BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 6, pp. 1179-1188, 1995

0032-3861/95/$10.00+0.00

Effect of processing conditions on the dynamic mechanical properties of starch and anhydride functional polymer blends

Utpal R. Vaidya, Mrinal Bhattacharya* and Dongmei Zhang
Department of Agricultural Engineering, University of Minnesota, 1390 Eckles Avenue, St Paul, MN 55108, USA
(Received 10 January 1994; revised 28 April 1994)

Reactive blending of starch with ethylene-propylene-*g*-maleic anhydride (EPMA) and styrene maleic anhydride (SMA) copolymers was carried out in a batch mixer. The effect of processing conditions, such as mixer speed and mixing time, on the dynamic mechanical properties and morphology, was studied. Starch/EPMA blends showed two distinct glass transitions in the G' and G'' plots, one corresponding to the starch and the other corresponding to EPMA. Starch/SMA blends exhibited one broad transition, since the glass transition temperatures of starch and SMA were in close proximity to one another. The starch in the blend was sensitive to the processing conditions used in this study. Increasing the mixing time from 10 to 20 min and increasing mixing speed from 50 to 100 rev min^{-1} resulted in increased melting of starch granules. Increasing the mixing speed and mixing time also resulted in increased degradation of starch, as evident from the gel permeation chromatography.

(Keywords: reactive blending; glass transition; dynamic mechanical properties)

INTRODUCTION

Polymer blending is one of the most popular methods used in developing new materials with desired combinations of properties. This is probably the cheapest and fastest route to developing new plastics. However, most of the useful polymers are not miscible with each other and tend to phase-separate in the melt state. In most cases, the major component of the blend forms a continuous matrix, while the minor component forms a dispersed phase in this matrix. Depending on the composition, both the phases can become continuous and interpenetrate (co-continuous). In addition to the properties of the individual polymer components, the final properties of these immiscible blends depend to a significant extent on the phase morphology and interfacial adhesion. Generally, a fine size of the dispersed phase and a good adhesion between the two phases, lead to improved blend properties.

Most polymers are viscoelastic in nature. Their mechanical properties exhibit a pronounced dependence on the temperature and the rate of deformation. In a number of applications, the material is subjected to complex dynamic stress conditions over a broad temperature range. The viscoelastic response of the material can be studied using a temperature sweep at a fixed frequency (i.e. rate of deformation) or in a frequency sweep at the required temperature. Subjecting the specimen to a torsional deformation could yield useful information related to the complex shear modulus. The complex modulus, G^*, can be represented as:

$$G^* = G' + iG''$$

where G' is the ratio of the stress in phase with the strain to the strain, and G'' is the ratio of the stress 90° out of phase with the strain to the strain. G' and G'' are termed the storage modulus and loss modulus, respectively. G' represents the elastic response of the material, related to the potential energy stored by the material under deformation, and viscous response of the material is characterized by G'', which signifies the dissipation of energy as heat during the deformation. The ratio of the two moduli is represented as:

$$\tan\delta = G''/G'$$

Tan δ represents the internal friction or damping and is termed the loss factor. The mathematical relationships between these parameters and their physical significance is well described in the literature[1].

All the parameters described above are directly related to the molecular motions under stress, and therefore yield useful information about the material structure. The value of the storage modulus G' signifies the strength of the material. At any fixed rate of deformation, the temperature at which the value of G' starts to decrease rapidly, corresponds to the glass transition temperature. Weaker molecular transitions, such as side group or small segmental motions, are seen more clearly in the G'' or in the $\tan\delta$ response. The G'' or $\tan\delta$ peaks reflect the energy dissipation or damping property of the material. The secondary transitions, γ and β peaks in the $\tan\delta$ plot, are due to side groups and small segmental motions.

---

*To whom correspondence should be addressed

Nearly all tough/ductile glassy polymers and those with high impact strength have prominent secondary transitions[2]. The primary α-transition corresponds to the glass transition. The shift in the α-transition peak position indicates a change in the transition temperature. In a phase-separated polymer blend, separate glass transitions for the two phases can be observed by dynamic mechanical analysis (d.m.a.). In fact, the use of d.m.a. is one of the most popular ways to determine the phase separation in polymer blends. Thus, dynamic mechanical analysis helps elucidate the structure and properties of the material.

D.m.a. has been extensively used to study the phase separation of synthetic polymer blends[3–11]. Several researchers have correlated dynamic mechanical properties with the morphology in order to characterize the miscibility of blends. Liang and Williams[3] studied blends of polypropylene and polyamide with and without compatibilizer. The compatibilized blends showed finer dispersion and better interfacial adhesion. For the compatibilized blends, the storage modulus in extension, E', varied linearly as a function of composition, while for non-compatibilized blends it showed significant deviation from linearity. The effect of compatibilization was most prominent for 50/50 blend compositions, where the poor adhesion between the co-continuous phases for a non-compatibilized blend resulted in lower modulus compared to the compatibilized blend. Compatibilized blends also differed from non-compatibilized blends in E'' and $\tan\delta$ plots. Hayashi *et al.*[4] studied the effect of crosslinking and composition on the morphology and dynamic mechanical properties of the styrene–divinylbenzene (DVB)/poly(vinyl chloride) (PVC) system. The system was found to be phase-separated. The glass transition temperature and the modulus of the polystyrene–DVB phase increased with the crosslinking. Thomas and George[5] studied blends of polypropylene and ethylene–vinyl acetate copolymers with respect to blend composition and crosslinking of the rubber phase. They correlated dynamic mechanical properties with the morphology. The extent of crosslinking improved the miscibility of the blends, as evident from the increased modulus and broadened transition peaks. They also discussed models to predict the storage modulus of these blends. Natansohn *et al.*[16] reported the effect of ionic interactions on the miscibility of the blends. Several other reports[7–11] on blends of synthetic polymers are also available in the literature.

In recent years, issues concerning environmental pollution have prompted a great deal of activity in the development of biodegradable plastics from renewable resources. Several patents are being filed in this area. Many of these patents describe blends of a natural polymer, namely starch, with synthetic polymers[12–16]. Starch is a highly hydrophilic polymer and therefore not miscible with most of the synthetic hydrophobic polymers. In spite of the increased level of academic and commercial interest, no detailed studies on the dynamic mechanical properties of these blends are available in the literature.

Recently, we have reported improvement in the physical properties of starch and synthetic polymer blends by using synthetic polymers having anhydride functional groups[17]. In this paper we extend our previous study and report the dynamic mechanical properties of these blends. The dynamic mechanical properties and the scanning electron micrographs were correlated to the processing conditions in the batch mixer. To the best of our knowledge, this is the first time that the dynamic mechanical properties of starch/polymer blends have been reported in the scientific literature.

EXPERIMENTAL

Materials

Industrial corn starch, containing 75–80% amylopectin and 20–25% amylose (SMP 1100), was obtained from Cargill Inc. Styrene maleic anhydride (SMA) copolymer (Dylark 232) was obtained from Arco Chemicals. This grade of SMA contains about 8% maleic anhydride. Ethylene–propylene-*g*-maleic anhydride (EPMA) copolymer (VA1801) was obtained from Exxon Chemicals and contained approximately 0.8% maleic anhydride.

