Synthesis of Casein-*g*-Poly(methyl Acrylate). II

D. MOHAN,* GANGA RADHAKRISHNAN, and S. RAJADURAI,
Polymer Division, Central Leather Research Institute, Adyar, Madras 600 020, India

Synopsis

The synthesis of casein-*g*-poly(methyl acrylate) was studied using the potassium peroxydisulfate–ascorbic acid redox system. The effect of synthetic variables has been investigated in the light of rates of conversion of monomer, graft copolymerization and homopolymerization, percent grafting, and grafting efficiency. The results are compared with the system initiated by pure potassium peroxydisulfate alone.

INTRODUCTION

The properties of the natural and synthetic polymers can be tailored effectively through graft copolymerization of vinyl and acrylate monomers onto them. The literature abounds with examples of successful formation of copolymers[1-19] from natural[1-16] and synthetic[17-19] macromolecules. The casein contains H bonds between $\diagdown C{=}O$ and $-NH$ groups which have negative influence on film formation. This property may be altered by weakening these intermolecular bonds through graft copolymerization of some acrylic ester groups onto casein. Thus grafting favors the formation of more elastic casein film and the modified casein may be applied as top coats for leather.

However, the knowledge on the grafting of acrylate monomers onto casein is scanty. The graft copolymerization of acrylate monomers onto protein had been successfully achieved by employing either potassium peroxydisulfate[1,9,10,14,15,20] alone or as part of a redox system, H_2O_2–Fe^{2+},[21] and ceric ion.[22] Even tri-*n*-butyl borane had been used to graft poly(methyl methacrylate) onto blood.[23] Further, potassium peroxydisulfate in combination with ascorbic acid had been reported to be the best initiator for polymerization of vinyl monomers in aqueous medium,[24-26] including graft copolymerization.[12,13] In continuation of our earlier studies,[12,13] a systematic investigation onto graft copolymerization of methylacrylate onto casein in heterogeneous medium had been carried out using potassium peroxydisulfate–ascorbic acid redox system (KPS–AA) in order to understand the pathway of the reaction kinetics and the results are compared with our earlier system.[1,9,10,12,13]

*Reverse Osmosis Discipline, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364002, India.

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EXPERIMENTAL

Materials

Casein (E. Merck, A. G., Germany), Potassium peroxydisulfate (E. Merck, A. G., Germany) and Ascorbic acid (LR, BDH, India) were used as such without further purification. Methylacrylate (BDH, U.K.) was freed from inhibitor by washing successively with sodium hydroxide and water, dried over anhydrous sodium sulfate and finally distilled under vacuum. The middle fraction of the distillate was used for the graft copolymerization reaction.

Graft Copolymerization Procedure

A known weight of casein was dispersed in water kept at constant stirring in a three necked flask of 100 mL capacity under nitrogen atmosphere. After sufficient time, required amount of monomer was added, followed by potassium peroxydisulfate and ascorbic acid in succession and the total volume was made up to 50 mL. After a specified time interval, the reaction products were cooled to 5°C and filtered through a weighed sintered crucible and dried to a constant weight in vacuum. The unbound homopolymer was then Soxhlet extracted with acetone and the resultant polymer was dried *in vacuo*.

The rates of conversion of monomer, R_p, graft copolymerization, R_g, and homopolymerization, R_h, were calculated gravimetrically while percent grafting PG and grafting efficiency GE were calculated as follows.

$$R_g = R_p - R_h$$

$$\text{GE} = \frac{R_g}{R_g + R_h} \times 100 = \frac{R_g}{R_p} \times 100$$

$$\text{PG} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the weight of casein taken and W_2 is the weight of casein-g-poly(methyl acrylate).

Infrared Analysis

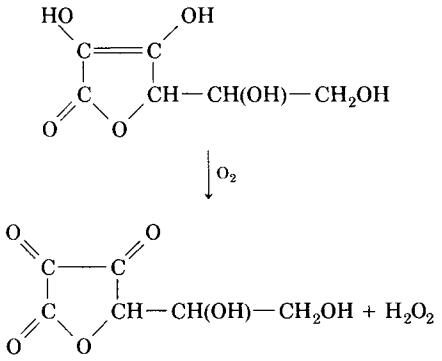
Casein-g-poly(methyl acrylate) was characterized, after exhaustive Soxhlet extraction to remove homopolymer, by IR analysis using a Perkin-Elmer Model 337 grating spectrophotometer in the potassium bromide medium.

