

Properties of Blends of Starch and Synthetic Polymers Containing Anhydride Groups. II. Effect of Amylopectin to Amylose Ratio in Starch

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SYNOPSIS

Corn starch with different amylopectin to amylose ratios was blended with styrene maleic anhydride copolymer (SMA) and ethylene-propylene-g-maleic anhydride copolymer (EPMA). The starch had an amylose content of approximately 0, 50, and 70%. The concentration of starch in the blend was kept constant at 60% by weight. The samples were melt blended in a corotating twin screw extruder. Scanning electron micrographs showed that the amount of starch granules remaining in the samples varied with the torque. Optical micrographs showed that starch/EPMA blends formed a cocontinuous phase in all blends irrespective of starch variety. For starch/SMA blends, the starch granules remained dispersed in the SMA phase. The torque during blending, tensile strength, water absorption, storage and loss modulus, and data on biodegradability of the blends are presented. Tensile strength and water absorption correlated well with the torque generated during blending: the higher the torque, the lower the tensile strength and the higher the water absorption. The tensile strength of blends containing SMA decreased when the humidity increased. Fractured surfaces of starch/SMA blends exhibited brittle failure; for the ductile starch/EPMA blends, shear tearing appeared to be the major failure mechanism. For blends containing EPMA, the percentage elongation increased with increased humidity. Dynamic mechanical analysis of the blends showed two sharp peaks for $\tan \delta$ vs. temperature plot for starch/EPMA plots, but showed a single peak for starch/SMA blends. Starch/EPMA blends had a higher percentage of water absorption that became constant after 20 days. Using the ASTM test method D5902, the starch content in the samples was found to degrade. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends containing varying amounts of starches and other polysaccharides are being investigated as possible replacements for pure synthetic polymers.¹⁻⁴ It is expected that the polysaccharide portion will degrade in the environment and thus lead to a decrease in solid-waste pollution. Also, increased use of polysaccharides would reduce our dependence on nonrenewable petrochemicals from which the synthetic polymers are derived.

Starch is composed of repeating 1,4- α -D-glucopyranosyl units. It is a mixture of linear (amylose) and branched (amylopectin) polymers. The molecular weight of amylose is on the order of several hundred thousand, while that of amylopectin is several million. Commonly used native corn starch has an amylose content of about 25%, although starches containing varying amylose contents can also be produced for specialty uses. Typically, commercially available corn starches have an amylose content ranging from 0% (waxy) to a high of 70%. Blends made from starches containing different amylopectin to amylose ratios would be expected to have considerably different physical properties. Indeed, in the food industry where starches find most of their uses,

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the amylopectin to amylose ratios have been known to have a profound effect on properties.⁵

Starch by itself is unsuitable for most uses as plastic. It is difficult to process and is extremely sensitive to humidity. Depending on the environment, the physical properties such as elasticity, hardness, and dimensional stability are affected. To overcome the problems caused by the poor physical properties of pure starch, it is often blended with water insoluble synthetic polymers.⁶⁻¹¹ The technique of blending two or more components into one material to impart new characteristics is a well-known procedure in the synthetic polymer industry. Because starch and hydrophobic synthetic polymers are immiscible at the molecular level, simple mixing produces blends that tend to phase separate.

Compatibility between two immiscible polymers can be improved by introducing a reactive functional group on each polymer. The functional group is expected to react during blending. In the case of starch-polymer blends, we look for functional groups on the synthetic polymer that can react with the hydroxyl group of starch (or the carboxyl group in modified starch). The functional group on the synthetic polymer can form a hydrogen or covalent bond with the hydroxyl group on the starch. Otey and coworkers⁶⁻⁸ reported on blends of starch and poly(ethylene-*co*-acrylic acid). Willet⁹ made starch blends with copolymers of olefin. Jane and coworkers¹⁰ used blends of starch, oxidized polyethylene, and low density polyethylene. In a recent patent issued to the Novon division of Warner Lambert,¹¹ numerous possible blends of destructured starch, compatibilizer, and optionally thermoplastic synthetic polymers is described. A recent paper by George and coworkers¹² revealed that in blends of starch and poly(ethylene-*co*-vinyl alcohol), as the amylose content in the starch increased, the elongation increased.

In an earlier study,¹³ we reported on the properties of blends of native corn starch and synthetic polymer (styrene or ethylene-propylene rubber) containing a maleic anhydride functional group. The concentration of starch in the blend was varied. The water absorption of the blends increased with increasing starch content and was sensitive to mixing time and speed, particularly for starch/styrene maleic anhydride blend composition. When non-functionalized polystyrene or ethylene-propylene rubber was blended in the same concentration, the tensile strength was found to be inferior to that obtained by using maleated polymer in the blend. Starch/ethylene-propylene-*g*-maleic anhydride (EPMA) blends showed two glass transitions, one

corresponding to starch and the other to EPMA.¹⁴ Starch/styrene maleic anhydride (SMA) blends exhibited one broad glass transition. The starch in the blend was found to be sensitive to processing conditions and degraded as evident from gel permeation chromatography.

In this study, we extend on our previous work by incorporating starches of varying amylopectin to amylose ratios in the blend. The objective of this study is to compare the effect of the amylopectin to amylose ratios in the blend on the properties of starch/maleated polymer blends. As reported earlier,^{13,14} we used SMA and EPMA as the synthetic polymer. The concentration of the starch in the blend was 60% by weight. The amylose content of the starch was 0, 50, and 70% by weight. The torque during blending, tensile strength, water absorption, storage (G') and loss (G'') modulus, and optical and scanning electron microscopy (SEM) of the blends are presented.

EXPERIMENTAL

Materials

The corn starches used in this study had amylose contents of approximately 0, 50, and 70% by weight. Thermoflow (0% amylose), Hylon V (50% amylose), and Hylon VII (70% amylose) were obtained from National Starch and Chemical Co. SMA 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 continuously in an extruder. 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. A torque meter attached to the extruder was used to monitor the torque continuously. The moisture content of the starch was approximately 10% to enhance processability. 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

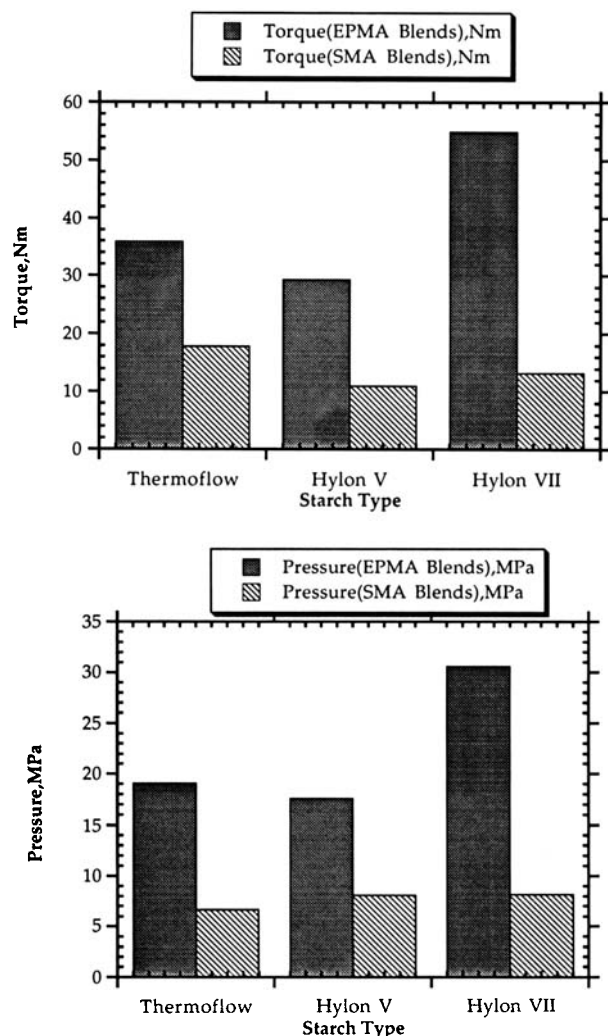


Figure 1 (a) Torque during melt blending of various SMA/starch and EPMA/starch compositions. (b) Pressure during melt blending of various SMA/starch and EPMA/starch compositions.

of 63 rpm. The resulting 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 resulting extrudate was in the form of a flexible rope. The minimum residence time for each case was approximately 45 s.

