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Fracture behaviour of casein films – II

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Casein was grafted with acrylonitrile and with a binary mixture of acrylonitrile and n-butyl methacrylate. Mechanical properties and the fracture of these films were studied at different temperatures. Due to possible transition, fracture behaviour changed ca. 60 °C in both systems. The effect of the polymer (grafted chains and homopolymer) present in the system affected the morphology and the fracture behaviour of casein films grafted with binary mixtures of the monomer.

1. Introduction

Polymer properties can be altered by chemically modifying the polymer by graft or block copolymerizations. The main and branch chains are usually thermodynamically incompatible, hence, most graft copolymers can be classified as multiphase polymers [1–3] in the solid state. An important characteristic of the two phase graft is the feasibility for blending well with the respective homopolymers.

Vinyl [4, 5], acrylic [6–13] and methacrylic [14–17] monomers were used to graft casein. Acrylonitrile (AN) grafted casein has been studied in detail by many workers [18–24]. Grafting of casein with AN is advantageous when compared to other monomers, as a glazable film is formed [13]. This property is useful when casein is used as a coating material. At higher temperatures AN forms a stable cyclic compound [25]. Therefore, casein grafted with AN is stable even after the glazing process. During the glazing process an instantaneous increase in temperature on the surface of the film occurs.

AN grafted film tends to be brittle at room temperature as the T_g of poly(AN) is between 80 and 100 °C. Properties of AN grafted casein can be changed by using small quantities of other monomers. The choice should take into account the compatibility of the monomer with casein as well as AN, and the glazability of the resulting grafted film.

Despite extensive studies of the chemical aspects of AN grafted casein films, little attention has been given to the analysis of the mechanical behaviour under processing and end use conditions. This paper deals with the tensile fracture behaviour of AN and n-butyl methacrylate (n-BMA) grafted casein films.

Casein was grafted with 2 mol dm^{-3} of AN monomer and the mechanical properties and fracture behaviour were studied at different temperatures. In another experiment casein was grafted with a binary mixture of AN and n-BMA and the properties of grafted casein films were studied at different temperatures.

2. Experimental procedure

Grafting of casein was done with AN (2 mol dm^{-3}) by following the procedure discussed in an earlier publication [26]. Grafting was done at 60 °C for 3 h using potassium persulphate (9.7×10^{-3} mol dm^{-3}) as the initiator.

To graft binary mixtures of AN and n-BMA stock solutions of binary mixtures, consisting of 0.9 mol of AN and 0.1 mol of n-BMA in one case (System A) and 0.8 mol of AN and 0.2 mol of n-BMA in the second case (System B) were prepared. For grafting purposes, the concentrations of the binary mixtures used were 0.4, 0.8, 1.2 and 1.6 M, respectively (A_1, A_2, A_3, A_4 and B_1, B_2, B_3, B_4) in each system. The reaction was performed at 60 °C for 3 h using potassium persulphate as the initiator [26].

2.1. Preparation and testing of films

The films were cast from the grafted polymeric material without removing the ungrafted homopolymer. Films were cast, conditioned and tested at 25 ± 2 °C and 65 ± 2% RH. Dumb-bell shaped specimens were cut as per ASTM standards [27]. The uniaxial stress–strain characteristics of the films were tested by using an Instron universal tensile testing machine model 1112. Mechanical properties of AN grafted casein films (Ca-g-AN) (2 mol dm^{-3}) and casein grafted with a binary mixture (System A_3) were studied at different temperatures by using a specially made cell attached to the tensile testing machine. Details of testing are given in an earlier publication [28].

Surface and cross-sectional morphology of the fractured samples were studied using a Stereoscan S-150 scanning electron microscope, after sputter coating the sample with gold.