Thermal Analysis of Graft Copolymer

The thermal stability of casein and its graft copolymers with poly(methyl acrylate) were analyzed by employing DuPont Thermal Analyzer (Model 951). Thermal analytical experiments were carried out under nitrogen at atmospheric pressure, with a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The most important auto-oxidizable hydroxy ketone or enediol is probably ascorbic acid. The initiation reaction is



The reaction is autocatalytic, being accelerated by dehydroascorbic acid.

The reduction of peroxydisulfate by ascorbic acid is a two-electron transfer in which ascorbic acid is oxidized to dehydro-ascorbic acid and the ascorbate ion ($A\bar{H}$) in aqueous medium is believed to be responsible for the vigorous reducing action.[27]

With a view to understanding the reaction mechanism and the role of activator, ascorbic acid, on grafting of methyl acrylate onto casein, the effects of synthetic variables such as concentrations of monomer, initiator, activator, and backbone and temperature are investigated and compared with the system initiated by pure peroxydisulfate alone.[10]

Effect of Monomer Concentration

The graft copolymerization of methyl acrylate onto casein has been investigated at various monomer concentration by keeping the amounts of initiator, activator and backbone, time and temperature as constant and the results are depicted in Figure 1. An increase in methyl acrylate concentration was found to increase the rates of conversion of monomer, graft copolymerization and homopolymerization, percent grafting, and grafting efficiency, as expected. This may be due to the fact that, as monomer concentration increases, a larger number of monomer radicals are available near the close proximity of casein matrix and thereby influence R_p, R_g, R_h, PG, and GE.

A similar observation was also noted in our earlier publications.[1,9-15] At higher monomer concentrations, due to gel effect, the polymeric molecules become more and more immobilized, and tightly coiled through entanglements, the collective diffusion of more than a few segments, such as at the radical site is greatly hampered. Hence, the termination of free radicals by combination will greatly be impeded resulting in increasing percent grafting, grafting efficiency, R_p and R_g. Further, the R_p and R_g are found to be many times higher than that observed in the earlier system.[10] This may be due to the fact that, in addition to $SO^{\cdot}_4^-$ radicals, the ascorbate ion ($A\dot{H}^-$) radicals are also involved in polymerization reaction resulting in higher rates of conversion of monomer and graft copolymerization. However, vinyl acetate[12] exhibits less percent grafting, grafting efficiency, R_p and R_g compared to

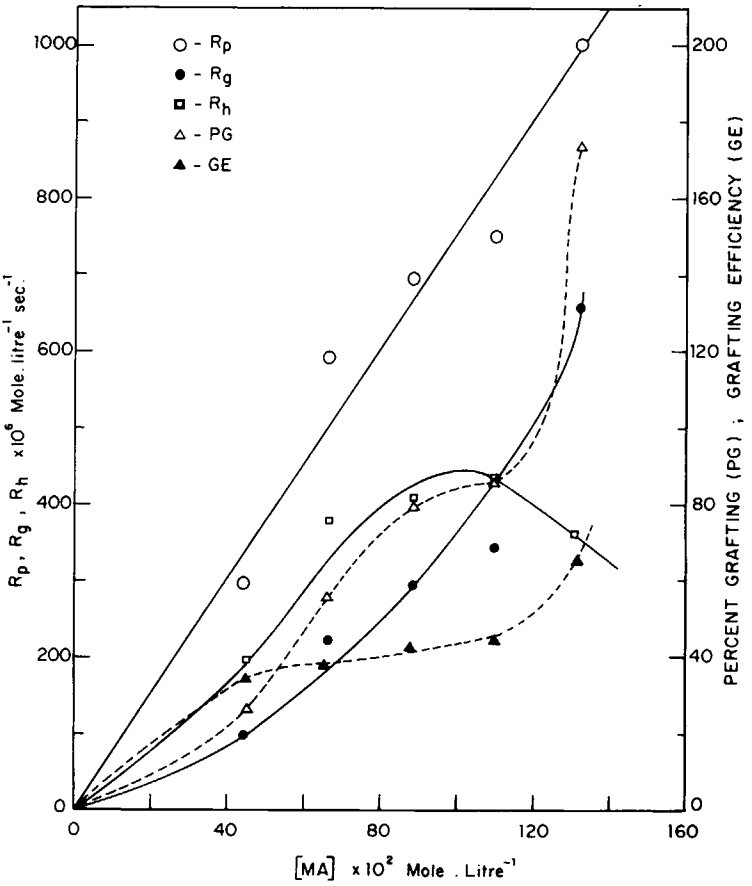
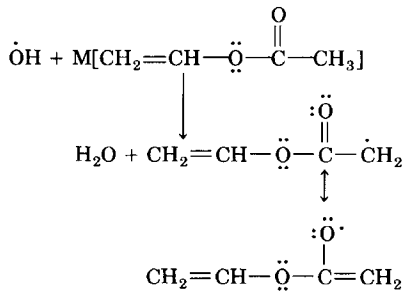


