

# Properties of ternary blends of starch and maleated polymers of styrene and ethylene propylene rubber

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The properties of starch/styrene maleic anhydride (SMA)/ethylene propylene maleic anhydride (EPMA) were studied at a constant starch composition of 60% by weight. The synthetic polymer content was 40% of total weight and contained 30, 20 and 10% SMA by weight, the rest being EPMA. Blends were made in a batch mixer as well as continuously in an extruder. The water absorption data showed that samples made by extrusion have less water resistance than samples made in a batch mixer. Dynamic mechanical analysis indicated three distinct glass transitions, corresponding to the glass transitions of EPMA, starch and SMA. Tests showed injection moulding gave higher tensile strength compared to compression moulding, and tensile strength increased with SMA content. Gel permeation chromatography data indicated there was degradation during mixing. Blending using an extruder caused more degradation of starch in the blends than when a batch mixer was used. Both scanning electron microscopy and optical microscopy showed that some starch was not melted during blending though the number and average size of unmelted starch granules decreased with decreasing SMA content. Scanning electron microscopy indicated the different morphologies of injection moulded samples at different locations in the mould. Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

There is a great potential to develop materials that have a significant component of renewable materials such as starches. The successful development of such materials would have a significant impact on the farm economy as well as reducing US dependence on imported oil.

Our goal has been to increase the use of starch in plastics while minimizing any detrimental loss in properties or functionalities of the resulting blend. Polymer blending is one of the most popular methods used in developing new materials with a desired combination of properties. Multicomponent polymer systems are often intended to meet the requirements of a familiar application more cheaply and effectively. On the other hand, some polymer blends provide a novel combination of properties, thus opening up the possibility of new applications.

Several studies have been conducted on blends of starch and poly(ethylene-co-acrylic acids) by Otey and co-workers<sup>1–3</sup>. Their primary purpose was to use these blends to produce films for agricultural and land applications. Bagley and co-workers<sup>4</sup> studied the properties of various starch-g-polystyrene blends. Buchanan and co-workers<sup>5,6</sup> reported on the properties of starch xanthate and styrene butadiene rubber blends. Patil and Fanta<sup>7</sup> evaluated the properties of starch-g-methyl

acrylate films. George and co-workers<sup>8</sup> investigated the effect of poly(ethylene-co-vinyl alcohol) concentration on the properties of different types of starches.

In our previous articles<sup>9–12</sup> we have dealt with the properties of the binary blends of starch and styrene maleic anhydride (SMA) or starch and ethylene propylene maleic anhydride (EPMA). Using a functionalized polymer such as SMA or EPMA increased tensile properties over simple mixtures containing non-functionalized polystyrene or ethylene-propylene copolymer. Starch/SMA blends containing 60% by weight of corn starch had a tensile strength of 18 MPa<sup>9</sup> which increased to 25 MPa when high amylose corn starch was used<sup>10</sup>. When starch was blended with EPMA at a level of 70% by weight, the tensile strength of the blend was comparable to that of pure EPMA. However, the elongation decreased dramatically as the starch content in the blend was increased. Starch/EPMA blends showed two distinct glass transitions ( $T_g$ ), one for each polymer, while starch/SMA blends showed one broad transition<sup>11</sup>. Processing history was found to affect the morphology and the viscosity of the blends<sup>12</sup>.

The objective of this research was to evaluate the properties of ternary blends of starch, SMA and EPMA. To our knowledge this is the first attempt to study the properties of ternary blends containing starch. To keep the study manageable the starch content of the blend was fixed at 60% by weight, the remaining being the synthetic polymers SMA and EPMA which was varied in different ratios. The effects of type of blending (batch *versus*

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continuous) and the type of moulding (compression versus injection) on the physical and morphological properties were studied.

## MATERIALS AND METHODS

### Materials

Industrial corn starch (SMP 1100) was obtained from Cargill Corporation. The starch contained 25% by weight of amylose, the rest being amylopectin. SMA (Dylark 232) was obtained from Arco Chemicals. This grade of SMA contained about 8% maleic anhydride by weight (melt flow index (MFI)  $\approx$  1.8 at 190°C). EPMA (VA 1801) was obtained from Exxon Chemicals and contained approximately 0.8% maleic anhydride by weight (MFI  $\approx$  0.13 at 170°C).

### Blend preparation

For the starch/SMA/EPMA system, both batch mixer and extruder were used to make the blend. The batch mixer was equipped with roller blades (C. W. Brabender Instruments Inc., South Hackensack, NJ, USA) and connected to a variable speed motor through a torque meter. Starch, SMA and EPMA were dried in a vacuum oven at 100°C and  $-100$  kPa overnight. The required quantities of starch and synthetic polymers were hand mixed in a plastic beaker and introduced into the mixer preheated to 180°C. The speed of the mixer was 50 rev min<sup>-1</sup> and mixing time was 10 min. During the blending process, the torque and the melt temperature were recorded continuously and stored in a microcomputer (IBM PC/AT). At the end of 10 min, the mixer was quickly dismantled and the material was removed with a spatula.

The extruder used in the blending is a laboratory-scale twins screw with a corotating screw (Haake Instruments, Paramus, NJ, USA). 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 (0.635 $\phi$   $\times$  65 mm). The starch contained approximately 10% moisture on a dry weight basis. No additional water or other plasticizers were added to the blend. The first zone temperature was set at 80°C; the second and the third zone temperatures were set at 170°C; the die temperature was 120°C. Extrusion was carried out at a screw speed of 60 rev min<sup>-1</sup>. The torque was recorded continuously during the experiment. The resultant extrudate was in the form of rope and had a smooth texture. The residence time was approximately 45 s.

### Moulding

Samples for testing were made by both compression and injection moulding. Compression moulding was accomplished using an OTC compression moulding machine (Owatonna Tool Co.). Samples were put in a dog-bone (neck dimension of 50  $\times$  6  $\times$  3 mm) for tensile measurement or in a rectangular strip (65  $\times$  10  $\times$  2 mm) for water absorption studies. A constant force of 10 tons was applied to the platens preheated to 180°C for a fixed period of time (10 min). The platens were then cooled with tap water while maintaining the force until the temperature dropped below 40°C, after which the samples were removed and stored for analysis.

A Boy 50M injection moulding machine with reciprocating screw was used to mould dog-bone samples with a

**Table 1** Injection moulding conditions of starch/SMA/EPMA

Sample	IP (bar)	IS (mm s <sup>-1</sup> )	T (°C)
SMA30/EPMA10	160	109	100/170/170/160
SMA20/EPMA20	100	109	100/160/160/160
SMA10/EPMA30	100	109	100/160/160/160

IP, injection pressure (system pressure, not the pressure in the cavity); IS, injection speed

neck dimension of 50  $\times$  6  $\times$  3 mm. A number of parameters, such as melt temperature, mould temperature, mould cooling time and injection speed could affect the mechanical properties of the sample. However, to keep this study manageable, samples were injection moulded using the conditions summarized in Table 1. The conditions were selected based on visual acceptability of the samples.

### Water absorption

After mixing starch/SMA/EPMA in an extruder or in a batch mixer, compression moulding at 180°C and 10 tons for 10 min was used to make rectangular thin strip samples with dimensions of 65  $\times$  11  $\times$  2 mm. The moulded strip samples of the blend were weighed and immersed in distilled water. The samples were then removed at specified time intervals, gently blotted with Kimwipes paper to remove excess water on the surface, and weighed, and the weight was recorded. The process was repeated at several time intervals. Two samples were dried in a vacuum oven at  $-100$  kPa and 60°C overnight before conducting the water absorption test to determine if drying will affect the water resistance of the materials.

### Dynamic mechanical analysis

A Rheometric Mechanical Spectrometer (RMS-800) was used to evaluate the dynamic mechanical properties. Blend samples were compression moulded into rectangular strips of 65  $\times$  11  $\times$  2 mm by pressing each sample into a rectangular shaped mould at a constant force of 10 tons at 180°C for 10 min. The samples were subjected to sinusoidal strain in the torsion mode. The magnitude of strain was 0.1% and the test was concluded at a temperature between  $-100$  and 120°C, and a frequency of 1 rad s<sup>-1</sup>. The temperature was increased at the rate of 10°C min<sup>-1</sup>. Each sample was analysed in triplicate.

A temperature/frequency sweep was done at a fixed strain of 0.1% with temperature starting from  $-20$ °C and ending at 90°C with a temperature ramp of 10°C. Two samples were chosen, one from extrusion, the other from batch mixing. Time-temperature superposition was done to get a master curve by shifting the different temperature values along the time or frequency axis.

### Tensile test

Both compression and injection moulded dog-bone samples were used to obtain tensile strength measurement. The samples were put into two chambers, one containing saturated LiCl solution (relative humidity of approximately 15%) and the other containing saturated KCl solution (relative humidity of approximately 85%) for two weeks to let samples equilibrate with the moisture. The tensile testing was done using an MTS tensile testing machine type T5002 and a crosshead speed of 3 mm min<sup>-1</sup> according to the procedures outlined in

ASTM test method D-638. All samples were tested at least in triplicate.

