Effect of crystallinity on the mechanical properties of starch/synthetic polymer blends

D. H. S. RAMKUMAR, M. BHATTACHARYA

Department of Biosystems and Agricultural Engineering, University of Minnesota, St Paul, MN 55108 USA

Crystallization behaviour of starch and maleated blends was studied at 50 °C over a period of 20 weeks using wide angle X-ray diffraction (WAXS). The variation of mechanical properties (tensile and flexural) and stress relaxation behaviour of the blends stored at 50 °C and -10° C were studied over the same period. The starch content in the blends was 70% by weight. The synthetic polyolefins used in the blends were two grades of ethylene-co-vinyl acetates (EVA) containing 28% and 18% VA, two grades linear low-density polyethylene (melt index of 40 and 20) and high density polyethylene. An increase in the tensile properties of all the blends was observed in the first 5 weeks for samples kept at both temperature conditions. Blend samples kept at 50 °C had higher tensile strengths than the ones at -10 °C. Flexural strength remained constant over the duration of time. Freshly moulded specimens relaxed faster than the samples aged at either temperature. X-ray diffraction patterns showed that the starch was completely melted and had lost its crystallinity. Also, starch blends with EVA did not show any crystalline structure. The crystallinity in the starch blends with polyethylene was mainly due to the crystallinity of the synthetic polymer. The X-ray patterns of pure synthetic polymers were not found to be different from their functionalized counterparts. Crystal intensity was found to decrease for all the polyethylene blends. The effect of crystallinity on the mechanical properties is discussed.

1. Introduction

Injection moulding is one of the commercially important polymer processes used in the fabrication and manufacturing of a wide range of thermoplastics. Many plastic parts are produced by injection moulding of polymer materials. It is well known that injection-moulded articles often contain residual stresses due to non-uniform cooling rates. The presence of such stresses causes anisotropy in their mechanical properties [1] and a change in their magnitude or distribution during post-processing ageing is therefore important.

We have been working on blends of starch and synthetic polymer [2–7]. It has been shown that the mechanical properties of blends of incompatible starch and synthetic polymers can be significantly improved by the addition of functional groups (maleic anhydride) on the synthetic polymer capable of interacting with the hydroxyl groups on the starch. Recently we have presented data [6, 7] on the injection moulding of starch and maleated polyolefin blends.

The optimum process conditions for injection moulded starch/polyolefin blends, their water absorption characteristics, the effect of various amounts and size of fillers, and degradation behaviour were published earlier [6, 7]. Since blends containing significant amounts of starch are moisture sensitive, they need to be stored in a dry atmosphere. During storage and handling, and depending on the climatic conditions and geographical locations, the finished products are likely to encounter extreme temperature conditions. Hence, the product performance under those temperature conditions needs to be studied to optimize the shelf life of the moulded article.

In the injection moulding process, the moulded article may have residual stresses and orientation. The stresses can result in poor mechanical properties. The rates of decay of stresses vary with time. Though decay of stresses occurs mostly in the melt state, it is interesting to see the effect of temperature on the solid samples. Also, since the crystallinity of semi-crystalline polymers changes with time and temperatures, it may influence the ultimate properties of the moulded product. The crystallization behaviour of the blend is expected to depend on its constituents. The presence of the amorphous component and its influence on the crystallization behaviour of a semi-crystalline material needs to be investigated.

In the work reported here, blends of injection moulded starch/maleated polyolefins were aged at two temperatures and their properties as a function of time are reported. The maleated polyolefins include high-density polyethylene (HDPEMA), linear lowdensity polyethylene (EMA), and ethylene vinyl acetate (EVAMA). The starch content was fixed at 70% by weight. The properties studied were tensile and flexural strengths. An assessment of the residual stresses was obtained from the stress relaxation method. Since moulding and storage conditions affect the morphology, crystallinity of these blends as a function of time was evaluated.