3. Results and discussion

Stress–strain characteristics of the grafted casein films tested at different temperatures are presented in Fig. 1. It was found that the stress at break increased, showed a maximum value at 40 °C and then decreased. The reverse trend was seen in the case of strain at break. At lower temperatures the stress at break was low [27]. At 28 °C there was a pronounced yield point and neck

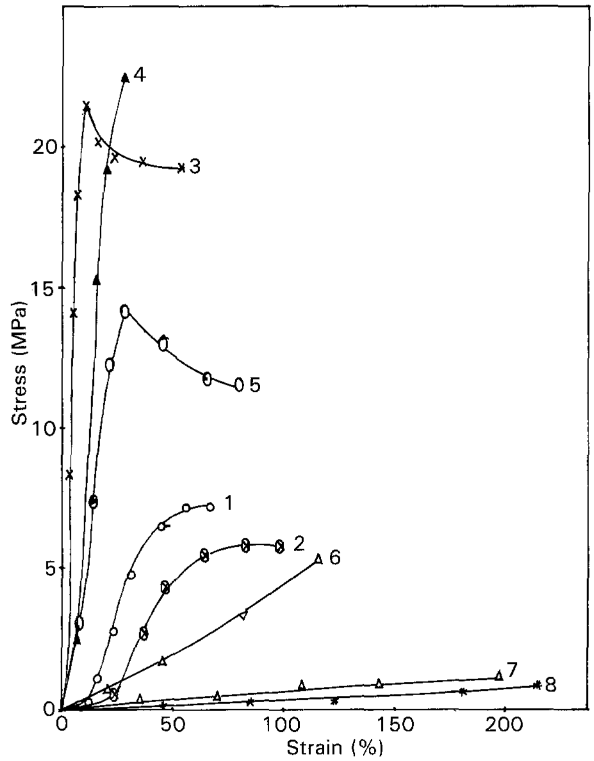


Figure 1 Stress–strain curves of Ca–g-AN at different temperatures (°C).

formation, but the sample broke before restabilization of the neck. The stress–strain curves at 40 °C show that the sample fractured before yield point. The strain at break suddenly increased to 79% at 60 °C, from 28% at 40 °C. Thereafter, the strain continuously increased and the stress decreased with an increase in temperature.

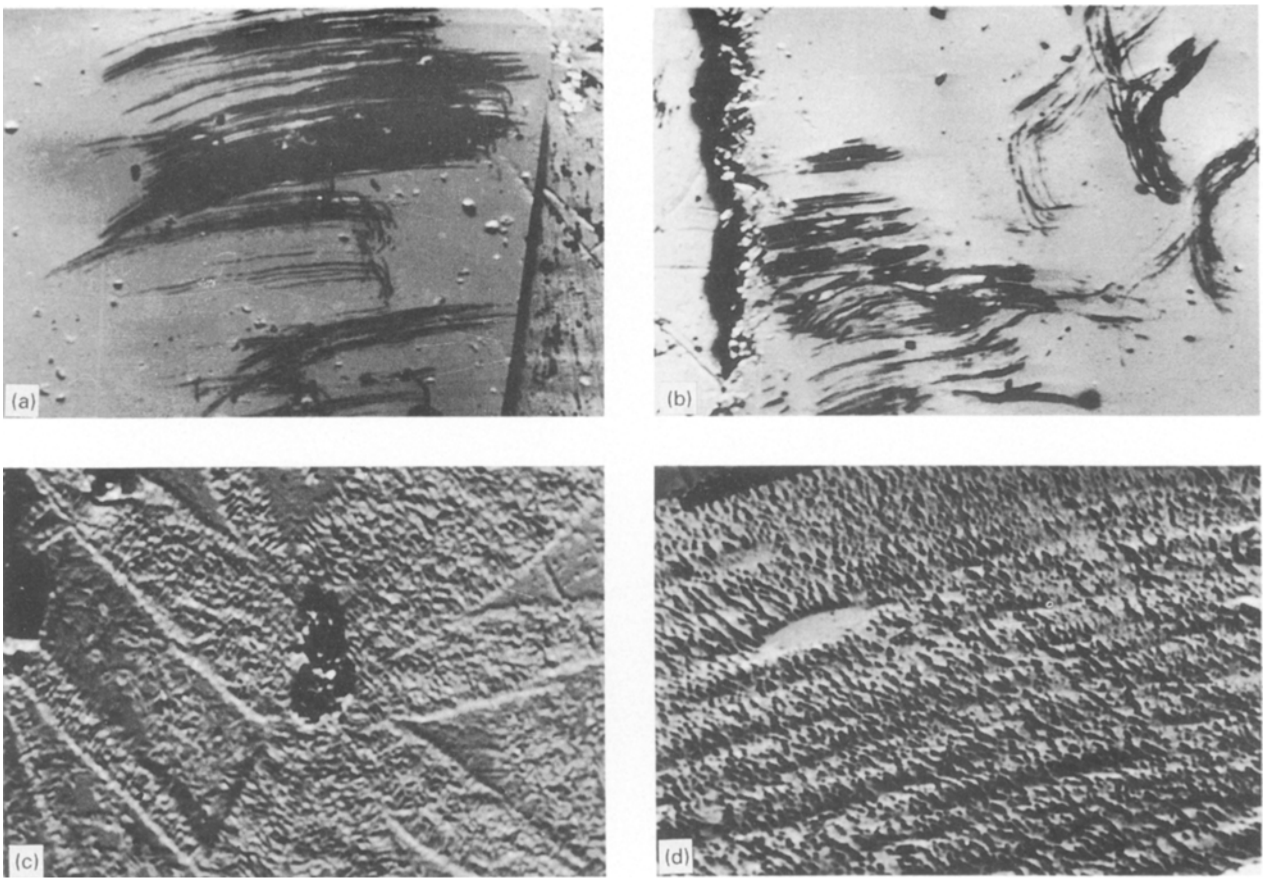
To obtain further insight on the effect of temperature morphological studies were done with the samples fractured at different temperatures. The surface morphology of the sample tested at 28 °C is shown in Fig. 2a. The surface shows a structure similar to multiple crazing lines near the fracture edge [30]. At 40 °C the number of lines increased when compared to the surface at 28 °C. At 28 °C the lines were seen only perpendicular to axis of stress propagation, whereas at 40 °C criss-cross lines were also seen. It has been stated [30] that in many polymers both crazing and localized shear yielding may be observed simultaneously, and that interactions occur between them. Bucknall *et al.* [31] have proposed that such interactions may be important in imparting a high toughness to multiphase system. The surface structure of Ca–g-AN at 40 °C also showed interactions between the two types of lines. The surface structure of the films at 80 °C is shown in Fig. 2c and that at 100 °C in Fig. 2d and e. The surface morphology at higher temperatures shows that the material had flown in the direction of stress application and that microcracks had formed in the material.