#### Gel permeation chromatography

A Waters 150 LC/GPC was used with a refractive index detector to measure the molecular size of starch. A Phenogel (Phenomenex, Torrance, CA, USA) column (300 × 7.8 mm) with 10 mm particle size was used for separation. HPLC grade dimethyl sulfoxide (DMSO) was used as a mobile phase at the flow rate of 1 ml min<sup>-1</sup> during analysis. A solution of about 0.2% w/v samples containing a blend of starch in DMSO was filtered through a 0.45 mm filter to remove insoluble particles. Since the ternary blend is insoluble in DMSO, three organic solvents – xylene (boiling point (b.p.) 147°C), 1,2-dichlorobenzene (b.p. 178°C) and 1,1,2,2-tetrachloroethane (b.p. 147°C) – were used to dissolve and extract EPMA from blends. They were compared for solubility and boiling point, then boiling 1,1,2,2-tetrachloroethane (b.p. 147°C) was used to flux and extract the EPMA. Finally, the insoluble part was filtered out and dissolved in hot DMSO. SMA, though soluble, was isorefractive with DMSO and hence did not affect gel permeation chromatography (g.p.c.) analysis. No standard starch samples could be run, hence the analysis was based on relative increase or decrease of high/low molecular weight fractions and shift of peak position of the starch component of the blend. Thus, the absolute average molecular weight cannot be obtained. Only the relative increase or decrease can be known.

#### Optical microscopy

An optical microscope was used to study the effects of processing condition and composition on the distribution of starch in the blends. For starch/SMA/EPMA ternary blends, the samples were first fixed with 5% glutaraldehyde solution followed by dehydration using ethanol, n-propanol and n-butanol. Finally, the samples were encapsulated in an acrylic resin. Thin sections (~0.2 mm) of the encapsulated samples were cut at -50°C with a glass knife on cryomicrotome. 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 of the object.

#### Scanning electron microscopy

After blending, samples were fractured in liquid nitrogen and stuck to aluminium stubs. Similarly, the fractured surfaces of samples after tensile testing were evaluated by cutting the samples using a blade and affixing the slices to aluminium stubs. The samples were coated with gold (Au)/palladium (Pd) alloy by vapour deposition and observed under a Hitachi S-450 electron microscope.

## RESULTS AND DISCUSSION

During the reactive blending of SMA and EPMA with starch, the anhydride groups from synthetic polymers can react with hydroxyls of starch to form ester linkages. Such a reaction during blending improves the interfacial adhesion and physical properties of the blend. The carboxylic groups, resulting from the hydrolysis of the anhydride, can form hydrogen bonds with the hydroxyl

groups of starch to further improve the properties of the blends. We have attempted to determine the esterification reaction by i.r.<sup>13</sup>. Because of the large absorption peak of starch between 1708 and 1730 cm<sup>-1</sup>, it was difficult to detect the half ester which absorbs in the same region. However, we were able to detect the disappearance of the anhydride from the blend by Fourier transform (FT) i.r. under dry conditions (to prevent hydrolysis) which could be due to the reaction between the hydroxyl on the starch and the anhydride on the synthetic polymer.

#### Torque

In the batch mixer, as the polymers start to melt, a viscous mass is formed and the torque value increased. A representative plot of torque and temperature is shown in *Figure 1*. The temperature of the melt also increased due to external and viscous heating, leading to a reduction in the melt viscosity and therefore the torque. During extrusion, the mechanical energy (SME) imparted by the rotating screws also helps to melt the starch granules. As the percentage of EPMA increased, the magnitude of the torque increased for both the blending techniques (*Table 2*), probably due to the higher viscosity of the EPMA polymers.

#### Gel permeation chromatograph

The g.p.c. results obtained for starch in starch/SMA/EPMA blends of various compositions from a batch mixer and an extruder are shown in *Figures 2a* and *2b* respectively. The sample solutions were filtered to remove the insoluble part of the blend. The insoluble part may include the reacted and/or associated polymer/starch particles. Two peaks in each figure were observed. This means that there were two groups of starch with different molecular weights in the blend. The first peak is the amylopectin fraction in starch and corresponded to high molecular weight; the second peak is the amylose fraction and corresponded to lower molecular weight. The position of the peak at the *x*-axis (elution volume) corresponds to the average molecular weight of that group.

The first peak of pure starch was at an elution volume of 6.3 ml, while the second peak was at 9.0 ml. The first peak of starch from batch-mixed samples was at approximately 6.6 ml, while the second peak ranged between 9.1 and 9.4 ml (*Figure 2a*). Compared to starch in a blend made by a batch mixer, the pure starch (no processing history) had peak positions at lower elution volumes, and this indicated that the starch in the blends underwent molecular degradation during the mixing process. A similar result was obtained for the starch from the extruded sample (*Figure 2b*). Data for the elution volumes of the various blends are summarized in *Table 3*. The ratio of the peak heights of the low molecular weight (second) to those of the high molecular weight (first) for starch could be used to indicate the relative amount of starch degradation. In order to obtain the height of the peaks, we should be very careful with the baseline for the peak. For pure starch and some samples like SMA30/EPMA10-B, the baseline did not return to the starting position. It is a common practice to connect the starting position of the first peak and the end position of the second peak as the baseline, and then compare the ratio of the two peak heights. For batch-mixed samples, the

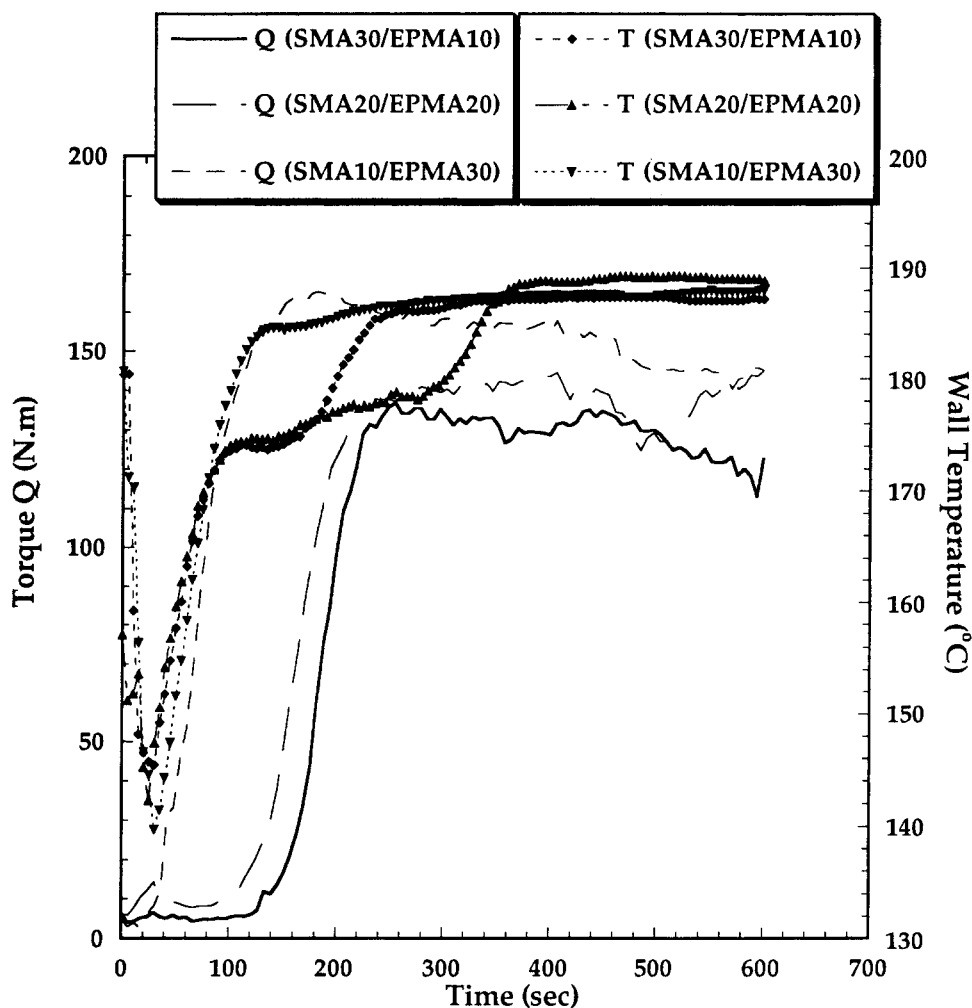


Figure 1 Torque (Nm) and wall temperature (°C) versus time for the blends in a batch mixer

Table 2 Torque (Nm) for starch/SMA/EPMA blends in batch and extrusion mixing

Sample	Torque (batch)	Torque (extrusion)	Flow rate (g min <sup>-1</sup> )	SME (kJ kg <sup>-1</sup> ) (extrusion)
SMA30/EPMA10	12	17.0	20.0	320.3
SMA20/EPMA20	15	25.1	19.9	476.5
SMA10/EPMA30	18	26.7	24.9	403.4

ratio of the low to high molecular weights of SMA10/EPMA30 was the highest; both peak heights are very close (Table 4). This means that the starch in the starch60/SMA10/EPMA30 blend experienced the most degradation. Also, as the SMA content in the blend increased or the EPMA content decreased, the starch molecules underwent less degradation.