2. Experimental procedure

2.1. Materials

Industrial corn starch (SMP 1100) containing approximately 25% amylose and 75% amylopectin was obtained from Cargill, Inc. Ethylene vinyl acetate (ELVAX 240, melt flow index \sim 43), ethylene vinyl acetate (VA) maleic anhydride (MC 190D, 28% VA, melt flow index ~ 20) (EVAMA-28), ethylene vinyl acetate maleic anhydride (MC 197D, 18% VA, melt flow index ~ 2.5) (EVAMA-18), ethylene maleic anhydride (MB 226D, melt flow index ~ 1.5) (EMA-800), ethylene maleic anhydride (MB 110D, melt flow index \sim 40) (EMA-80), and high-density polyethylene maleic anhydride (MB265D, melt flow index ~ 2.0) (HDPEMA) were obtained from DuPont, Canada. The maleic anhydride content of EVAMAs, HDPEMA and EMAs was approximately 0.8 mol %. Low-density polyethylene (Type 955 I, melt flow index ~40 and Type 993I, melt flow index ~25) and high-density polyethylene (melt flow index \sim 4) was obtained from the Dow Chemical Company, USA.

2.2. Extrusion compounding

The various compositions used in this study are summarized in Table I. Each blend composition contained 70% starch, 10% functionalized polymer (HDPEMA, EMA, or EVAMA) and 20% non-functionalized polymer (HDPE, LLDPE, or EVA). The method of processing these blends has been described in our earlier publication by Ramkumar and coworkers [6, 7]. A laboratory-scale twin screw extruder with corotating screws was used for continuous melt compounding. The barrel-length-to-diameter ratio was 20:1 and the extruder was divided into four zones for temperature control. The temperature of the first zone of the extruder was 80 °C, and those of the second and third zones were 140 °C and 150 °C, respectively. A capillary die maintained at 120 °C was attached to the end of the extruder. The die diameter was 0.64 cm and had a length of 7.6 cm. 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 the processability, and the flow rate ranged between 2.5 and 3.5 kg h^{-1} . The various compositions blended are summarized in Table I.

2.3. Injection moulding

Injection moulding was accomplished in a 50-tonne Boy injection moulding machine. Blends containing EVAMA were tested for tensile properties only, while

TABLE I Blend compositions (%) for storage studies

Starch	EVAMA	EVA	EMA	LDPE	HDPEMA	HDPE
70	10 (28% VA)	20				
70	10 (18% VA)	20				
70	. ,		10 (EMA80)	20 (40 MI)		
70			10 (EMA800)	20 (20 MI)		
70			· · · ·	· · ·	10	20

those containing EMA and HDPEMA were studied for both tensile and flexural properties. The pelletized blend extrudate was injection moulded to form ASTM D-638-68 Type I dog-bone specimens approximately 3 mm thick. Flexural bars were moulded as per the specifications given in ASTM D638. Tensile specimens without weldlines and flexural specimens with and without weldlines were moulded. The mould temperature was kept constant by circulating water. Blends containing EVAMA had the following processing conditions: barrel temperature 170 °C, mould temperature 20 °C, screw speed 100 r.p.m., back pressure 4 MPa, and injection pressure of 12 MPa. Blends containing EMA and HDPEMA had the following processing conditions: barrel temperature 155 °C, mould temperature 40 °C, screw speed 100 r.p.m., back pressure 0.5 MPa, and injection pressure of 8 MPa. These parameters were selected based on our previous work [6, 7]. All samples were conditioned in a freezer $(-10^{\circ}C)$ and in an oven (50 °C) for a specific period of time. Before testing, the samples were allowed to come to room temperature.