To study the effect of torque during processing on the properties of the sample, blends containing Hylon V and EPMA were made at three different torque levels. The torque level was varied by altering the mass flow rate in the extruder. These samples were compression molded and tested for tensile strength as described below.

Molding

The extruded 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 D638. 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, 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 tons. 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 excess water on the surface, and the weight recorded. This process was repeated at several time intervals.

Table I Specific Mechanical Energy (SME) of Samples During Melt Blending

Sample Composition	Flow Rate (g/min)	Torque (Nm)	SME (kJ/kg)	Tensile Strength (MPa)
Thermoflow/EPMA	29.28	35.86	554.2	6.1
Hylon V/EPMA	23.05	29.26	508.21	8.7
Hylon VII/EPMA	25.43	54.92	977.07	6.9
Thermoflow/SMA	7.95	17.87	889.87	19.5
Hylon V/SMA	7.48	11.00	582.14	25.1
Hylon VII/SMA	5.78	13.24	906.74	23.5

$$\text{SME (J/kg)} = [\text{torque (Nm)} \cdot \text{angular velocity (s}^{-1}\text{)}] / [\text{throughput (kg/s)}].$$

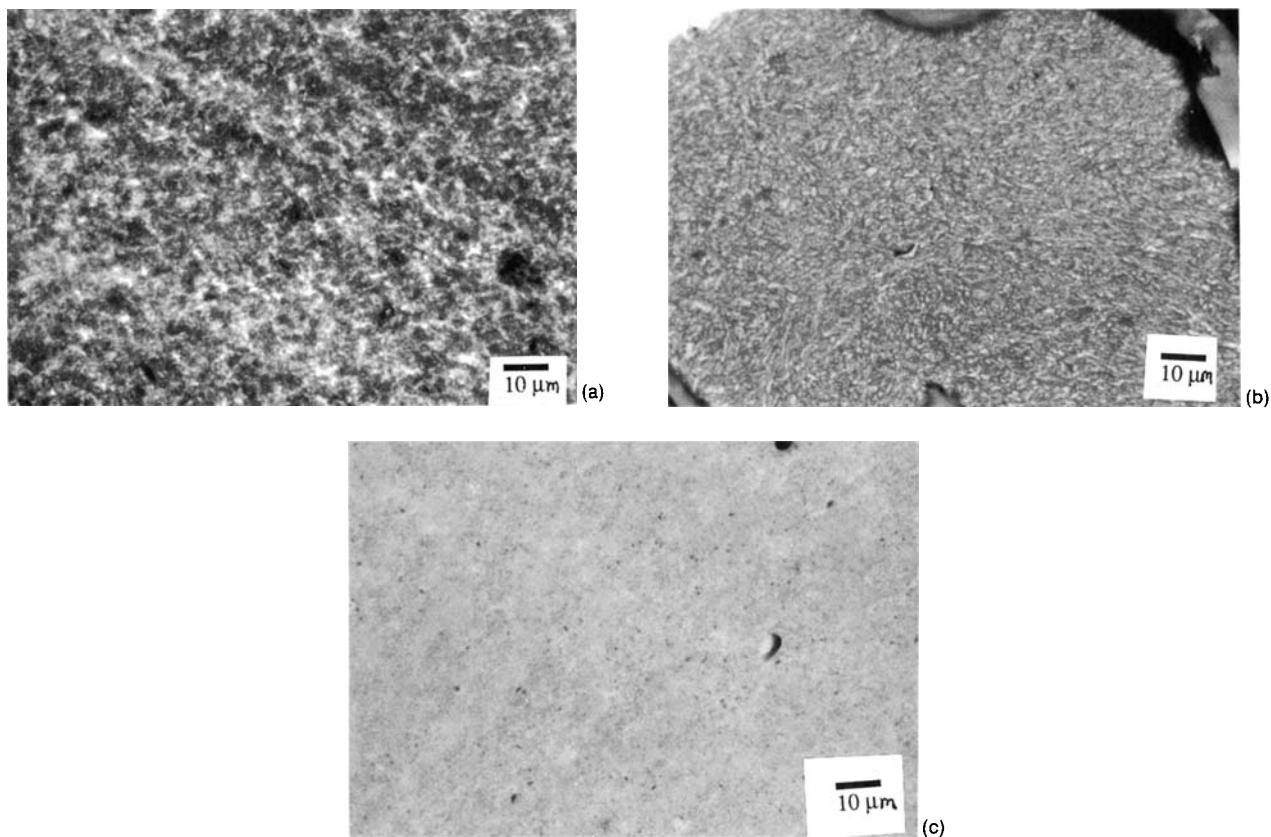


Figure 2 Optical microscope of (a) EPMA/Hylon VII, (b) EPMA/Hylon V, and (c) EPMA/Thermoflow blends.

Tensile Strength

Tensile testing was done on an Instron Universal testing machine according to the procedure outlined in ASTM test method D638. To study the effect of humidity on the tensile strength, samples were stored in a closed chamber containing a saturated solution of lithium chloride, which corresponds to a relative humidity (rh) of 11%, and a saturated solution of potassium chloride, which corresponds to an rh of 85%. These samples were kept in the enclosed chamber for a period of 4 weeks to equilibrate. They were then removed and tested immediately using a tensile tester. For blends containing EPMA, the crosshead speed was 10 mm/min corresponding to an initial strain level of $1.67 \times 10^{-3} \text{ s}^{-1}$. For blends containing SMA, the crosshead speed was 5 mm/min corresponding to an initial strain level of $8.33 \times 10^{-4} \text{ s}^{-1}$.

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was accomplished in a Rheometrics Spectrometer (RMS-800).

All testing was done in the torsional mode to obtain the storage (G') and loss (G'') modulus. The sample dimensions were $0.2 \times 10 \times 65 \text{ mm}$. For all blends the frequency was 1 rad/s. The percent strain for starch/SMA blends was 0.1% for the entire temperature range of 30–150°C. For starch/EPMA blends, the percent strain was 0.1% for temperatures between –100 and 20°C, which was raised to 1% for temperatures between 20 and 150°C. This increase in the strain was necessary to raise the torque to a range that could be detected by the transducer.

SEM

The fractured samples obtained after tensile testing were cut about 2–3 mm below the fracture surface and stuck to aluminum stubs. The samples were then coated with an Au/Pd alloy by vapor deposition and observed under a Hitachi 80 electron microscope.