Fig. 1. Reaction conditions: $[S_2O_8^{2-}] = 6.0 \times 10^{-3}M$; [AA] = $0.6 \times 10^{-3}M$; [casein] = $0.6667 \times 10^{-3}M$; temperature = 60°C; time = 10 min; total volume = 50 mL. R_p = plot of rate of conversion of monomer vs. monomer concentration. R_g = plot of rate of graft copolymerization vs. monomer concentration. R_h = plot of rate of homopolymerization vs. monomer concentration. PG = plot of percent grafting vs. monomer concentration. GE = plot of grafting efficiency vs. monomer concentration.

methylacrylate and butyl acrylate.[13] This may be explained by the fact that the hydroxyl radical (ȮH)[25] is formed and can abstract hydrogen atom from suitable vinyl monomer leading to the wastage of vinyl monomer. This assumes significance, when vinyl acetate is used as monomer, since the hydrogen abstraction reaction with vinyl acetate is facilitated owing to resonance stabilization of the resulting radical species as shown below:



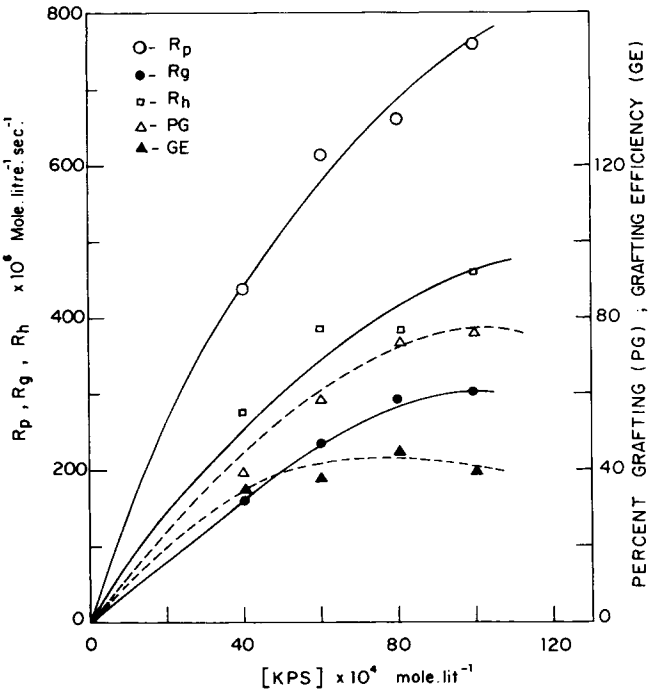


Fig. 2. Reaction conditions: [MA] = 0.7268*M*; [AA] = 0.6 × $10^{-3}M$; [Casein] = 0.6667 × $10^{-3}M$; temperature = 60°C; time = 10 min; total volume = 50 mL. R_p = plot of rate of conversion of monomer vs. initiator concentration. R_g = plot of rate of graft copolymerization vs. initiator concentration. R_h = plot of rate of homopolymerization vs. initiator concentration. PG = plot of percent grafting vs. initiator concentration. GE = plot of grafting efficiency vs. initiator concentration.

