. At the end of the 10-min run, the torque for the starch/SMA blend containing 60% starch was about 18.6 Nm, while for a blend containing 80% starch it was about 25.5 Nm. The starch/SMA blend, containing 60% starch, exhibited higher torque (18.6 Nm) compared to the nonfunctional polystyrene/starch blend (13.7 Nm) containing the same percentage of starch. This could be attributed to the increase in the viscosity of SMA/starch blends due to the reaction and/or the association between starch and SMA molecules. Though the temperature of the mixer was set at 180°C, the viscous heating increased the melt temperature above the set temperature. Figure 4 shows the increase in the melt temperature with time for various SMA blends. The increase in the temperature was proportional to the starch contents of the blends. The melt temperature depends on the viscosity and the reaction exotherm. The greater the viscosity, the higher the increase in the

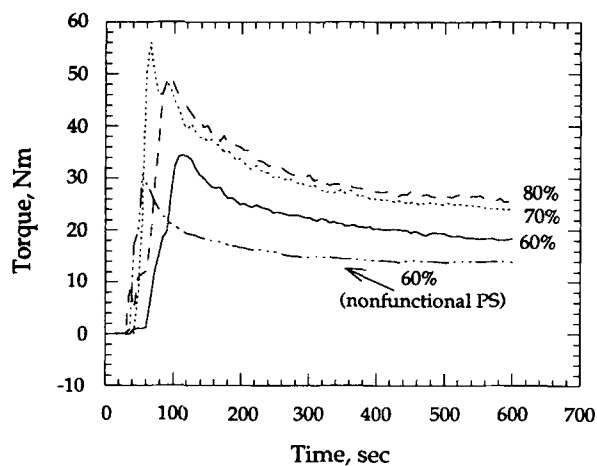


Figure 3 Torque versus time for starch/SMA and starch/nonfunctional PS blends in the mixer.

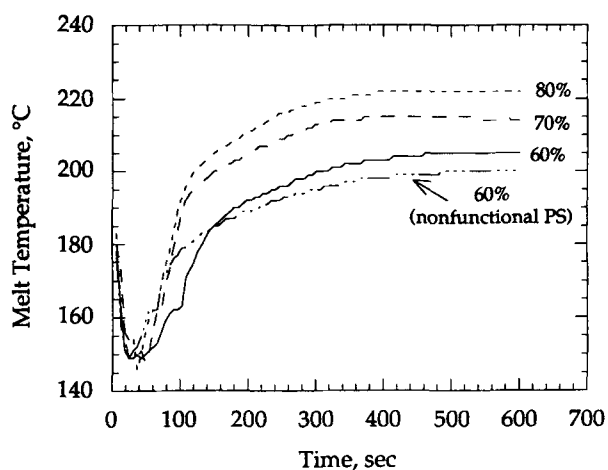


Figure 4 Melt temperature profile for starch/SMA and starch/nonfunctional PS blends in the mixer.

melt temperature. The nonfunctional polystyrene/starch blend displayed lower melt temperatures (200°C) due to lower viscosity and absence of the reaction than the corresponding SMA/starch blend (205°C). For 80% starch the melt temperature reached 222°C. Performance of starch/SMA blend containing 70% starch, in terms of torque and melt temperature, was in between that of blends containing 60 and 80% starch. It should be noted that the torque measurements could not be made at the same melt temperatures for different blends (due to viscous dissipation rise). Because small increases in the temperature lowers the viscosity, the actual torques for the SMA blends would be higher than the nonreactive blend at a same given temperature. The presence of polystyrene melt prevented discoloration or burning of the starch at such high temperatures, except for the blends made at very high rpm and/or mixing times, as described earlier.