Optical Microscopy

Optical microscopy was used to study the effect of the extrusion process on the distribution of starch

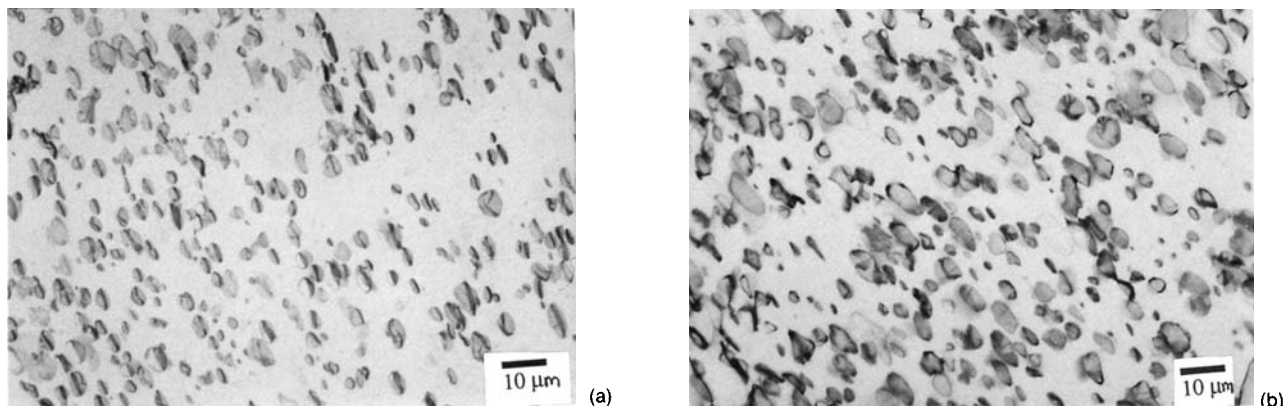


Figure 3 Optical microscope of (a) SMA/Hylon VII and (b) SMA/Hylon V blends.

in the blends. For starch/SMA blends, the samples were first fixed with a 5% glutaraldehyde solution followed by dehydration using ethanol, *n*-propanol, and *n*-butanol. Finally the samples were encapsulated in an acrylic resin. Thin sections (0.12–0.25 μm) of the encapsulated samples were cut at room temperature with a glass knife. Since the glass transition temperature of EPMA is approximately –40°C, starch/EPMA blend samples were cut at –60°C. These samples were stuck directly to a stub (without encapsulation) and cut with a glass knife to obtain sections approximately 0.2-μm thick. These thin sections were transferred onto optical microscope slides and stained with an iodine/KI solution. The sections were observed under the optical microscope at 40× magnification.

Biodegradation

This method is used to determine the degree and rate of aerobic biodegradability of polymeric materials in the presence of municipal sludge waste. Return activated sludge (RAS) from the wastewater treatment plant was used to prepare an inoculum and the polymeric material was exposed to this inoculum. The test determines the degree of aerobic biodegradation by measuring the evolved carbon dioxide as a function of time and assessing the degree

of degradability by reporting the percentage carbon conversion. This test was carried out per ASTM D5209 with some modification. The Bushnell–Hass Broth (Difco) was used as the source of nutrients from the microorganism, instead of the media specified by ASTM D5209. The composition of the Difco broth is as follows: anhydrous MgSO₄ 0.2 g, anhydrous CaCl₂ 0.02 g, K₂HPO₄ 1.0 g, anhydrous K₂HPO₄ 1.0 g, and anhydrous FeCl₃ 0.05 g. The test solution contained 4.9 g of Difco broth, 1.5 g of the test material, and 15 mL of the sludge inoculum. Water was added to the flask and brought to 1500 mL. The test sample was ground to fine mesh size prior to exposure to the sludge inoculum.

RESULTS AND DISCUSSION

Torque

The torque and the pressure generated during the melt blending are shown in Figures 1(a) and 1(b). The torque and pressure decreased and then increased as the amylose content in the blend increased. The mechanical input (specific mechanical energy) is given in Table I. Generally, high amylose corn starches have higher viscosities¹⁵ and hence generate higher torque values. However,

Table II Effect of Torque and Specific Mechanical Energy (SME) on Tensile Strength and Elongation of Hylon V/EPMA Blends

Torque (Nm)	Mass Flow Rate (g/min)	SME (kJ/kg)	Tensile Strength (MPa)	Elongation (%)
33.9	9	1728.6	6.2	15
50.93	54	432	4.7	30
90.38	80	518.3	5.1	19

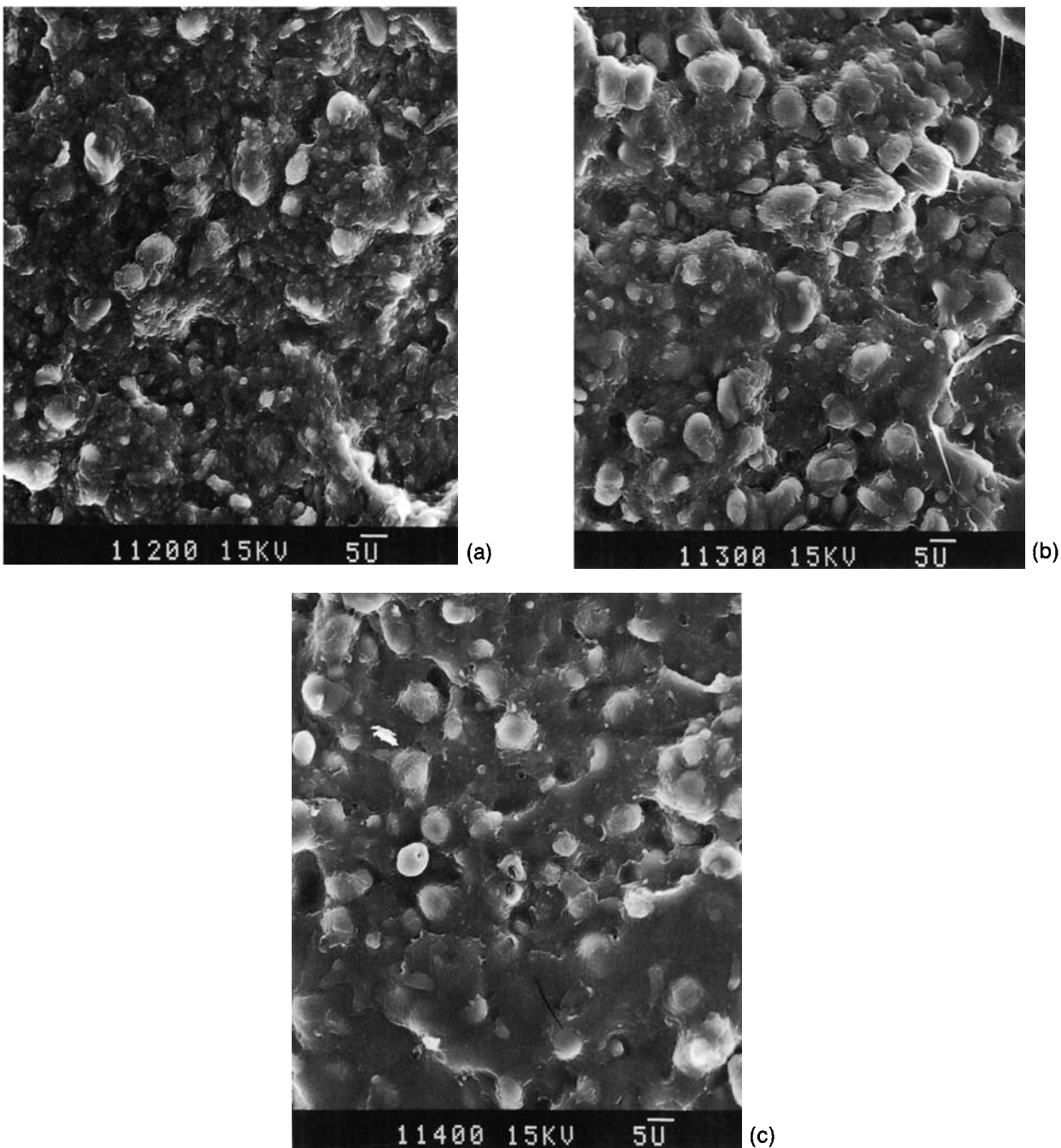


Figure 4 SEM of the effect of torque/SME on the morphology of EPMA/Hylon V blends: (a) torque is 33.9 Nm and SME is 1728.6 kJ/kg, (b) torque is 50.93 Nm and SME 432 kJ/kg, and (c) torque is 90.38 and SME 518.3 kJ/kg.