Effect of Initiator Concentration

Figure 2 illustrates that an increase in potassium peroxydisulfate concentration in presence of an activator enhances the rates of conversion of monomer, graft copolymerization and homopolymerization, percent grafting, and grafting efficiency. With increasing initiator concentration, a large number of primary radicals are produced which are employed in the activation of casein and methylacrylate at higher rates and thereby influence grafting and hence the observed result. However, a further increase in the initiator concentration accelerates the rate of homopolymerization more than that of graft copolymerization resulting in decreased grafting efficiency, which is in good accordance with earlier reported results.[1,9,10,12,14,15,28,29] Further, the expected low PG and GE in this system may be attributed to the formation of homopolymer to a great extent in conjunction with the graft copolymer than that observed in KPS system.[10] Further, as the size of the monomer increased the diffusion of the monomer to all available sites on the casein backbone is considerably hindered. As a result, PG, GE, R_p, and R_g are lower in the case of bulkier monomer butyl acrylate[13] than methyl acrylate.

Effect of Activator Concentration

The rates of conversion of monomer, graft copolymerization and homopolymerization, and percent grafting were found to increase with ascorbic acid

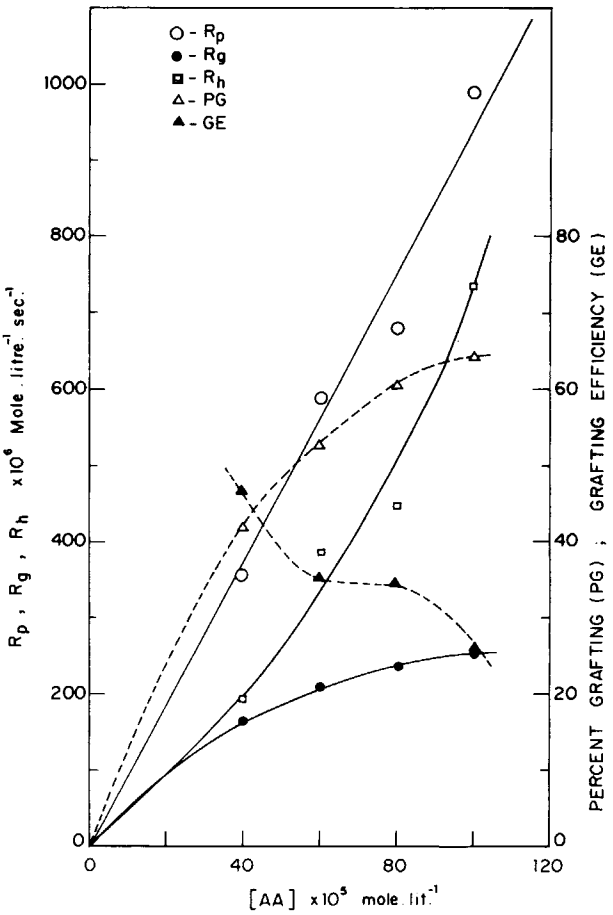


Fig. 3. Reaction conditions: [MA] = 0.7268M; [$S_2O_8^{2-}$] = 6.0 × $10^{-3}M$; [Casein] = 0.6667 × $10^{-3}M$; temperature = 60°C; time = 10 min; total volume = 50 mL. R_p = plot of rate of conversion of monomer vs. activator concentration. R_g = plot of rate of graft copolymerization vs. activator concentration. R_h = plot of rate of homopolymerization vs. activator concentration. PG = plot of percent grafting vs. activator concentration. GE = plot of grafting efficiency vs. activator concentration.

concentration while grafting efficiency showed a decreased trend (Fig. 3). These may be explained on the basis that at higher concentrations of ascorbic acid, the rate of generation and the concentration of reactive species increased[24,25] and thereby increase R_p, R_g, R_h, and percent grafting. However, it must also be considered that the casein acts as a cocatalyst in the redox system, with peroxydisulfate anion causing accelerated peroxydisulfate decomposition as well as sites for grafting. When ascorbic acid is added as cocatalyst, it competes with casein–peroxydisulfate decomposition and is less effective in providing grafting sites in the casein[11] hence the decreased grafting efficiency with increasing activator concentration and also the observed lower values of grafting efficiency in the present system than the earlier reported system.[10]