When the g.p.c. results for both batch-mixed and extruded blends having the same compositions are plotted<sup>14</sup>, it is observed that both peak positions of the extruded samples were at higher elution volumes than those of batch-mixed samples for all three blends. The results also indicated that the double effect of both peak positions moved to a higher elution volume and that the ratio of the heights of low molecular weight to high molecular weight was higher for the extruded sample. This confirmed that extrusion caused more degradation of starch than batch mixing.

Table 3 Peak positions in g.p.c. analysis. The letters B and C indicate batch mixing and extrusion mixing respectively

Sample	First peak position (ml)	Second peak position (ml)
Pure starch	6.3	9.0
SMA10/EPMA30-B	6.5	9.2
SMA20/EPMA20-B	6.6	9.1
SMA30/EPMA10-B	6.7	9.4
SMA10/EPMA30-C	7.1	10.2
SMA20/EPMA20-C	6.9	9.3
SMA30/EPMA10-C	6.9	9.8

Table 4 Peak heights (mm) and their ratio in g.p.c. analysis. The letters B and C indicate batch mixing and extrusion mixing respectively

Sample	First peak height	Second peak height	Ratio of second/first
Pure starch	77	50	0.65
SMA10/EPMA30-B	32	26	0.81
SMA20/EPMA20-B	56	37	0.66
SMA30/EPMA10-B	70	42	0.60
SMA10/EPMA30-C	45	37	0.82
SMA20/EPMA20-C	53	42	0.79
SMA30/EPMA10-C	91	66	0.73

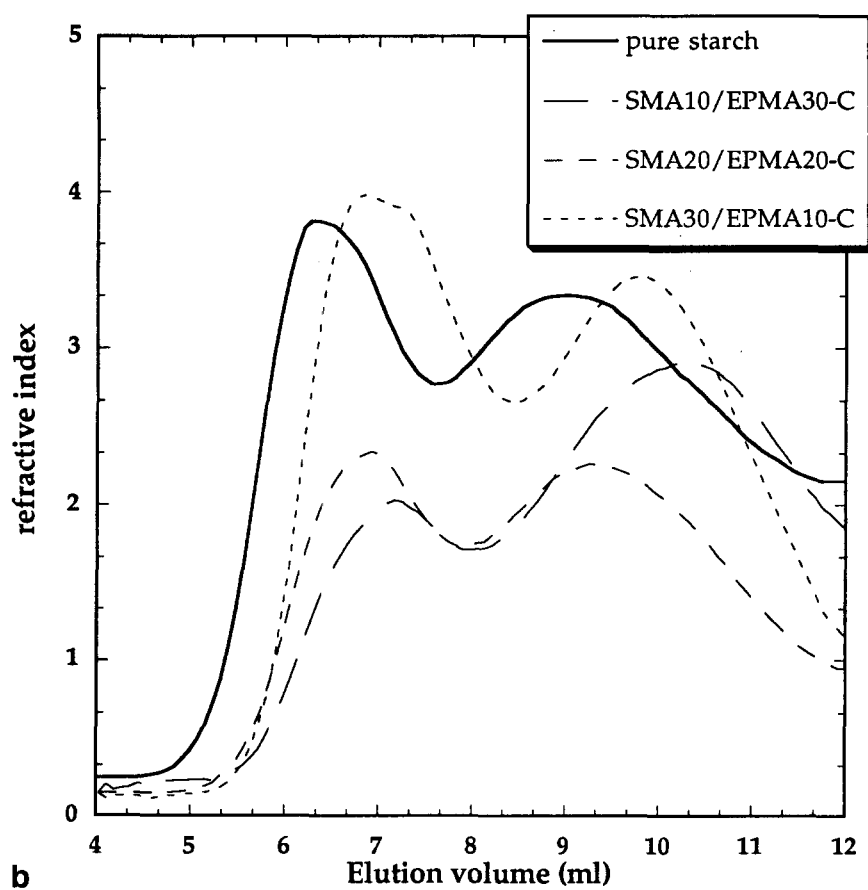
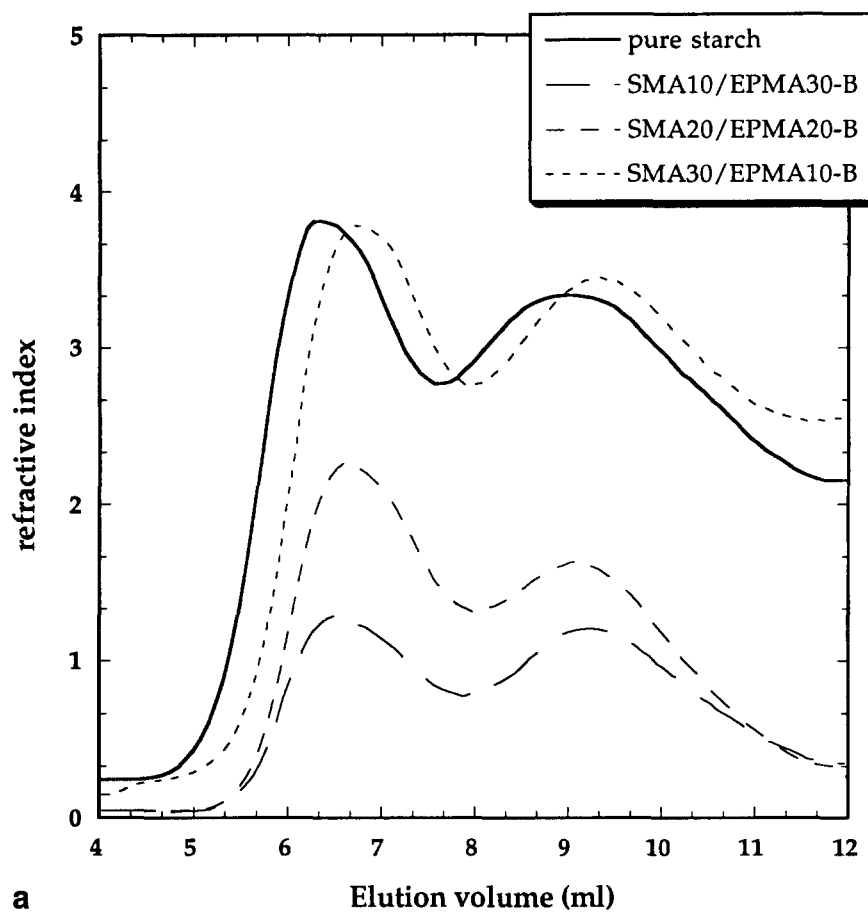
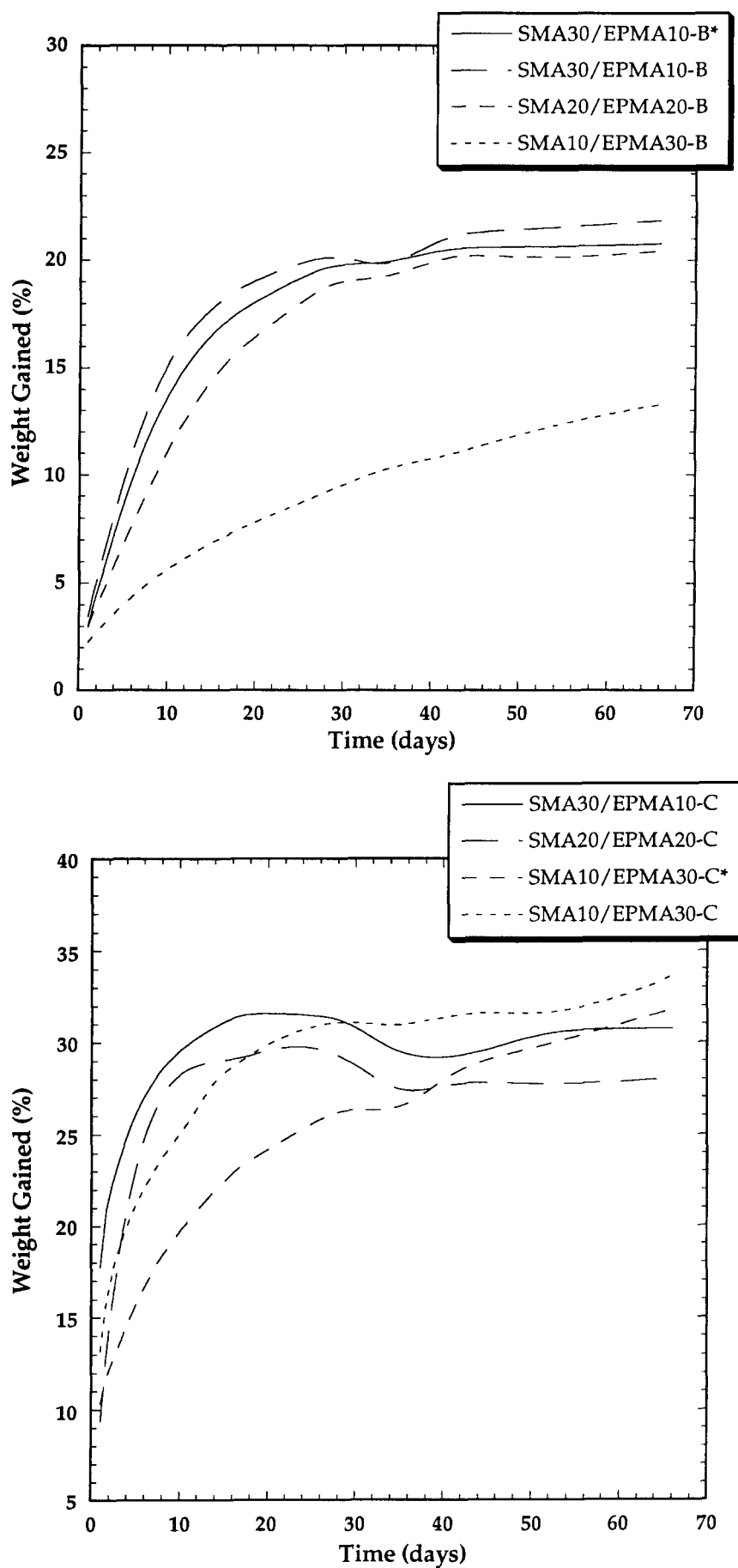


