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GRAFT CO-POLYMERIZATION OF CASEIN WITH ACRYLONITRILE AND *n*-BUTYL METHACRYLATE

N. SOMANATHAN,* R. SANJEEVI, C. RAMI REDDY and N. RADHAKRISHNAN
Central Leather Research Institute, Adyar, Madras 600 020, India

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Abstract—Casein was grafted using acrylonitrile and *n*-butyl methacrylate. The mechanical properties of the grafted co-polymer films were studied using an Instron Universal Testing Machine. The morphological characteristics were studied by scanning electron microscopy. The tensile strength was found to increase and elongation at break to decrease with increasing monomer content. The compatibility of the graft co-polymer and homopolymer formed was found to be important in governing the morphological features of the films.

INTRODUCTION

One of the oldest types of finish used in leather industry is the glazed aniline finish; this protein finish can be friction glazed. Casein is the basic material for any protein finish. Strength, dyeability and resistance to oil, grease and solvents make casein good enough for machinability and glazability, but the wet rub fastness of casein finish is very poor so that modification is needed.

Attempts have been made to reduce the hydrophilicity of casein finishes in a number of ways [1–3]. A modern approach for modification of a natural or synthetic polymer is the use of a grafting technique with a suitable monomer, without affecting the overall properties of the backbone chain. A significant amount of literature refers to the formation of graft co-polymers of natural polymers such as collagen [4, 5], gelatin [6, 7], cellulose [8], starch [9], wool [10], natural rubber [11] and casein [12, 13]. Grafting of casein with acrylonitrile prevents growth of micro-organisms to some extent and also improves the wet rub fastness.

In the present investigation, grafting acrylonitrile and *n*-butyl methacrylate onto casein is undertaken with a view to improving the fastness properties. The optimum conditions and appropriate composition of monomers and also the mechanical properties of these graft co-polymers were studied. Morphological characteristics of the grafted polymers were also studied.

EXPERIMENTAL

(*A*) *Materials*

The monomers acrylonitrile (AN) and *n*-butyl methacrylate (*n*-BMA) were freed from inhibitors. Stock solutions of a binary mixture consisting of 0.9 mol of AN and 0.1 mol of *n*-BMA in one case (system I) and 0.8 mol of AN and 0.2 mol of *n*-BMA in second case (system II) were prepared. For the reaction, the concentrations of the binary mixture used were 0.4, 0.8, 1,2 and 1.6 mol l^{-1} respectively in both cases.

(*B*) *Preparations of graft co-polymers*

Casein (2.5 g) was soaked overnight in water (25 ml) and then treated with a solution of triethanolamine (0.5 g) in 10 ml of water). After complete dissolution of casein, the solution was kept at 60°C for 1 hr, and then cooled to room temperature. This 10% solution was taken in a three-necked R.B. flask and was placed in a bath maintained at $60 \pm 0.5°C$; N_2 was bubbled through the solution throughout the reaction.

The monomer mixture and the initiator (potassium persulphate solution of 9.7×10^{-3} mol l^{-1}) were added simultaneously over a period of 10 min. The reaction was allowed to proceed for 3 hr and the system was then cooled. Films cast from the above products were used for studying mechanical properties. Parameters such as percent grafting and efficiency were determined from precipitation studies using 10% acetic acid.

(*C*) *Isolation of graft co-polymer*

Isolation of ungrafted co-polymer from the grafted co-polymer was carried out by subjecting the precipitate obtained by means of solvent extraction in a tumbled bottle method using dimethylformamide as solvent for the extraction of ungrafted co-polymer. The solvent layer was separated from the undissolved residue and from the solvent layer; ungrafted co-polymer was extracted. The undissolved residue was repeatedly washed with water and dried in vacuum to give the weight of the graft co-polymer. From these weights of graft polymer, total polymer and the backbone weight, the percent grafting and grafting efficiency were calculated.

(*D*) *Preparation of polymer films*

Films were cast on a mercury surface from a solution of the graft co-polymer. The concentration of the co-polymer corresponded to 15% solid content on drying. The films were cast at 65% r.h. The films thus obtained were removed from the mercury bed, dried in vacuum and conditioned for 7 days at $25 \pm 2°C$ and $65 \pm 2\%$ r.h. in a desiccator.

(*E*) *Study of the mechanical properties*

Mechanical behaviour was studied to understand the stress response of a system to the applied strain. Since these films have a specific end-use, both stress and strain have to be studied. Tensile strengths of films were important in that they have some bearing on the adhesion of the finish to leather [14]. Many experiments have been carried out on the mechanical properties of coatings [15–17]. Films prepared with different compositions were subjected to the mechanical behaviour experiments.

