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MODIFICATION OF GELATIN BY GRAFTING WITH METHYL METHACRYLATE

A Rasheed Khan[a]*, A F K Ifrahim[b], Kausar Ali Syed[b] and Tehzeeb Akhtar[b]

[a]Fuel Research Centre, PCSIR Karachi-75280, Pakistan

[b]Plastic and Polymer Research Centre, PCSIR Laboratories Complex, Karachi-75280, Pakistan

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Modification of gelatin by grafting with methyl methacrylate in the presence of potassium persulphate was studied and the results were discussed with respect to grafting ratio (GR) grafting efficiency (GE), rate of grafting (Rg) and rate of conversion of monomer (Rp). The lower concentration of gelatin favours more grafting. Homopolymerization of monomer is not observed in most of the cases.

Key words: Gelatin, Grafting, Methyl methacrylate.

Introduction

To achieve improved physical and chemical properties, the natural and synthetic polymers like nylon (Lenka 1982), silk (Misra *et al* 1982), collagen (Brauer and Termini *et al* 1974), casein (Khan *et al* 1994) and gelatin (Kim Songky *et al* 1990) are modified by grafting with vinyl monomers. These graftings may be accomplished by use of radical forming initiators like sodium or potassium persulphate, ceric ammonium nitrate etc. Gelatin is a heterogeneous protein or protein fraction derived from collagen on boiling with water. It consists of a mixture of soluble proteins of high molecular weight which is capable of forming a firm gel in an aqueous medium and which on digestion yields various amino acids in definite ratios. Gelatin is generally used in foods, pharmaceutical preparations and photographic products etc. It is a good adhesive for glass and paper but loses its strength at high humidity and (unless containing a preservative such as boric acid, β-napthol and zinc sulfate) is subject to attack by moulds (Roff 1956).

Many useful applications of vinyl monomers grafted gelatin can be found in leather industry. The product possesses high mechanical properties, high elasticity and thermal stability and may be used in coating formulations of leather finishes. This paper deals with grafting of methyl methacrylate onto gelatin using potassium persulfate as initiator.

Experimental

Materials. Methyl methacrylate, $H_2C=C(CH_3)COOCH_3$ (BDH) was freshly distilled and the middle fraction was used. Acetone and other organic solutions were distilled before use. Gelatin (E. Merck, food grade), potassium persulfate (E. Merck, G R) were used without further purification.

Procedure. The copolymerization reactions were carried out in 500 ml reaction vessel with nitrogen inlet and outlet. A 10% solution of gelatin was prepared in warm water. Gelatin was precipitated from a portion of this solution to confirm its percentage concentration. Required quantity of gelatin (from 10% solution), methyl methacrylate and potassium persulfate were transferred to the reaction flask. The total volume was made upto 100 ml by adding water. The temperature of the reaction vessel was maintained at 60°C. After the required reaction time (30 min or more), the ingredients were poured into acetone and grafted gelatin was precipitated. Any loosely bound poly (MMA) present would be dissolved into acetone. The product was further treated with THF to dissolve any residue homopolymer still present. Finally it was dried and weighed. The product was analysed for nitrogen. The IR spectra of the product and gelatin were recorded to identify the attachment of growing polymer chain of PMMA onto gelatin from the appearance of characteristic absorption bands which were not present in the spectrum of pure gelatin (Fig 1).

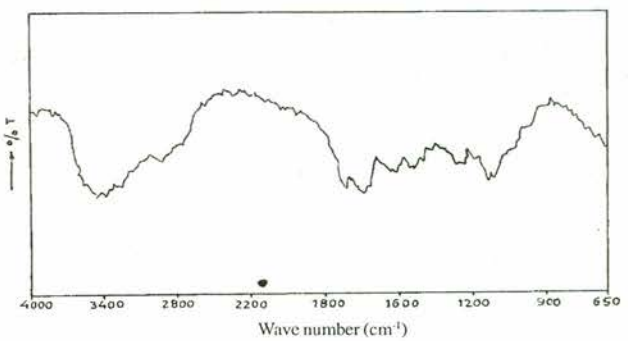

Fig 1. Spectrum of gelatin-g-MMA.