2.4. Mechanical properties

The tensile testing of the samples was done at a crosshead speed of 3 mmmin^{-1} , and flexural testing was done at a crosshead speed of 9.5 mm min^{-1} using a MTS universal tester. The definitions of the parameters evaluated are outlined in the aforementioned ASTM test methods. Stress is the measured force-perunit cross-sectional area of the sample. An initial jaw separation of 4.2 cm was maintained. The gauge length at any time was calculated from the time elapsed from the start of the test and the crosshead speed. Percent elongation is the ratio of the change in the gauge length at any time to the original gauge length of the sample. Results for the elongation are compared on the basis of time to break. Stress relaxation experiments were performed on the blends at room temperature. A stress value of about 60 to 70% of the maximum stress to break was applied to the sample and the decay in stress was monitored with time for 1000 s. All the mechanical properties reported are the average of five specimens. The maximum variation in the tensile and flexural properties was within 10% of the value.

2.5. X-ray analysis

X-ray measurements were conducted on injectionmoulded samples using a Siemens wide angle X-ray diffraction apparatus and a Rigaku Geigerflex camera operating at a voltage of 40 kV and a current of 40 mA. Nickel-filtered CuK_{α} radiation ($\lambda = 0.154$ nm) was used. X-ray scans were made over a 2 θ range of 10 to 35° with a step size of 0.05. In the case of semicrystalline materials, the relative areas of crystalline and amorphous regions were computed by drawing a smooth curve.

3. Results and discussion

3.1. Tensile properties

The tensile properties of samples aged at 50 °C (oven) and at -10° C (freezer) were measured at room temperature every 5 weeks up to 20 weeks. The results are shown in Fig. 1. The tensile strengths of the starch blends (fresh samples) were in the following decreasing order by synthetic polymer component in the blend: HDPEMA, EMA-800, EMA-80, EVAMA-18 and EVAMA-28. It is observed that the tensile strengths of the blends are comparable or greater than the tensile strengths of the synthetic polymers, though the percent elongation is drastically lowered. This trend in the tensile strength for different blends continued for samples aged in the oven and in the freezer over the entire testing period. Except for the blends of starch/EVAMA-28, all other blends displayed higher tensile strengths by about 12% when aged at 50°C than when aged at -10° C (Fig. 1). The tensile strength of the starch/EVAMA-28 blends were unaffected by the storage temperature. The non-EVAMA blends turned somewhat brittle when aged in the oven. Irrespective of the temperature at which these samples were aged, the tensile strengths of all the blends increased in the first 5 weeks and remained constant with further ageing time. The increase in tensile strength for the samples stored in the oven after 5 weeks was approximately 35% over the tensile strength of the freshly moulded values. The blends that showed the least increase in tensile properties after 5 weeks of storage were the EVAMA blends, with EVAMA-28 being the least sensitive. The lower sensitivity of the change in mechanical properties with ageing could be due to the complete amorphous microstructure of EVAMA blends. An exception to this behaviour is with EVAMA18 blends aged at 50 °C, which behaved similarly to the polyethylene blends.

The order of elongation behaviour of the freshly moulded blends is EVAMA-28 > EVAMA-18 > EMA-800 > HDPEMA > EMA-80 (Fig. 2). The elongation of starch blends followed the same order as the elongation of the pure synthetic polymer, i.e. the higher the elongation of the synthetic polymer, the higher the elongation of the blends. For EVAMA-28 blends, the elongations are the same for freezeraged and oven-aged samples up to 10 weeks. Beyond a period of 10 weeks, elongation of oven-aged samples was lower than the freezer-aged samples.



Figure 1 Variation of tensile strength with time for starch blends. Filled symbols and solid lines correspond to oven aged samples. Unfilled symbols and dashed lines correspond to freezer aged samples. ($\mathbf{\nabla}, \nabla$) HDPEMA; ($\mathbf{\Delta}, \Delta$) EMA-800; ($\mathbf{\Box}, \Box$) EMA-80; ($\mathbf{\Phi}, \diamond$) EVAMA-18; ($\mathbf{\Phi}, \bigcirc$) EVAMA-28.



Figure 2 Variation of elongation with time for starch blends. Notation for symbols and lines are the same as those in Fig. 1.