Blend preparation

All blends were prepared in a batch mixer (C. W. Brabender Instruments Inc., South Hackensack, NJ). The batch mixer was equipped with a pair of roller blades 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 EPMA and 190°C for SMA blends. For starch/EPMA experiments, the amount of starch in the blend was 60, 70 and 80% by weight. For starch/SMA experiments, the amount of starch in the blend was 50 and 80% by weight. For each composition, the mixer speed was set at 50, 100 or 200 rev $\min^{-1}$ and mixing time was either 10, 20 or 30 min. During the blending process, the torque and the melt temperatures 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.

Gel permeation chromatography (g.p.c.)

A Waters 150 LC/GPC was used with a refractive index detector to measure the molecular size of starch. A Phenogel (Phenomenex, Torrance, CA) column (300 mm × 7.8 mm), with 10 μm particle size, was used for separation. H.p.l.c. grade dimethyl sulfoxide (DMSO) was used as a mobile phase. Due to the lack of a mutual solvent for EPMA and starch, only starch/SMA blends could be analysed by g.p.c. About 0.2% (w/v) solution of samples containing blends of starch/SMA in DMSO was filtered through a 0.45 μm filter to remove insoluble particles. Since polystyrene was not soluble in DMSO, and SMA, although soluble, was isorefractive with DMSO, no standard samples could be run. Hence, the analysis is based on relative increase or decrease of high/low molecular weight fractions of the starch component of the blend.

Scanning electron microscopy (*SEM*)

Samples were fractured in liquid nitrogen and stuck to aluminium stubs. The samples were then coated with Au/Pd alloy by vapour deposition and observed under a Hitachi 80 electron microscope.

Dynamic mechanical analysis

Blend samples were moulded into rectangular strips of dimensions 0.2 mm × 10 mm × 65 mm. A Rheometrics Mechanical Spectrometer (RMS-800) was used to evaluate the dynamic mechanical properties. The samples were subjected to a sinusoidal strain in the torsion mode. Starch/EPMA blends were subjected to 0.1% strain between -100 and 20°C and to 1% strain between 20 and 150°C at a frequency of $1\,\mathrm{rad\,s^{-1}}$. Starch/SMA blends, on the other hand, were subjected to 0.1% strain between 20 and 180°C at $1\,\mathrm{rad\,s^{-1}}$ frequency. The temperature was increased at the rate of $10°\mathrm{C\,min^{-1}}$. Each sample was analysed in triplicate.

RESULTS AND DISCUSSION

In its natural state, starch exists in a granular form. The size and shape of the starch granules vary depending on their origin. Native corn starch consists of polygonal or round granules ranging from 5 to 25 μm in diameter[18]. Starch behaves like a thermoplastic only under high shear and high moisture ($>10\%$) conditions. At lower moisture content ($<10\%$), the starch granules may melt when subjected to high shear and temperature, but that could also lead to the partial degradation of starch macromolecules, resulting in the lowering of molecular weight. When the native starch, at low moisture content, is blended with a functionalized synthetic polymer in a batch mixer, the resulting blend contains a mixture of molten polymer, molten starch, unmelted or partially melted starch granules and a small amount of graft copolymer of starch and polymer. The small concentration of graft copolymers formed during the blending can significantly improve the properties of the blend. The authors are investigating the reaction between starch and anhydride functional polymers using Fourier transform infra-red spectroscopy[10]. The extent of starch melting and degradation depends on the blending conditions. The blending conditions of the batch mixer had a considerable effect on the dynamic mechanical properties of the starch/polymer blends. These properties could be related to the melting and degradation of starch by using g.p.c. and SEM data.

Starch/EPMA blends

Glass transition. Dynamic mechanical analysis of the starch/EPMA blends revealed two distinct glass transitions, indicating the phase separation of the blend components. These transitions are observed in approximately the same temperature ranges, irrespective of the blend composition and the blending conditions. The first transition, corresponding to EPMA copolymer, was observed roughly between -40 and 0°C. The second glass transition, between 30 and 50°C, was due to starch[20].

Effect of blend composition. Blends prepared with 60, 70 and 80 wt% starch were analysed using the dynamic mechanical analysr. The storage modulus (*Figure 1*) of the blends was dependent on the amount of starch and increased with increased starch content in the blend. This effect was more pronounced with the increase in temperature during d.m.a. It is a common practice to compare values of the modulus in the rubbery region, which is a measure of the inherent rigidity due to the chemical structure and/or crosslinking. At 100°C, the blend containing 80% starch displayed the highest storage modulus (3.5×10^6 Pa), followed by those containing 70% (8.5×10^5 Pa) and 60% starch (5×10^5 Pa). A similar trend is seen in *Figure 2* for the loss modulus, indicating that the material became more rigid with increased percentage of starch in the blend. Scanning electron micrographs of different blend compositions are shown in *Figures 3a–c*. In the blend containing 80% starch (*Figure 3c*), most of the granules remained intact and the material appeared more like a filled system, wherein the unmelted starch granules are coated and held together by EPMA copolymer. With lower starch content (*Figures 3a* and *b*) the number and the average size of unmelted granules decreased. The increase in the starch content from 60 to 70 and then to 80% resulted in a reduction in the mixer torque from 28 to 11 to <1 Nm, respectively[17]. This decrease in the mixing torque caused a decrease in the extent of melting of starch granules with increasing starch content.

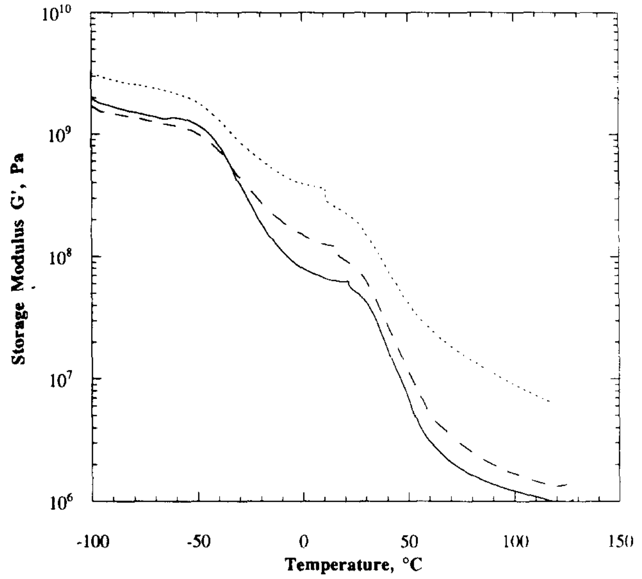

Figure 1 Effect of blend composition on the storage modulus of starch/EPMA blends: ——, 60% starch; – – –, 70% starch; . . . , 80% starch