higher viscosities also lead to higher stresses and caused the starch granules to melt and degrade, thus lowering the viscosity. For waxy corn starch, which has a highly branched structure, the high torque value is an indication of a crosslinked polymer between starch and the synthetic polymer. It

is interesting to note that the torque and specific mechanical energy (SME) generated by blends containing waxy starch is higher (554.2 vs. 349.3 kJ/kg for EPMA and 889.87 vs. 540.6 kJ/kg for SMA) than that of a similar 60/40 blend containing normal corn starch.¹⁶

Table III Effect of Relative Humidity (rh) on Tensile Strength

Sample Composition	Tensile Strength (rh 11%) (MPa)	Elongation (%)	Tensile Strength (rh 85%) (MPa)	Elongation (%)
Thermoflow/EPMA	6.8	13.1	6.7	51.5
Hylon V/EPMA	8.9	2.9	8.1	15.6
Hylon VII/EPMA	8.6	4.9	5.3	22.5
Thermoflow/SMA	19.7	1.63	5.9	1.05
Hylon V/SMA	22.4	1.78	14.13	1.5
Hylon VII/SMA	17.2	1.63	13.53	1.43

Morphology

For optimum mixing during melt blending, both the starch and the synthetic polymer should be in the molten state. While the synthetic polymer, like any thermoplastic will melt at temperatures above its melting point, the starch granules will melt only under conditions of temperature and shear energy. Under the conditions of melt blending used in this process, the starch granules do not undergo complete melting.¹⁶ Thus we have a molten phase of starch and synthetic polymer in which discrete starch granules are imbedded. Because starch is a shear sensitive material, granules undergo degradation in addition to the melting whenever a high shear is imparted.^{14,16}

The morphology of the molded blends are shown in Figures 2 and 3. Starch and EPMA formed a co-continuous phase in all three starch/EPMA blends (Fig. 2). The starch phase became finer as the amylopectin content in the blend increased. In the blend containing waxy starch [Fig. 2(c)], the granules of starch completely melted and are dispersed with the rubbery phase. In starch/SMA blends, the starch granules do not undergo complete melting and remain dispersed in the SMA phase (Fig. 3). Blends made from Thermoflow/SMA are not shown because during the microtoming the sections were very fragile and water sensitive and hence could not be transferred onto the optical microscope slide. The starch granules for Hylon VII blend [Fig. 3(a)] are smaller than the granules in Hylon V [Fig. 3(b)]. This is because Hylon VII blends were subjected to a much higher SME than Hylon V blends (Table I). The blends were subjected to different torques, with Hylon VII being intermediate between a high with waxy and low with Hylon V. It should be noted that the SMEs of starch/EPMA and starch/SMA blends are comparable. The torques for starch/EPMA blends are significantly higher than that for starch/SMA blends. This is due to the fact that the processing temperatures are lower for starch/EPMA

blends than for starch/SMA blends. Hence, the viscosity is higher for starch/EPMA blends than for the corresponding starch/SMA blends.¹⁶ Thus, besides the viscosity ratio and surface tension, it appeared that torque had more influence on morphology than SME.

To further study the effect of SME and torque on the tensile properties, samples of Hylon V and EPMA were made up in the extruder by altering the flow rate of the material into the extruder. The amount of material in the extruder influenced the shear experienced, and hence the SME and torque required during processing. The SME and the torque for the blends are also given in Table II. The SEMs for the blends are shown in Figure 4. As seen from Table II and Figure 4, SME has a much more pronounced influence on the granule size than does torque. The blend subjected to the highest SME (1728.6 kJ/kg) and the lowest torque (34 Nm) had the lowest granule size.

Because the granular structure (shape, size, and hardness), composition (amylose and amylopectin ratio), and viscosities of the three starch varieties are different, the SME required to melt the starch granules (and hence destroy the granular structure) will be different. Therefore, it is difficult to compare the effect of torque and SME on the morphology of blends made from different varieties.

Tensile Strength

The variation in tensile strength with amylose content of starch is shown in Table I. Both the blends containing EPMA and those containing SMA show the same trend, i.e., increased strength at amylose content of 50% (Hylon V) and then decreased strength at an amylose content of 70% (Hylon VII). The tensile strengths for pure EPMA and SMA are 6.6 and 33 MPa, respectively. The addition of starch to EPMA reduced the tensile strength only slightly but significantly reduced the

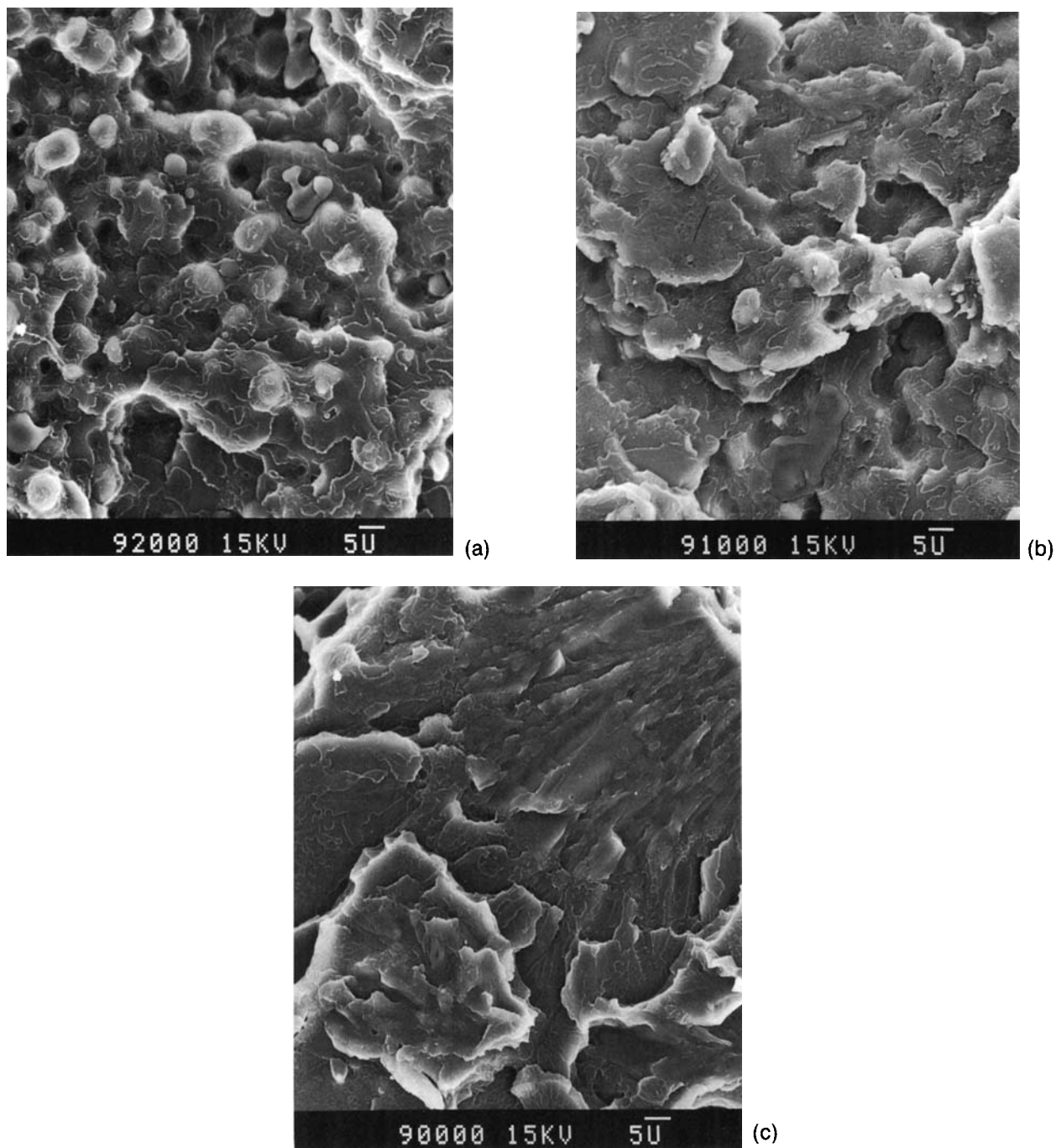


Figure 5 SEM of failed surface (in tensile) of blends conditioned at 11% rh: (a) SMA/Hylon VII, (b) SMA/Hylon V, and (c) SMA/Thermoflow blends.

percentage elongation from 1000 to less than 5% for high amylose blends. Addition of starch to SMA reduced the tensile strength of the blend, while the percentage elongation was unaffected. There appeared to be an inverse relationship between the torque and SME during blending and the tensile strength. The highest tensile strength

was obtained for EPMA and SMA blends containing Hylon V. The Hylon V blends required the lowest torque and the lowest SME during processing. For any given amylose to amylopectin ratio, higher SME tended to disrupt and degrade the starch molecules to form a low molecular weight product with inferior physical properties.