However, the elongation of samples stored in the freezer increased by 39% over its 10 week value. The increase in elongation for freezer samples could be due to moisture absorption which acted as a plasticizer. However, the tensile strengths are not affected during the same period of time. For EVAMA-18 blends, the elongation pattern is similar to that of the EVAMA-28 blends, except that the delineation started after the first 5 weeks of storage. The elongation of annealed EVAMA-18 blends after 20 weeks is about 32% lower than that of those stored in the freezer. This behaviour is consistent with the tensile strength of this material. Tensile strengths of oven-aged samples are higher than those of freezer samples. As explained under the X-ray section, this material behaviour is similar to that of polyethylenes.

A common observation in all the polyethylene blends and freezer-aged EVAMA-18 blends is that there is a maxima in the elongation at approximately 10 weeks. As will be seen later, this maxima in the elongation corresponds to a minima in the crystallinity. With a few exceptions, the elongation of ovenaged samples is lower than that of the freezer-aged samples at all times, which can be attributed to the effect of annealing on crystallinity.

3.2. Flexural properties

The order of flexural strengths for the blends is HDPEMA, EM-800 and EMA-80. The variation of flexural strength with time is shown in Fig. 3. All weldline samples have lower flexural strengths than non-weld samples. Blends with HDPEMA had the highest average weldline to non-weldline strength, followed by blends of EMA-800 and EMA-80.

The flex strengths of annealed non-weld samples of EMA-800 and HDPEMA are higher than similar non-weld freezer-aged samples. The flex strengths for all non-weld samples remained constant with ageing. The flexural strength of EMA-80 were the same for freezer and oven-aged samples and remained constant for a period of 10 weeks; further ageing increased the flex strengths of samples stored in the freezer over those stored in the oven. The exact reasons for the difference in the flex strengths of these blends are not known.

The flex strengths of EMA-80 and HDPEMA blends with weldline stored at both the temperatures remained constant with time of ageing. The freezer-aged weldline samples of EMA-80 and HDPEMA are slightly higher than those of the oven-aged samples. The variations in flex strength with storage temperature for HDPEMA blends are different for weld and non-weld samples. For samples stored at -10 °C, the flexural strength is higher than that of similar weldline samples that were annealed. Low temperatures decreased the chain mobility and helped heal the weldlines more than that was possible for the ovenaged samples of HDPEMA. However, there were no



Figure 3 Variation of flexural strength with time for weld (WL) and non-weld (NWL) starch/maleated polyethylenes. Notation for symbols and lines are the same as those given in Fig. 1.

differences in the flexural strengths for HDPEMA blend samples aged at both the temperatures at the 20-week point.

3.3. Stress relaxation

The tensile stress relaxation of the samples aged at 50° C and -10° C was plotted with time using reduced stress (i.e. instantaneous stress divided by applied stress) on the vertical axis. Representative plots of the stress relaxation are shown in Figs 4 and 5. These materials show a sigmoidal stress relaxation when the stress is plotted against the logarithm of time. The relaxation process has two regions, the exponential region at shorter durations and the power law region at relatively longer durations. For freshly moulded blend samples, the relaxation followed the following order: EVAMA-28 > EVAMA-18 > HDPEMA > EMA-80 > EMA-800. For EVAMA-28, the stresses relaxed to 45-63% of the applied stress, depending on the time and condition of storage. For EMA-800 the range fell between 66-81%. It was observed that for all blends, the freshly moulded specimens relaxed faster than the samples aged at either temperature. However, relaxation of the applied stress was quicker for the samples aged in a freezer than those aged in an oven. This behaviour is similar to the elongation behaviour and could be due to the plasticizing effect of moisture, which is absorbed by the samples in the freezer. The stress relaxation behaviour is the same for all the blends, including the blends of starch with semi-crystalline polyethylenes.

Ageing has been known to introduce chemical changes and the likely formation of bulky groups which will be explained in greater detail below. These changes could increase the relaxation times for the aged samples as was observed in this study. The effect of annealing on the oven-aged samples increased the crystallinity. The enhanced crystallization reduced chain mobility for semi-crystalline blends and further reduced the relaxation rates. The effect of ageing time on the stress relaxation is similar to that observed in the crystallinity variation with storage time. For amorphous blends of starch/EVA, the difference in the stress relaxation with ageing time was not found to be significant.