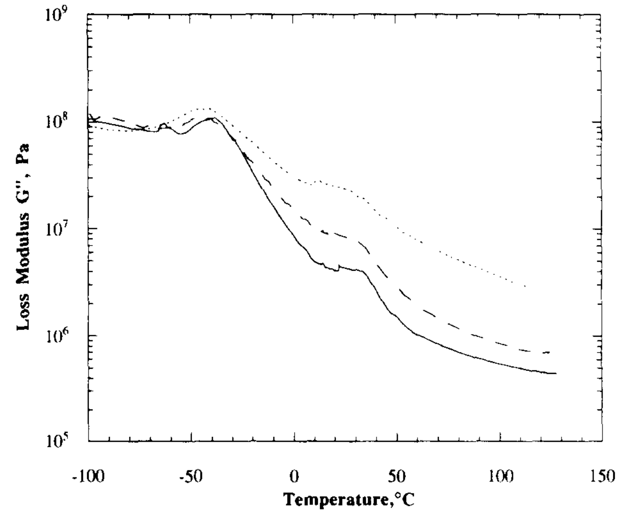

Figure 2 Effect of blend composition on the loss modulus of starch/EPMA/blends: ——, 60% starch; – – –, 70% starch; . . . , 80% starch

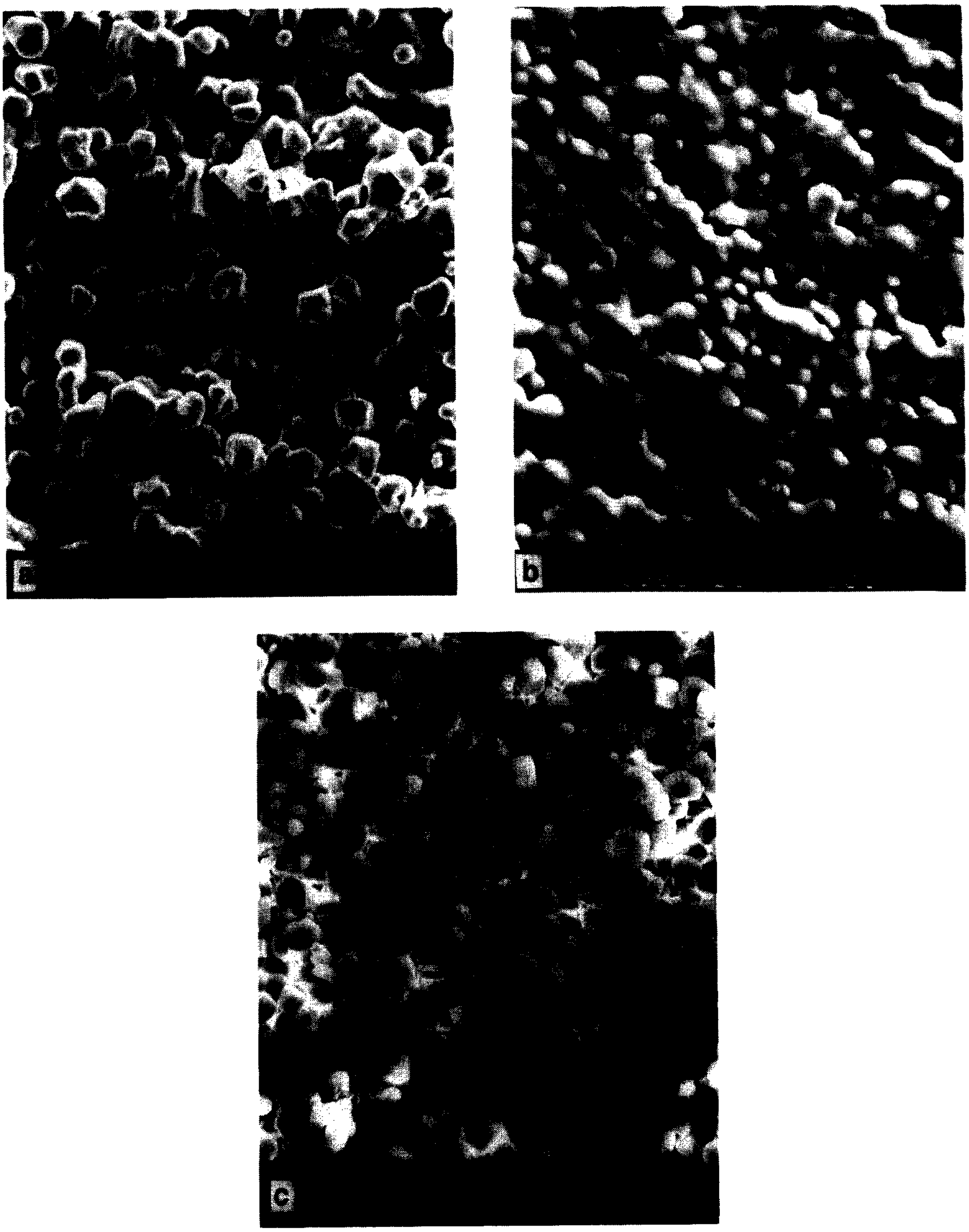

Figure 3 Scanning electron micrographs of starch/EPMA blends made at 50 rev min^{-1} mixer speed and 10 min mixing time: (a) 60% starch/40% EPMA; (b) 70% starch/30% EPMA; (c) 80% starch/20% EPMA

Effect of mixer speed. The effect of mixer speed on the storage modulus is shown in *Figure 4*. Increasing the speed from 50 to 100 rev min^{-1} marginally increased the storage modulus of the blends. This was observed for all compositions. This increase could be due to the increased melting of starch granules resulting from the higher shear stress generated at higher mixer speeds. Increasing the speed to 200 rev min^{-1} increased the stresses considerably and caused excessive thermal degradation, resulting in a burnt material. The increased melting of the starch granules when the speed was increased from 50 to 100 rev min^{-1} is also evident by comparing *Figures 3a* and *5*. The number and size of unmelted starch granules are smaller in *Figure 5* than in *Figure 3a*. The loss modulus displayed a similar effect, i.e. it increased slightly with increased mixing time. At higher mixing times (20 or 30 min), even a moderate speed of 100 rev min^{-1} led to some degradation and burning.

Effect of mixing time. The mixing time had a similar effect as the mixing speed on the dynamic mechanical properties of the blend. An increase in the mixing time from 10 to 20 and then to 30 min marginally increased the modulus for the blend made at 50 rev min^{-1} (*Figure*

6). For a 70/30 starch/EPMA blend, the storage modulus in the rubbery region at 100°C increased from about 1.5×10^6 Pa to about 6×10^6 Pa when the mixing time was increased from 10 to 30 min. For a mixing time of 20 min, the value of the modulus was intermediate (3.5×10^6 Pa) to that obtained during the 10 and 30 min experiments. This trend may again be related to the increased melting and mixing of starch at higher mixing times. Increased melting would also improve reaction/interaction between starch and the polymer and may result in increased crosslinking. The electron micrographs in *Figures 3a, 7a* and *7b* show increased melting of the starch granules with increased mixing time. At 100 rev min^{-1} and 30 min mixing time, the starch in the blend began to discolour slightly. When the speed was increased to 200 rev min^{-1}, the product was found to be significantly degraded or burnt at 10 min mixing time.