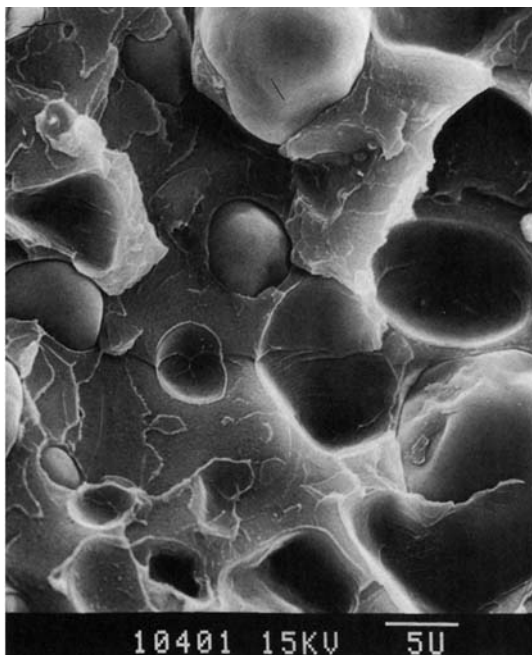


Figure 6 SEM of failed surface (in tensile) of normal (25% amylose) corn starch/nonreactive polystyrene blends.

The effect of relative humidity on tensile and elongational properties is shown in Table III. The tensile strengths of blends containing EPMA (except Hylon VII) remained unaffected with a change in relative humidity. However, the percentage elongation increased significantly as the humidity was increased. This can be explained from the morphology of the starch/EPMA blends. For a cocontinuous morphology, the material that has the highest modulus determines the elongation of the blends in the tensile mode. For starch/EPMA blends, thermoflow absorbed the most water, which could act as a plasticizer. When water was added to pure starch, its elongation increased.¹¹ Thus, at higher humidity, elongation of the samples will increase.

For starch/SMA blends, the tensile strength decreased sharply without any change in the percent elongation. For these blends, the starch particles are dispersed in the SMA matrix. In such cases, the dispersed phase (starch) does not contribute to the elongation. At higher humidity, starch particles absorb more moisture and the interphase becomes weaker, which results in lower strength without any change in the percent elongation.

The effect of SME and torque on the tensile strength and elongation of Hylon V/EPMA blends are shown in Table II. The blend subjected to the highest SME had the highest tensile strength but

the lowest percentage elongation. As the SME encountered during the blending decreased, the tensile strength decreased but the percent elongation increased. At low SME when the starch was not fully melted (Fig. 4), the system behaved similarly to a filled system and the tensile strength was high. With increased SME, more and more starch was melted and formed a cocontinuous phase with the rubber which increased the modulus and reduced the elongation.

Fracture Mechanics

The fracture surface morphology is also helpful in elucidating the failure mechanism of these blends. For starch/SMA blends, which are mostly brittle, the fracture surface after tensile failure showed the presence of cavities in the form of ridges and valleys (Fig. 5). A valley is present on one fracture surface and a corresponding ridge on the other. The crack seemed to propagate through both the starch and SMA phases. This was observed for all three different types of starches. The failure appeared to be a combination of pop-in and shear mode with pop-in mode dominating [Fig. 5(b,c)]. Shear tearing is an accepted mode of failure in metals and polymers.¹⁷⁻¹⁹ The absence of any deep voids indicates that materials snapped at the point of stress. The presence of a rough surface indicates that the fracture is similar to that of a planar fracture surface.²⁰ There appeared to be no evidence of interfacial failure between the starch and the SMA. To elucidate what effect the functional group on the SMA has on the mode of failure, we examined the fractured surface of the starch (containing 25% amylose)/polystyrene blend from our prior study.¹³ Because polystyrene has no functional group capable of reacting with the hydroxyl group of the starch, the blend is a simple mixture that is expected to display poor interfacial tension. It can be seen that the failure occurred at the starch/polystyrene interface (Fig. 6) and resulted in the starch granules being separated from the polystyrene matrix. These blends had a much lower tensile strength¹³ compared to starch/SMA blends. This supports the theory that the reactive blending improves the interfacial adhesion.

Compared to the starch/SMA blends, which had a fairly smooth surface, the corresponding starch/EPMA blends displayed a much rougher surface. For starch/EPMA blends, which are primarily ductile, the main fracture mechanism appeared to be due to shear tearing. A significant number of internal voids and cavities are apparent (Fig. 7). The largest of these voids ranged between 1 and 2 μm . There

