Mechanical Properties of Grafted Casein Films

N. SOMANATHAN,* V. ARUMUGAM, R. SANJEEVI, and V. NARASIMHAN, *Bio-physics Laboratory, Central Leather Research Institute, Adyar, Madras 600 020, India*

Synopsis

Casein was grafted with mixtures of acrylonitrile (AN) and *n*-butyl methacrylate (*n*-BMA). The mole ratios of AN : *n*-BMA were 0.9 : 0.1 and 0.8 : 0.2. The mechanical properties of the grafted casein films were studied under uniaxial and biaxial stress conditions. A reduction in longitudinal stress and elongation at break was observed with the simultaneous application of lateral stress. Scanning electron micrographs of the stretched films (uniaxial and biaxial stress) are also presented.

INTRODUCTION

Grafted casein films have a number of applications in the surface coating industry. Grafting should be done with suitable monomer without affecting the overall properties of backbone chain of the polymer. Casein films are grafted with different monomers mainly to improve surface characteristics.

The properties of a polymer, like those of any other substance, depend on its chemical constitution, which determines the flexibility of macromolecular chains. The mechanical properties of polymers depend on a number of so-called structural modifications, orientations of macromolecules and super molecular structures, the size of the latter, compounding, plasticization, etc. In addition, mechanical properties depend on the crosslink density of a polymer.

Mechanical behavior of the finish films is studied to understand the stress response of a system to the applied strain. Since these films have a specific end use, the strain–stress relationship has to be studied. Films which give high stress with low strain and films which give high strain with low stress may not be useful for practical applications.

In the present investigation, grafting of acrylonitrile and *n*-butyl methacrylate onto casein was undertaken with a view to improve the fastness properties and to optimize the conditions for preparation.

Casein and grafted-casein find much use as a protective film in leather finishing. Mechanical properties such as tensile strength, elongation, etc. of these films are normally studied only uniaxially (i.e., in the longitudinal direction only) to assess their suitability in leather finishing. However, in actual application one finds that these films undergo stresses in more than one direction thus warranting a study of the mechanical properties in lateral direction too. Hence, in the present investigation, both uni- and biaxial stress responses of the casein-grafted films were studied to understand better, how these films would perform under actual application conditions.

Journal of Applied Polymer Science, Vol. 34, 2299–2311 (1987)

CCC 0021-8995/87/062299-13$04.00

EXPERIMENTAL

Preparation of Graft Copolymers

Grafting of casein was done with acrylonitrile (AN) and *n*-butyl methacrylate (*n*-BMA). A detailed description of the grafting procedure adopted is presented in our earlier publication.[1]

In the present work, stock solutions of binary mixtures consisting of 0.9 mole of AN and 0.1 of *n*-BMA in one case (system I) and 0.8 mole of AN and 0.2 mole of *n*-BMA in the second case (system II) were prepared. For grafting purposes, the concentrations of the binary mixtures used were 0.4, 0.8, 1.2, and 1.6 M, respectively, in both cases.

Parameters like grafting efficiency and percentage grafting were determined from precipitation studies using 10% acetic acid. The precipitates were extracted with dimethyl formamide which was the solvent for ungrafted copolymer.

The films were, however, cast from the grafted polymeric material *without* removing the ungrafted homopolymer. These films were used for studying mechanical properties.

Preparation and Testing of Films

Films were cast from a solution of the graft copolymer over mercury surface. The concentration of the copolymer corresponded to 15% solid content on drying. The films were cast at 65% relative humidity (RH). The film thus obtained was removed from the mercury bed, dried in vacuum and conditioned for 7 days at a temperature of 25 $\pm$ 2°C and 65 $\pm$ 2% RH in a desiccator.

Dumb-bell-shaped specimens were cut as per ASTM standards.[2] Thickness of the specimens were measured. The uniaxial stress–strain characteristics of the films in the longitudinal direction were studied using an Instron universal tensile testing machine model 1112.