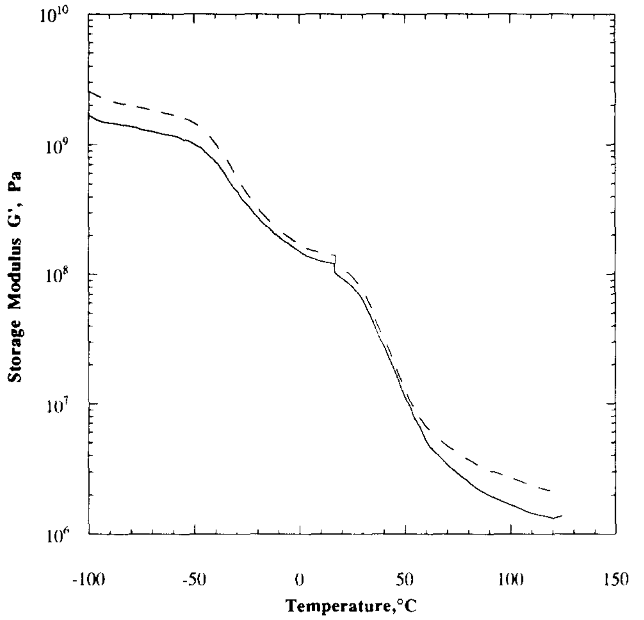

Figure 4 Effect of mixer speed on the storage modulus of the blend containing 70% starch and 30% EPMA: ——, 50 rev min^{-1}; – – –, 100 rev min^{-1}

Figure 5 Scanning electron micrograph of 60/40 starch/EPMA blend made at 100 rev min^{-1} mixer speed and 10 min mixing time

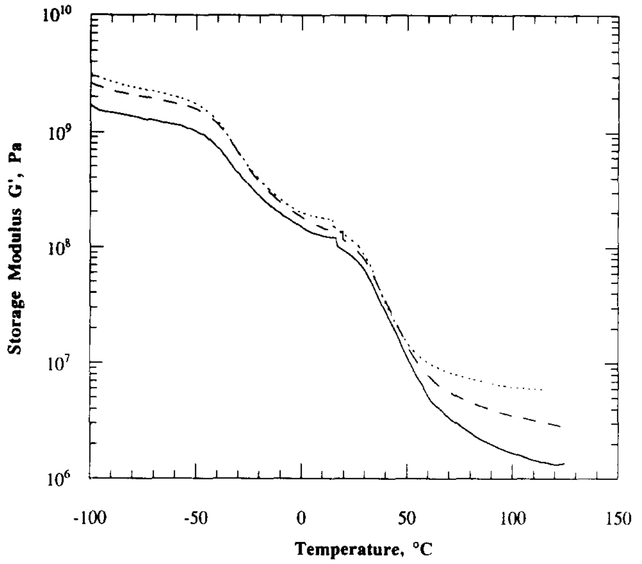

Figure 6 Effect of mixing time on the storage modulus of the blend containing 70% starch and 30% EPMA: ——, 10 min; – – –, 20 min; ..., 30 min

Starch/SMA blends

Glass transition. Unlike starch/EPMA blends, starch/SMA blends displayed a single, broad glass transition (*Figure 8*) that ranged between 80 and 110°C. A careful study of temperature *versus* loss modulus and tan δ plots in *Figures 9* and *10* for the blend containing 80% starch revealed two additional weak transitions, the first between 40 and 60°C and the second between 105 and 115°C. The range for the first transition (40–60°C) is very close to the glass transition range for starch in the starch/EPMA blends. However, the magnitude of these two transitions is so small that the value of the storage modulus (*Figure 8*) is practically unchanged in this region. The α-transition between 105 and 115°C is noticeable in tan δ (*Figure 9*), as well as in the storage modulus response (*Figure 8*). The blend containing 50% starch displayed only one transition. The glass transition of starch is known to vary considerably with the amount of water[19], which acts as a plasticizer. It may be possible that in a 50/50 blend the glass transition for SMA and starch overlap, whereas for an 80/20 blend the glass transition of starch moves to a higher temperature range (105–115°C) and is manifested as a small transition after the glass transition of SMA. Hayashi *et al.*[4] reported a similar observation for polystyrene/PVC system. At lower concentrations of polystyrenes, only a single broad glass transition was observed, but when the polystyrene/PVC ratio was increased to 4, a second peak, corresponding to the glass transition of polystyrene, appeared in the loss modulus spectrum. They attributed this phenomenon to the crossover from a dispersed to a continuous nature of the polystyrene phase. A similar phenomenon may occur with our blends. A detailed study is necessary to evaluate this hypothesis.

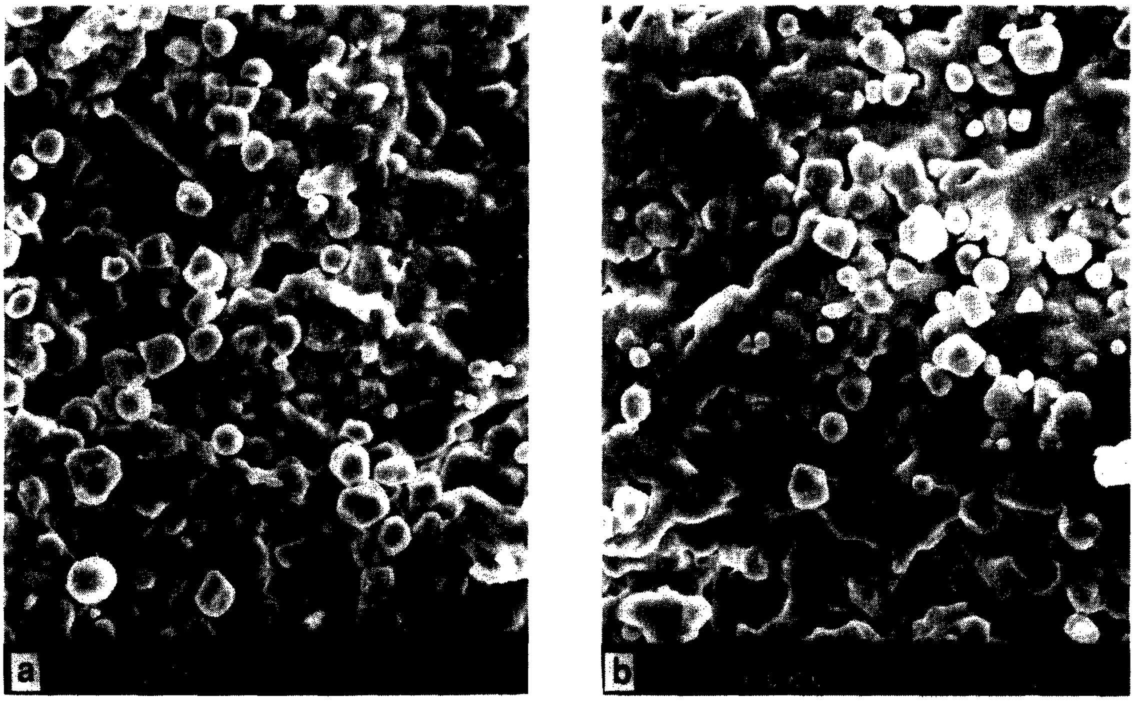

Figure 7 Scanning electron micrographs of 60/40 starch/EPMA blends made at 50 rev min^{-1} mixing speed: (a) 20 min mixing time; (b) 30 min mixing time