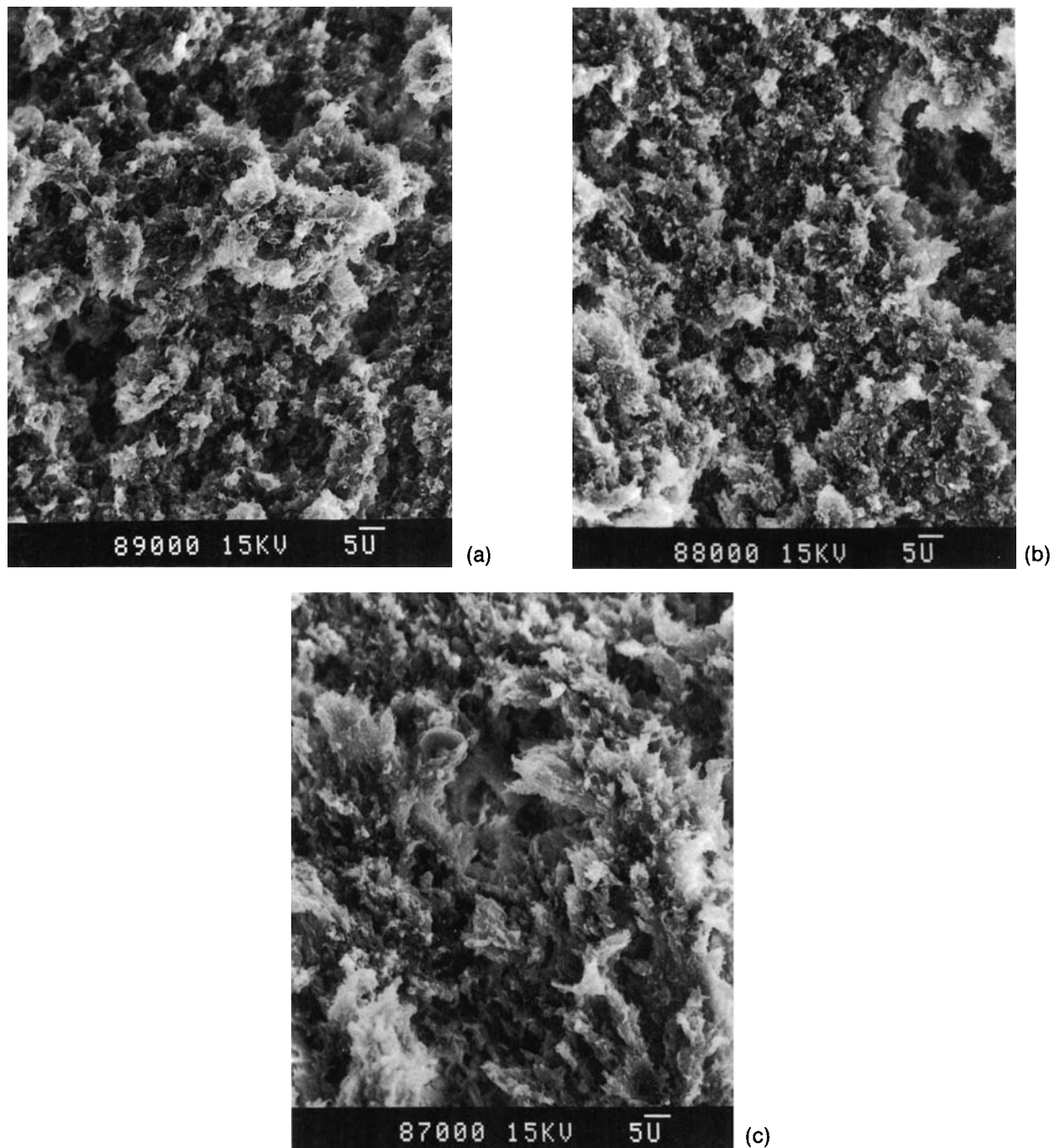


Figure 7 SEM of failed surface (in tensile) of blends conditioned at 11% rh: (a) EPMA/Hylon VII, (b) EPMA/Hylon V, and (c) EPMA/Thermoflow.

was no evidence of a matching fracture surface in the other part. The pulled-out portion in Figure 7 that created the cavities or voids was probably the rubbery phase (EPMA) in the blend. The EPMA domains appeared to have fractured by tearing. Because EPMA has a much higher elongation than starch at low humidity, the rubber phase elongated

even after the starch phase had failed. Apart from the cavities left behind by the pulled-out rubber particles, no voiding was observed. At higher humidity (Fig. 8), the number of voids decreased significantly. This is probably because the blend samples were more ductile, and both the phases elongated to a certain degree before failing (thus leaving

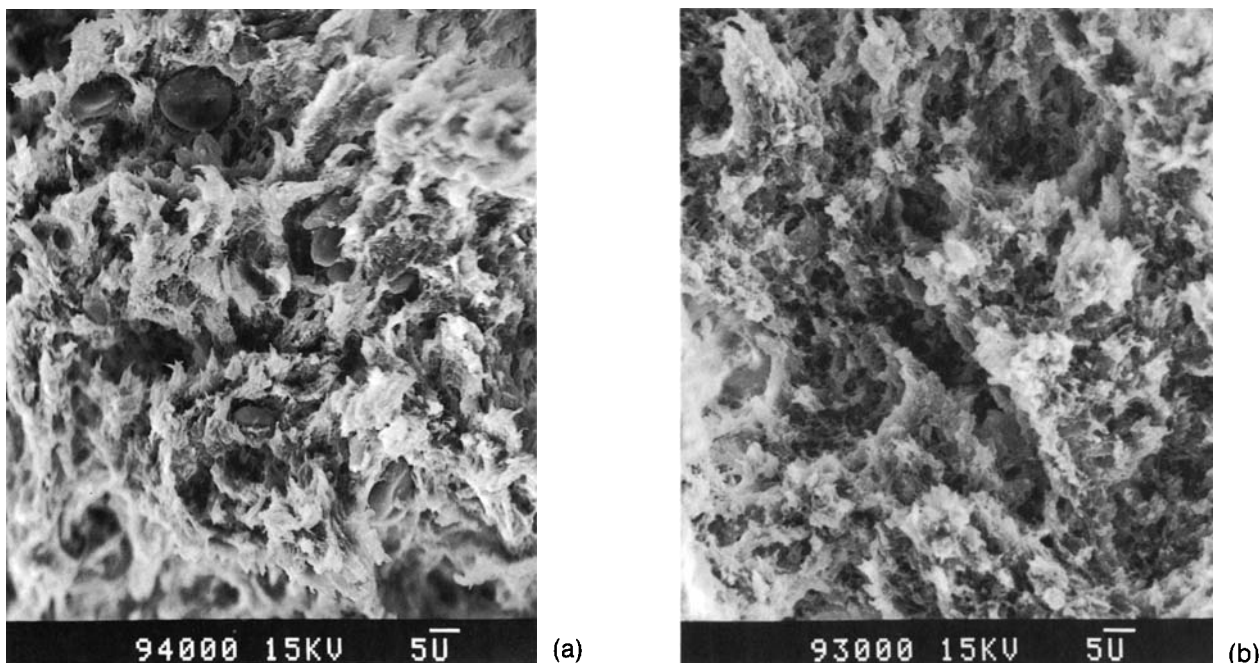


Figure 8 SEM of failed surface (in tensile) of blends conditioned at 85% rh: (a) EPMA/Hylon V and (b) EPMA/Thermoflow.

behind a filamentlike structure). Cavitation is a commonly encountered mechanism in blends with finely dispersed phases.¹⁷ Because of the higher torque that starch/EPMA blends encountered during processing,¹⁶ the morphology is much finer than that of starch/SMA blends. This encourages adhesion between the phases and leads to cavitation of the lower modulus rubber particles.

Water Absorption

The plot of water absorption with time for the starch/EPMA and starch/SMA blends is shown in Figure 9. Starch/EPMA absorbed more water than starch/SMA contrary to the results reported in our earlier article.¹³ This is because when the blending was achieved in a batch mixer, as in our previous study,¹³ the torque displayed by starch/SMA blends was much higher than the torque of the corresponding starch/EPMA blends. A careful look at these data revealed that water absorption is related to the mechanical energy during processing: the higher the energy during melt blending, the higher the amount of melting and degradation of starch and the higher the percent water absorbed. The water absorption leveled off between 7 and 22 days. For EPMA blends, samples containing higher amylose content had a lower percentage of water absorption. For SMA blends, the water absorption was the highest for the

samples containing Hylon V. Hylon VII/EPMA and Thermoflow/SMA blends actually showed a slight decrease in water absorption. This was probably due to small amounts of starch that leached out in the presence of water.

DMA

The temperature dependence of the G' , G'' , and $\tan \delta$ of starch/EPMA blends are shown in Figures 10 and 11. The glass transition (T_g) for pure EPMA in DMA is between -40 and -30°C . It was not possible to obtain the DMA of pure starch, because it was difficult to mold the samples. Two distinct glass transitions are observed for each blend. The first transition is due to the EPMA phase, which occurred between -45 and -25°C . The second transition represents the glass transition of the starch phase. The T_g of starch depends on its moisture content as well as its amylose to amylopectin ratio.²¹ Higher moisture and amylose content would tend to decrease the glass transition temperature. The moisture content of the starch/EPMA blend dropped to between 2 and 3% after extrusion. At such low moisture content, the T_g of starch has been reported to be above 100°C .²¹ From the $\tan \delta$ peak in Figure 11 it is seen that the T_g ranges from 85°C for Hylon VII to a high of 115°C for the waxy starch. This trend is in accordance with the values available in