Fig. 2c shows that the crack grew from the flaw present in the system and propagated in the material. Due to the anisotropy in the material, the stress taken by different points in the sample were different. Therefore, the sample flowed in the direction of high stress and formed into a star-like pattern, as seen in Fig. 2c. When the temperature was increased (100 °C) the material flowed in the direction of stress and oriented uniformly, as seen in Fig. 2d. Fig. 2e shows the formation of ridge-like structures, which could transmit the energy to produce slits parallel to the direction of draw [32]. Fig. 2d also suggests that there may possibly be more than one microphase in the system and that failure possibly occurs near the interface of the microphases present in the system. Microphase separation in the solid state, of block and graft copolymers, is generally caused by the incompatibility of constituent polymer. Hence the grafted system forms into domains [33] in the case of casein grafted with AN. Stress–strain curves show that the strain increased rapidly beyond 60 °C, suggesting that the material then started flowing due to possible transition.

In the next stage, casein was grafted with the binary mixture of AN and n-BMA and the tensile properties of the films were studied. Stress–strain curves of Systems A and B are shown in Figs 3 and 4, respectively. The percentage of grafting and grafting efficiency of Systems A and B are given in Table I. In general, the stress–strain curves followed the same pattern in both systems. Initially the stress increased with the increase in strain and with the formation of pseudo-yield point, the stress increased further with the increase of strain similar to an effect produced by orientation hardening. The increase in polymer content (grafted or homo) moved the curve towards the stress axis, making the sample more brittle.

Due to the difference in the percentage of grafting in the two systems more graft copolymer would be present in System A than B, while in system B larger amounts of ungrafted polymer would be present. Although in graft polymer the side chain is covalently linked, the properties of the graft copolymer has similarities with polyblends, which are formed by mixing two polymers [2]. The ungrafted copolymer formed during the grafting reaction had the possibility of forming a miscible blend with grafted chain forming into domains. Therefore, the morphology of grafted casein films were studied to get further correlation of the mechanical properties.