Effect of Backbone Concentration

The influence of casein concentration is illustrated in the Figure 4. It is evident that the rates of conversion of monomer, graft copolymerization and homopolymerization, percent grafting, and grafting efficiency are increased. These may be due to the fact that at higher backbone concentrations a larger number of grafting sites are created along the casein which are utilized for grafting. A further increase in backbone concentration leads to deactivation of backbone radicals by primary radical termination and also by termination between backbone radicals itself, resulting in observed decrease in R_p, R_g, and R_h. Further, the ratio between the weight of side chain grafted to casein decreases with increasing casein concentration and resulted in decreased percent grafting, which is in good accordance with the results of other investigators.[7,22,23] In addition, the graft radicals are almost immobile due to segmental movement and thus the relative decrease in R_g is less when compared to that in R_h and thereby increases the grafting efficiency even beyond the optimum concentration.[1,9,10,13,22] The grafting efficiencies in casein poly(vinyl acetate)[12] graft copolymers are lower than those of casein–poly(methyl acrylate) and casein–poly(butyl acrylate).[13] This appears to be due to higher rates of termination of the growing grafted chains by homopolymer radicals in the former system than for the latter cases.

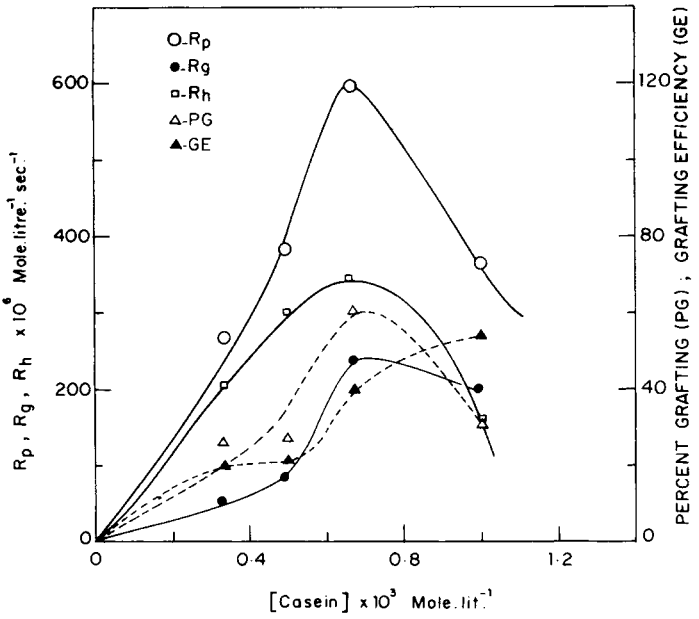


Fig. 4. Reaction conditions: [MA] = 0.7268M; [$S_2O_8^{2-}$] = 6.0 × $10^{-3}M$; [AA] = 0.6 × $10^{-3}M$; temperature = 60°C; time = 10 min; total volume = 50 mL. R_p = plot of rate of conversion of monomer vs. backbone concentration. R_g = plot of rate of graft copolymerization vs. backbone concentration. R_h = plot of rate of homopolymerization vs. backbone concentration. PG = plot of percent grafting vs. backbone concentration. GE = plot of grafting efficiency vs. backbone concentration.

Effect of Temperature

The role of temperature in the graft copolymerization has been investigated and it was found that temperature influences the rates of conversion of monomer, graft copolymerization and homopolymerization, percent grafting, and grafting efficiency as in normal polymerization reaction (Fig. 5). A contributing factor here is the uncatalyzed decomposition of $S_2O_8^{2-}$ that becomes more predominant as the reaction temperature rises. Further, the dependence of rates of grafting on the increase in temperature could be ascribed to the greater activation energy. The swellability of casein and diffusion rates of methylacrylate and homopolymer radicals are enhanced by increasing the reaction temperature and thereby influences R_p, R_g, R_h, PG, and GE. However, at higher temperature, the mutual termination between homopolymer radicals is faster than between graft and homopolymer radicals, which in turn is faster than two graft radicals.[30] This is because the homopolymer radicals are highly mobile while the graft radicals are almost immobile, due to reduced segment movement, and resulting in decreased grafting efficiency, which is similar to earlier reported results.[1,9,10,12,13,22] This is supported by the continuous increase in the rates of conversion of monomer and homopolymerization.