For biaxial studies, sample of the type shown in Figure 1 was used. A load was suspended in the lateral direction (i.e., perpendicular to longitudinal axis) and the stress–strain characteristics in the longitudinal axis were studied. The stress in the lateral direction was varied from 2.5 to 45 kg cm^{-2}. The creep studies for the lateral load applied were, however, not worked out in this investigation.

The specimens were prepared as follows for morphological studies using scanning electron microscope (SEM). In the case of uniaxial studies, samples were subjected to a predetermined stress (a stress very close to but less than breaking stress) arrived at through previous experiments, for 24 h. The

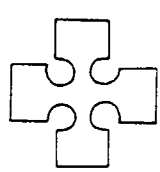

Fig. 1. Figure showing shape of the biaxial test sample.

specimens were relaxed for a further 24-h period, and then taken up for SEM studies. In the case of biaxial studies, in addition to the longitudinal stress, a lateral stress of 5 kg cm^{-2} was applied and a similar procedure followed. This lateral stress was arrived at by experimentation (see Results and Discussion).

Samples were cut and mounted on the aluminium stubs with silver dag. The samples were then coated with gold and were scanned at 10 kV with a filament current of 2.5 amps using Stereoscan S-150 scanning electron microscope.

RESULTS AND DISCUSSION

The kinetics of grafting and characterization of graft copolymers have been studied extensively in recent years by several workers.[3-9] However, the study of kinetics of graft copolymerization in heterogeneous conditions is of recent origin.

Table I presents the effect of variation of monomer concentrations on the kinetic parameters, *viz.* percent grafting and grafting efficiency. The increase in percent grafting with increase in concentration is linear in system I, while there is no appreciable change in percent grafting with increased monomer concentration in system II (Fig. 2). It is very likely that the large pendant group of *n*-BMA is responsible for the decrease in the rate of diffusion to the grafting site as a whole. The grafting efficiency increases initially with monomer concentration, but drops and levels off in system I (Fig. 2). There is an initial decrease in grafting efficiency which levels off at higher monomer concentrations in system II (Fig. 2).

In actual leather finishing applications, the graft copolymers are normally used without separating the ungrafted homo- (and possibly co-) polymers. Therefore, in this study, the material used for the preparation of films is the grafter copolymer, which also contains the ungrafted polymers.

Due to the difference in percent grafting in the two systems, in system I there will be more graft copolymer, while in system II a larger amount of ungrafted polymers will be present.

TABLE I

Casein = 2.5 g/50 mL $K_2S_2O_8$ = 9.7 × 10^{-3} M

Temperature = 60°C Total volume = 50 mL

Time = 3 h

S. no.	Compn. of AN : *n*-BMA (mole fracn.)	AN + *n*-BMA concn. moles l^{-1}	Percent grafting	Percent grafting efficiency
1.		0.4	4.59	28.13
2.	0.9 : 0.1	0.8	30.62	78.92
3.		1.2	47.27	55.47
4.		1.6	75.67	56.30
5.		0.4	8.09	67.72
6.	0.8 : 0.2	0.8	11.09	24.60
7.		1.2	15.10	30.01
8.		1.6	9.81	28.39

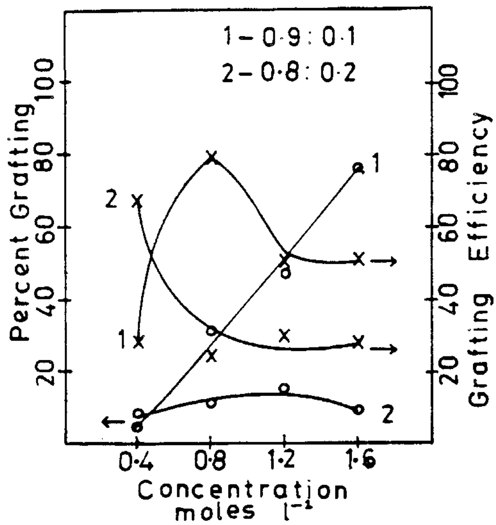

Fig. 2. Effect of monomer concentration on percent grafting and grafting efficiency. 1 = 0.9 : 0.1; 2 = 0.8 : 0.2.