As can be seen in Figs 4 and 5, the stress does not decay to zero but reaches an asymptotic level σ_{∞} in the limit of long durations. When polymeric materials solidify in a mould, internal stresses are frozen-in due to the differences in the solidification rate between the surface and the interior of the object. According to Kubat et al. [8], the magnitude of the internal stress is equal to σ_{∞} . The applied stress (σ_0) at the time of the experiment can be considered to be the sum of the internal stresses due to the deformation of the sample and the residual internal stresses present in the virgin sample due to processing conditions. While the internal stresses induced by a deformation can be assumed to be a function of the applied stress, the internal stresses remaining after processing are likely to be a constant. Alternately, the Kubat-Rigdahl [9] analysis can be applied to estimate the residual internal



Figure 4 Stress relaxation of starch/maleated ethylene vinyl acetates. (a) EVAMA-18, freezer; (b) EVAMA-18, oven; (c) EVAMA-28, freezer; (d) EVAMA-28, oven. (\longrightarrow) 0 weeks; (---) 5 weeks; (---) 10 weeks; (---) 15 weeks; (---) 20 weeks.

stress. From the exponential flow region, the maximum slope of the stress versus logarithmic time $(-d\sigma/d \log(t))$ is plotted versus the initial stress σ_0 and the intercept with the σ_0 axis gives the values of the residual internal stress σ_i . The magnitude of σ_i from stress relaxation procedure is summarized in Table II. For starch/synthetic polymer blends, the magnitude of σ_i obtained from the stress relaxation procedure are much higher both in magnitude and as a ratio of σ_i/σ_0 than those of most of the synthetic polymers tested [8, 9].

3.4. X-ray results

The X-ray patterns of the functionalized and nonfunctionalized synthetic polymers are shown in Fig. 6. As can be seen from Fig. 6, they display a similar pattern. This meant that the grafting of maleic anhydride to the polymer chains did not alter their crystalline structures. This behaviour can be expected since the amount of maleic anhydride in a functionalized polymer is approximately 0.8%. X-ray patterns of the pure synthetic polymers showed a crystalline behaviour for polyethylenes (HDPEMA and both EMAs) only. No crystallinity was observed in the EVAMA polymers. The crystallinity of polyethylenes of freshly moulded samples are in the order HDPEMA (58%) > EMA-80 (47%) > EMA-800 (42%). The X-ray patterns of these materials have distinct peaks at 20 values of 21.5 and 23.8 for HDPEMA and 21.3 and 23.6 for both EMAs. Both of the pure components of EVA with 18% VA and 28% VA have broad amorphous hills. Changes in the crystalline state of the materials with varying vinyl acetate contents was investigated by Salyer and Kenvon [10]. Our results support their findings that at the vinyl acetate levels used in our work the EVA copolymers are in amorphous state. However, the X-ray patterns of EVAMA-18 revealed that a sharp peak is developing in this material. As the vinyl acetate (VA) substitution in polyethylene copolymer is only 18%, compared to 28% in EVAMA-28, the behaviour of this material is somewhat closer to that of the polyethylenes. Native starch granules, on the other hand, have semi-crystalline structure due to the presence of amylose.

Blends of starch/EVAs do not show any crystalline peak, while the blends containing starch with polyethylenes show a distinct peak. After extrusion and injection moulding, the starch granules in the blends are melted and the crystallinity is destroyed. These starches, whose crystallinity is destroyed, are



Figure 5 Stress relaxation of starch/maleated polyethylenes. (a) EMA-80, freezer; (b) EMA-80, oven; (c) HDPEMA, freezer; (d) HDPEMA, oven. Notation for lines as for Fig. 4.