*Author for correspondence

Results and Discussion

Tables 1-4 include the data obtained from grafting of PMMA onto gelatin using potassium persulfate as catalyst. Proof of the grafting was obtained from elemental analysis, solubility and the IR spectra of the graft copolymers. Gelatin and 21 samples of product were estimated for nitrogen. Gelatin contains 16.5% nitrogen whilst the product samples contain 3.7 - 15.5% nitrogen. The variation in percentage of nitrogen suggests the grafting of growing polymer chain of poly (MMA) onto reactive centres of gelatin. Gelatin gets dissolved in cold or hot water, dilute alkali whereas the product samples are partially soluble in alkali (1%) and swells in water showing swelling uptake 13.45%. The swelling tests of gelatin and grafted gelatin were also carried out to ensure the assumption based on elemental analysis to be confirmed (Table 5).

Gelatin swelled with different solvent uptake in xylene (90%), acetone (7%), butyl acetate (20%), choloroform (0.0%), ethyl alcohol (0.0%), ethyl acetate (9%), methyl ethyl ketone (8%), DMF (88%), carbon tetrachloride (19%) whereas grafted gelatin shows solvent uptake in different solvents as xylene (123%), acetone (0.0%), butyl acetate (44%), chloroform (219%), ethyl alcohol (4.3%), ethyl acetate (10%), methyl ethyl ketone (43%), DMF (464%) and carbon tetrachloride (127%). The solvent behaviour of gelatin and grafted gelatin towards different solvents revealed attachment of growing polymer chain of MMA onto gelatin. IR spectral studies also support the assumption that the product is graft copolymer. The presence of ester carbonyl absorption band at 1725 cm^{-1} and amide group at 1650 cm^{-1} and 1550 cm^{-1} provide a definite proof that graft polymer (MMA-g-gelatin) has been formed. Consequently all these evidences confirm the formation of this graft copolymer.

The total conversion, the grafting ratio (GR), grafting efficiency (GE), rate of conversion of monomer (Rp), rate of grafting of monomer on gelatin (Rg) and rate of homopolymerization (Rh) were calculated as follows,

$$\text{Total conversion } \% = \frac{\text{Total weight of vinyl polymer formed}}{\text{Weight of vinyl polymer}} \times 100$$

$$\text{GR } \% = \frac{\text{Weight of vinyl polymer in graft}}{\text{Weight of gelatin}} \times 100$$

$$\text{GE } \% = \frac{\text{Weight of vinyl polymer in graft}}{\text{Weight of total polymer}} \times 100$$

$$\text{Rp} = \frac{\text{Total conversion of vinyl monomer (in mole)}}{\text{Time in sec}}$$

$$\text{Rh} = \frac{\text{Vinyl monomer in graft (in mole)}}{\text{Time in sec}}$$

$$\text{Rg} = \text{Rp-Rg}$$

The effect of monomer concentration was investigated by changing the monomer concentration at a fixed concentration of catalyst, backbone, temperature and time (Table 1). These results show that an increase in monomer concentration the values of GR, GE, Rp, Rg and Rh get enhanced. It might be due to the higher availability of the monomer molecules in the vicinity of gelatin macroradicals. The more growing polymer chains of MMA are available which combine onto the reactive sites of gelatin. The similar things also happen in the grafting of butylacrylate onto gelatin (Joseph *et al* 1982) using H_2O_2 - ascorbic acid redox system. Grafting of acrylamide (Khan *et al* 1994) in the presence of persulfate is another example where same effects are also observed. The contents of nitrogen in product samples decrease with increasing concentration of monomer. This is probably due to the attachment of higher growing polymer chains of MMA onto reactive sites of backbone which drops the total conversion of nitrogen in graft copolymers. The values of GE indicates that maximum quantity of MMA gets grafted onto gelatin which supports the elemental analysis.