In order to evaluate the differences in the magnitudes of torque between the reactive and nonreactive blends, experiments were conducted with SMA, polystyrene, and their blends with 60% starch. When the same mass of pure SMA and polystyrene was melted in the mixer at 180°C, the steady-state torques for SMA and polystyrene were 14.4 and 8.7 Nm, respectively. When these two polymers were blended with 60% starch the corresponding torques were 20.0 and 13.1 Nm, respectively. The difference in torque between the SMA and polystyrene was 5.7 Nm. This difference increased to 6.9 Nm for their blends at the same starch content indicating some possible interaction between SMA and starch. Torque is proportional to the melt viscosity. Assuming no interaction between nonfunctionalized polystyrene and starch, the torque contribution, due

to the starch component in the blend, can be calculated. For incompatible polymer blends using the logarithmic mixing rule¹⁷ the melt viscosity (η) is given by

$$\ln \eta = \sum_{i=1}^n w_i \ln \eta_i.$$

Hence, the expression for torque (τ) is

$$\ln \tau = \sum_{i=1}^n w_i \ln \tau_i$$

where w and τ is the mass fraction and torque, respectively, of component i in the blend. The contribution of torque, due to starch, can be calculated by knowing the torque for polystyrene (8.7 Nm) and blend of starch and polystyrene (13.1 Nm). When this estimated value was used to predict the torque of starch/SMA blends, the predicted value was found to underpredict the observed torque for the blend by 20%. Although somewhat indirect, these calculations support our hypothesis that there is some physical and/or chemical interaction between SMA and starch.

The torque and the melt temperatures, with respect to mixing time for starch/EPMA blends at 60, 70, and 80% starch contents is shown in Figures 5 and 6. As with starch/SMA blends, a reference blend with nonfunctional EP and starch was made at 60% starch content. The torque and the melt temperature profile was different compared to SMA blends. The average torque decreased with the increasing starch contents. A substantially higher

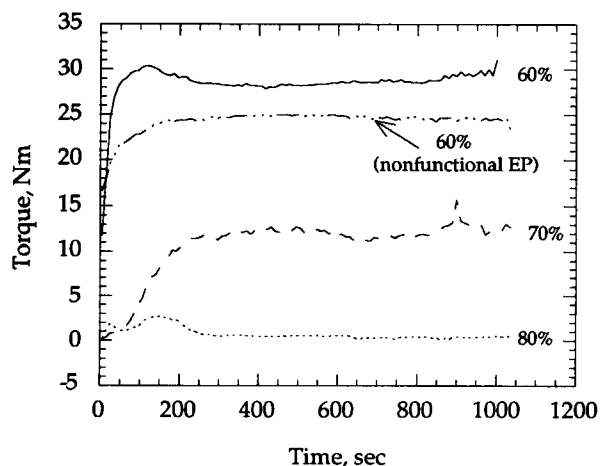


Figure 5 Torque versus time for starch/EPMA and starch/nonfunctional EP blends in the mixer.

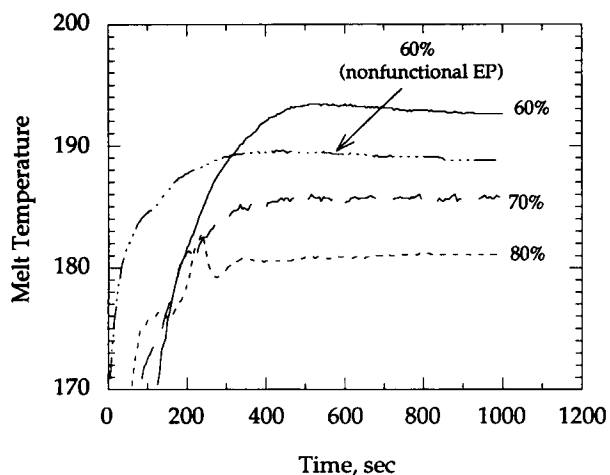


Figure 6 Melt temperature profile for starch/EPMA and starch/nonfunctional EP blends in the mixer.