Figure 2 Gel permeation chromatographs for starch in (a) batch-mixed and (b) extrusion-processed samples



**Figure 3** Water absorption *versus* time for blends made in (a) batch mixer and (b) extruder. The letters B and C indicate batch mixing and extrusion mixing respectively. The asterisks indicate samples that were dried before the test

### Water absorption

Starch-based materials tend to absorb water because the hydroxyl group in starch can form a hydrogen bond with water. Compression-moulded samples of both batch and continuously made blends were used for water absorption determination. The weight gained with time for batch and continuously processed samples is shown in *Figures 3a* and *3b*, respectively. It is seen that the blends prepared by extrusion processing absorbed more water than batch-mixed samples. This could be due to increased gelatinization and probably degradation of starch during extrusion processing<sup>14</sup>, which made the starch in the blend more sensitive to water. During the period of 60 days, some samples made using extrusion blending had a net weight loss instead of a weight gain. For these blends, it was visually observed that a small amount of solids extracted out. This could be due to the degradation of starch molecules to fragments of smaller molecular weight that are more water soluble than particles of higher molecular weight.

The extruded samples quickly saturated to a weight gain of approximately 30% in the first 2 weeks and then remained almost constant (*Figure 3b*). Batch-mixed samples, on the other hand, continued to gain weight for a period of 20 to 30 days (*Figure 3a*). For both batch-mixed and extruded samples, water absorption increased with increased SMA. This could be due to the carboxylic groups that resulted from the hydrolysed anhydride forming hydrogen bonds with the hydroxyl groups from starch. Since there are more maleic anhydride groups in SMA (~8%) than in EPMA (~1%), the water resistance of the blends increased with increased amounts of EPMA. It should also be noted that, compared to the undried samples, dried samples have more water resistance, i.e. less water absorption (*Figures 3a* and *3b*). This is surprising since the reverse was expected to be true. It could be that the evaporation of moisture changed the materials aggregation and made the materials denser during drying, although no shrinkage was detected.

### Tensile test

The blends obtained from the batch mixer were in the form of chunks of irregular shape. Blends containing significant amounts of starch melt and flow only under conditions of high shear<sup>12</sup>. In the absence of shear during compression moulding, the blends did not melt properly, resulting in the formation of weld lines where separate pieces fused together due to poor diffusion of the melt. When subjected to tension, failure often occurred along the weld line. Therefore, the tensile test was not pursued for batch-mixed samples.

Tensile testing was done with the extruded blends. Both the compression and injection moulding techniques were used to make dog-bone shaped samples. The extruded strips were cut into pieces equal to the length of the mould cavity and compression moulded. This procedure reduced the weld line significantly and, if present, the weld lines were aligned in the direction of the force applied during tensile testing and would have minimal effect on the sample failure.

The tensile strengths of compression- and injection-moulded blends are shown in *Table 5*. The samples stored in lower relative humidity (15%) had higher tensile strength than those stored in higher relative

**Table 5** Tensile strength of starch/SMA/EPMA from extrusion. The numbers in parentheses indicate the standard deviation

Sample	RH (%)	Tensile strength (MPa)	Elongation (%)
Compression moulded			
SMA30/EPMA10	15	6.94 (1.0)	2.60 (0.3)
SMA30/EPMA10	85	5.07 (0.7)	1.90 (0.2)
SMA20/EPMA20	15	5.06 (0.66)	3.56 (0.42)
SMA20/EPMA20	85	3.50 (0.42)	2.65 (0.32)
SMA10/EPMA30	15	3.78 (0.42)	5.80 (0.65)
SMA10/EPMA30	85	2.97 (0.30)	5.15 (0.64)
Injection moulded			
SMA30/EPMA10	15	18.73 (3.62)	1.97 (0.2)
SMA30/EPMA10	85	14.85 (2.08)	1.52 (0.2)
SMA20/EPMA20	15	17.40 (2.96)	4.75 (0.52)
SMA20/EPMA20	85	10.30 (1.70)	3.67 (0.48)
SMA10/EPMA30	15	14.96 (2.40)	5.10 (0.60)
SMA10/EPMA30	85	8.53 (1.28)	3.85 (0.54)

**Table 6** Peak positions of  $G''$  and  $\tan \delta$  for different samples. The letters B and C indicate batch mixing and extrusion mixing respectively

Sample	$G''$ peak position			$\tan \delta$ peak position		
	First	Second	Third	First	Second	Third
SMA10-B	-43.3	30	80.9	-34.0	40.5	87.6
SMA20-B	-41.9	26	79.8	-34.9	42.8	88.5
SMA30-B	-46.2	25	80.5	-38.9	46.0	89.6
SMA10-C	-45.6	25	82.0	-33.7	30	87.2
SMA20-C	-46.2	28	81.7	-40.7	32	90.1
SMA30-C	-45.5	30	83.7	-40.6	36	92.7

humidity (85%). The tensile strength increased with increased SMA content in the blend. This is consistent with the fact that pure SMA has a higher tensile strength than pure EPMA. At both humidities and for all blend compositions, the injection-moulded samples had a much higher tensile strength than compression-moulded samples. In compression moulding, in which the material is subjected to squeeze type flow, there is the presence of weld lines as well as air bubble formation in the tensile test sample because of high viscosity. The modest deformation and the absence of high stress regions (such as runners and gates) prevent the complete melting of starch in the blend and thus preclude a truly homogeneous mixture as is obtained during injection moulding, in which the high shear causes the materials to melt and the screws impart a degree of mixing. It should be noted that we were unable to injection-mould samples of starch with non-reactive polystyrene and ethylene propylene copolymer. In most cases, the samples disintegrated while handling. This would indicate that there is poor adhesion between starch and molten polymers without functional groups.

### Dynamic mechanical analysis

The dynamic mechanical analysis of starch/SMA/EPMA displayed three distinct glass transitions indicating the phase separation of the blend components (*Table 6*). The transitions can also be observed in the plot of  $\tan \delta$  and  $G'$  with temperature and is shown in *Figure 4a* for blends made in a batch mixer and in *Figure 4b* for blends made in an extruder. These glass transitions are observed in approximately the same temperature ranges, irrespective of the blend compositions. The first glass transition, corresponding to EPMA,