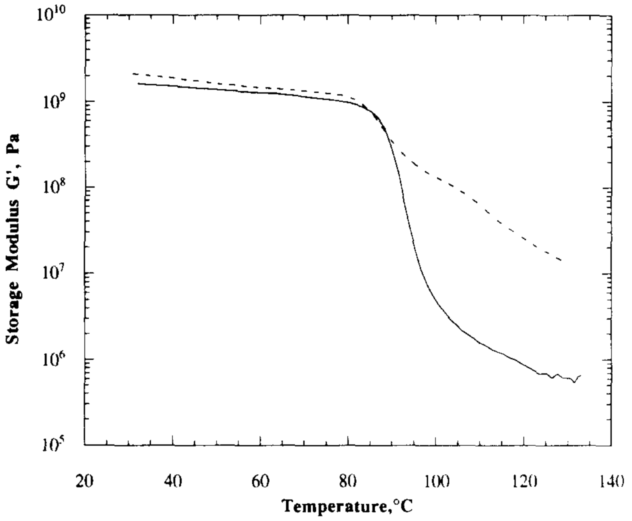

Figure 8 Effect of blend composition on the storage modulus of starch/SMA blends: —, 50% starch; ---, 80% starch

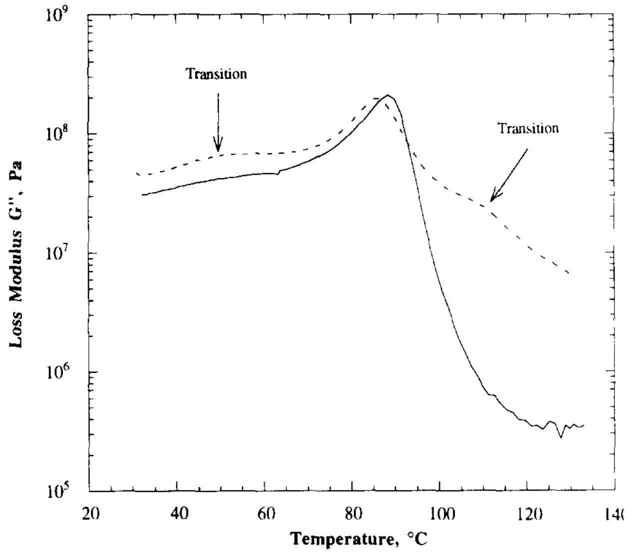

Figure 9 Effect of blend composition on the loss modulus of starch/SMA blends: —, 50% starch; ---, 80% starch

Effect of composition. *Figures 8* and *10* show the change in storage modulus and tan δ with temperature for the two compositions studied. A major glass transition is observed between 80 and 100°C for both compositions. The storage modulus of the sample containing 80% starch was higher by more than an order of magnitude (1×10^7 Pa) in the rubbery region at 130°C (*Figure 8*) compared to the sample containing 50% starch (6×10^5 Pa). Electron micrographs (*Figure 11*) again show the presence of unmelted starch granules. As the starch content in the blend decreased, the amount and size of unmolten starch granules decreased (*Figures 11a* and *b*). During the blending of starch/SMA compositions, the torque increased with increased starch content[17]. In spite of this increased torque, there is a significant number of unmelted granules for 80/20 starch/SMA blends. This is,

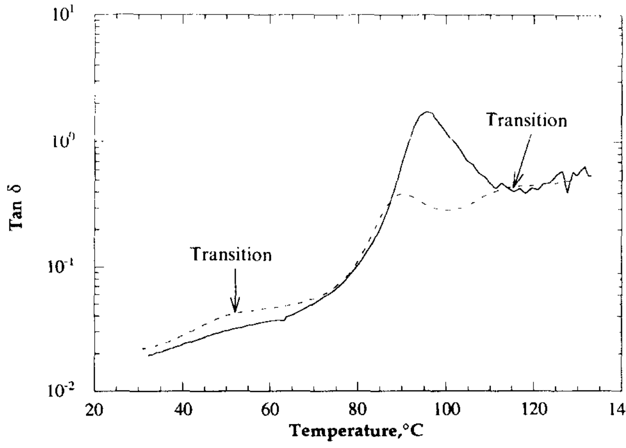

Figure 10 Effect of blend composition on the loss factor of starch/SMA blends: —, 50% starch; ---, 80% starch

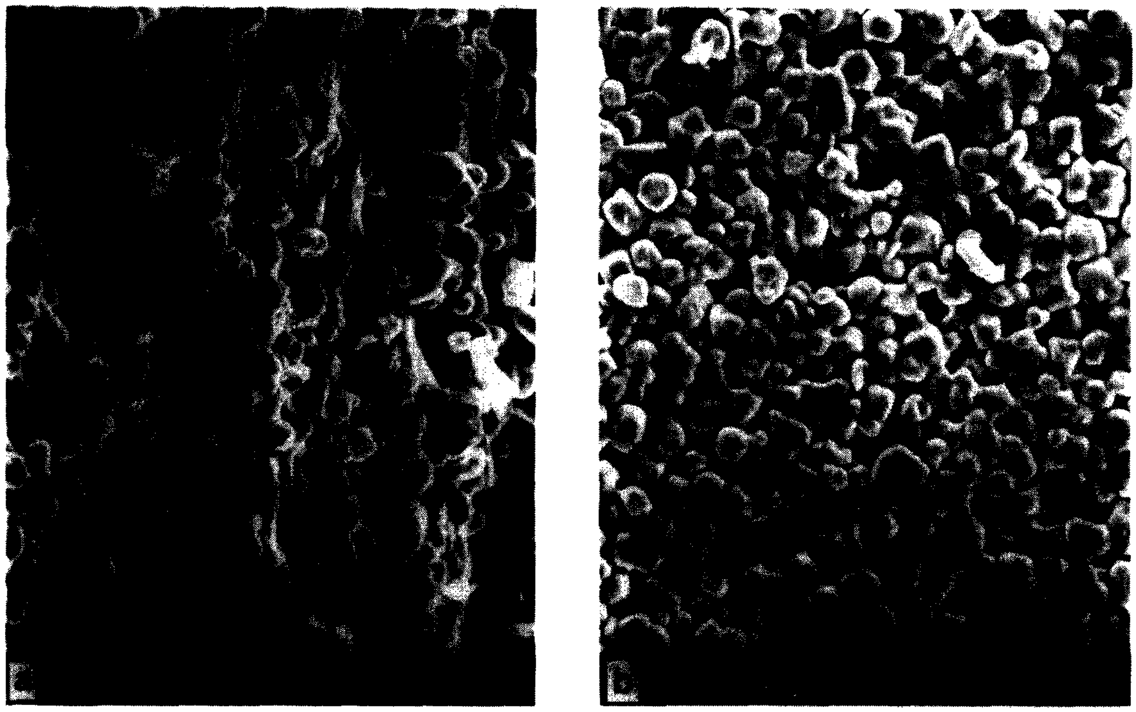

Figure 11 Scanning electron micrographs of starch/SMA blends made at 50 rev min^{-1} mixing speed and 10 min mixing time: (a) 50% starch/50% SMA; (b) 80% starch/20% SMA