torque of 28.4 Nm for the blend containing 60% starch reduced to about 11.8 Nm when the starch content was increased to 70%. At 80% starch, the observed torque was less than 1 Nm and the blend appeared extremely dry and powdery. As mentioned earlier, starch melts and flows only under high pressure and shear. At 40% polymer concentration (60% starch), the viscosity of the polymer melt probably generated enough torque to melt the starch and the molten starch further increased the torque. With the increasing starch content and decreasing polymer contents in the blend, the shear stress was considerably reduced probably due to slippage (evident from the reduced torque) that prevented the starch from melting. At 80% starch, torque was low enough (< 1 Nm), that a large fraction of starch remained unmelted and the composition appeared more like a highly filled system than a blend. The blend of nonfunctional EP and 60% starch exhibited lower torques than the corresponding reactive blend. The melt temperature followed the torque profile exactly. The higher the torque, the higher the melt temperature. For 60% starch and EPMA blend the melt temperature was 193°C, while for the nonreactive EP and starch blend of the same composition it was 189°C. For EPMA starch blend containing 70% starch, the temperature was 186°C. At 80% starch, the temperature practically stayed at 180°C because of the extremely low torque.

Experiments similar to those described for the SMA blend were conducted with functional and nonfunctional EP and their blends. Torque for EP polymer kept decreasing during a 20-min run. In fact, the torque for EP was higher than for EPMA for the first 10 min yet, during their blending with

60% starch, the torque of EPMA blend was always higher than the EP blend. For the EPMA/starch blending, the torque appeared to increase with time, which is an indication of some interaction between EPMA and starch.

Thus, the higher torques for blends made from SMA and EPMA compared to nonfunctional polystyrene and EP, do not conclusively prove a reaction, but at least indicate some interaction with the starch. A thorough investigation of blends, using techniques like FTIR and GPC, is currently in progress.

Water Absorption

SMA/starch blends containing 50 and 80% starch were investigated to study the effect of the mixing time and mixer speed (rpm) of the batch mixer on the water resistance of the blends. Molded rectangular samples of these blends were immersed in water and the weight gain was observed with time. The blending conditions had a significant effect on the water absorption or water resistance characteristics of the blends. At 50% starch content, the blends were prepared at three different speeds (50, 100, and 200 rpm), keeping the mixing time constant at 10 min. The percent weight gained by the samples, over a 60-day period when immersed in the water is shown in Figure 7. When the mixer speed is increased from 50 to 100, although the weight gain increased by a very small percentage (11.0 to 11.5%), an increased amount of solids were extracted from

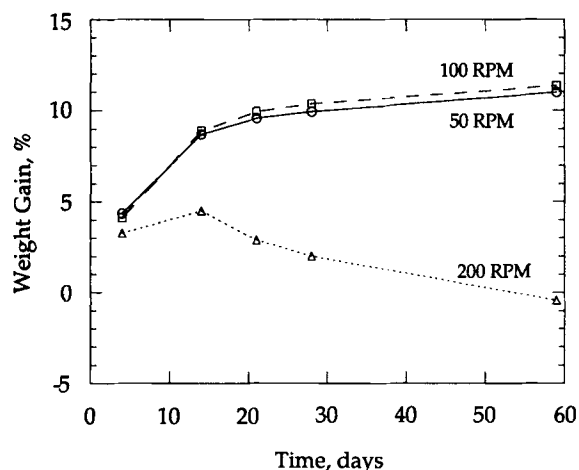


Figure 7 Effect of mixer speed at a constant mixing time of 10 min on the percentage weight gain of starch/SMA blend containing 50% by weight of starch in the blend.

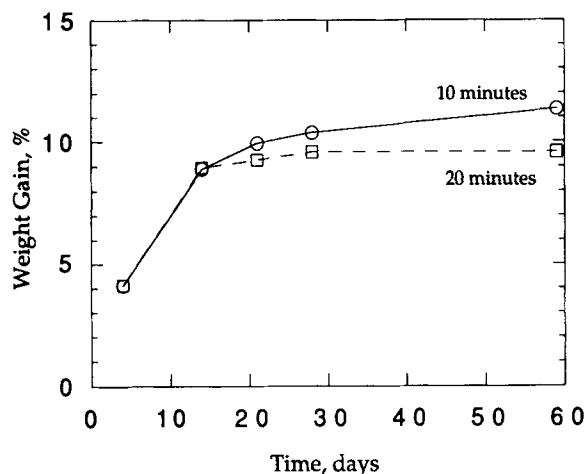


Figure 8 Effect of mixing time at a constant mixing speed of 100 rpm on the percentage weight gain of starch/SMA blend containing 50% by weight of starch in the blend.