The uniaxial stress–strain characteristics were studied by varying the concentration of monomer mixtures (0.4, 0.8, 1.2, and 1.6 M). The results are shown in Figure 3 for the two systems. The amount of casein was kept constant in all these systems. It is seen that the tensile strength increases with increasing concentrations of the monomer mixture, whereas elongation at break decreases.

The effect of grafting on mechanical properties may be one of increasing stress (and of a reduction in elongation at break) due to possible cross links. The effect of ungrafted polymers on these properties will be similar to that of a loading material. That is, when a material is loaded the stress increases and

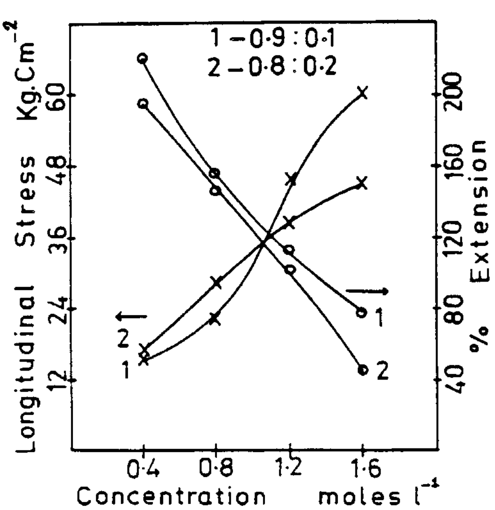

Fig. 3. Effect of monomer concentration on longitudinal stress and percent extension, at break. 1 = 0.9 : 0.1; 2 = 0.8 : 0.2.

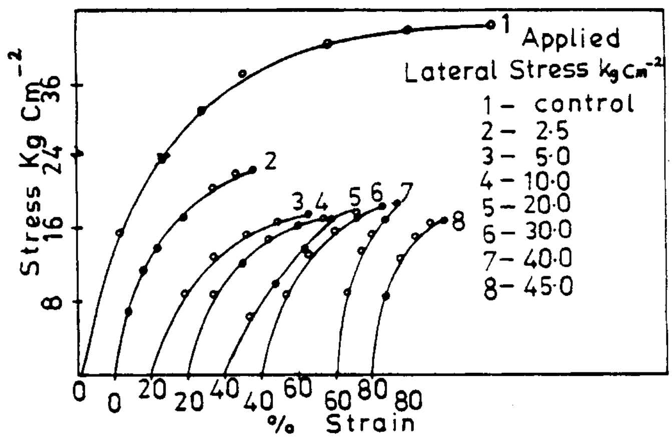

Fig. 4. Stress–strain curves of system I (1.2 M monomer concentration) at different applied lateral stress (kg cm^{-2}). 1 = control; 2 = 2.5; 3 = 5.0; 4 = 10.0; 5 = 20.0; 6 = 30.0; 7 = 40.0; 8 = 45.0.

elongation at break decreases. While in system I, we have more of grafted material (and less of ungrafted), as the amount of monomer increases, in system II we find that the amount of ungrafted material increases with increase of monomer concentration. However, with the composite nature of the material given, it is very difficult to predict in a quantitative way, which of these effects will predominate. From the results (Figs. 2 and 3) however, we have reason to believe that the effect of both grafted and ungrafted polymers have significant roles to play.