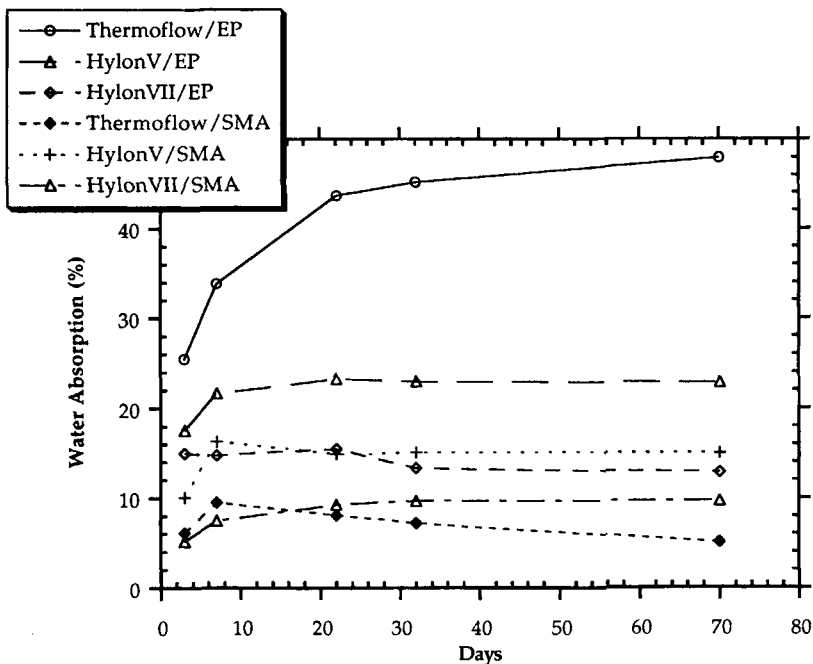


Figure 9 Water absorption with time for different starch/SMA and starch/EPMA blends.

the literature. The maximum $\tan \delta$ value is the highest for the waxy starch (0.375) and minimum for Hylon V (0.24) with Hylon VII (0.298) exhibiting the intermediate value. The value of $\tan \delta$ decreased as the molecular weight increased.²² This would be unusual, given that unprocessed waxy starch has the highest molecular weight. However, the higher mechanical energy encountered during melt blending

would reduce the molecular weight of waxy starch more than the corresponding high amylose starch. Also, the starches with higher amylose content tend to recrystallize. This would lead to a lower $\tan \delta$ value than would occur in higher molecular weight waxy starch. The addition of starch to EPMA increased the magnitude of the modulus. The higher the amylose content in the starch, the higher the

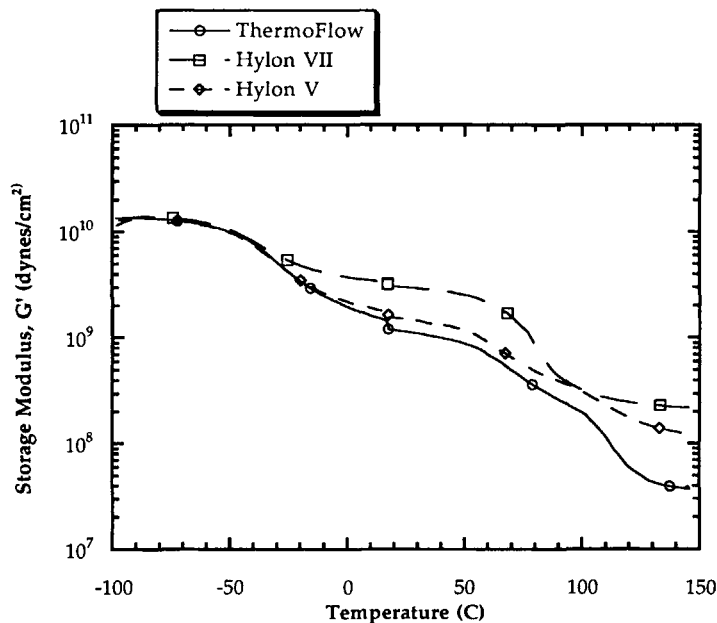


Figure 10 Storage modulus vs. temperature of starch/EPMA blends.

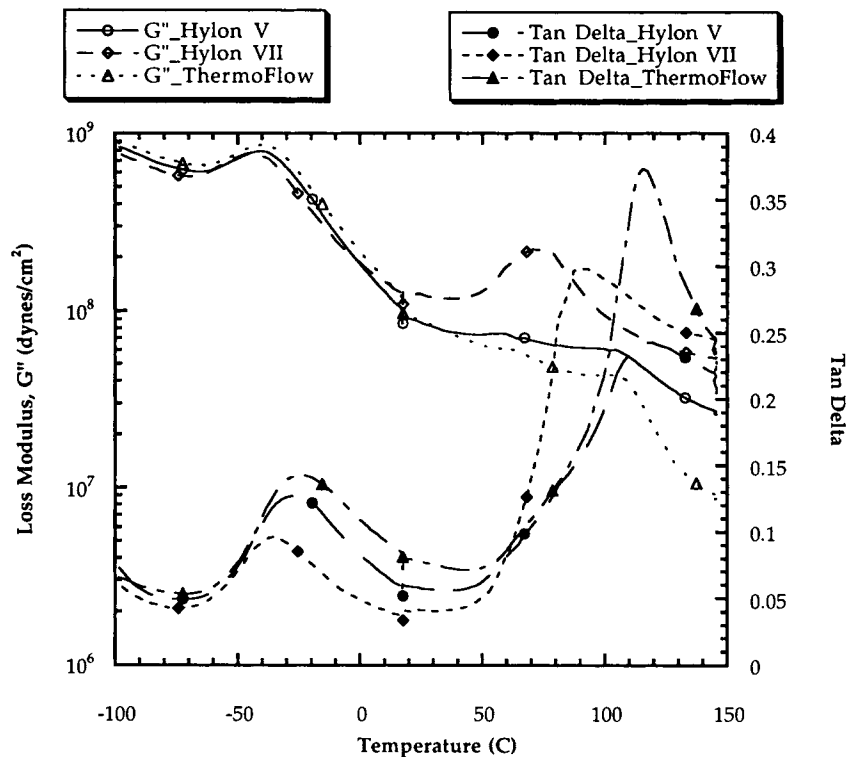


Figure 11 Loss modulus and tan δ vs. temperature for starch/EPMA blends.

magnitude of the storage modulus (Fig. 10). At 75°C, in the rubbery region, the storage modulus is 1.7×10^9 dynes/cm² for the blend containing Hylon VII, 6×10^8 dynes/cm² for the blend containing Hylon V, and 4×10^8 dynes/cm² for the blend containing waxy starch. Hence, the material becomes more rigid as the amylose content of the starch increases. This

can also be seen in the tensile strength data where the percentage elongation decreases when the amylose content is increased.

The dynamic mechanical properties of the starch/SMA blends as a function of temperature are shown in Figures 12 and 13. The T_g of pure SMA ranged between 90 and 100°C. A single broad T_g is observed

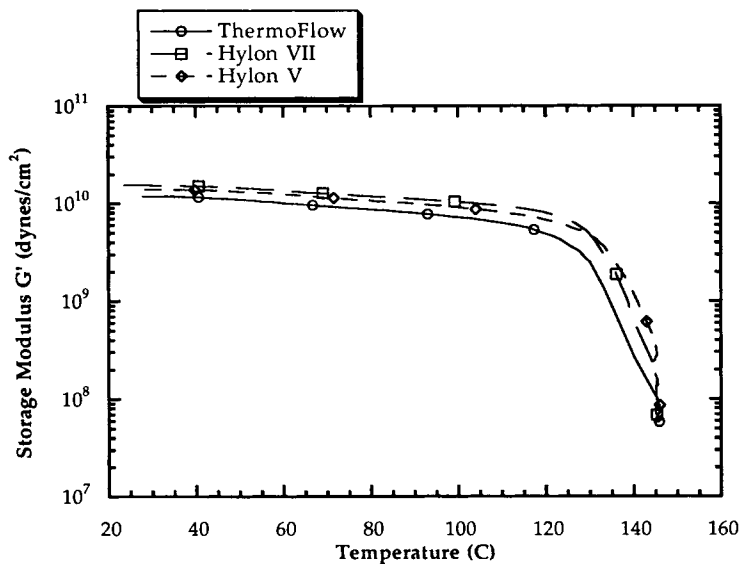


Figure 12 Storage modulus vs. temperature of starch/SMA blends.