the blend made at 100 rpm. This could be due to increased gelatinization and probable degradation of starch that make the blend more water sensitive. The sample made at 200 rpm was degraded to a greater extent as is evident from the significant amount of solids that were extracted out and the sample exhibited weight loss instead of weight gain. At 50 rpm, when the blending time was increased from 10 to 20 min, the water absorption remained practically unchanged except for a slightly hazy appearance of water for the higher mixing time sample. When the same blend composition was mixed at 100 rpm, increased degradation of the starch component was evident from the larger amount of solids extracted from the sample. The weight gain (9.5%) for the sample mixed for 20 min was lower (due to the extraction of solids) compared to the 10-min sample, which gained 11% weight without much solid extraction (Fig. 8). A similar effect was seen for the 80/20 blends. The blend made at 50 rpm for a 10-min duration absorbed about 22% water in the first 4 days (Fig. 9). The sample quickly saturated to about 27% weight gain in the first 15 days and then the weight practically remained unchanged. When the same blend was made at higher rpm (100) or higher mixing time (20 min), the water absorption increased to about 26% in the first 4 days; but instead of gaining weight further, the weight actually decreased with time due to extraction of solids from the sample. In most of the cases, samples made at 200 rpm or 30-min mixing time were significantly degraded and were not suitable for molding.

Starch/EPMA blends exhibited reasonably good

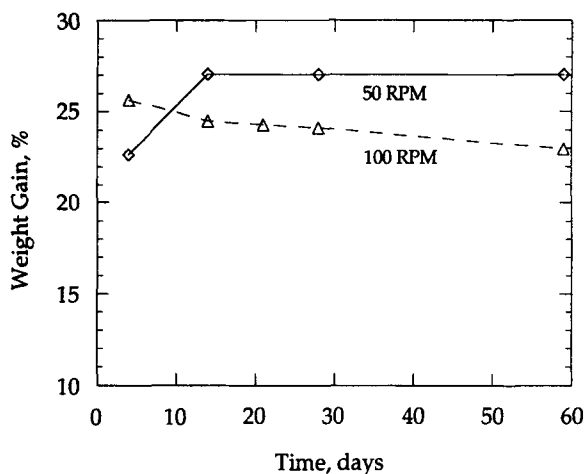


Figure 9 Effect of mixer speed at a constant mixing time of 10 min on the percentage weight gain of starch/SMA blend containing 80% by weight of starch in the blend.

water resistance compared to starch/SMA blends. The clarity of the water during the water absorption test indicated negligible extraction of the solids. In the first 4 days, the blends containing 80% starch, absorbed about 4% water (Fig. 10), whereas the one containing 60% starch absorbed only about 1.5%. The water absorption slowly increased over a period of 60 days, by which time the blends containing 60, 70, and 80% starch absorbed about 11, 14, and 18% water, respectively. The processing conditions did not have much effect on the water absorption prop-

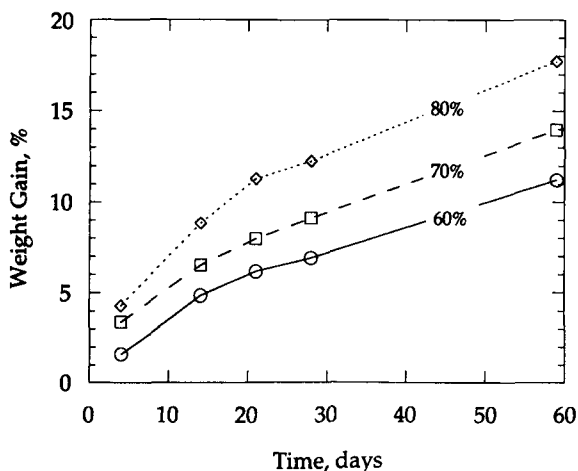


Figure 10 Effect of starch content at a constant mixing time of 10 min and mixing speed of 50 rpm on the percentage weight gain of starch/EPMA blends.

