Effect of Extension Rate on the Stress–Strain Characteristics of Grafted Casein Film

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Synopsis

Casein was grafted with a binary mixture of acrylonitrile and *n*-butyl methacrylate. The mechanical properties of the grafted casein films were studied at various extension rates. The fractured surfaces were analyzed using scanning electron microscopy. With the increase in extension rate, the strain at yield increases to a maximum value and then decreases to a limiting value. The stress at yield and the energy at break steadily increase with the increase in the rate of extension.

INTRODUCTION

Casein is widely used as a surface-coating material. It has very good machinable and glazable properties. But it has a very high susceptibility to attack by microorganisms, poor wet rub fastness, and low stretchability. These properties make it impossible for it to be used without modification. Grafting of casein with suitable monomers is done mainly to improve its resistance to both microorganisms and wet rub. Grafted casein is generally used for coating leather surfaces that are to be friction glazed. During normal usage, the film along with the leather is subjected to different rates of stretching, which affects its properties—the mechanical properties in particular.

Mechanical properties are those that determine the response of the bodies to the external mechanical forces. Environmental conditions of testing, such as temperature and rate of stretching greatly influence the mechanical properties of the coatings. A study was undertaken to investigate the influence of the rate of straining on the stress–strain characteristics of grated casein films.

Much work has been done on the effect of straining rate on the mechanical properties of materials.[1–8] The effect of strain rate on the static modulus of polyethylene was studied by Strella and Newmann[1] and on polypropylene by Hall.[2] Variation of loading rates was also found to affect the viscoelastic properties of rubber[3] and it was found that an increase in the speed of testing correlated to a decrease in temperature.[4] Amborski and Mecca[5] have reported the effect of strain rate on the tensile properties for such materials as polyethylene, amorphous polyethylene terephthalate, mylar plastics, suran-coated cellophane, polystyrene, etc. They have also reported the critical strain

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rates for the above-mentioned polymeric materials. Effect of extension rate on tensile tests of different types of vulcanized rubbers at two different temperatures were studied by Greensmith.[7] The effect of strain rate on the mode of tensile fracture of elastoidin fibers in dry and wet conditions was reported by Arumugam and Sanjeevi.[8]

EXPERIMENTAL

Grafting of casein was done[9] with a binary mixture of acrylonitrile (AN) and *n*-butyl methacrylate (*n*-BMA) (mole ratio 8:2) at 60°C for 3 h with potassium persulfate (9.7×10^{-3} mol/L) as the initiator. The concentration of the binary mixture used was 1 mol/L. Acrylonitrile-grafted casein forms a relatively hard and tough polymer, but the extension of the film is lessened. Therefore, *n*-BMA was chosen as a second monomer in grafting casein with acrylonitrile.

Films were cast from the solution of the graft copolymer over mercury surface. The concentration of the graft copolymer corresponded to 15% solid content on drying. Dumbbell-shaped specimens were cut as per ASTM standards[10] (length of the specimen = 22.25 mm). Specimen thickness was measured using a thickness gauge (Mitutoyo Manufacturing Co. Ltd., Japan) having a sensitivity of the order of 0.0001 inch (0.000254 cm). The thickness of the samples used in the experiment was $\simeq 0.01$ cm.

Stress–strain measurements were made using an Instron Universal tensile tester (Model 1112). Tests were performed at various extension rates. The effect of extension rate on the mechanical properties of pure casein films could not be studied, because of the very low stretchability and high tensile strength[9] mentioned earlier. The tensile strength and the percent strain were calculated using the following expressions:

$$\text{Tensile strength} = \frac{\text{breaking load (kg)}}{\text{cross-sectional area (cm}^2\text{)}}$$

$$\text{Percent strain} = \frac{\text{increase in length of the sample}}{\text{original length of the sample}} \times 100$$

The morphological characteristics of the fractured films were studied with scanning electron microscopy. First, the samples were removed from the jaws of the Instron tester after break and were fixed to aluminium stubs with electrodag so that the broken edge could be scanned. This was followed by sputter coating with gold to improve the conductivity of the material. The coated samples were scanned at an operating voltage of 10 kV, in a Cambridge stereoscan S-150 scanning electron microscope (SEM). Several samples were scanned to identify the representative characteristics of fractured surface before recording them.