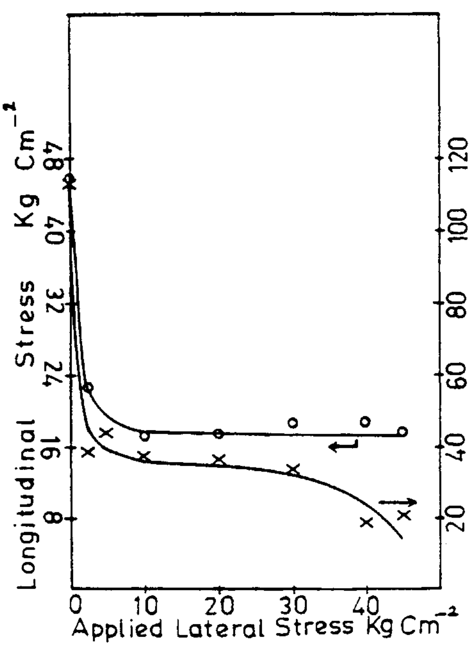

Fig. 5. Effect of applied lateral stress on longitudinal stress and percent extension, at break, of system I (1.2 M monomer concentration).

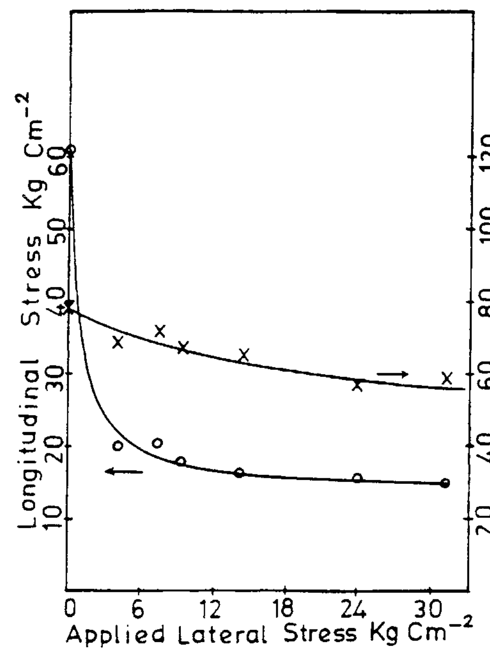

Fig. 6. Effect of applied lateral stress on longitudinal stress and percent extension, at break, of system I (1.6 M monomer concentration).

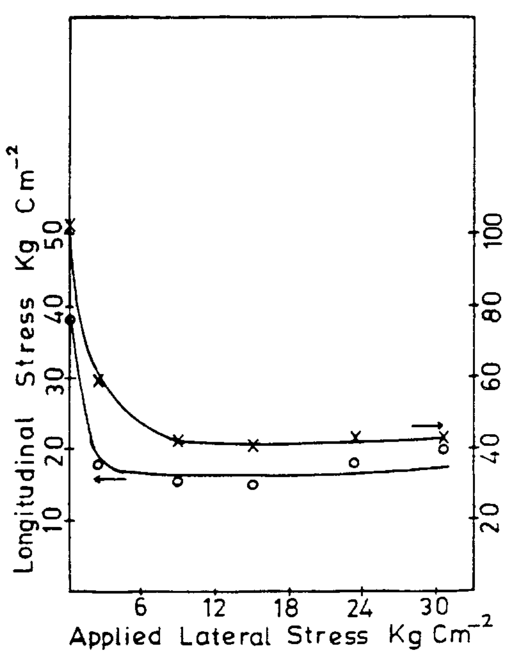

Fig. 7. Effect of applied lateral stress on longitudinal stress and percent extension, at break, of system II (1.2 M monomer concentration).

The films were then viewed in SEM and the films showed orientation toward the stress axis. The films were found to contract perpendicular to the direction of stretch.

The biaxial stress–strain characteristics under various applied stress levels of the films prepared with monomer concentration of 1.2 and 1.6 M of system I and 1.2 M of system II alone were studied, since the kinetic parameters for these were higher compared to those of others. The stress–strain characteristics for system I (1.2 M) are presented in Figure 4. Similar curves were obtained for the other two cases also. The relationship of the tensile strength and elongation at break to the applied lateral stress is presented in Figures 5–7, respectively, for all the three cases mentioned above.