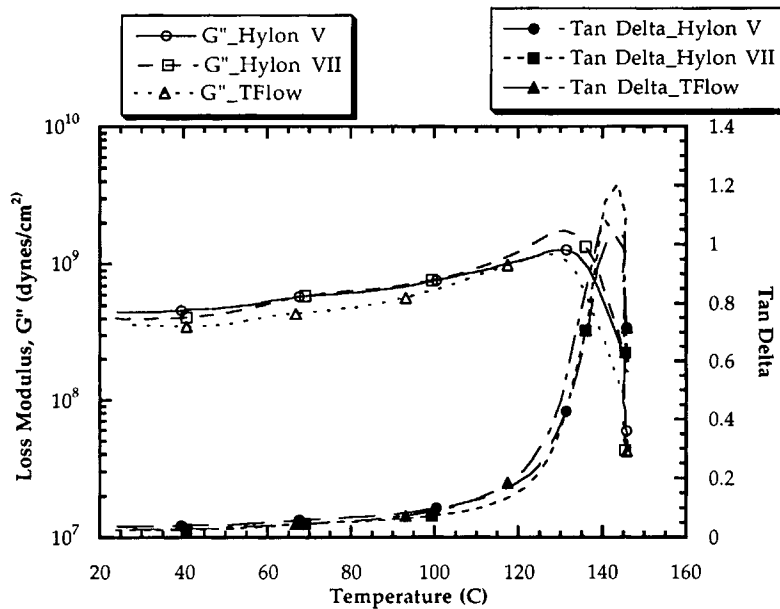


Figure 13 Loss modulus and $\tan \delta$ vs. temperature for starch/SMA blends.

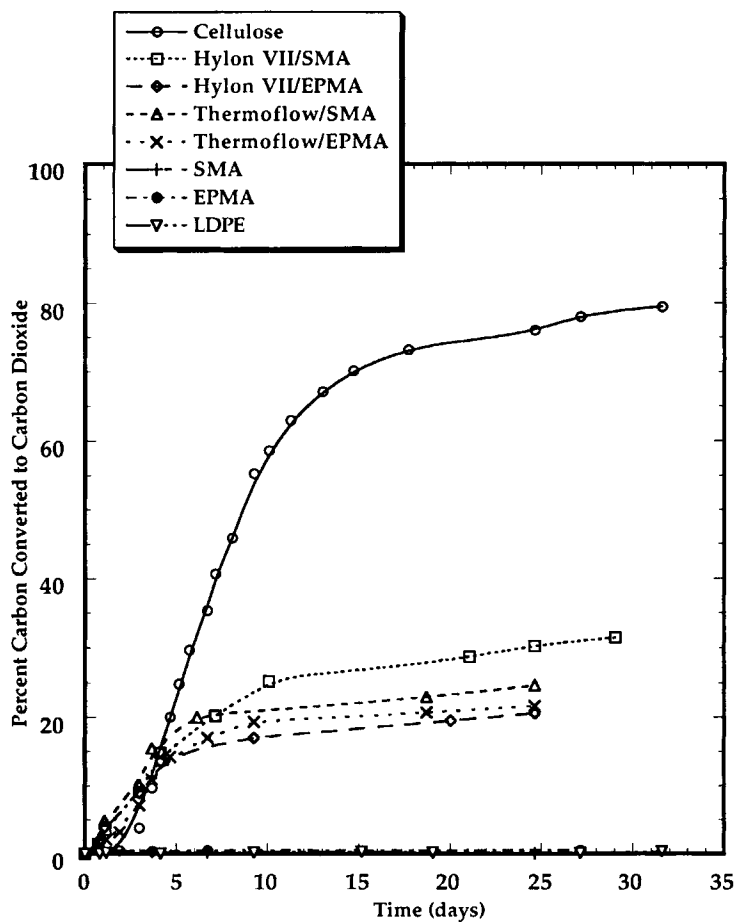


Figure 14 Aerobic biodegradation of blends in the presence of municipal sewage sludge.

for these blends. Normally the presence of single T_g is an indication of a homogeneous or a crosslinked blend. In our opinion, the single T_g occurs because of the close proximity of the individual glass transitions of starch and SMA, which cannot be delineated by the DMA technique. There is a peak of decreased intensity on the loss modulus plot near 65°C (Fig. 13) that could correspond to the T_g of starch at high moisture content. However, at the moisture content at which the DMA experiment was conducted (2–3%) the expected T_g of starch should be much higher. The magnitude of this transition is very small and is not apparent in the storage modulus or $\tan \delta$ plot. We conducted a separate experiment in which the sample was immersed in water prior to conducting the temperature sweep in the hope that the plasticizer would depress the T_g of the starch component. The plot of G' and G'' with temperature was unchanged as compared to blends containing 2–3% water. There may be a possibility that the increased concentration of the functional group could have led to a slightly crosslinked blend. This observation is under further investigation. Also, the T_g of the blend is about 10°C higher than that of pure SMA and roughly 20–40°C higher than the T_g of starch in the starch/EPMA blends. The T_g was slightly higher for the blends containing high amylose starch (135–140°C) than for waxy starch (125°C). The maximum $\tan \delta$ value was the highest for Hylon VII (1.3) and lowest for Hylon V (1.05), with waxy starch (1.175) occupying the intermediate position. The modulus of the blend was higher than that of pure SMA and, as was the case with starch/EPMA blends, increased with increased amylose content (Fig. 12).

Biodegradation

The percentage of polymeric carbon converted to carbon dioxide with time is shown in Figure 14. It is seen that cellulose biodegrades to about 60% within the first 10 days. The pure synthetic polymers SMA, EPMA, and low density polyethylene showed no biodegradation. The two blends of Hylon VII with EPMA and SMA showed biodegradation of approximately 20 and 30%, respectively. Because SMA and EPMA does not biodegrade, the carbon that is being converted to carbon dioxide comes from the starch component in the blend. Blends containing EPMA have lower rates of biodegradation than do blends containing SMA. Blends containing Thermoflow also showed biodegradation. Because this biodegradation is carried out in liquid environments, the rate of biodegradation generated here is expected to

be different from that during composting. However, the basic trends would still be valid, i.e., that the natural component in the blend would degrade while the synthetic component does not.

CONCLUSIONS

Starch containing different amounts of amylose and amylopectin were melt blended with synthetic polymers (styrene and ethylene-propylene rubber) containing a maleic anhydride group. Hylon V required the minimum torque and SME for both EPMA and SMA blends. In starch/EPMA blends, the starch in the blend formed a cocontinuous phase with the rubbery phase. The starch phase became finer as the amylopectin content in the starch increased. In starch/SMA blends, the starch granules were still intact, presumably because the torque generated was lower than that used for corresponding starch/EPMA blends. For Hylon V blends, the size and number of the unmolten starch granules were related to the SME encountered during processing; the higher the SME, the lower the size and number of the granules. Addition of starch to EPMA caused a significant reduction in the percent elongation of the blends but little reduction in the tensile strength. For starch/SMA blends the tensile strength dropped to between 60 and 80% of that of pure SMA. Higher humidity increased the elongation of starch/EPMA blends, but for starch/SMA blends, caused a significant decrease in the tensile strength, this observation being most prominent for blends containing Thermoflow. While shear tearing appeared to be the major failure mechanism in tension for starch/EPMA blends, starch/SMA blends failed due to a combination of pop-in and shear modes. In the absence of a functional group on the synthetic polymer (and hence the absence of reaction), the starch/polystyrene blend failed at the interface of the polymers. Water absorption was lower for blends containing SMA and correlated with the SME during processing: the higher the SME, the higher the percent of water absorbed. Blends containing Thermoflow absorbed the most water. Starch/EPMA blends showed two glass transitions, one corresponding to each polymer; starch/SMA blends displayed one broad T_g .

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