The surface morphology of Systems A_1 and A_3 after 10% straining are shown in Fig. 5a and b, respectively. The surface morphology of unstretched film of System B_3 is given in Fig. 6. Since these types of systems contain grafted casein as well as ungrafted copolymer they form matrix-like lamellar structures, seen in the respective figures. The compatibility of the components present in the systems have been found to alter the two components present in the system and the interpenetration of the lamellar structures between the two domains. When the ungrafted polymer formation was less, a uniform homogeneous film was formed, as evident in Fig. 5a. As the content of ungrafted polymer increased (with the increase of monomer concentration) the film showed two mutually interpenetrating networks, one surrounded by the other [34], as seen in Figs 5b and 6. Fig. 6b shows a magnified view of the



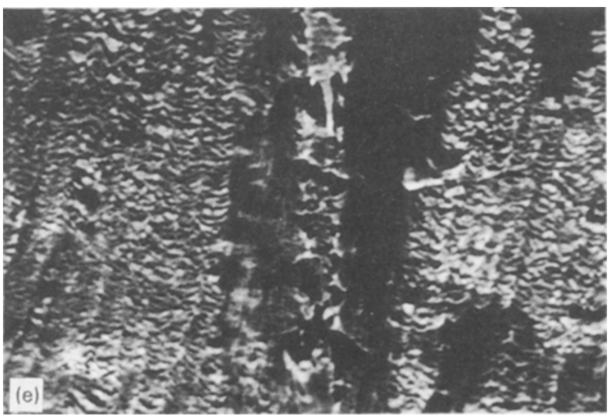


Figure 2 SE micrographs showing the surface morphology of fractured Ca–g-AN film at different temperatures (°C): (a) 28 (60 ×); (b) 40 (60 ×); (c) 80 (150 ×); (d) 100 (150 ×); (e) magnified view of (350 ×).

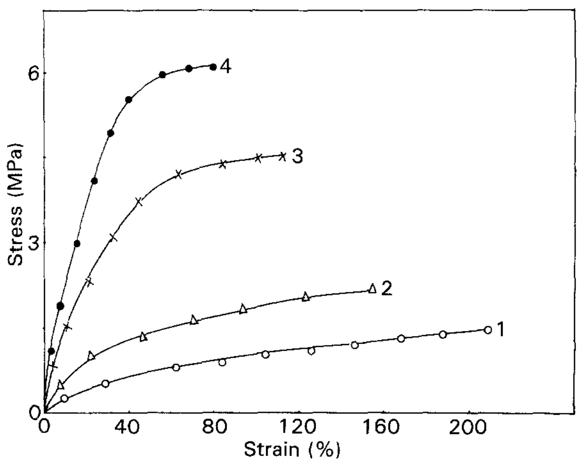


Figure 3 Stress–strain behaviour of System A (0.9:0.1). 1 = 0.4 mol dm^{-3}; 2 = 0.8 mol dm^{-3}; 3 = 1.2 mol dm^{-3}; 4 = 1.6 mol dm^{-3}.

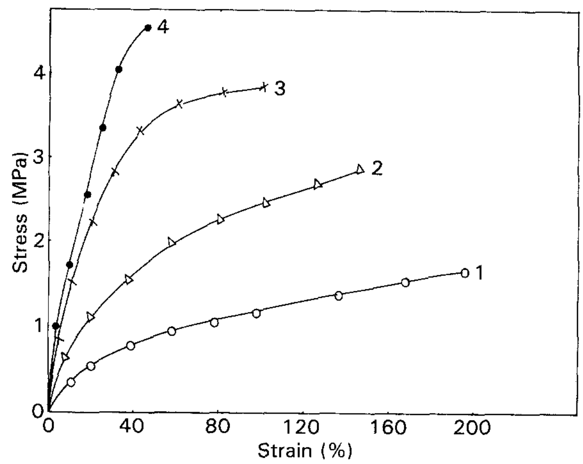


Figure 4 Stress–strain behaviour of System B (0.8:0.2). 1 = 0.4 mol dm^{-3}; 2 = 0.8 mol dm^{-3}; 3 = 1.2 mol dm^{-3}; 4 = 1.6 mol dm^{-3}.

boundary between the two phases and the interpenetration of one with the other. When the grafted film was stretched cracking took place between the interfaces of the two components, with the result that the extension of the films [28] was low compared to that of the films with low ungrafted polymer components.