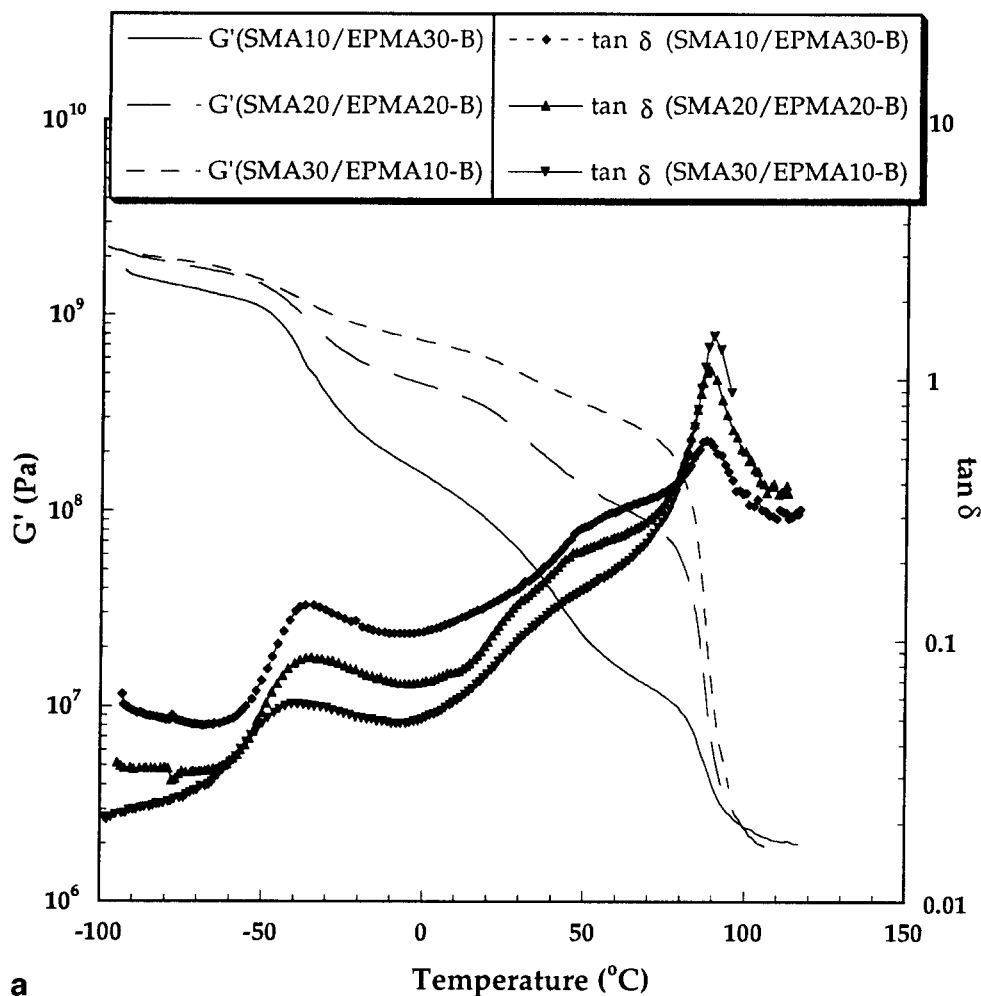


Figure 4 Storage shear modulus and  $\tan \delta$  versus temperature for samples made in (a) batch mixer and (b) extruder

was observed roughly between  $-50^{\circ}\text{C}$  and  $-30^{\circ}\text{C}$ ; the second glass transition (which looked like a plateau because of overlap) due to starch was between  $30^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ , and the third due to SMA at about  $80^{\circ}\text{C}$  to  $90^{\circ}\text{C}$ . This is in contrast to our earlier studies<sup>11</sup> in which starch/EPMA blends showed two distinct  $T_g$  values, one for each polymer, while starch/SMA blends showed one broad transition. The single  $T_g$  observed for starch/SMA blends could be due to the close proximity of the  $T_g$  of the two individual polymers.

A careful look at Figures 4a and 4b indicated that as the EPMA content in the blend decreased and the SMA content increased, the magnitude of the  $\tan \delta$  peak decreased. For blends made in a batch mixer, most of the moisture evaporated during mixing as the temperature exceeded  $100^{\circ}\text{C}$ . The moisture content of the final blend was less than 0.1%. For blends made in an extruder, the moisture content of the final blend ranged between 3 and 4%. Thus, moisture plays a minimal effect in controlling the  $T_g$  of starch. This is also validated in our earlier publication<sup>11</sup> where the synthetic and natural polymers were dried prior to processing. Addition of a low  $T_g$  material like EPMA to the blend appeared to induce a plasticizing effect on the starch, thus lowering its  $T_g$ . Similar results were observed by Ramkumar and co-workers<sup>15</sup> where 'bone-dry' starch, when blended with a synthetic polymer having low  $T_g$ , underwent increased

melting after each successive processing as observed from the decreased melting endotherm in a differential scanning calorimetry experiment.

The storage modulus of the blend is affected by the amount of SMA or EPMA. Temperature had a more pronounced effect on the storage modulus than on the loss modulus. There were three regions in the  $G'$  versus temperature plot that need to be discussed. The first region is below  $-50^{\circ}\text{C}$ , the second is from  $-50^{\circ}\text{C}$  to  $90^{\circ}\text{C}$ , and the third is above  $90^{\circ}\text{C}$ . In the first and the third regions, the moduli for various compositions were close because all three components were either in their glassy states or in their rubbery states. In the second region, the storage modulus increased with increased SMA or decreased EPMA content in the blend. A similar trend was seen in the data for loss modulus ( $G''$ ), indicating that the materials became more rigid (smaller  $G''$ ) with increased SMA or decreased EPMA contents.  $\tan \delta$  increased with increased EPMA or decreased SMA content when temperature was lower than the third peak. Around the third peak,  $\tan \delta$  increased with increased SMA or decreased EPMA content. It is possible that as SMA entered its rubbery state, both the storage modulus and the loss modulus were controlled by SMA (rigid component), while near the first peak, EPMA dominated the properties of the blend since EPMA has higher viscosity. It was also observed that the glass transition



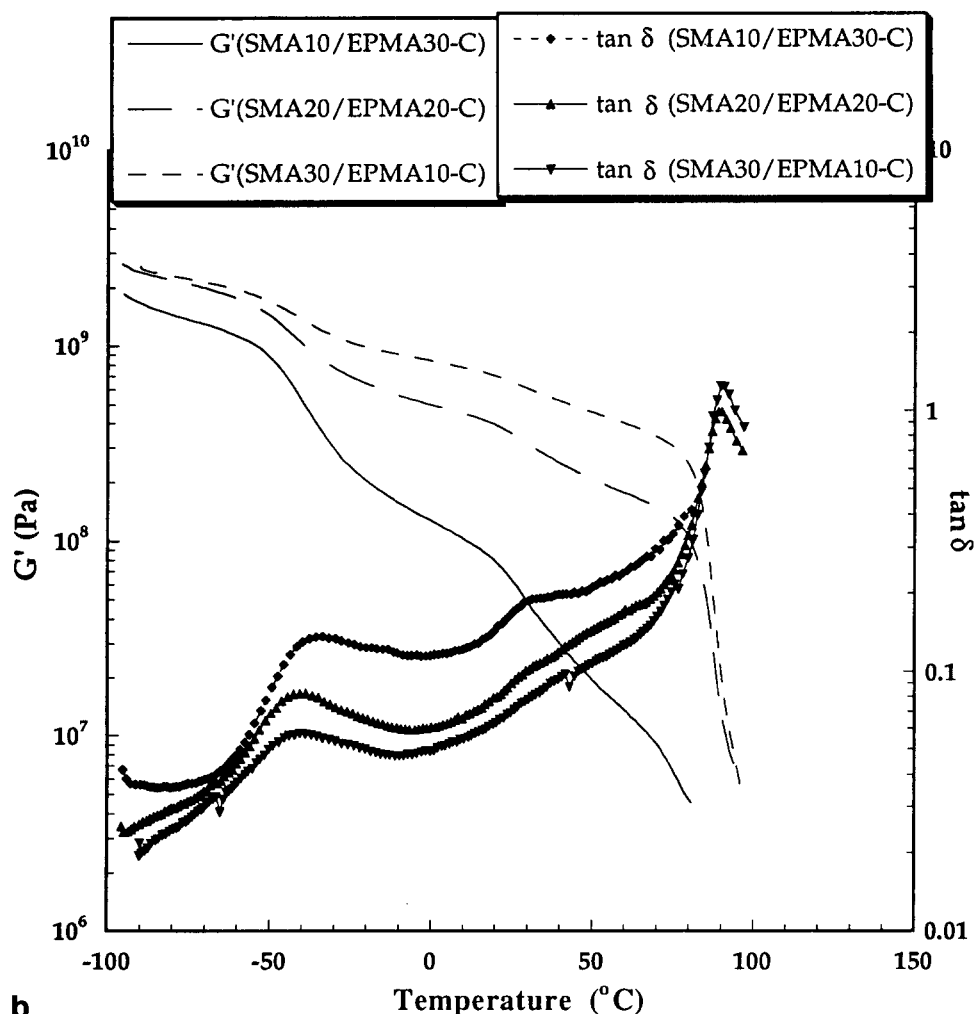


Figure 4 (Continued)

temperatures from  $\tan \delta$  peaks are several degrees higher than from  $G''$  peaks (Table 6).

During batch mixing and during extrusion, materials are subjected to different shear and thermal histories. The residence times are also different for the two processes. For SMA10/EPMA30 and starch blends, both  $G'$  and  $G''$  of the material made in a batch mixer were higher than  $G'$  and  $G''$  of the blends made in an extruder. For SMA20/EPMA20 and starch blends, both  $G'$  and  $G''$  of material made in a batch mixer are close to  $G'$  and  $G''$  of the material made using an extruder. For SMA30/EPMA10 and starch blend, both  $G'$  and  $G''$  of material made in a batch mixer were lower than  $G'$  and  $G''$  of the material made using an extruder. This is in contrast to the result for SMA10/EPMA30 and starch blends. The  $\tan \delta$  peaks (both magnitude and temperature at which it occurs) for EPMA and SMA were very close for all three blends. However, the peak at which the transition of starch occurred for the batch-mixed samples was significantly different from the starch peak of the extruded sample. The peak temperatures for samples made in an extruder were always lower than that of those obtained from a batch mixer. This indicated that starch in extrusion experienced a very different processing history than the starch in batch mixing. In extrusion, the materials were subjected to higher shear force than

experienced in batch mixing. This could cause increased gelatinization and probably degradation during extrusion<sup>16</sup>. This explanation is consistent with the water absorption results in which the extruded blends were found to have less water resistance.