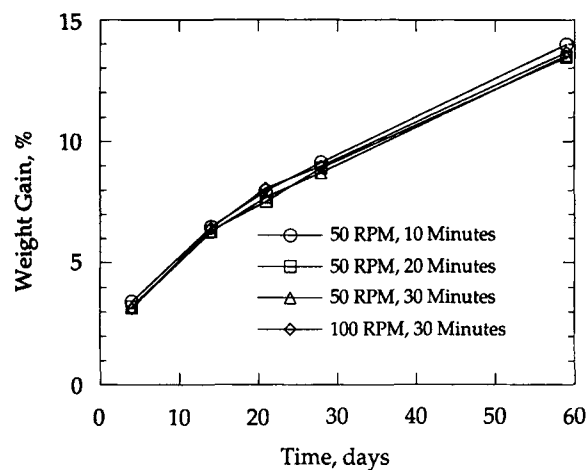


Figure 11 Effect of mixing time and mixing speed on the percentage weight gain of starch/EPMA blends containing 70% starch by weight.

erty, indicating minimum degradation even at high speed (200 rpm) and mixing time (30 min) (Fig. 11).

As seen from Figure 8, EP blends absorb considerably less water than the SMA based blends. A blend containing 50% SMA and 50% starch absorbed about 4% water in the first 4 days, which is equal to the water absorption of a blend containing 20% EPMA and 80% starch. It is clear from the slopes of the absorption plots that starch/SMA blends absorb at a faster rate and reach saturation quicker than the starch/EPMA blends. A significant difference is seen at 80% starch loading. EPMA blend absorbed only 4% water in the first 4 days, which slowly increased to about 18% in 60 days, whereas the SMA blend absorbed about 23% in the first 4 days and quickly saturated to about 27%, with a considerable amount of visible solids extracted in the water. SMA blends were quite sensitive to the mixing conditions. Under severe conditions of mixer speed and mixing time, the blends became more water sensitive, probably due to starch degradation. On the other hand the EP blends showed a negligible effect of mixing conditions on the water absorption.

We also autoclaved the molded samples of starch/SMA and starch/EPMA containing 60% starch by subjecting it to high pressure steam (121°C and 20 psi) for 10 min. The surface appearance of starch/SMA was affected and some cracks were developed in the sample. The starch/EPMA blend, however, was unaffected by the sterilization process. This again indicates a superior water resistance of starch/EPMA blends compared to blends containing SMA.

It is worth noting that even under these severe conditions the autoclaved samples did not lose their mechanical integrity.

Thus, the composition and the mixing conditions affected the blend properties. This type of study is useful in optimizing the reaction conditions to get the desired water sensitivity depending on the end use. If the application is such that the material should retain the mechanical strength and should not leach out, a lower rpm and mixing time is suitable. However, if the application is such that the material should weaken and break down when put in the water, higher rpm and mixing times could be useful. Thus, blends containing large amounts of starch (50–80%) could be made significantly water resistant. The samples retained their original shape and absorbed only 10–30% water when immersed in water for 60 days.

Tensile Strength

The blends obtained from the mixer were in the form of chunks of irregular shapes. To fill the molds, these chunks had to be broken into small pieces, and upon molding, caused the formation of weld lines. Starch melts and flows only under conditions of high shear. In the absence of shear during compression molding, the blend did not melt or flow properly, resulting in the formation of weld lines where different pieces fused together due to poor diffusion of the melt. The presence of weld lines were more prominent in the blends containing higher starch content (> 70%). When subjected to tension, sample failure often occurred along the weld line. Hence, data from the mixer experiment is not reported.