Table 1 Kinetic parameters of grafted casein with various monomer concentrations. Casein = 2.5 g/50 ml; $K_2S_2O_8 = 9.7 \times 10^{-3}$ mol l^{-1}; temperature = 60°C; total volume = 50 ml; time = 3 hr

Sl. No.	Composition of AN: *n*-BMA (mol fraction)	AN + *n*-BMA concentration (mol l^{-1})	Wt of polymer formed Total (g)	Wt of polymer formed Grafted (g)	Grafting (%)	Grafting efficiency (%)
1		0.4	0.408	0.115	4.59	28.13
2	0.9:0.1	0.8	0.970	0.766	30.62	78.92
3		1.2	2.130	1.182	47.27	55.47
4		1.6	3.360	1.892	75.67	56.30
1		0.4	0.299	0.202	8.09	67.72
2	0.8:0.2	0.8	1.127	0.277	11.09	24.60
3		1.2	1.258	0.378	15.10	30.01
4		1.6	0.864	0.245	9.81	28.39

Dumb bell shaped specimens were cut as per ASTM standards [18]. Thickness of the specimens was measured using a thickness gauge having a sensitivity of the order of 0.0001 in. The specimens were tested by using an Instron universal tensile testing machine model 1112. From the graphs, tensile strength and percent elongation were calculated.

(*F*) *Stress relaxation*

When the polymeric samples are strained to a given stress level and the strain is maintained constant, then the stress undergoes a decay, known as stress relaxation. The stress relaxation experiments at 10% and 20% strain were studied by using an Instron universal tensile testing machine and the stress decay patterns were plotted (σ against time).

(*G*) *Morphological studies of the films*

The morphological characteristics of the films are altered by varying the composition. This study is essential, since these systems are mainly to be used as top-coats, which in turn will govern the morphological features of leather.

In order to study the surface cracking and the special morphological features due to stretching, the following procedure was adopted. The samples were strained up to 10% and 20% separately for a period of 24 hr. Then specimens were cut from the central portion of the samples. The specimens were mounted on the aluminium stubs with silver dag. They were coated with gold and then scanned with a filament current of 2.5 A in stereoscan S-150 scanning electron microscope.

RESULTS AND DISCUSSION

Grafting of vinyl monomer onto casein is expected to improve its fastness properties. For this purpose, a comprehensive understanding of the kinetics of grafting is essential.

Table 1 shows the effect of variation of monomer concentration on the kinetic parameters viz. percent grafting and grafting efficiency. The increase in grafting with increase in concentration of monomer is less in the case of system II. It is likely that the large pendant groups of *n*-BMA units are responsible for the decrease in the rate of diffusion to the grafting site as a whole. With increasing concentrations of monomer in the reaction system, increased amounts of ungrafted co-polymer are formed, i.e. the grafting efficiency decreases with increasing monomer concentration.

The film formed from the pure casein solution gave a very small extension and very high tensile value (Fig. 1). For a film forming material, on the other hand, very high extension is essential. So casein has to be modified and this was effected using the grafting procedure discussed earlier.

The stress–strain characteristics were studied by varying the concentration of monomer mixture. The amount of casein was kept constant in all cases. The tensile strength has a direct relationship with the concentration of monomer used. Figure 2 shows that the tensile strengh increases with concentration and elongation at break decreases with concentration. We are interested in an optimum elongation from the point of view of the end-use. Figures 3 and 4 clearly suggest that, at moderate concentrations viz. around 1 mol l^{-1} of monomer, we will be able to obtain a suitable product. Twelve samples were tested on each system and standard deviations for the tensile strength and elongation at break are quite small (see Table 2).

The stress relaxation of the samples were studied at 10% and 20% strain levels. Stress relaxation was studied by plotting the stress against time (σ = stress at a given time and σ_0 = stress at time zero). This will give an idea of the viscous component of the stress at a given strain level. The viscous component (Fig. 5a,b) was very high for all cases. The same trend was also observed at 20% strain.

The morphological characteristics were studied by observing the surface features using SEM. Figure 6(a–c) show the morphological features of the films of system I (0.4 mol l^{-1}).

It is reported that the compatibility of the materials present in a film will alter the morphological characteristics [19]. Systems where the compatibility is very

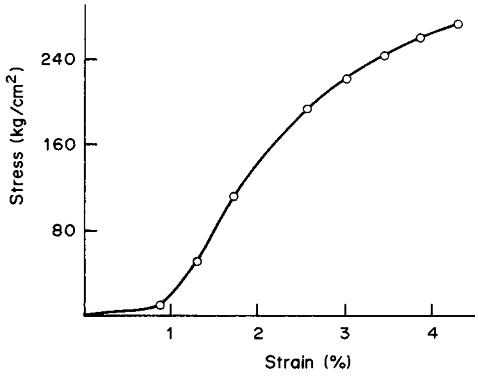

Fig. 1. Stress–strain behaviour of pure casein film.