Table 2 contains the results of the influence of backbone concentration on GE, GR, Rp, N, Rg, Rh. These results reveal that GE is not changed with the increase or decrease in concentration of gelatin whereas the values of Gr, Rp and Rg decrease with in-

Table 1

Effect of monomer concentration on grafting of poly (MMA) onto gelatin using potassium persulphate as catalyst

S.no.	MMA in feed	Total conversion of MMA		Elemental analysis	Grafted MMA	GR	GE	Rate of polymerization x10^7 mole sec^{-1}		
	(g)	(g)	%	%N	(g)	%	%	R_p	R_g	R_h
1.	0.94	0.165	17.5	9.7	0.163	16.3	98.8	9.1667	9.0566	0.1111
2.	1.88	0.966	51.4	8.9	0.962	96.2	99.6	53.6667	53.4444	0.2227
3.	2.35	1.941	82.6	5.9	1.940	194.0	99.9	107.8330	107.7778	0.0555
4.	3.76	3.008	80.0	4.3	2.990	299.0	99.4	167.1110	166.1110	1.0000
5.	4.23	3.370	79.8	4.0	3.35	335.0	99.4	187.2220	186.1110	1.1110
6.	5.64	4.230	75.0	3.71	4.20	420.0	99.3	235.000	233.3330	1.6670

Gelatin, 1.0g; Temp, 60°C; Time, 30 min; Persulfate, 2.7g.

Table 2

Effect of backbone concentration on grafting of poly (MMA) onto gelatin using potassium persulphate as catalyst

S. No.	Gelatin in feed (g)	Total conversion of MMA (g)	Total conversion of MMA %	Elemental analysis %N	Grafted MMA (g)	GR %	GE %	Rate of polymerization x10^7 mole sec^{-1} R_p	R_g	R_h
7.	1.0	1.941	82.6	5.90	1.940	194.0	99.9	107.8330	107.7778	0.0552
8.	1.5	1.882	80.0	9.70	1.882	125.0	100.0	104.5550	104.5550	0.0000
9.	2.0	1.670	71.1	9.50	1.670	83.5	100.0	92.7778	92.7778	0.0000
10.	3.0	1.400	59.6	12.50	1.400	46.7	100.0	77.7778	77.7778	0.0000
11.	4.0	1.175	50.0	11.20	1.75	29.4	100.0	65.2778	65.2778	0.0000
12.	5.0	1.050	44.7	15.50	1.050	21.0	100.0	58.3333	58.3333	0.0000

MMA, 2.35g; Temp, 60°C; Time, 30 min; Persulfate, 2.7g.

Table 3

Effect of catalyst concentration on grafting of poly (MMA) onto gelatin using potassium persulphate as catalyst

S. No.	Persulfate (g)	Total conversion of MMA (g)	Total conversion of MMA %	Elemental analysis %N	Grafted MMA (g)	GR %	GE %	Rate of polymerization x10^7 mole sec^{-1} R_p	R_g	R_h
13.	1.0	0.9719	51.7	9.5	0.9719	38.9	100	53.9944	53.9944	0.0
14.	2.0	1.2152	64.5	10.3	1.2152	48.6	100	67.5110	67.5110	0.0
15.	3.0	1.2588	66.9	9.6	1.2588	50.3	100	69.9330	69.9330	0.0
16.	4.0	1.3748	73.1	11.3	1.3748	55.0	100	76.3780	76.3780	0.0
17.	4.5	1.3887	73.9	11.4	1.3887	55.6	100	77.1500	77.1500	0.0

MMA, 1.88g; Gelatin, 2.5g; Time, 30 min; Temp, 60°C.

crease in concentration of gelatin. This may be due to the fact that with higher gelatin concentration more graft radicals are formed which may interact and lead to termination. The lower concentration of gelatin favours more grafting as is obvious from the amount of grafted MMA onto gelatin (Table 2). These results also show that homopolymerization of MMA does not take place. The reactive sites of gelatin utilizes all growing polymer chains formed during the reaction.

Table 3 includes the observations obtained from the effect of catalyst concentration on grafting of MMA onto gelatin. These results indicate that the values of Gr, Rp and Rg increase with increase in concentration of persulfate.The enhancement of these values is due to more available active species produced by different concentration of catalyst in the system. The results of grafted monomer and value of GE show that the growing polymer chains of MMA are not left ungrafted.

Table 4 summarizes the data obtained from the effect of time onto grafting of MMA gelatin. At the initial stages of grafting reaction percentage of grafting was low but increased progressively with added time. This may be attributed to the fact that in the initial stages the primary radicals produced are used to activate the backbone polymer instead of homopolymerization is favoured. Further with greater intervals of time these primary radicals (growing polymer chains MMA) may form a redox system with reducing group present in the gelatin thereby increasing the percent grafting considerably (Nagabhushanam *et al* 1978). Similar results were also observed in the grafting of methyl acrylate on to gelatin with different initiators including persulfate (Kuwajima *et al* 1978) and grafting of polyvinyl alcohol with potassium persulfate (Ikada *et al* 1974). Grafting efficiency is maximum (100%) at all intervals of time. It is due to the utilization of all growing polymer species of MMA in grafting on gelatin. Further active centres of the gelatin also favour gelatin reactions at all concentration (Khan and Khalil 1995) and (Mohan *et al* 1989).