The stress–strain characteristics along the longitudinal direction when a lateral stress is applied are presented in Figure 4. This stress in the lateral direction is varied from 2.5 to 45 kg cm^{-2}. It is clearly seen that the strain in the longitudinal direction is very much affected by the lateral stress. The longitudinal stress at break initially shows a steep decrease and shows practically no change beyond a lateral applied stress of 5 kg cm^{-2} (Fig. 5). The results obtained for other concentrations are similar (Figs. 6 and 7).

Effect of Lateral Stress

The lateral stress is applied instantaneously while the longitudinal stress is applied at the strain rate of 0.5 cm/min.

It is seen from Figure 8 that the applied lateral stress helps to break at lower longitudinal stresses. When the load is zero on the lateral direction, the longitudinal stress is maximum, registering a value of 45.63 kg cm^{-2} and is indicated as "AB" in Figure 8. There is a marked decrease in the longitudinal stress at break for even small values of lateral stress applied. Any further increase in the lateral stress has only a marginal effect in further reducing the longitudinal stress at break.

Orientation of the Polymer Film at the Arms

It is expected, that when uniaxial stress is applied in the longitudinal direction (Y axis) only, the material wil have an orientation[10] as shown in

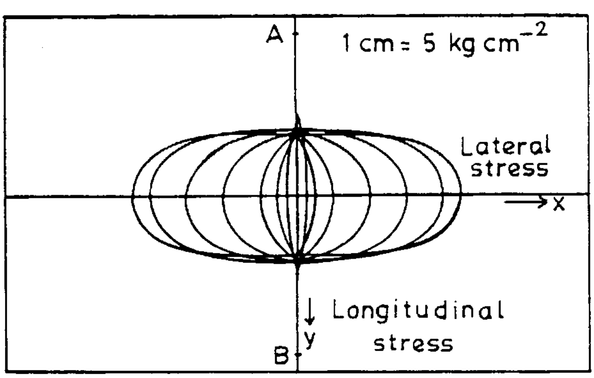

Fig. 8. Effect of longitudinal stress on applied lateral stress of system I (1.2 M monomer concn.).

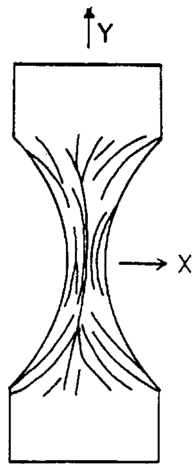

Fig. 9. Figure showing the orientation of streaks in an uniaxial test sample.

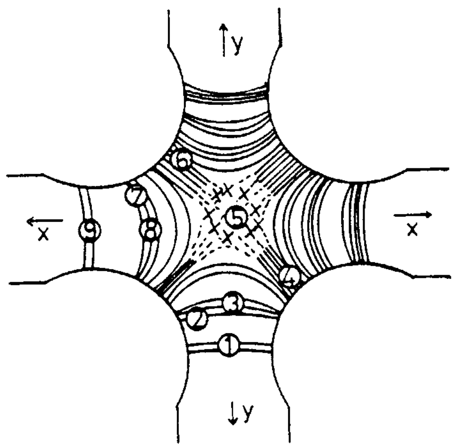

Fig. 10. Mapping of orientation of streaks in a biaxially stretched sample.

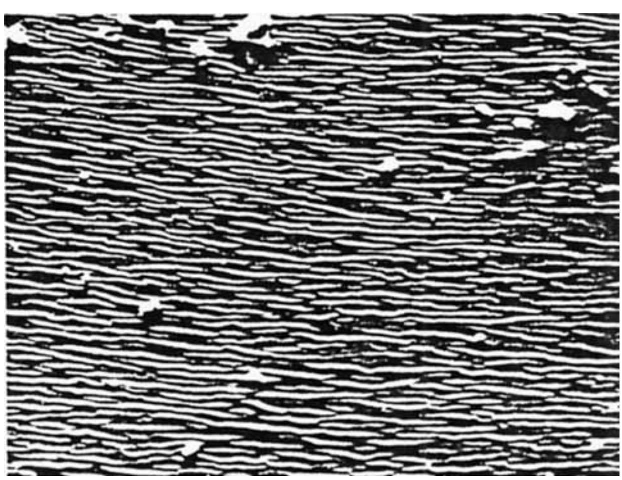

Fig. 11. Figures 11–19 correspond to the locations marked 1 to 9 on Fig. 10.