RESULTS AND DISCUSSION

The stress-strain characteristics of the grafted casein films at various extension rates are given in Figure 1. At all strain rates, there is a well pronounced yield point beyond which the stress decreases with increasing strain. Energy values at yield point and at break were calculated from

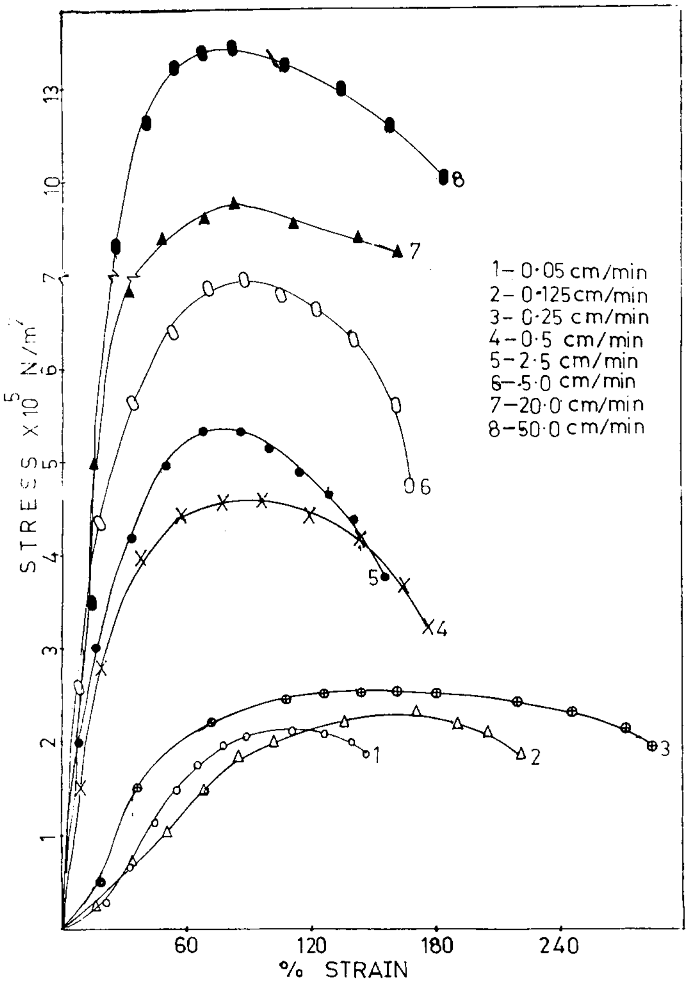


Fig. 1. Stress–strain characteristics of casein-g-AN-*n*-BMA films at various extension rates.

stress-strain curves (Table I). The initial modulus increases with the increase in extension rate, as can be seen from Figure 1.

The influence of extension rate on the ratio of the stress–strain, as well as energy at break to those at yield, is presented in Figure 2. The ratio decreases in all cases with the increase in extension rate. The effect of extension rate on stress at break and at yield is given in Figure 3 and that on the strain is given in Figure 4.

From Figure 4 it is seen that with increased extension rate, the strain at yield point increases, attains a maximum, and then decreases to a limiting value, whereas the strain at break increases initially and then decreases. Stress at yield steadily increases with increased extension rate. At lower extension rates, there is very little difference between the stress at yield point and at break, whereas at very high speeds they show large deviation.

The stress–strain graphs indicate a general trend of load rise followed by a fall before breaking. But this phenomenon is more pronounced at higher extension rates, which corresponds to necking rupture. At higher extension

TABLE I
Energy Values Calculated from Stress-Strain Graphs

Extension rate cm/min	Energy at break ($\times 10^7$ ergs)	Energy at yield ($\times 10^7$ ergs)
0.05	3.32	2.18
0.125	5.65	4.08
0.250	9.48	5.61
0.50	10.88	5.59
2.50	10.73	5.63
5.00	15.55	7.32
20.00	20.55	8.97
50.00	32.73	12.76