A compression-moulded rectangular strip was used to conduct the frequency/temperature sweep on RMS-800. Only blends containing starch/SMA20/EPMA20 were used. The shift factor  $a_T$  can be obtained as  $a_T = \omega_s/\omega$  at the same  $G'$  for different temperatures, where  $\omega_s$  is the frequency from the reference curve (20°C),  $\omega$  is the frequency from any curve which has the same  $G'$  as the point  $\omega_s$ . Using the shift factors above,  $G'$  curves were moved along the  $x$ -axis to obtain the time-temperature superposition master curve. The master curves for the batch and extruded sample containing starch 60/SMA20/EPMA20 are shown in Figures 5a and 5b respectively. The shift factors at different temperatures for the material processed in batch or in an extruder are shown in Table 7. The shift factors are larger for extruded samples than for batch-mixed samples at temperatures below the reference (20°C). At temperatures above the reference, shift factors are lower for extruded samples than for batch-mixed samples. The range of shift factors is wider for extruded blends ( $10^{10}$  to  $10^{-13}$ ) than for batch-mixed blends ( $10^8$  to  $10^{-9}$ ). Hence, extruded samples are more temperature

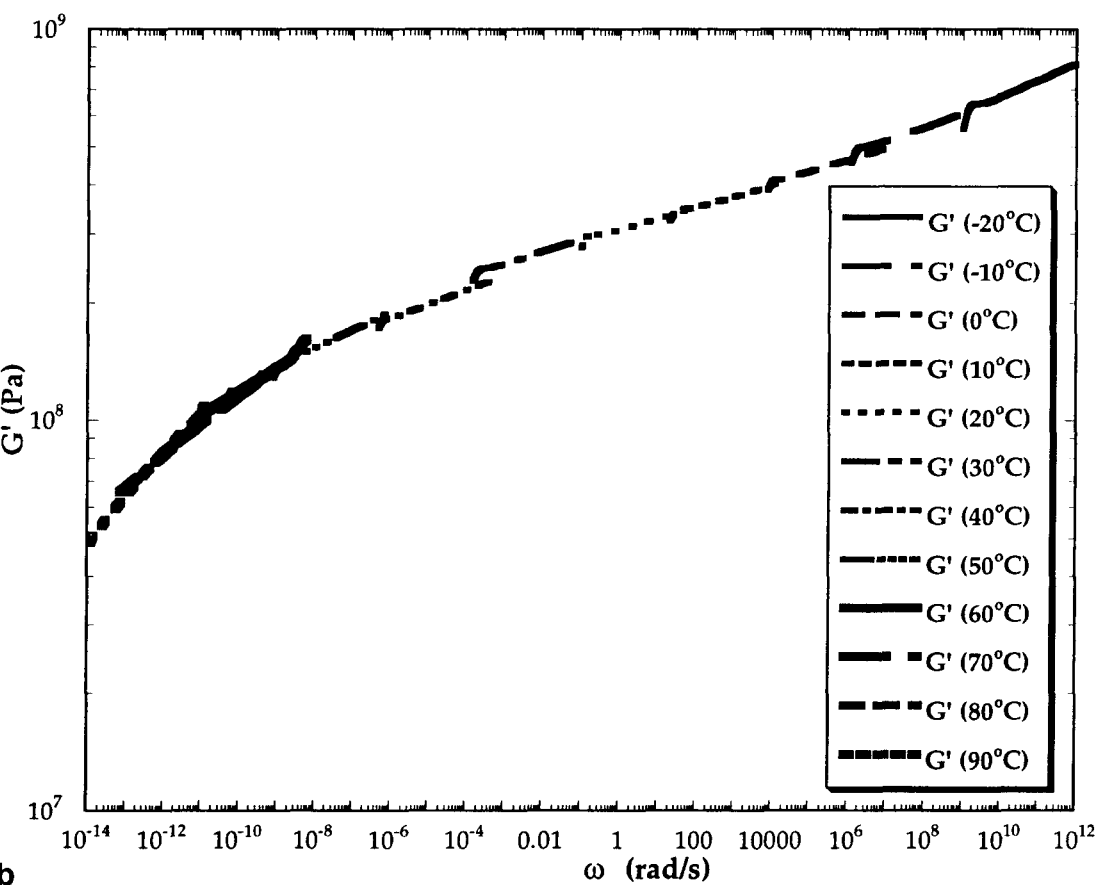
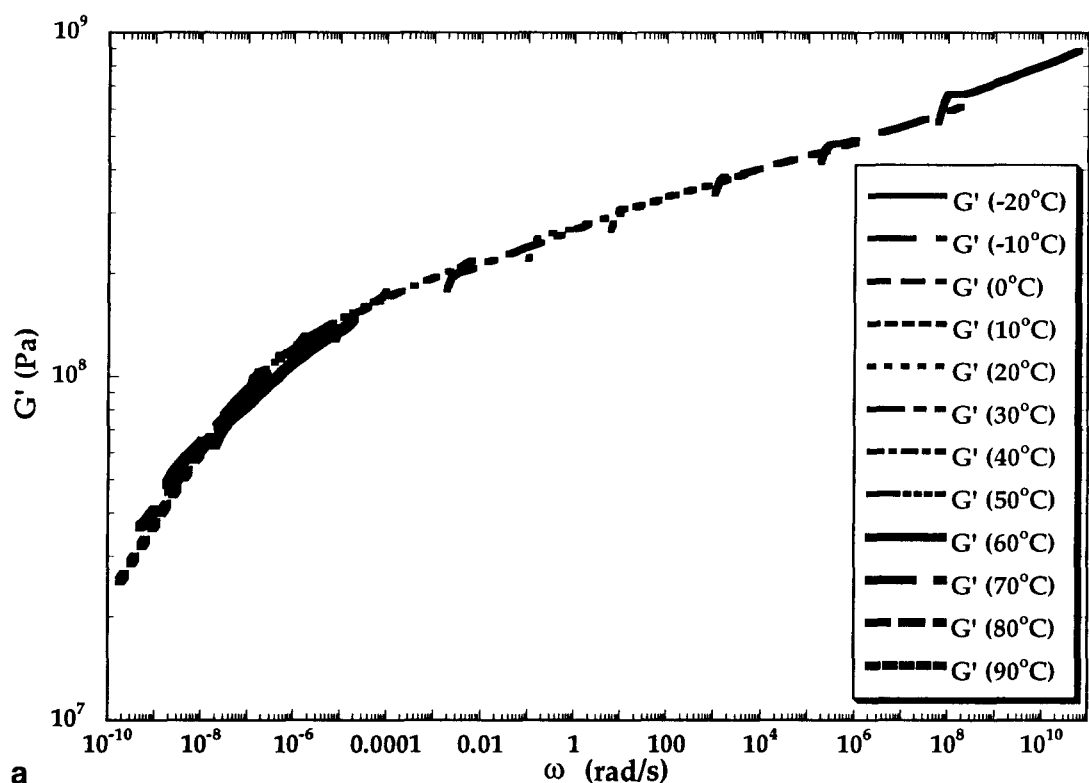


Figure 5 Storage shear modulus versus frequency reduced to 20°C for starch60/SMA20/EPMA20 for (a) batch-mixed and (b) extrusion-processed blends

sensitive than batch-mixed samples. This is consistent with the results obtained in the temperature sweep. The difference is again due to increased gelatinization and/or degradation of starch in the extruder.

*Blend morphology*

In its natural state, starch exists in a granular form. The size and the shape of the starch granules vary depending on the origin. Native corn starch consists of

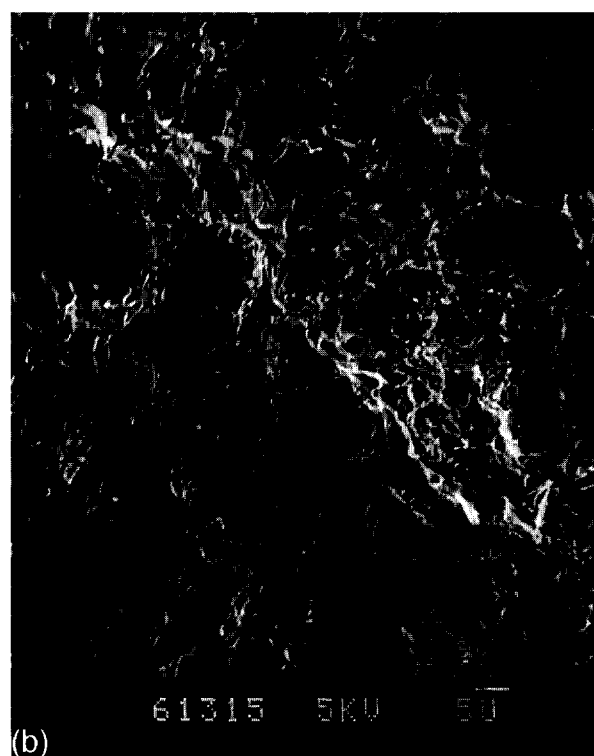
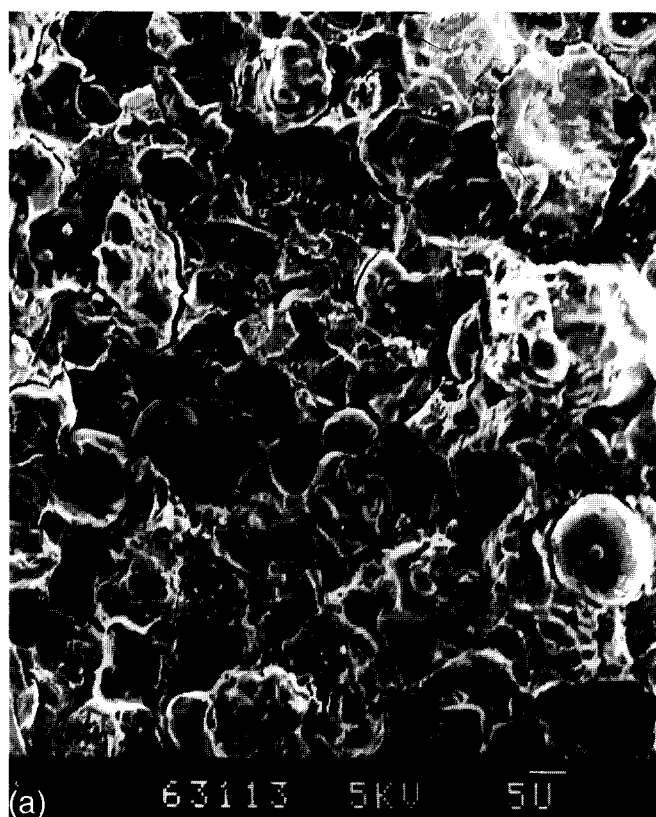
**Table 7** Shift factors for starch60/SMA20/EPMA20. The letters B and C indicate batch mixing and extrusion mixing respectively