The tensile strength was measured for blends obtained from extrusion. The extruded rods were cut into pieces equal to the length of the mold cavity and compression molded. This procedure reduced the weld lines significantly, and if present, the weld lines were aligned in the direction of the force during tensile testing and would have minimum effect on sample failure. The tensile strengths of the virgin polymers and their blends with starch made in an extruder are shown in Table I. For starch/SMA blends, as the starch content increased, the tensile strength was practically unchanged. For starch/EPMA blends, as the starch content in the blend was increased, the tensile strength of the blend was found to increase. The presence of starch reduces the strength of starch/SMA blends over pure SMA. For EPMA the reverse holds true, that is, the presence of starch increased the tensile strength of the

Table I Tensile Strengths

Sample	Tensile Strength (MPa)
SMA	33.2
Polystyrene (nonfunctional)	31
Starch/SMA, 60/40	18.4
Starch/SMA, 70/30	17.7
Starch/polystyrene (nonfunctional), 60/40	9.58
EPMA	6.2
EP (nonfunctional)	> 8.92 ^a
Starch/EPMA, 60/40	6.37
Starch/EPMA, 70/30	8.30
Starch/EPMA, 60/40 ^b	4.48
Starch/EP (nonfunctional), 70/30 ^b	2.79

^a The samples slipped out of the grip beyond this load.

^b Blends made in a batch mixer.

blend over pure EPMA. These results are in direct contrast to those present by Jane et al.⁸ and Willet.⁹ The tensile strength of pure SMA and polystyrene are comparable yet the blend of polystyrene with starch displayed much lower tensile strength compared to the blend containing SMA. Because not enough nonfunctional EP could be procured for extrusion, its blend was not made in the extruder. However, a similar trend was observed with blends made from EPMA and nonfunctional EP in the batch mixer. In fact, the tensile strength of the nonfunctional EP was much higher than EPMA. Yet the tensile strength of the blend made from nonfunctional EP was lower than the blend made from EPMA. It should be noted that while the magnitude of tensile strength obtained from samples made in the blender was lower, the same general trend as in the case of extruded samples were observed. The improved properties of starch/anhydride functional polymers could be due to increased interfacial adhesion resulting from the reaction between starch and the polymers.

Biodegradation

All the samples supported fungus growth. The fungus growth could be seen with visual observations after 2–4 days. Fungus kept growing rapidly with time. As seen from the photographs in Figure 12, the rate of fungus growth increased with the amount of starch in the blends. Starch, being a natural polymer, could be readily used as a carbon source by the fungus. On the other hand, a synthetic polymer does