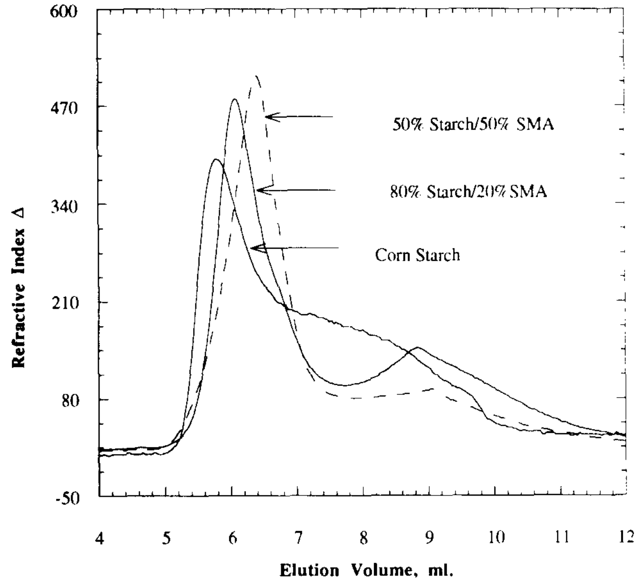

Figure 12 Gel permeation chromatograph of native starch and starch in starch/SMA blends

of course, due to the higher starch concentration of the sample in *Figure 11b*. The gel permeation chromatographs (*Figure 12*) showed that the starch in the blends had undergone molecular degradation during the blending process. The sample solutions were filtered to remove the insoluble part of the blends. The insoluble part of the blends may include the reacted and/or associated polymer/starch particles. The ratio of the low molecular weight peak to the high molecular weight peak for starch is higher in the 80/20 blend than in the 50/50 blend. This would result from the higher torque generated for 80/20 blends during melt blending, leading to more degradation. Surprisingly, however, the high molecular weight peak is shifted more towards the low molecular weight side in the 50/50 blend than in the 80/20 blend. This may result from the greater interaction/reaction between high molecular weight starch and SMA in a 50/50 blend, generating more high molecular weight insolubles that were removed by filtration before the g.p.c. analysis.

Effect of mixing speed and time. Shear sensitivity of starch makes it an extremely difficult material to process. A combination of different phenomena may result from changing the mixing time and speed. Increased mixing time or speed would facilitate the melting and mixing of starch, resulting in improved reaction/interaction and stronger material. On the other hand, these very same changes in the mixing conditions may increase the degradation and burning of starch, thus leading to a weaker material. One has to strike a balance between these two parameters to achieve the optimum properties in the blend. For the 50/50 blend only one glass transition was observed. The values of the storage and loss moduli before and after the glass transition seem to be unaffected by the mixing conditions. However, the temperature range in which the transition occurs did vary for some of the blending conditions. Increasing the mixing time from 10 to 20 min at 50 rev min^{-1} for 50/50 starch/SMA blends, shifted the transition temperature to a higher value, as seen from the storage modulus plot in *Figure 13*. The tan δ peak for the same blend composition (*Figure 14*) shifted from about 95 to 105°C. This may result from better melting and mixing of starch with SMA. However, a similar increase in the mixing time at 100 rev min^{-1} did not result in a higher transition temperature. In this instance, the increased degradation of starch, resulting from higher mixing speed and time, could have nullified the effect of increased melting and reaction/interaction. On the other hand, increasing the mixer speed from 50 to 100 rev min^{-1} for a 10 min mixing time did not result in any change in the transition temperature (*Figure 15*),

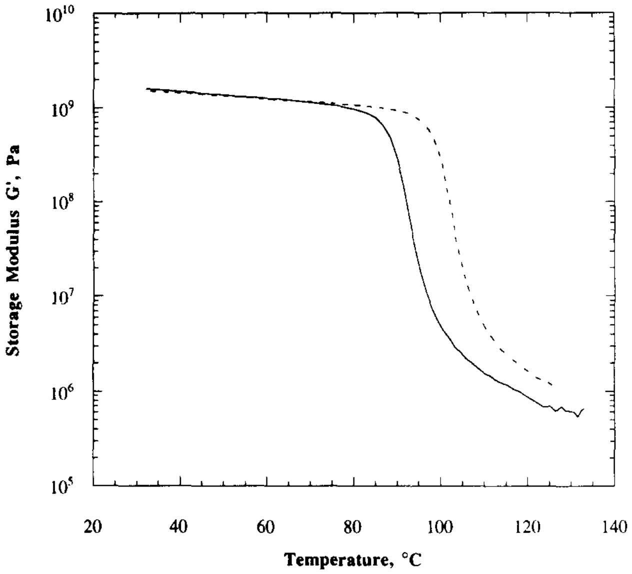

Figure 13 Effect of mixing time on the storage modulus of the 50/50 starch/SMA blend: ——, 10 min; – – –, 20 min

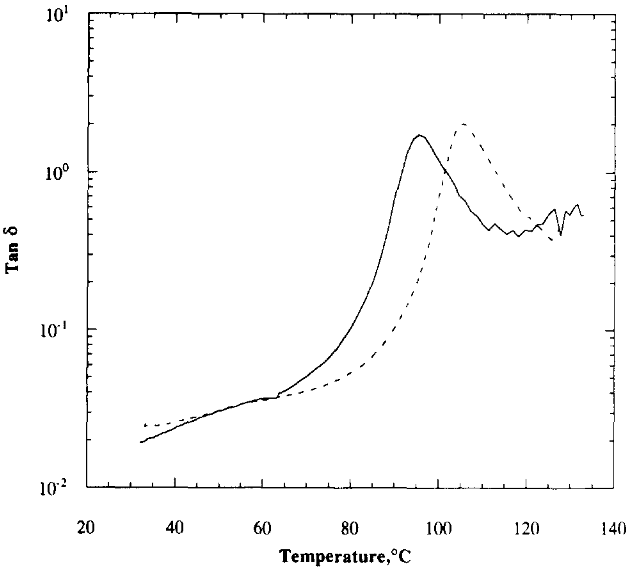

Figure 14 Effect of mixing time on the loss factor of the 50/50 starch/SMA ——, 10 min; – – –, 20 min