All the copolymer samples are light yellow solid substances and become powdery on crushing. They dissolve partially in 1% NaOH and swells in water showing uptake as 134.5%. When copolymer sample (expt.22) was heated at 100-120°C for 45 min it appeared to retain its original and colour. On heating at 160°C for 45 min the samples becomes light brown and loose its weight 10%. When the temperature is raised to 200-210°C it starts becoming dark brown within the same time period of 45 min and loses 0.5% its weight. This decomposed product was found insoluble in aqueous solution of NaOH

Table 4
Effect of time on grafting of poly (MMA) onto gelatin using potassium persulphate as catalyst

S. No.	Effect of time in (min)	Total conversion of MMA (g)	Total conversion of MMA %	Elemental analysis %N	Grafted MMA (g)	GR %	GE %	Rate of polymerization x10^{7} mole sec^{-1} R_p	R_g	R_h
18.	10	0.3729	15.9	10.4	0.3729	12.40	100	62.1500	62.1500	0.0000
19.	20	0.8592	36.6	12.9	0.8592	28.64	100	71.6000	71.6000	0.0000
20.	30	1.4152	60.2	9.8	1.4152	47.20	100	47.7330	47.7330	0.0000
21.	45	1.5078	64.2	8.2	1.5068	50.20	100	83.7670	83.3711	0.0000
22.	55	2.0990	89.3	7.5	2.0890	69.60	100	116.0550	116.0550	0.0556

Gelatin, 3.0g; MMA, 2.35; Temp, 60; Persulfate, 3.7g.

Table 5
A comparative study of solvent uptake shown by gelatin and (MMA-g-gelatin)

Solvent	% Solvent uptake	
	Gelatin	MMA-g-gelatin
Acetone	7	insoluble
Butyl acetate	20	44
Chloroform	0	219
Carbontetra cloride	19	127
D M F	88	464
Ethyl acetate	9	10
Ethyl alcohol	0	43
Methyl ethyl Ketone	8	45
Sodium hydroxide (1%)	soluble	Partially soluble
Xylene	90	123
Water	soluble	1345 (Cold)

and does not swell in the solvent given in Table 5. The change in weight is due to the distillation of PMMA grafted onto gelatin, whereas the change in colour might be due to intermolecular and intramoleculer rearrangement of reactive groups of gelatin in the copolymer chain. The colouration of copolymer by heat or radiation is usually attributed to the formation of a long chain conjugated double bonds (Jellinek 1962).

When the heterogeneous mixture of MMA, gelatin catalyst and water is heated at 60°C, three or four types of radicals are formed. The primary radicals produced by the decomposition of persulfate ($\dot{SO}_4$, $\dot{OH}$) are used in activating the reactive sites of gelatin and react with monomer to form monomer radicals. At the early stage of reaction, the formation of macroradicals of gelatin and monomer takes place and thus graft copolymerization proceeds. It is quite probable that with greater intervals of time, the primary radicals may form a redox system with reducing groups present in the gelatin there by increasing the percent of grafting considerably. Fundamentally, the behaviour of gelatin indicates an arrangement in which amino acid residues are joined together through peptides (amide) linkages - CH_2 - NH - CO. These are aliphatic (glycine, aniline etc.) aromatic (phenylalamine, tyrosine) sulfur containing (cystine, methionine) hetrocyclic (pyroline, hydroxypyroline) acidic (aspiratic acid, glumatic acid) and basic (arginine, lysine). Due to presence of these reactive groups at lower concentration of gelatin, percentage grafting is increased and reactive sites onto gelatin are not left unturned by monomer radicals and this hinders the homopolymerization of MMA. Table 1-4 provides evidences that homopolymerization of MMA could not take place, occasionally if more gelatin is available in the system, monomer radicals can not turn each activated side of gelatin, and gelatin radicals mutually terminate themselves forming gelatin macroradicals. This results in decrease in grafting ratio.

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