Figure 9. In the arms region of the sample, the orientation is more or less parallel to the Y axis.

In a biaxial stress, when lateral stress is applied in addition to longitudinal stress, the break occurs at a lower applied longitudinal stress compared to the value when lateral stress is zero. This reduction in longitudinal stress is marked, even when the lateral stress applied is minimum possible under the experimental conditions. The elongation at break is also much lower compared to the value for uniaxial longitudinal stress. Thus, the lateral stress applied effects a reduction in longitudinal stress as well as elongation at break. This, in turn, can be expected to affect the orientation of the material in the Y direction.

A difference is expected in the orientation of the material as compared with the one under unidirectional stress conditions depicted in Figure 9.

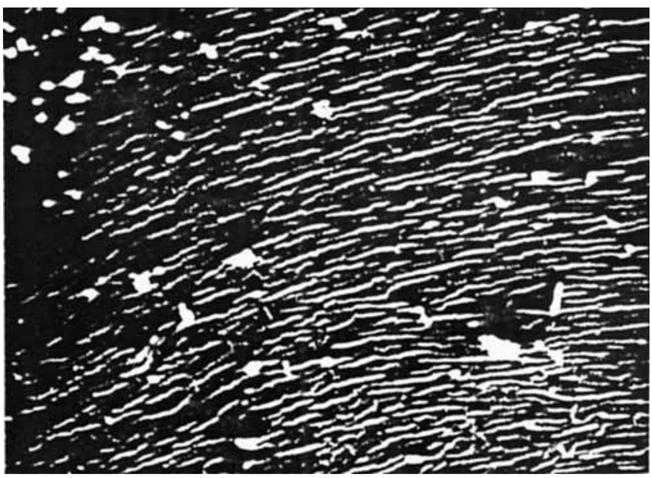

Fig. 12.

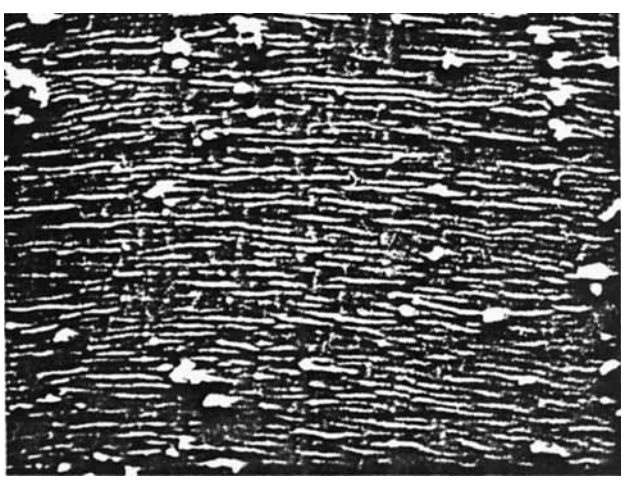

Fig. 13.

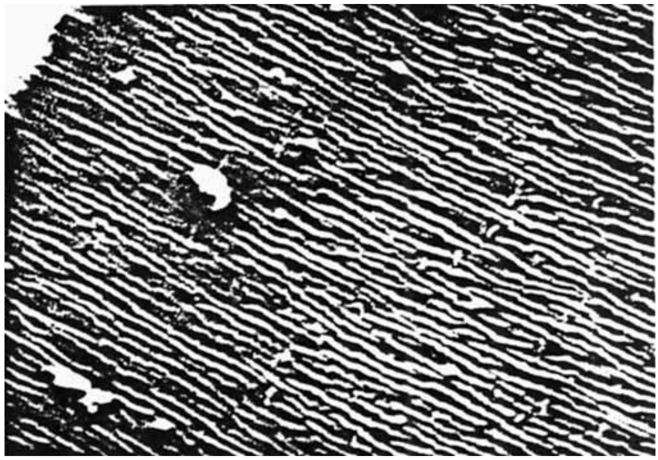

Fig. 14.