TABLE I Kinetic parameters of grafted casein with various monomer concentrations. Casein = 2.5 g/50 cm^3; temperature = 60 °C; $K_2S_2O_8 = 9.7 \times 10^{-3}$ mol dm^{-3}; total volume = 50 cm^3; time = 3 h

System	AN:nBMA (mol fraction)	[AN + nBMA] (mol dm^{-3})	Grafting (%)	Grafting efficiency (%)
A_1	0.9:0.1	0.4	4.59	28.13
A_2		0.8	30.62	78.92
A_3		1.2	47.27	55.47
A_4		1.6	75.67	56.30
B_1	0.8:0.2	0.4	8.09	67.72
B_2		0.8	11.09	24.60
B_3		1.2	15.10	30.01
B_4		1.6	9.81	28.39

In Fig. 7 stress–strain curves of System A_3 at different temperatures are given. At 28 °C there was a pseudo-yield point, and beyond that the strain increased with a marginal increase in stress. At other temperatures the behaviour was like uniform extension. It was found that the elongation was small below the transition temperature. The low values of stress at break at 10 °C were attributed to the presence of a polar group in the polymer [29].

The fractured cross-section morphology of the samples (System A_3) tested at 20 and 100 °C are presented in Fig. 8a and b, respectively. Fig. 8a shows a hill and valley-like structure in the cross-section, suggesting that the failure was like ductile fracture. Similar morphological features were seen in the samples tested at 28 and 50 °C. Fig. 8b shows that the fractured ends joined together to form an agglomer. Similar morphology was also seen on the sample fractured at 70 °C;

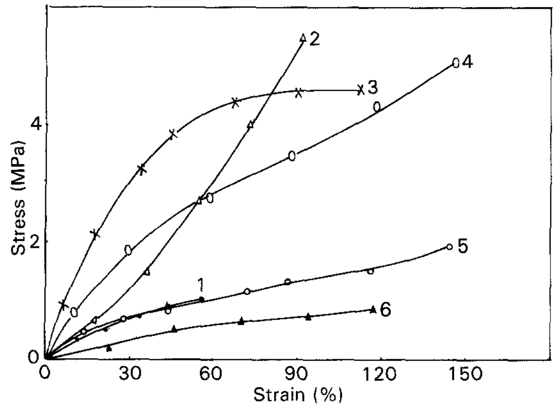


Figure 7 Stress–strain curves of System A_3 at different temperatures (°C): (1) 10; (2) 20; (3) 28; (4) 50; (5) 70; (6) 100.

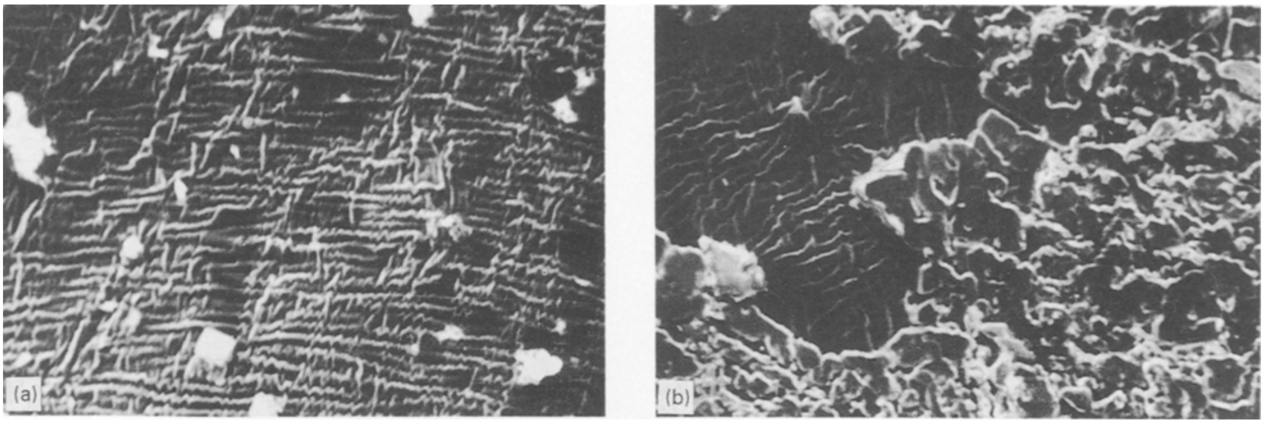


Figure 5 SE micrographs showing the surface morphology of 10% strained Ca-g-AN-co-nBMA films (System A). (a) A_1 (650 ×); (b) A_3 (650 ×).