Temperature (°C)	SMA20/EPMA20-B	SMA20/EPMA20-C
-20	$6 \times 10^8$	$1 \times 10^{10}$
-10	$1.8 \times 10^6$	$1.2 \times 10^7$
0	$1 \times 10^4$	$8 \times 10^4$
10	60	200
20	1	1
30	$9 \times 10^{-3}$	$1.5 \times 10^{-3}$
40	$8 \times 10^{-5}$	$5 \times 10^{-6}$
50	$1 \times 10^{-6}$	$8 \times 10^{-9}$
60	$9 \times 10^{-8}$	$6 \times 10^{-11}$
70	$1.8 \times 10^{-8}$	$6 \times 10^{-12}$
80	$5 \times 10^{-9}$	$7 \times 10^{-13}$
90	$1.8 \times 10^{-9}$	$1.2 \times 10^{-13}$

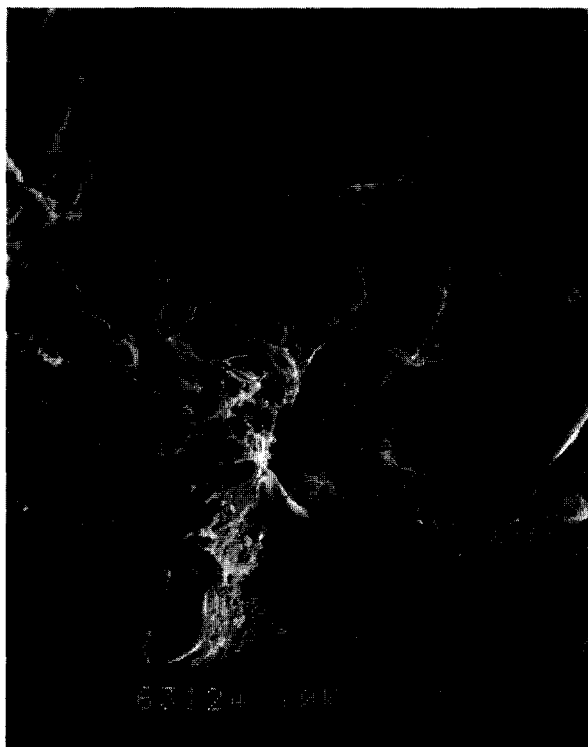
polygonal or round granules ranging between 5 and 25  $\mu\text{m}$  in diameter<sup>17</sup>. Starch behaves like thermoplastic polymers only under conditions of high shear and high moisture (>10%). At low moisture content (<10%), starch granules may melt when subjected to high shear, but this could lead to the degradation of starch molecules, resulting in the lowering of the molecular weight. When native starch at low moisture content is blended with synthetic polymer(s) in a batch mixer or in an extruder, the resulting blends contain a mixture of molten polymer, molten starch, and unmelted or partially melted starch granules. The properties of these blends depend on their morphology (phase structure) produced during processing. The extent of starch melting and degradation depends on the blending conditions such as melt temperature, moisture in the starch, extruder screw speed and screw configuration. The blending conditions either in a batch mixer (low shear) or in an extruder (high shear) have a considerable effect on the mechanical properties of starch/polymer blends. These properties could be related to starch melting and degradation by using g.p.c. data and scanning electron microscopy (SEM) graph.

Morphologies of blends were determined using a scanning electron microscope. Since the contrast between the starch and the polymer is poor, it is difficult to comment on the phase separation from the SEM graph. In such instances, an optical microscope was used. Each technique has its own characteristics. Using SEM one can get higher magnification. Under an optical microscope, after staining the starch there is enough contrast to see the phase behaviour and separation of starch blends.

SEM micrographs for batch-mixed samples are shown in *Figure 6*. Most of the starch granules in the starch60/SMA30/EPMA10 blend remained intact, and materials appeared more like a filled system, wherein the unmelted starch granules are coated and held together (*Figure 6a*). The size of the unmelted starch granules ranged between 5 and 15  $\mu\text{m}$ . With decreased SMA or increased EPMA content, as in the starch60/SMA10/EPMA30 blend, the number and the average size of unmelted starch granules decreased significantly (*Figure 6b*). Increased EPMA content resulted in an increase in the torque and viscous heating during blending (*Table 2*). This caused the increased melting of starch. Increased melting also improves the reaction and interaction between the starch and the synthetic polymer and may result in a slightly cross-linked polymer blend. For extrusion-blended samples, a similar trend regarding the number

**Figure 6** Scanning electron micrograph of (a) starch60/SMA30/EPMA10 and (b) starch60/SMA10/EPMA30 blends after melt compounding in a batch mixer

and the average size of unmelted starch granules with decreasing SMA content or increasing EPMA content was observed. An SEM micrograph for an extruded sample is shown in *Figure 7*. The size of starch granules in starch60/SMA30/EPMA10 was less than 5–10  $\mu\text{m}$  (*Figure 7*). While examining samples of similar composition from an extruder and from a batch mixer, lower and

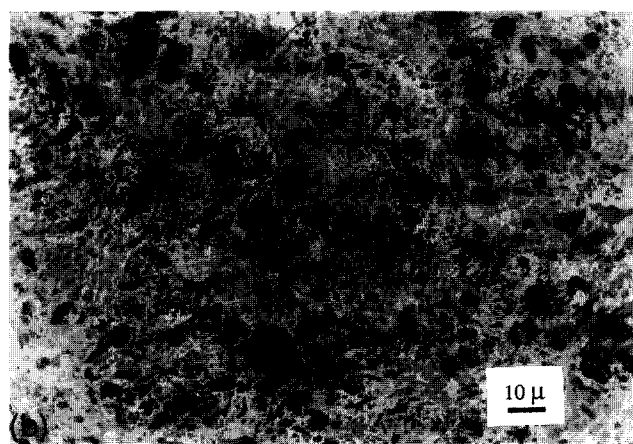


**Figure 7** Scanning electron micrograph of starch60/SMA30/EPMA10 blend after melt compounding in an extruder

smaller sized starch granules were observed in the extruded sample (*Figures 6a and 7*). This confirmed that the effect of a much higher shear force in the twin screw extruder causes more starch melting and degradation.

Photographs from an optical microscope for batch- and extrusion-blended samples are shown in *Figure 8*. It is easier to identify the starch granules because of the available contrast. In the photographs the discrete dark particles indicated the presence of unmelted starch granules and phase-separated starch. Typically, the size of starch particles in the batch-mixed sample of starch60/SMA10/EPMA30 was less than  $10\ \mu\text{m}$  (*Figure 8a*). With decreasing SMA content or increasing EPMA content, the number and the average size of unmelted starch granules decreased. During extrusion, due to the imparting of thermomechanical energy, the size of starch granules and the number of unmelted starch particles were reduced significantly. After compounding in the twin extruder, the number of unmelted starch granules in the blends is significantly reduced (*Figure 8b*). In the extruded starch60/SMA10/EPMA30 blend, the size of starch granules ranged from 1 to  $5\ \mu\text{m}$ . This is much smaller than the size of the starch granules in the corresponding blend made using a batch mixer (*Figures 8a and 8b*).