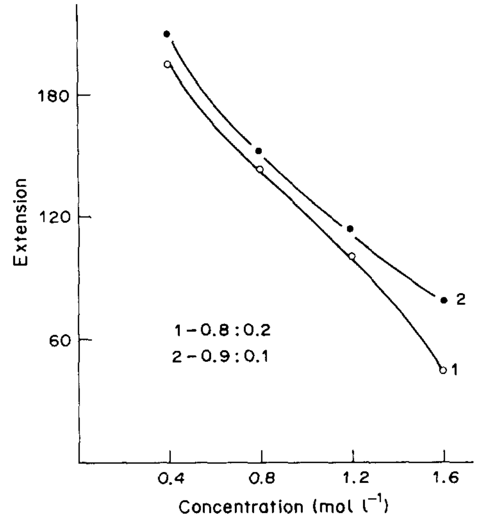

Fig. 2a. Effect of monomer concentration on extension at break.

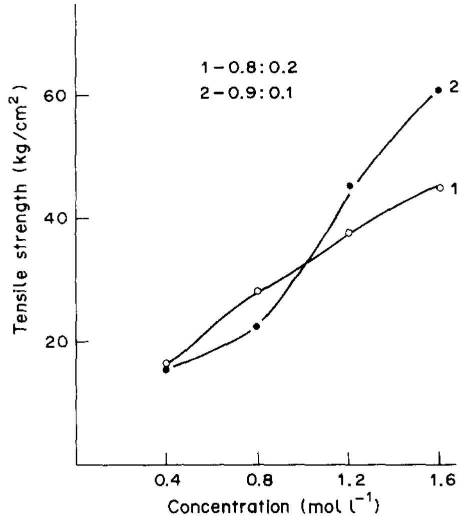

Fig. 2b. Effect of monomer concentration on tensile strength.

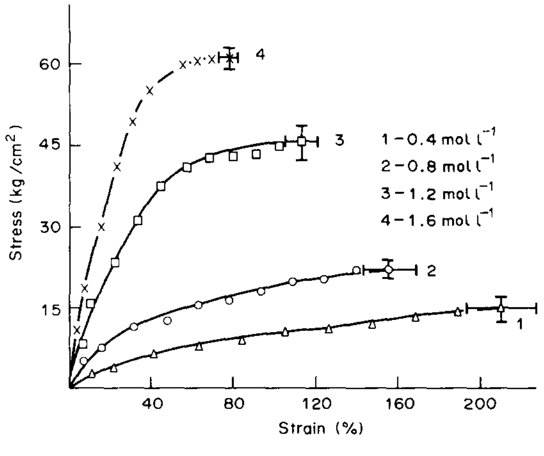

Fig. 3. Stress–strain behaviour of system I (0.9 : 0.1).

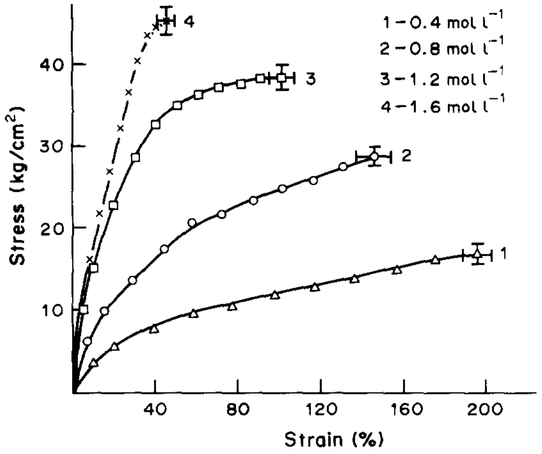

Fig. 4. Stress–strain behaviour of system II (0.8 : 0.2).