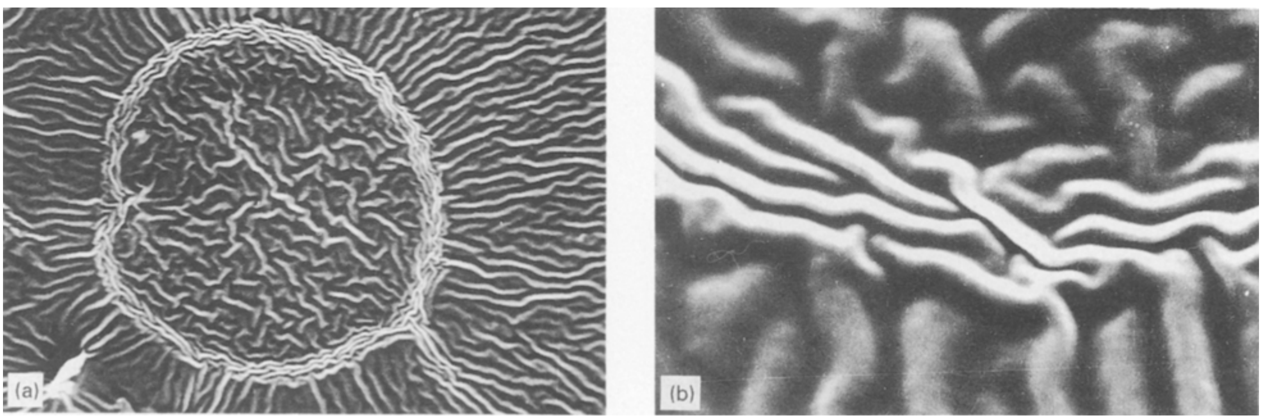


Figure 6 SE micrographs showing the surface morphology of System B_3. (a) Unstretched (900 ×); (b) magnified view of (4500 ×).