due to the opposing effects of degradation *versus* melting and reaction/interaction of starch. When the mixing speed was increased at a higher mixing time of 20 min, the effect of degradation dominated, resulting in the lowering of the transition temperature (tan δ peak) from 105 to about 90°C (*Figure 16*). Thus, low speed (50 rev min^{-1}) and higher mixing time (20 min) resulted in a material superior to those made at higher mixing speeds. A similar effect was observed for the 80/20 blends. However, instead of displaying a noticeable change in transition temperature, these samples exhibited changes in the magnitude of the storage modulus (*Figure 17*). At 50 rev min^{-1}, increasing the mixing time from 10 to 20 min increased the storage modulus. Similarly, at 10 min mixing time, when the mixer speed was increased from 50 to 100 rev min^{-1} the modulus increased, particularly in the rubbery region. Samples made at higher speed and mixing time were extremely brittle and could not be successfully moulded into test specimens. Increased melting of starch with increased mixing speed and time can also be seen by comparing the electron micrographs shown in *Figure 11a* and *Figures 18a* and *b*. The g.p.c. data shown in *Figure 19* indicate that the increase in the mixer speed and mixing time increased the degradation of starch.

CONCLUSION

The dynamic mechanical properties and the morphology of starch/EPMA and starch/SMA blends could be correlated to the processing conditions in the batch mixer. These blends comprised melted polymer, melted starch and unmelted starch granules. Starch/EPMA blends displayed two distinct glass transitions, corresponding to

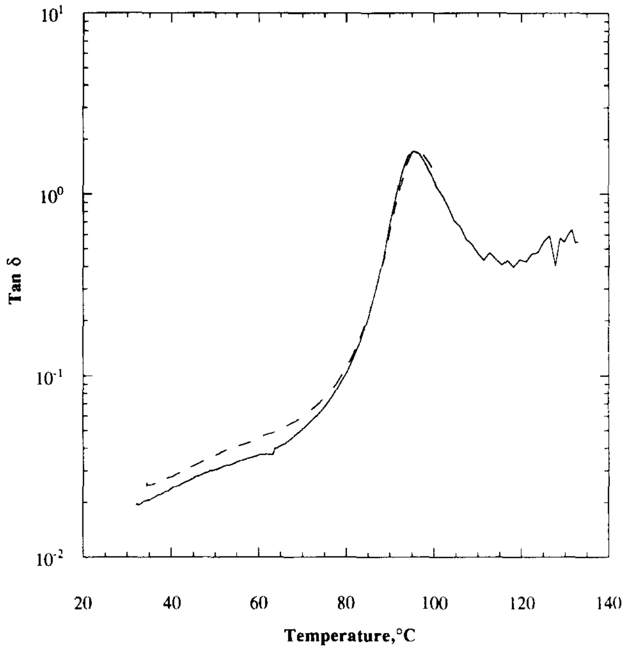

Figure 15 Effect of mixer speed on the loss factor of 50/50 starch/SMA blends made at 10 min mixing time: ——, 50 rev min^{-1}; – – –, 100 rev min^{-1}

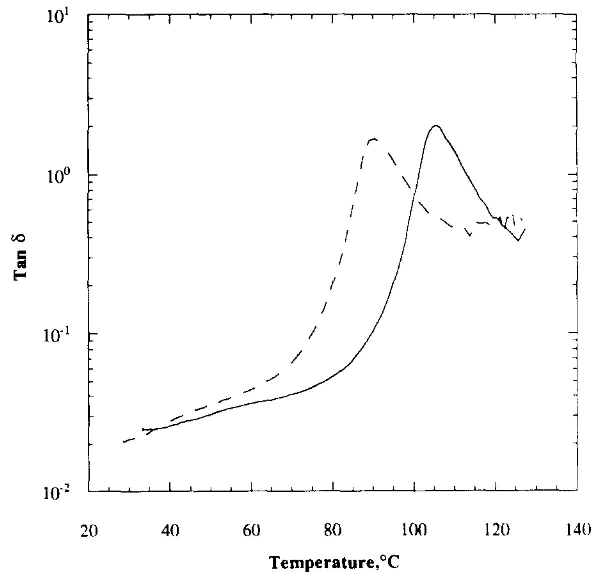

Figure 16 Effect of mixer speed on the loss factor of 50/50 starch/SMA blends made at 20 min mixing time: ——, 50 rev min^{-1}; – – –, 100 rev min^{-1}

the glass transitions of EPMA and starch phases. The storage modulus of the blend increased with increasing amount of starch for blends containing between 60 and 80% starch. Increasing the mixer speed from 50 to 100 rev min^{-1} and increasing the mixing time from 10 to 30 min facilitated the melting of starch granules and improved the storage modulus. Starch/SMA blends containing 50% starch displayed a single broad glass transition between 80 and 110°C. This is believed to be due to the close proximity of the glass transition temperatures of starch and polystyrene. However, when the starch concentration was increased from 50 to 80%, a small transition, corresponding to the starch phase, appeared between 105 and 115°C. The storage modulus in the rubbery region was higher for the blend containing 80% starch than for the one containing 50% starch. The processing conditions affected the transition temperature of the 50/50 blend and changed the modulus value for 80/20 blends. Increasing the mixing time from 10 to 20 min and the mixing speed from 50 to 100 rev min^{-1} facilitated the melting of starch; however, it also caused increased starch degradation, as observed by g.p.c. analysis. Starch/SMA blends made at 30 min mixing time or 200 rev/min^{-1} were excessively degraded and burnt. The resultant dynamic mechanical properties of the blends depended on whether the melting/mixing effect or the effect of starch degradation dominated during the processing. Starch in the starch/SMA blend was probably more susceptible to degradation than in the starch/EPMA blend.

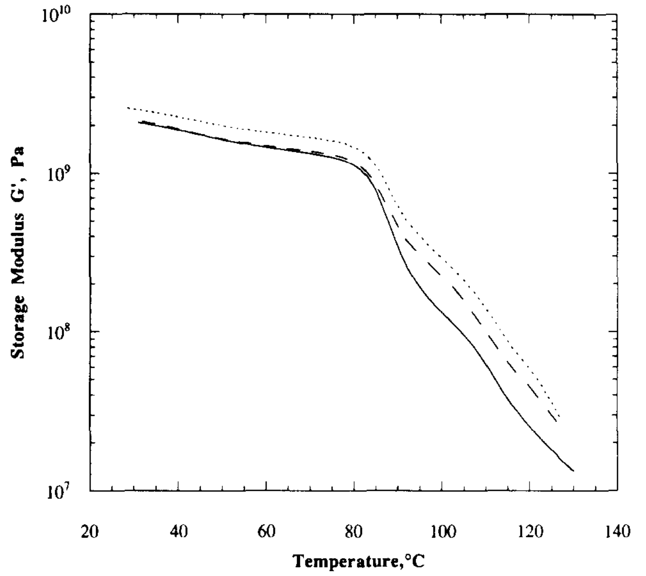

Figure 17 Effect of mixing time and mixer speed on the storage modulus of the 80/20 starch/SMA blend: ——, 50 rev min^{-1}, 10 min; ---, 100 rev min^{-1}, 10 min; ....., 50 rev min^{-1}, 20 min