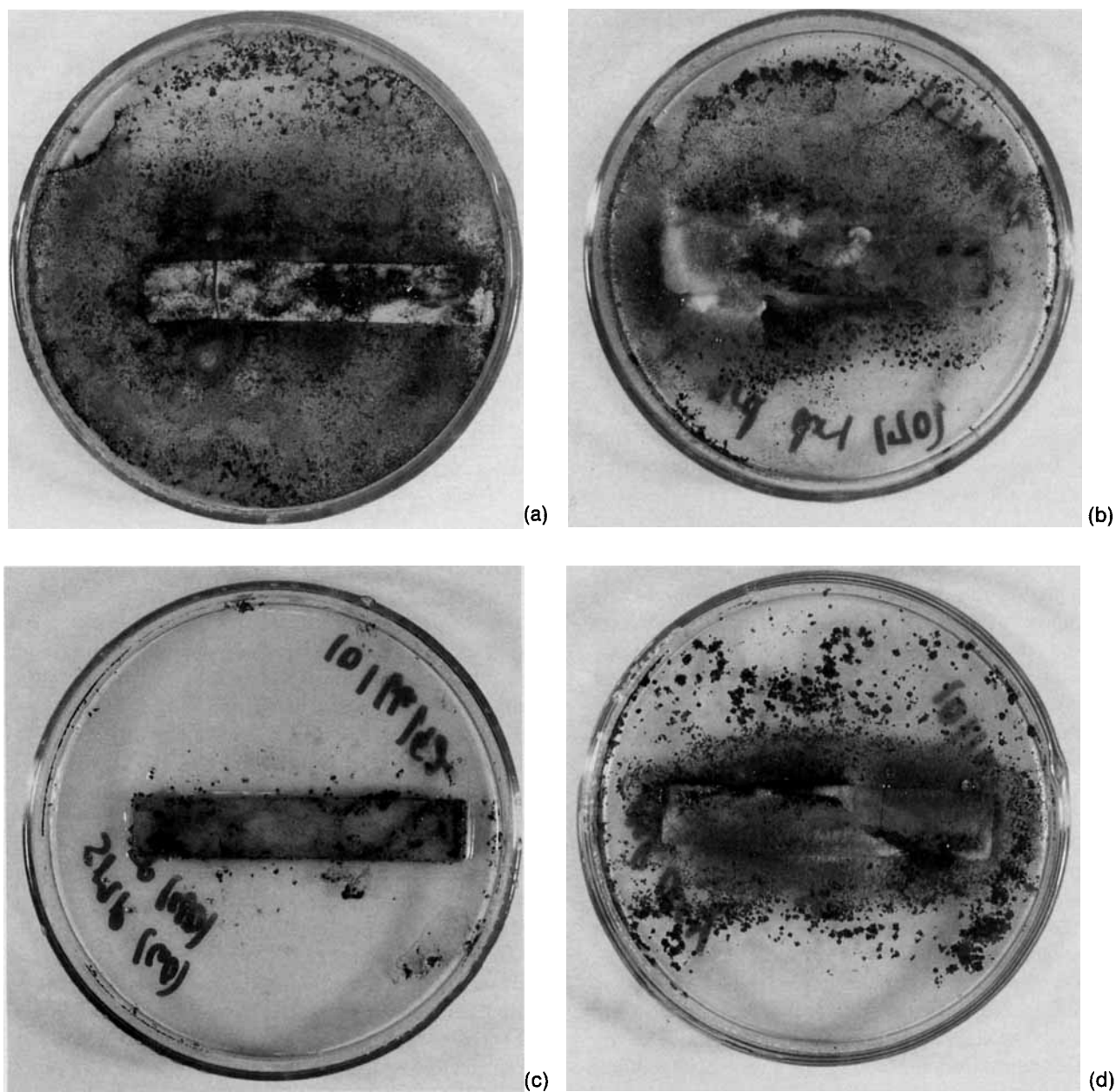


Figure 12 Fungus growth after the first 15 days since inoculation. (a) starch/SMA (60/40); (b) starch/SMA (70/30); (c) starch/EPMA (60/40); (d) starch/EPMA (70/30).

not serve as an efficient carbon source. Therefore, in a blend of the two, starch component degrades and is used up by the fungus, leaving SMA or EPMA largely unaffected. The rate of fungus growth depends on the relative ease with which the starch can be accessed by the organisms. As the starch content is increased, the starch becomes a continuous phase in the blend and can be easily accessed by the organisms. Samples made in the extruder showed faster growth than the blends made in the batch

mixer. When the native starch was first extruded and then blended with SMA or EPMA in a batch mixer, similar results were observed (see Fig. 13). During the extrusion process, the starch undergoes "cooking" due to higher shear, leading to greater amounts of gelatinization and degradation compared to the batch mixer. Thus, gelatinization/degradation further supports the faster fungus growth. At very low starch contents, the starch may remain encapsulated in the synthetic polymer thereby making