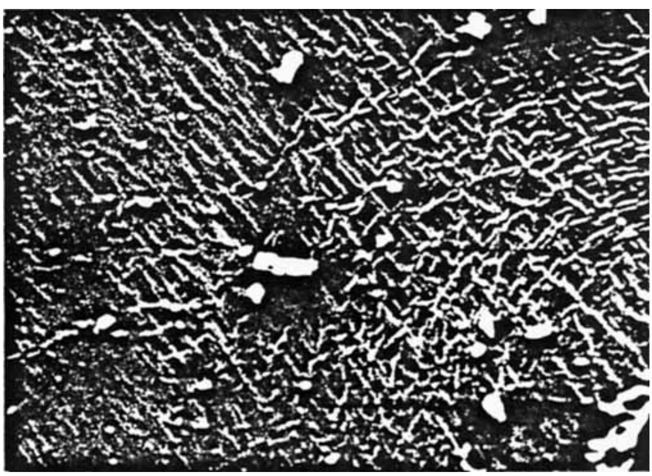

Fig. 15.

The scanning electron micrographs were taken at different regions of this specimen under biaxial stress conditions and a mapping was done (Fig. 10). It is seen that in the arms region, the orientation is certainly less perfect compared to the one seen under unidirectional stress conditions. Micrographs are also provided for different regions of the specimen (Figs. 11–19).

Orientation at the Central Portion

When longitudinal stress alone is applied along the Y axis, the streaks are normally found to be oriented in a direction almost perpendicular to the applied stress.[10] A stretch in the Y direction and a contraction in the X direction are observed. A similar effect may be expected, while applying a lateral force in the X axis, where a stretch in the X direction and contraction

Fig. 16.

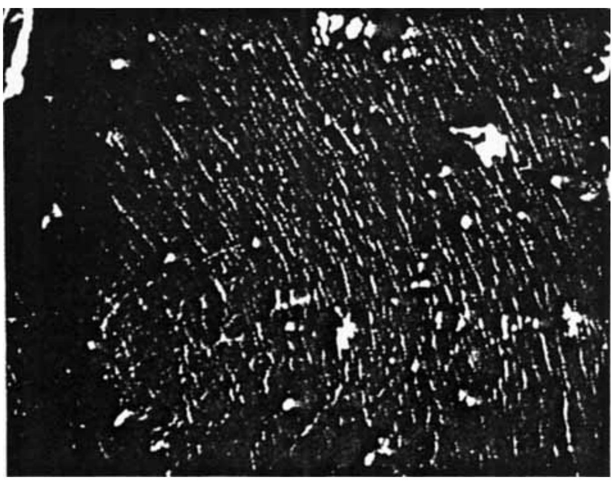

Fig. 17.

in the Y direction will be seen. Thus, when the longitudinal and lateral stresses are applied simultaneously, the net effect on the orientation of these streaks is expected to produce a checked square pattern, with the sides of the square parallel to the X and Y axes. If the two applied forces are unequal, the sides of the squares formed may be at an angle to the X and Y axes.

In our SEM studies of the films subjected to biaxial stress, the streaks form a square pattern with the sides of the squares at an angle to the X and Y axes, suggesting the validity of the expected pattern described earlier (Fig. 15).