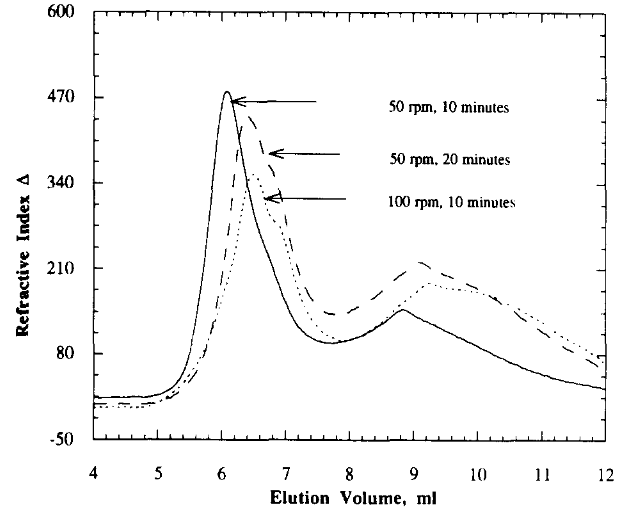

Figure 19 Gel permeation chromatographs of starch in the 80/20 starch/SMA blends

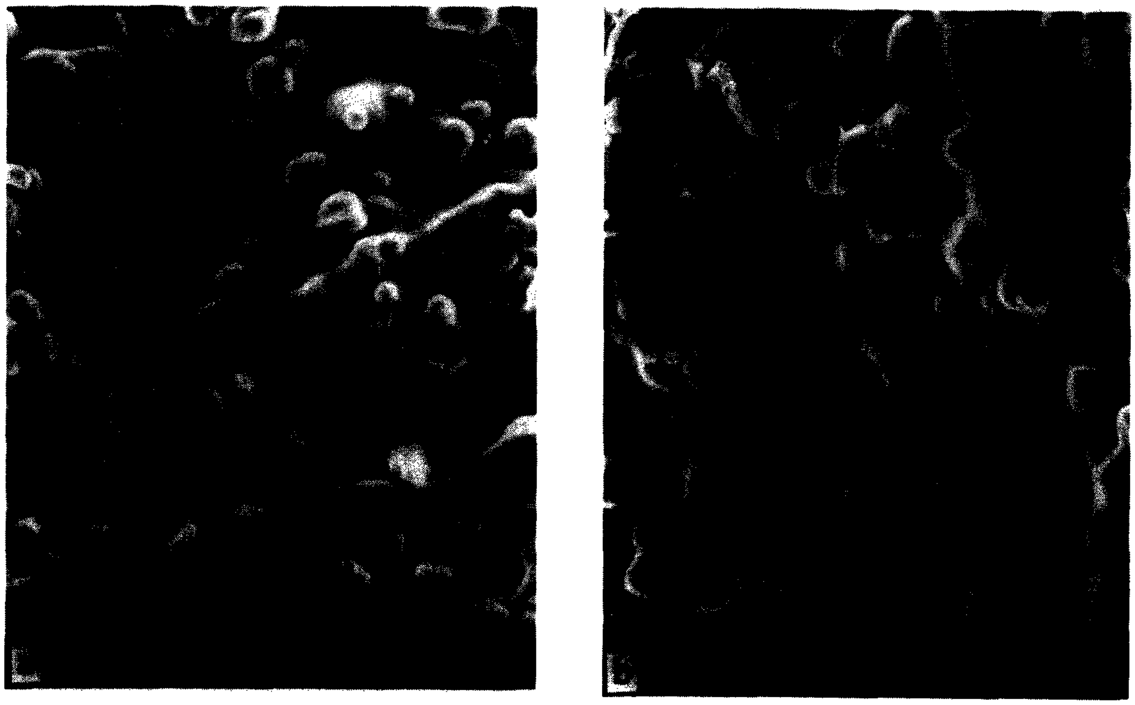

Figure 18 Scanning electron micrographs of 50/50 starch/SMA blends made at: (a) 50 rev min^{-1} mixer speed and 20 min mixing time; (b) 100 rev min^{-1} mixer speed and 10 min mixing time

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the United States Department of Agriculture (contract no. 93-03699 under the National Research Initiative Program). Published as paper number 21,103 of the scientific journal series of Minnesota Agricultural Experiment Station.

REFERENCES

1 Muruyama, T. 'Dynamic Mechanical Analysis', Elsevier Scientific, Amsterdam, 1978, Ch. 1
2 Nielsen, L. E. 'Mechanical Properties of Polymers and Composites', Marcel Dekker, New York, 1974
3 Liang, Z. and Williams, H. L. *J. Appl. Polym. Sci.* 1992, **44**, 699
4 Hayashi, T., Ito, J., Mitani, K. and Mizutani, Y. *J. Appl. Polym. Sci.* 1983, **28**, 2867
5 Thomas, S. and George, A. *Eur. Polym. J.* 1992, **28**, 1451
6 Natansohn, A., Murali, R. and Eisenberg, A. *Makromol. Chem., Makromol. Symp.* 1988, **16**, 175
7 O'Connor, K. M. and Orler, E. B. *Polym. Eng. Sci.* 1988, **28**, 1132
8 Brahimi, B., Ait-Kadi, A. and Fayt, R. *J. Polym. Sci. B* 1991, **29**, 945
9 Sjoerdsma, S. D., Dalmolen, J., Bleijenberg, A. C. A. M. and Heikens, D. *Polymer* 1980, **21**, 1469
10 Golovoy, A. and Cheung, M.-F. *Polym. Eng. Sci.* 1989, **29**, 85
11 Guest, M. J. and Daly, J. H. *Eur. Polym. J.* 1990, **26**, 603
12 Lay, G., Rehm, J., Stepto, R. F., Thomas, M., Sachetto, J.-P., Lentz, D. J. and Silbiger, J. US Patent 5095054, 1992
13 Jane, J.-L., Schwabacher, A. W., Ramrattan, S. N. and Moore, J. A. US Patent 5115000, 1992
14 Otey, F. H. and Westhoff, R. P. US Patent 4337181, 1982
15 Willet, J. L., US Patent 5087650, 1992
16 Bastioli, C., Bellotti, V., Del Tredici, G., Lombi, R., Montino, A. and Ponti, R. WO 92/19680, 1992
17 Vaidya, U. R. and Bhattacharya, M. *J. Appl. Polym. Sci.* 1994, **52**, 617
18 Wurzburg, O. B. in 'Modified Starches: Properties and Uses' (Ed. O. B. Wurzburg), CRC Press, Florida, 1991, p. 4
19 Ren, Q., Vaiday, U. R. and Bhattacharya, M. Unpublished data
20 Levine, H. and Slade, L. in 'Dough Rheology and Baked Product Texture' (Eds H. Faridi and J. M. Faubion), Van Nostrand Reinhold, New York, 1989, p. 157