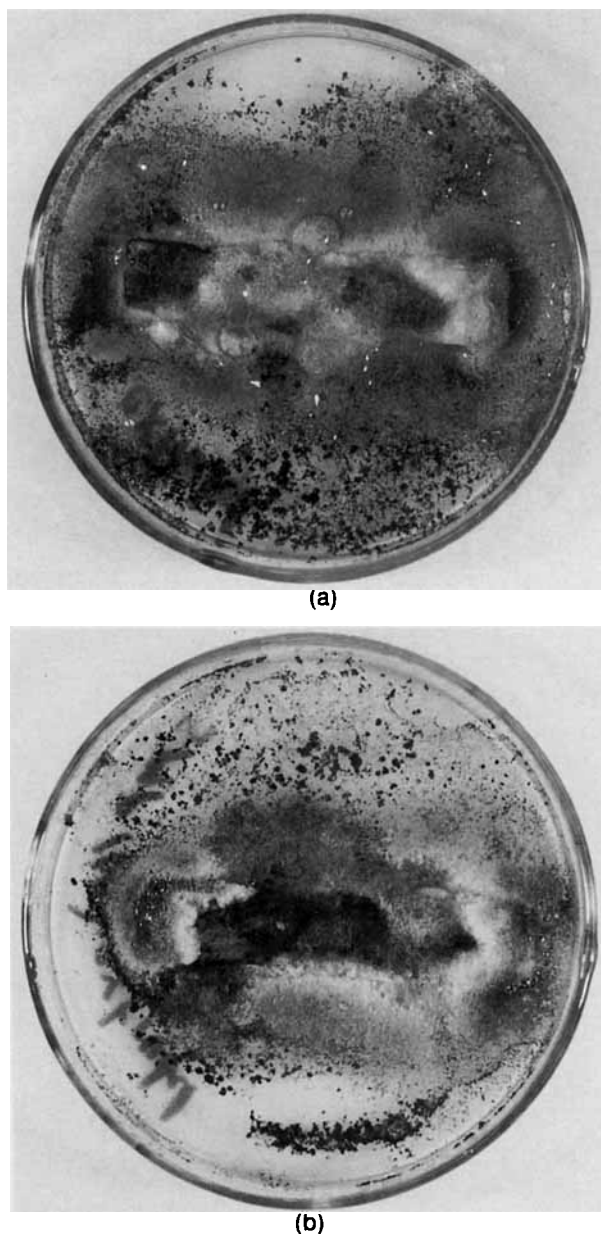


Figure 13 Fungus growth after the first 15 days since inoculation containing extruded starch. (a) Starch/SMA (60/40); (b) starch/EPMA (60/40).

it difficult for the organisms to access and use it as carbon source. In such a case the fungus growth will be slow. The control sample, made from pure SMA did not show any fungus growth. Fungus growth was noticeably faster in starch/SMA blends than in starch/EPMA blends.

CONCLUSIONS

Starch/polymer blends, containing in excess of 50% starch could be made in a batch mixer as well as in

an extruder. The mixing torque was found to be higher for blends containing starch and anhydride functional polymer than the corresponding starch and nonfunctional polymers. This could be due to the reaction of the anhydride group in the synthetic polymer with the hydroxyl group in the starch. For starch/SMA blends, the torque and the melt temperature increased with increasing amounts of starch. The reverse was true for starch/EPMA blends. Processing conditions affected the water resistance property of starch/SMA blends more than starch/EPMA blends. At higher rpm and/or mixing times, the starch in the blend was gelatinized or degraded, making the samples more water sensitive. This was particularly true for starch/SMA blends. Blends containing EPMA displayed better water resistance to blends containing SMA at the same weight fraction. Water resistance also decreased with increasing amounts of starch in the blend. The tensile strength of starch/SMA blends remained practically unchanged when the starch content increased from 60 to 70% by weight, whereas for starch/EPMA blends, the tensile strength actually increased. All of the blends supported fungus growth. The growth was faster for starch/SMA blends than on the corresponding starch/EPMA blends. Increasing the amount of starch in the blend increased the rate of fungus growth. The fungus growth was faster on samples containing extruded starch. In general, the rate of fungus growth depended on the ease with which starch could be accessed by the microorganism. Thus, higher starch content, higher degree of gelatinization/degradation of starch, and higher water permeability (as for blends containing SMA) were factors that favored the rapid growth of fungus.

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