Blend composition	Storage time (weeks)								
	0	5 (O)	5 (F)	10 (O)	10 (F)	15 (O)	15 (F)	20 (O)	20 (F)
EMA-800	0.664	0.784	0.71	0.78	0.58	0.82	0.73	0.75	0.71
EMA-80	0.685	0.72	0.75	0.75	0.70	0.83	0.67	0.71	0.71
HDPEMA	0.644	0.72	0.64	0.72	0.68	0.63	0.67	0.70	0.60
EVAMA-18	0.6	0.75	0.59	0.74	0.66	0.66	0.77	0.75	0.67
EVAMA-28	0.48	0.63	0.59	0.70	0.53	0.71	0.65	0.58	0.45

TABLE II Ratio of residual (σ_i) to applied stress (σ_0) from stress relaxation curves

O: oven.

F: freezer.

often referred to as "destructurized" or "gelatinized" starch.

Starch/polyethylene blends displayed distinct sharp peaks at the same 20 values as did pure polyethylenes (Fig. 7). In these figures, slight shifts in the peak positions can be observed, which are believed to be due to instrument drift. X-ray patterns of pure HDPEMA and of blends of starch/HDPEMA show that with ageing there is a gradual decrease in crystallinity of starch/polyethylene blends up to 10 weeks, followed by an increase in their crystallinity. It was then decided to observe the crystallinity of some of the starch/HDPEMA blends and pure HDPE more closely each week over a 5 week time period. A similar pattern was observed, i.e. a decrease in the crystallinity of starch/HDPE and pure HDPE for a period of 3 weeks followed by an increase. These results are summarized in Table III. The percent crystallinity of the materials for pure HDPE and its blends with starch are given in Table II. It can be seen that the addition of starch to HDPE increased the amorphous region in the blend. The time-dependent variation of



Figure 6 X-ray diffraction patterns of pure polyethylenes and pure maleated polyethylenes.



Figure 7 Variation of X-ray diffraction patterns of starch/ HDPEMA blends. Weeks: (——) 0; (–––) 5; (–––) 10; (····) 15.

TABLE III Percentage crystallinity of starch/HDPEMA blends

Week	Starch/HDPEMA	HDPEMA pure
0	31	58
1	37	55
2	23	57
3	18	49
4	27	56
5	33	54

crystallinity of pure semi-crystalline polymers and their starch blends are qualitatively similar. Since the variation of X-ray patterns for pure EMAs and their blends with starch are similar to those of HDPE, the results on EMA are not shown here. Also, the starch blends with EVAs did not indicate the formation of any crystalline patterns over a 20-week period. These findings would indicate that starch in the blends is not re-crystallizing. This also means that the crystallization behaviour of semi-crystalline polymers (HDPEMA and EMAs) are not affected by the presence of an amorphous component such as starch.

observed variation of crystallinity The of starch/polyethylene blends with ageing is mainly due to the variation in the crystallinity of the synthetic polymer. The decrease in crystallinity is not consistent with our tensile test results; the tensile strengths increased continuously over the first 5 weeks. The disagreement may be explained by the fact that macroscopic properties such as tensile strength are relatively insensitive to small changes in the crystallinity of the blends. The increase in crystallinity might be due to heat treatment of the samples at 50 °C. The initial decrease in the crystallinity is attributed to chemical changes in polyethylene. This interpretation of decrease in crystallinity is consistent with the Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) studies on HDPE by Pages et al. [11]. These authors have found a decrease in crystallinity due to formation of bulky groups, which leads to an increase of the amorphous content. They have also found a drastic reduction in impact strength (related to stiffness of the chains due to bulky groups) and invariance of tensile properties due to a decrease in the crystallinity of HDPE. Hence, the observed variations in crystallinity with ageing might be due to a combination of chemical changes as well as the annealing effects encountered in the oven.

The crystalline behaviour of EVAMA and EMA blends can also be used to explain the results from the water absorption studies reported in Ramkumar *et al.* [6]. Results indicated that the starch/EVAMA blends absorbed more water and showed mould growth than did starch/EMA blends studied over the same period. This finding can be correlated to the crystalline morphology of the blends with polyethylenes. In starch/EMA blends, the partial crystalline order of chains is hindering the access to water and microbes. Also, the higher tensile strengths achieved with starch/EMA can also be attributed to its crystalline structure.