The higher values of rates of conversion of monomer, graft copolymerization and homopolymerization, percent grafting, and lower grafting efficiency in the present system in comparison to the system initiated by pure potassium peroxydisulfate alone[10] supports that potassium peroxydisulfate–ascorbic acid

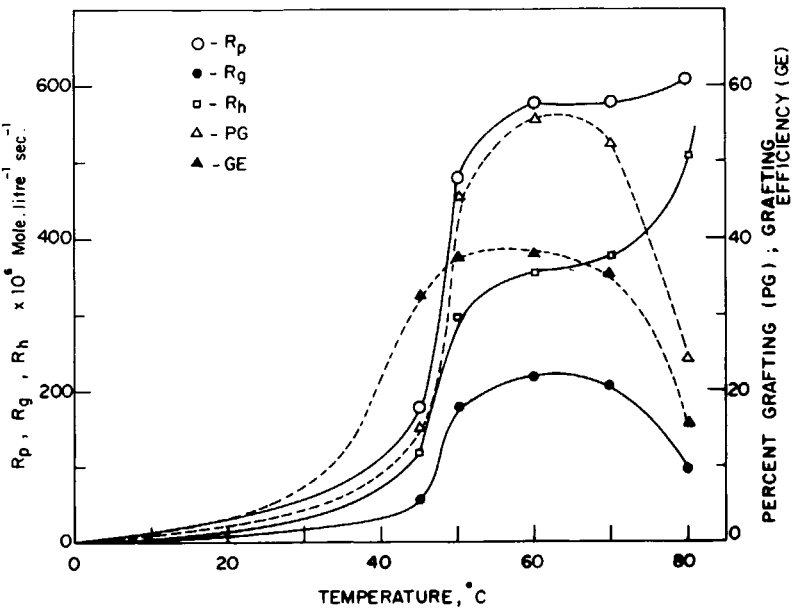


Fig. 5. Reaction conditions: [MA] = 0.7268M; $[S_2O_8^{2-}] = 6.0 \times 10^{-3}M$; [AA] = $0.6 \times 10^{-3}M$; [casein] = $0.6667 \times 10^{-3}M$; time = 10 min; total volume = 50 mL. R_p = plot of rate of conversion of monomer vs. temperature. R_g = plot of rate of graft copolymerization vs. temperature. R_h = plot of rate of homopolymerization vs. temperature. PG = plot of percent grafting vs. temperature. GE = plot of grafting efficiency vs. temperature.

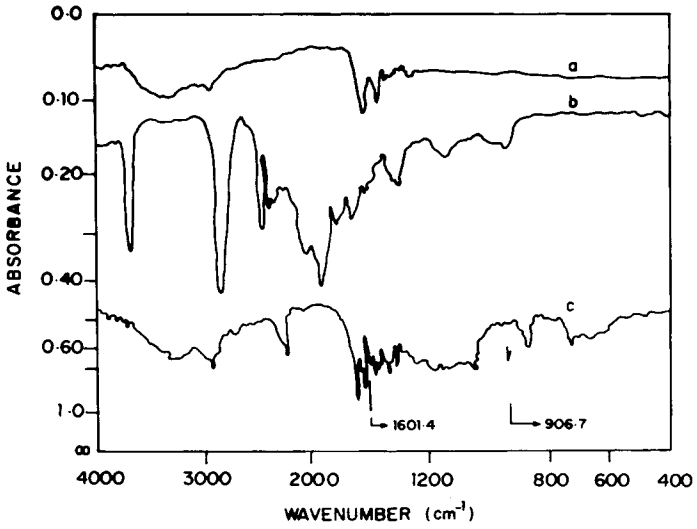


Fig. 6. Infrared spectra of (a) casein, (b) poly(methyl acrylate): and (c) casein-*g*-poly(methyl acrylate).

redox systems influences more the homopolymerization. Proof of graft copolymerization was obtained by employing the ninhydrin test and selective solvent extraction as reported in our earlier communication.[10]

The infrared spectra of pure and grafted casein are illustrated in the Figure 6. The additional peak at 1750 cm^{-1} in the grafted casein established the proof of graft copolymerization of poly(methyl acrylate) onto casein.

Figure 7 shows the thermal analysis of casein and the modified casein. The temperature profile against any accompanying weight changes in the corresponding polymer during thermal degradation is obtained both in integrated and its differential form. On comparison with pure casein, it is observed that graft copolymer exhibits two different peaks, one corresponding to the backbone moiety and the other corresponding to the grafted polymer. It is evident from the figure that casein grafted with poly(methyl acrylate) are thermally more stable than pure casein.