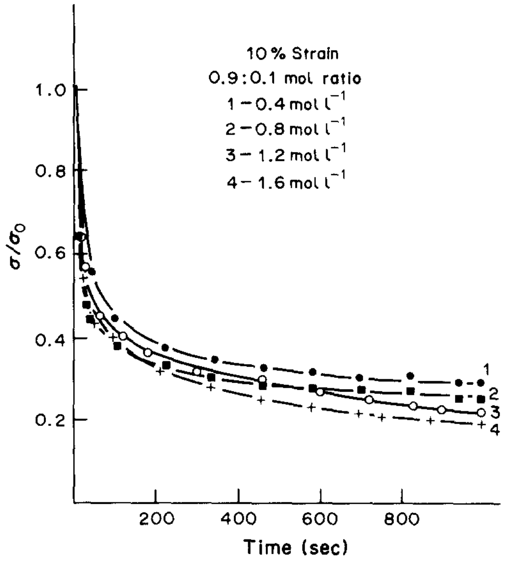

Fig. 5a. Stress relaxation pattern of system I at 10% strain level.

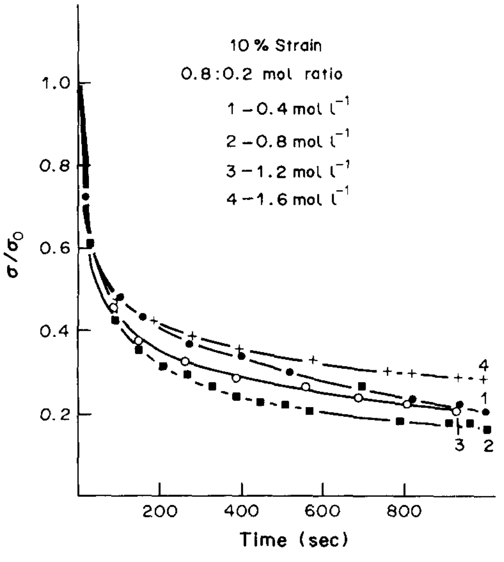

Fig. 5b. Stress relaxation pattern of system II at 10% strain level.

Table 2. Tensile properties of grafted casein films

Sl. No.	Composition (mol fraction)	AN + n-BMA concentration (mol l^{-1})	Tensile strength Mean	Tensile strength SD	Percent elongation Mean	Percent elongation SD
1	0.9:0.1	0.4	15.43	1.98	210.0	17.8
2		0.8	22.16	1.65	155.0	13.1
3		1.2	45.63	3.40	113.0	8.6
4		1.6	61.13	1.40	78.0	3.5
1	0.8:0.2	0.4	16.58	1.10	195.8	8.0
2		0.8	28.41	0.92	145.9	8.2
3		1.2	38.15	0.97	101.7	6.4
4.		1.6	45.15	1.68	46.8	3.8
	Control casein	—	272.0	—	4.3	—

good give very uniform surface, without wrinkles. In the scanning electron micrographs for the systems discussed, surface streaks are seen for all the monomer concentrations and are enhanced with increasing monomer concentration.

The stress–strain characteristics show a steady increase, thereby indicating the absence of crimps. The samples observed after 24 hr of stretch show surface cracking and it is more evident at 20% strain than at 10% strain level.

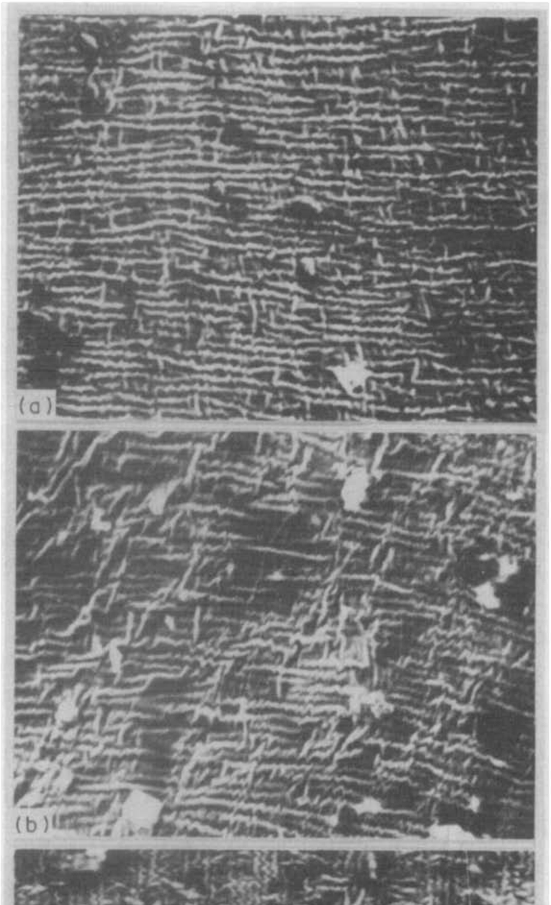

Fig. 6(a–c). Scanning electron micrographs showing the surface features of system I (monomer concentration 0.4 mol l^{-1}). (a) control, (b) 10% strained, (c) 20% strained.

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