4. Conclusions

The crystallization behaviour of starch blends showed that starch is in an amorphous state and does not recrystallize during storage. The observed variations of crystallinity of polyethylene/starch blends with time is primarily due to the variation in the crystallinity of the synthetic polymer. The variation of crystallinity of polyethylenes with time of ageing in their blends with starch are not affected by the presence of the amorphous component in starch. The variations of crystallinity with ageing time are attributed to the chemical changes and annealing effects. EVAMA-28 and EVAMA-18 and their blends with starch are in an amorphous state during ageing and do not crystallize. Blends of EVAMA-18 have property variations similar to those of polyethylenes.

Tensile strength of both oven-aged and freezer-aged samples increased during the first 5 weeks of storage and then remained relatively constant. Flexural strengths are not much effected by ageing in either oven or freezer-aged samples. However, the tensile and flexural strengths are slightly higher for annealed samples than for freezer-aged samples. However, no effect of ageing temperature was found on the tensile strengths of EVAMA-28. The flexural strengths of weldline HDPEMA blend samples were improved more by ageing in the freezer than in the oven. There is a reduction in the elongations of the blends due to ageing in an oven for all semi-crystalline blends. Elongation of EVAMA-18 blends is reduced by 32% due to annealing whereas that of EVAMA-28 is increased by 39% due to low-temperature ageing.

The time required for the stress to relax became longer for the blends because of ageing. Freezer-aged samples relaxed slightly faster than did the oven-aged samples. The chemical changes and increased crystallinity in the blends could be the reasons for increased stress relaxation process. EVAMA-28 blends relaxed the most, while blends containing EMA-800 relaxed the least. Starch/synthetic polymer blends have a much higher internal residual stress than their synthetic counterparts.

It can be concluded from this study that low temperatures are favourable for storing the EVAMA blends (elongations are important for these blends) and annealing helps polyethylene blends (strengths are important for these blends).

Acknowledgements

The authors would like to acknowledge the financial support of the US Department of Energy (Contract

#DE-FG02-96ER 12185) and the Minnesota Corn Research and Promotion Council.

References

- 1. A. I. ISAYEV and D. L. CROUTHAMEL, Polym. Plast. Technol. Eng. 22 (1984) 177.
- 2. U. R. VAIDYA and M. BHATTACHARYA, J. Appl. Polym. Sci. 52 (1994) 617.
- U. R. VAIDYA, M. BHATTACHARYA and D. ZHANG, Polymer 36 (1995) 1179.
- 4. M. BHATTACHARYA, U. R. VAIDYA, D. ZHANG and R. NARAYAN, J. Appl. Polym. Sci. 57 (1995) 539.
- K. SEETHAMRAJU, M. BHATTACHARYA, U. R. VAIDYA and R.G. FULCHER, *Rheologica Acta* 33 (1994) 553.
- D. H. S. RAMKUMAR, M. BHATTACHARYA, U. R. VAIDYA, M. HAKKAINEN, A. C. ALBERTSSON and S. KARLSSON, *Eur. Polymer J.* 32 (1996) 999.
- 7. D. H. S. RAMKUMAR, M. BHATTACHARYA and U. R. VAIDYA, *ibid.*, accepted.
- 8. J. KUBAT, M. RIGDAHL and R. SELDEN, J. Appl. Polym. Sci. 20 (1976) 2799.
- 9. J. KUBAT and M. RIGDAHL, Int. J. Polym. Mater. 3 (1975) 287.
- 10. I.O. SALYER and A. S. KENYON, *J. Polym. Sci. A-1* **9** (1971) 3083.
- 11. P. PAGES, F. CARRASCO, J. SAURINA and X.J. COLOM, *Appl. Polym. Sci.* **60** (1996) 153.

Received 8 July and accepted 23 October 1996