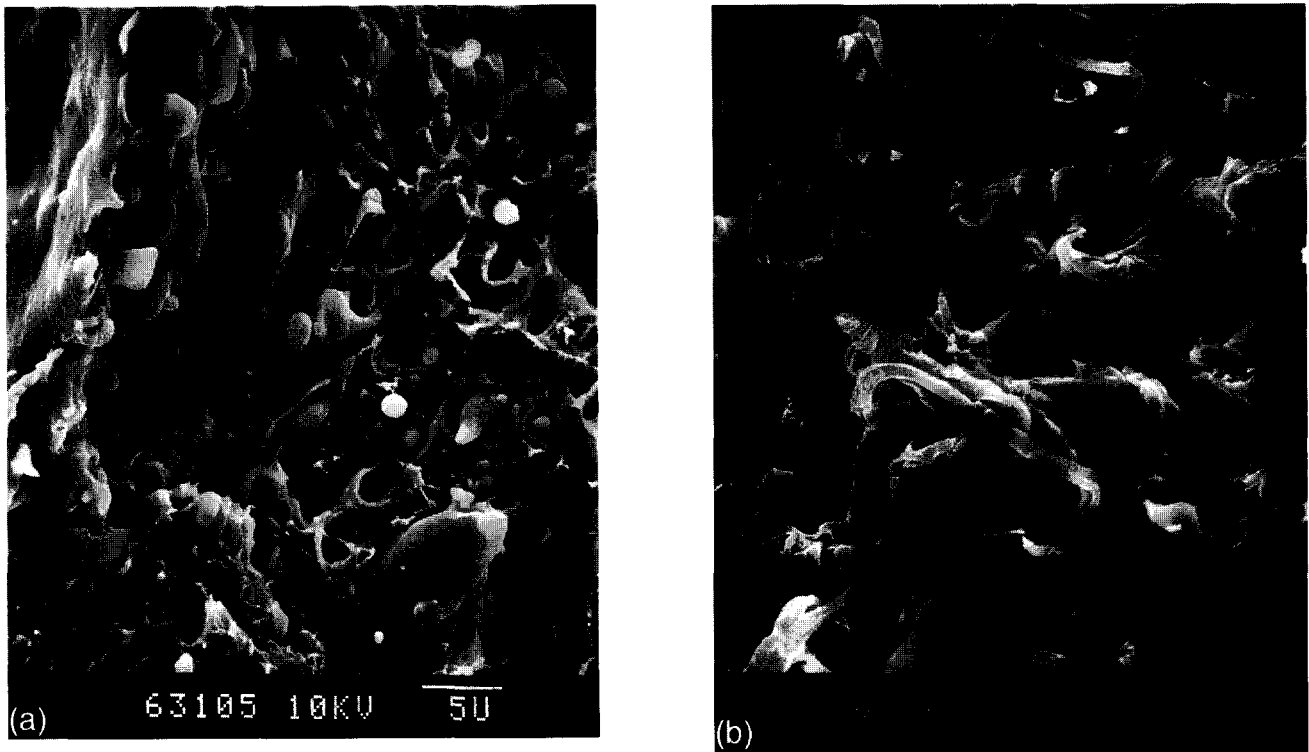
SEM micrographs for the morphology of the fracture surface after a tensile test of compression-moulded samples are shown in *Figure 9*. The size of starch granules in starch60/SMA30/EPMA10 was approximately  $5\ \mu\text{m}$  (*Figure 9a*). The fractured surface showed characteristics of a filled system where the unmolten starch granules detached themselves from the matrix. Some of the cavities or voids may be due to the EPMA phase being stretched until failure. This could be interpreted as evidence of poor



**Figure 8** Optical micrograph of starch60/SMA10/EPMA30 after melt compounding in (a) a batch mixer, (b) an extruder

interfacial adhesion resulting in poor mechanical properties. As the EPMA content increased, the fracture mechanism appeared to be shear tearing<sup>10</sup> (*Figure 9b*). A number of internal voids and cavities are observed. The pulled-out portions in *Figure 9b* that created the cavities are probably the rubbery phase. Comparing starch granules in a sample after extrusion to compression-moulded samples after tensile testing, there appeared to be fewer unmelted starch granules after moulding. This is because the tensile samples were made by heating and compression moulding. During heating and compression moulding, some starch granules had melted. It is generally believed that moisture is necessary for the melting of starch granules. The blends after extrusion had a moisture content of approximately 4%. Yet, after compression moulding, which involved heating under pressure only, the number of starch granules in the blends was reduced.

SEM micrographs for the morphology of different locations of injection-moulded dog-bone samples are shown in *Figure 10*. Samples were taken from near the gate and near the centre of the dog-bone for each composition. The starch granules have completely melted even in the starch60/SMA30/EPMA10 blend after injection moulding (*Figure 10a*). Near the gate the high SMA content samples indicate a layered structure. As the SMA content decreased the surface became more uniform (*Figure 10b*). In a typical tensile bar dog-bone, the melt entered the narrower section and imparted a certain amount of orientation in the direction of flow.

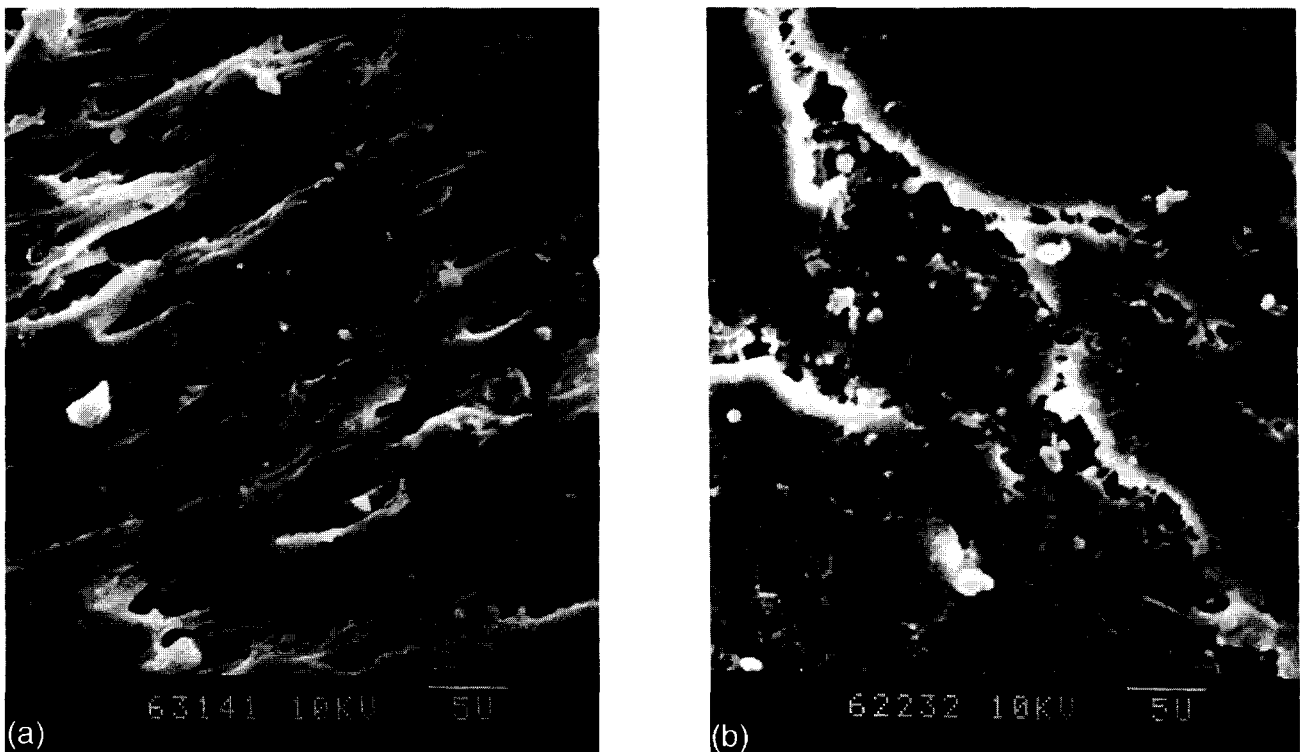


**Figure 9** Scanning electron micrograph of fracture surface of melt-compounded and compression-moulded blends of (a) starch60/SMA30/EPMA10 and (b) starch60/SMA20/EPMA20 blends after tensile testing

This is seen in *Figure 10a* which indicates there was a strong orientation at the centre of the dog-bone compared to the sample near the gate. This demonstrates the different morphology at different locations.

#### CONCLUSIONS

Ternary blends of starch/SMA/EPMA gave products with a range of physical properties which depended on the ratio of SMA to EPMA in the blend. As the SMA



**Figure 10** Scanning electron micrograph of injection-moulded samples of (a) starch60/SMA30/EPMA10 (centre) and (b) starch60/SMA20/EPMA20 (gate)

content increased, the samples were more rigid and had higher tensile strengths. The manner in which the blends were processed affected the quality of the final product. For example, samples made in a batch mixer, where the stresses are low, had lower water absorption and showed lower degradation of starch macromolecules as evidenced by g.p.c. measurements. Dynamic mechanical analysis data showed that the blends exhibited three distinct glass transitions, one for each component. The processing method (batch or extrusion) affected the temperature at which the transition occurred for starch. The  $T_g$  was always lower for extrusion-processed blends when compared to batch-processed blends of the same composition. The range of temperature shift factors is larger for extruded blends than for batch-processed blends, indicating that the extruded blends are more sensitive to temperature. SEM micrographs of samples showed that the starch granules did not melt completely during mixing. However, the granule size of starch did decrease after blending; this decrease was large for blends containing a greater percentage of EPMA. Successive processing such as compression or injection moulding further reduced the size of starch granules.

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