CONCLUSIONS

Casein was grafted with mixtures of AN and *n*-BMA monomers with different mole ratios of AN : *n*-BMA. The mechanical properties were studied

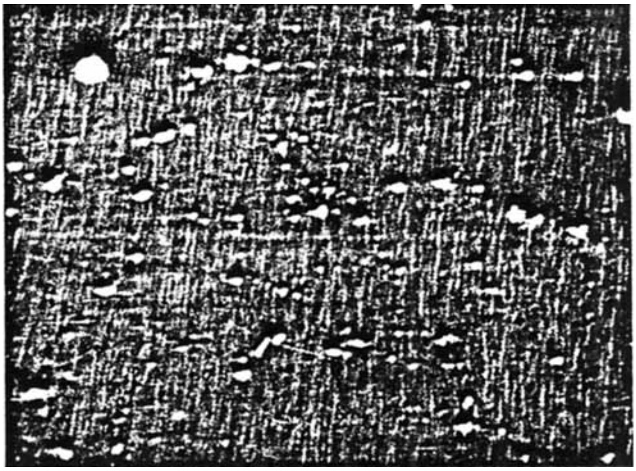

Fig. 18.

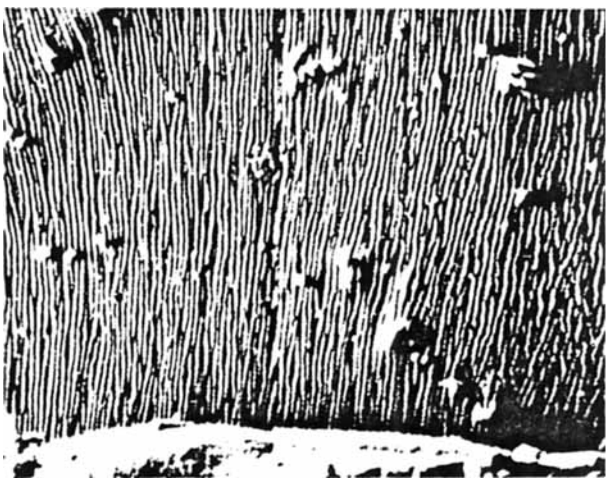

Fig. 19.

under uniaxial and biaxial stress conditions. The morphology of the films were also studied using SEM.

There is a marked decrease in the longitudinal stress at break for minimum values of lateral stress applied. Any further increase in the lateral stress has only a marginal effect in further reducing the longitudinal stress at break.

The orientation of the films under biaxial stress conditions show checked square patterns in the central portion of the specimen as is to be expected due to the simultaneous contribution of forces in perpendicular directions.

The authors are thankful to the Director, Central Leather Research Institute for his permission to publish this paper.

References

1. N. Somanathan, C. Rami Reddy, N. Radhakrishnan, and R. Sanjeevi, *Eur. Polym. J.* (in press).

2. Method of tensile testing: D-1708, Part 27, Book of ASTM Stds.; American Society for Testing of Materials, Philadelphia (1965).

3. K. Panduranga Rao, K. Thomas Joseph, and Y. Nayudamma, *J. Polym. Sci.*, A-1, **9**, 3199 (1971).

4. G. M. Barner and D. J. Termini, *J. Appl. Polym. Sci.*, **17**, 2557 (1973).

5. A. Joseph, G. Radhakrishnan, T. Nagabushanam, and K. Thomas Joseph, *J. Macromol. Sci. Chem.*, **A-15**, 515 (1981).

6. N. Gaylord, *J. Polym. Sci.*, *Poly. Symp.*, **C-37**, 153 (1972).

7. A. A. Kantouch, A. Hebeesh, and A. Bendak, *Eur. Polym. J.*, **7**, 153 (1971).

8. S. Amudeswari, C. Rami Reddy, and K. Thomas Joseph, *Eur. Polym. J.*, **20**, 91 (1984).

9. K. Kaleem, C. Rami Reddy, and S. Rajadurai, *J. Appl. Polym. Sci.*, **26**, 2305 (1981).

10. G. M. Bartener and Yu. S. Zuyev, Eds., *Strength and failure of visco-elastic materials*, Pergamon Press, New York, 1968, Chap. 3.

Received July 7, 1986
Accepted March 4, 1987