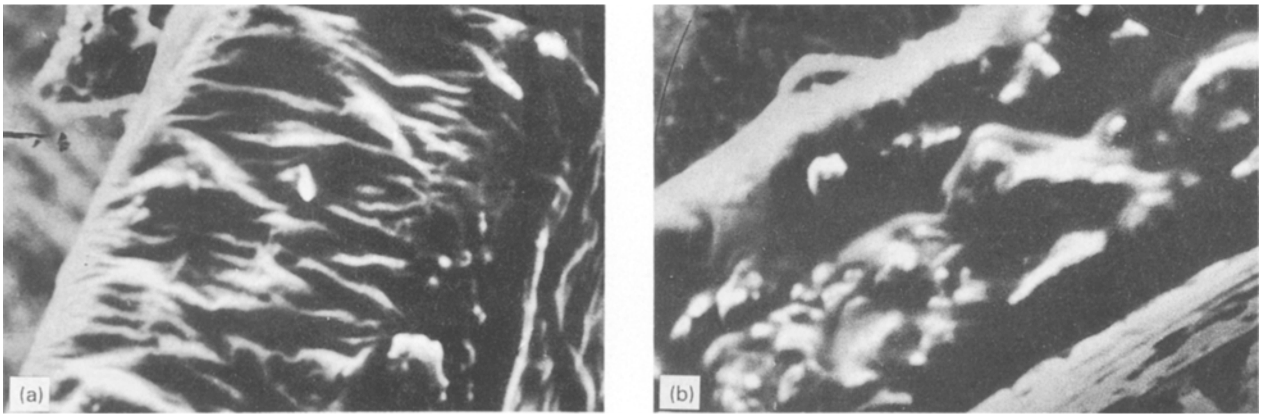
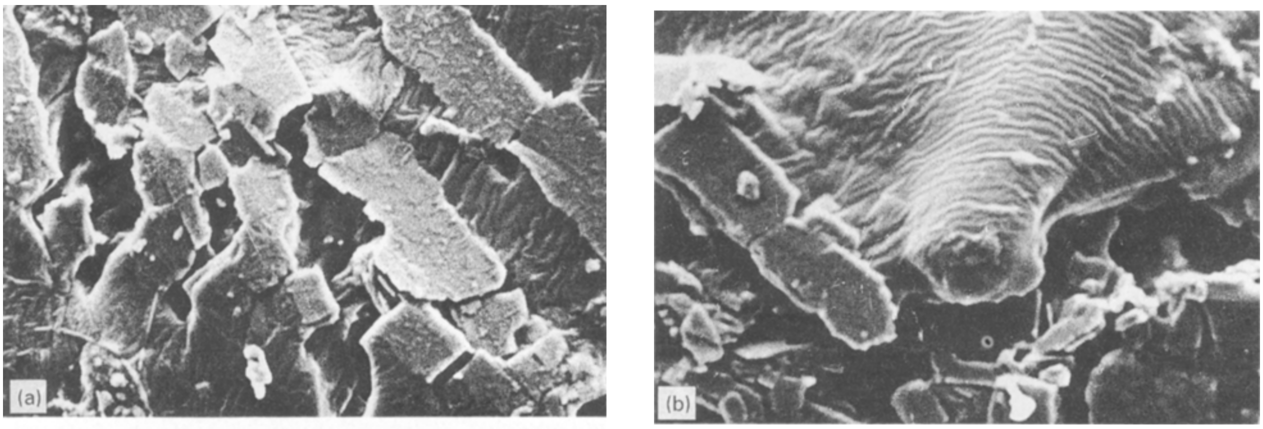


Figure 8 SE micrograph showing the fractured cross-section of System A_3 film tested at different temperatures (°C): (a) 20 (600 ×); (b) 100 (600 ×).



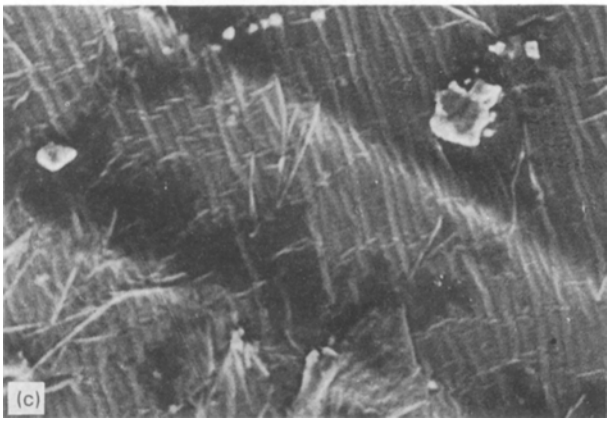


Figure 9 SE micrographs showing the fractured surface of System A_3 tested at different temperatures (°C) (600 ×): (a) 50; (b) 70; (c) 100.

the agglomers oriented perpendicular to the direction of applied stress.

The morphology of the samples tested at different temperatures suggests that above 50 °C some transition/rearrangement probably took place in the system, and because of that the sample flowed. This can also be seen in the stress–strain curves (Fig. 7). The orientation of lamellar structure was also seen on the surfaces of samples tested at 100 °C (Fig. 9c), whereas at 50 °C the surface morphology was totally different (Fig. 9a). Since the stress response of the phases are different the phases separate due to the application of stress, as shown by Fig. 9a. This effect is also clearly seen in Fig. 9b, which shows the fractured surface morphology of System A_3 at 70 °C. Fig. 9b shows the Hückel region [35] forming a concentric pattern, and the flaw point from where the cracks propagated with the separation of the two phases. Fig. 9 suggests that in these grafted films one phase is more flexible (T_g lower than the working temperature) than the other. Due to this, incompatibility arises and the sample breaks at lower extension (Fig. 3). Thus, the studies on the fracture behaviour of grafted casein films clearly shows their multiphasic nature.

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