Application of Modified Casein as Top Coats for Leather

The water absorption of casein is very high due to its hydrophillic nature and this inherent hydrophilicity impairs the water resistance and wet rub fastness of casein films deposited on leather. Further, casein does not form continuous film on evaporation. Leather, being a porous substrate, great care must be taken in choosing a top coat which will form a continuous film on the surface without sinking in. The grafting of acrylic monomers onto casein is to impart certain desirable properties such as good wet and dry rub fastness to this otherwise hard film forming material, casein. In order to apply on leather, the graft copolymer of methyl acrylate onto casein was prepared by emulsion

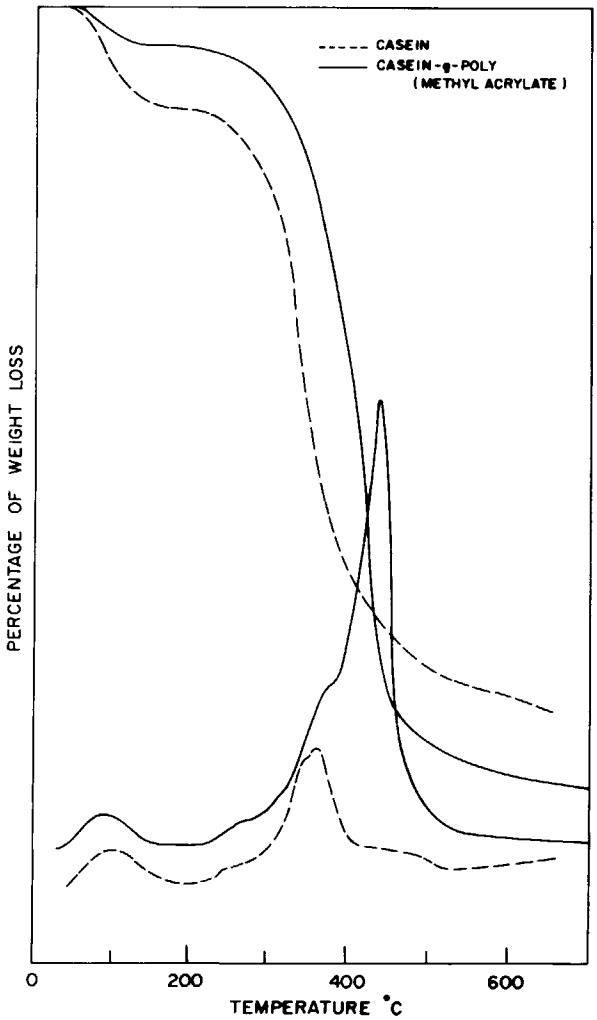


Fig. 7. Thermograms of casein and grafted casein.

polymerization,[11] applied on leather as top coats along with the homopolymer, and evaluated for use in leather finishing. No attempt was made to remove the ungrafted homopolymer from the formulation, as their presence is not in any way detrimental to the finishing property of these products. Film studies, practical finishing trials and physical testing of coated leather are carried out and compared with those coated with other graft copolymers of casein[11] with butylacrylate, vinyl acetate, acrylamide and acrylonitrile and are shown in Table I. Products I, II, III, and IV produced films with high elongation, but are not glazeable. The films get detached from the leather surface and they could not withstand the temperature produced on glazing. It is evident from the table that the formulation V gives the best result with respect to wet and dry rub fastness and flexural endurance. This may be due to the fact that the

TABLE I

Formulation	Composition	Flexing (does not crack into flexes)	Dry rub	Wet rub
	Pure casein	70,000	Good	Fair
I	Casein-*g*-methylacrylate	60,000	Good	Fair
II	Casein-*g*-butylacrylate	75,000	Good	Fair
III	Casein-*g*-vinylacetate	50,000	Good	Fair
IV	Casein–acrylamide	50,000	Good	Fair
V	Casein–acrylonitrile	90,000	Good	Good

chain of polyacrylonitrile (PAN) grafted at casein at random positions can undergo changes intramolecularly when two grafted chains are in close proximity and intermolecularly under the influence of heat and pressure during glazing. The formation of such cyclic structures[31] may be responsible for the improved wet rub fastness of the casein–PAN grafted copolymers.

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