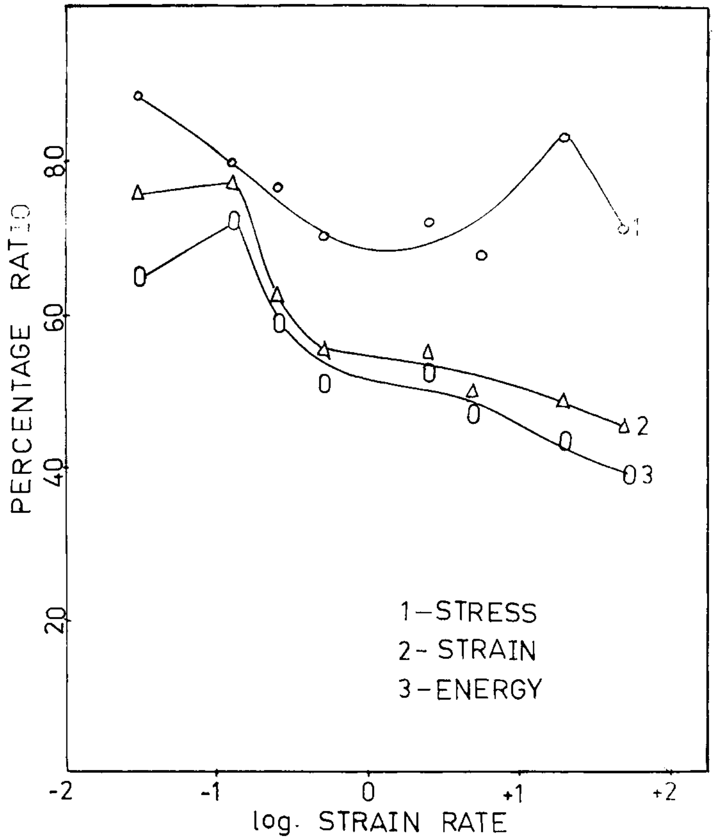


Fig. 2. Effect of extension rate on (1) the ratio of breaking stress to yield stress; (2) the ratio of yield strain to breaking strain; and (3) the ratio of energy at yield to energy at break.

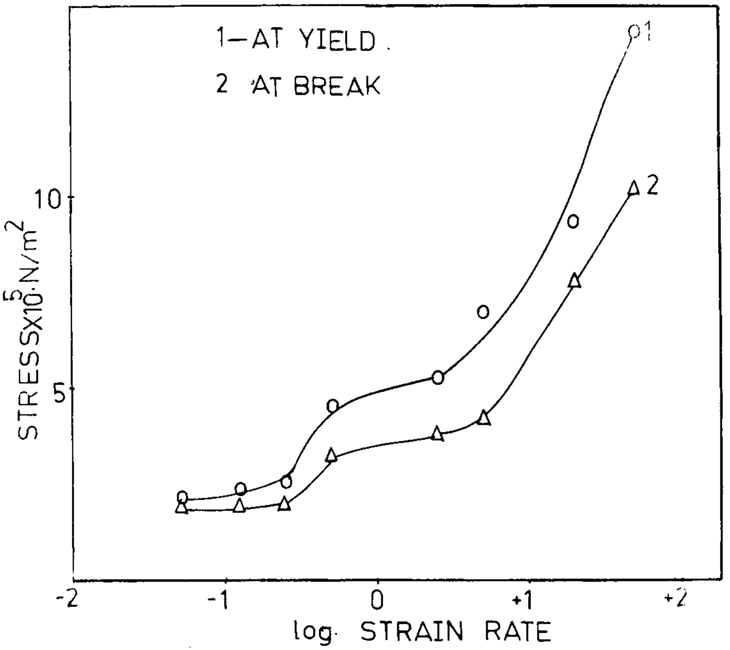


Fig. 3. Effect of extension rate on stress (1) at yield, (2) at break.

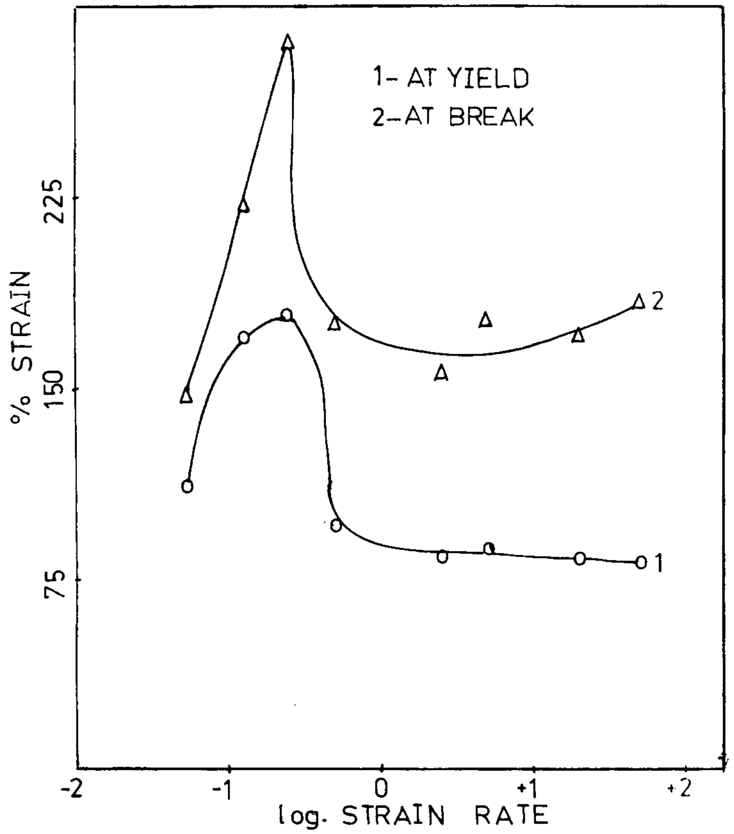
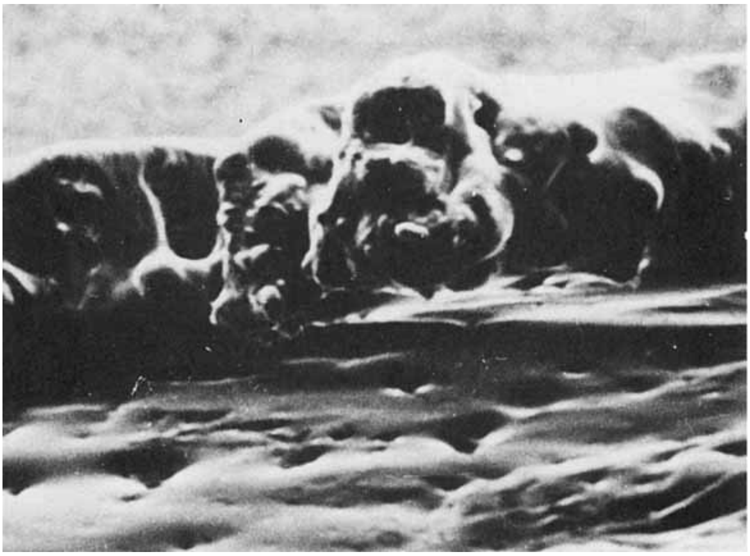


Fig. 4. Effect of extension rate on strain (1) at yield, (2) at break.



(a)

(b)

Fig. 5. Morphology of fractured edges, fractured at (a) 20 cm/min, (b) 0.5 cm/min extension rates (500 ×).

rates, there is little time for the restabilization of the neck.[4] Thus, when the rate of stretching is increased, the stress and initial modulus increase, whereas the total strain decreases.

Gruntfest[11] states that high-speed extensions are adiabatic rather than isothermal. The temperature rise tends to prevent cold drawing and favors necking rupture.[12] It has also been reported that higher temperature rises correspond to higher yield stresses, where the conversion of inelastic work to heat probably causes a localized temperature rise.[4]

In the present study, higher yield stresses were recorded for samples tested at higher extension rates, resulting in some kind of thermal softening.[4] This is seen in the scanning electron micrographs of the fractured edges of samples extended at 20 cm/min [Figure 5(a)]. This is in contrast to that at lower extension rate viz. 0.5 cm/min [Figure 5(b)], where there is a predominance of silver streaks. It has been reported,[13] that silver streaks form at places where there is considerable cold elongation and consolidation under prolonged stresses. With the increase of speed of deformation, the sample fails before the silver cracks form and at higher speed of deformation, they do not appear at all. Thus at lower extension rates, where the failure is closer to cold drawing, silver cracks are seen in the sample [Figure 5(b)], whereas at higher speeds which are adiabatic in nature, the effect of thermal softening is more pronounced. It has been reported[14] that on heating plasticization occurs in the polymeric material; however, on cooling some softening structure is formed. The structure seen in Figure 5(a) may be due to the above effect. This may result from van der Waals forces or hydrogen bonding of polymer segments either directly or through the plasticizer, as may occur from entanglement or crystallization of the polymer segments.

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References

1. S. Strella and S. Newmann, *Polymer*, **5**, 107 (1964).
2. I. H. Hall, *J. Appl. Polym. Sci.*, **54**, 505 (1961).
3. F. Bueche, *J. Appl. Phys.*, **26**, 1133 (1955).
4. *Mechanical Properties of Polymers*, Encyclopedia reprints,. N. M. Bikales, Ed., Wiley-Interscience, New York, 1971.
5. L. E. Amborski and T. D. Mecca, *J. Appl. Polym. Sci.*, **4**, 332 (1960).
6. R. E. Ely, *Plastics Tech.*, **3**, 100 (1957).
7. H. W. Greensmith, *J. Appl. Polym. Sci.*, **3**, 175 (1960).
8. V. Arumugam and R. Sanjeevi, *J. Mat. Sci.*, **22**, 8 (1987).
9. N. Somanathan, C. Rami Reddy, N. Radhakrishnan, and R. Sanjeevi, *Eur. Polym. J.*, **23**, (6) 489–492 (1987).
10. *1980 Annual Book of ASTM Stds.* Part 35, D-1708-79, American Society of Testing of Materials, Philadelphia, p. 566.
11. I. J. Gruntfest, *J. Polym. Sci.*, **18**, 449 (1955).
12. P. I. Vincent, *Polymer*, **1**, 7 (1960).
13. *Strength and Failure of Viscoelastic Materials*, G. M. Bartenew and Yu. S. Zuyev, eds., Pergamon Press, New York, 1968.
14. *Encyclopedia of Polymer Science and Technology*, Vol. 10, M. Norbert and Bikales, eds., Wiley-Interscience, New York, 1969.

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