Studies on Graft Copolymerization of Acrylic Acid onto Collagen Hydrolysate as High Performance Retanning Agent for Leather

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Abstract: Graft copolymerization of acrylic acid and methacrylic acid onto collagen hydrolysate (obtained from tannery leather waste which comes from trimmings, shavings and splits by removing non protein part and keeping the protein part intact by enzyme hydrolysis) has been carried out by free radical polymerization using potassium persulphate / sodium meta bisulphite redox system at 80^0c for 3 hours under controlled polymerization technique. The percent grafting (PG) and grafting efficiency (GE) were found to be better when it was separated from the ungrafted homopolymer by solvent extraction method using deionized water. The percent grafting and grafting efficiency were calculated and the reaction parameters viz. monomer concentration, initiator concentration, backbone concentration and variation in temperature were found out. The collagen hydrolysate and its graft copolymers were characterized by FTIR, solid state NMR, TGA, amino acid analysis and particle size analyzer .The collagen hydrolysate grafted acrylic copolymer was applied as a retanning agent on leather, which showed an overall improvement in properties such as physical appearance, feel, fullness, softness, smoothness of surface and better nap on the flesh side of the leather. The collagen hydrolysate-g- poly (acrylic acid) and poly (methacrylic acid) polymer treated leather exhibit higher tensile strength, maximum load, grain crack strength and distension than those treated with market product. The polymer treated leather was characterized by scanning electron microscope (SEM), which showed better filling of the voids.

Key words: graft copolymerization; acrylic acid; collagen hydrolysate; retanning agent

1 Introduction

Hides come to the tannery as a byproduct of the meat industry. The tanning process, in turn, generated much greater quantities of byproducts and wastes than leather. One ton of wet salted yields only 200kg of leather but over 600kg of solid waste i.e. byproduct if a market could be found. In the International scenario,1,60,000 metric tons of chromium containing solid wastes i.e. chrome shavings are generated by the leather industry each year approximately[1,2]. About 700 kilotons of fleshings are generated from India annually. Land application for the disposal of chromium-containing tannery and other leather wastes had been widely practiced earlier[2b] but fewer landfills sites can be found everyday and cost transportation and disposal increased, which causes pollution and water contamination and other environmental problems. On looking at this issue closely, it is proposed to investigate and establish a dedicated facility for the research and developmental activity with the aim of developing a new polymeric materials using these solid waste leather and hence an attempt has been made in this investigation to study

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the graft copolymerization of acrylic acid monomers onto collagen hydrolysate as a novel retanning agent for leather.

This study comes under the heading utilization of waste into useful products and recycling the wastes and to develop wealth from waste. These leather wastes could be utilized as useful products for leather and allied industries.

2 Experimental

2.1 Materials

Collagen hydrolysate (Ch), obtained from tannery wastes, acrylic acid monomers, potassium persulphate, sodium metabisulphite were obtained from Merck India, Ethanol from SD fine chemicals and deionised water.

2.2 Preparation of collagen hydrolysate

Pre treated chrome shavings were treated with alkaline protease (2u/g) of *Aspergillus tamarii* and incubated in a shaker at 55°C for 4 h. After the incubation period the samples were filtered through Whatman No.1 filter paper to separate the unhydrolysed residue into collagen hydrolysate.

2.3 Synthesis of acrylic acid graft collagen hydrolysate

The grafting reactions were carried out in a 3 necked flask of 250 ml capacity. Required amount of collagen hydrolysate was placed in the reaction flask under N_2. The monomer acrylic acid (AA) was placed in one dropping funnel. The required amount of initiator (potassium persulphate) was dissolved in distilled water and placed in another dropping funnel. The grafting reactions were carried out at various temperatures. The monomer and initiator was added drop wise into the flask simultaneously over a period of 30 min. and the reaction was conducted for 3 h for complete conversion of the monomer to polymer.

2.4 Separation of ungrafted polymer from total polymer

The graft copolymer solutions obtained from the experiment were treated with excess amount of ethanol and double distilled water in 1:1 ratio dissolution which was used as non solvent. Then the precipitate was carefully filtered and washed repeatedly with distilled water to remove ethanol completely. The residue was dried in vacuum and weighed, from which the weight of the polymer formed (graft as well as homo) was determined. To calculate the amount of grafted polymer on the backbone, isolation of ungrafted homopolymer was carried out by solvent extraction (tumble bottle method) for a period of 72 h using deionized water as the solvent for ungrafted homopolymer. The % grafting and grafting efficiency were calculated by standard procedure[4].

3. Results and discussion

Graft copolymerization of acrylic acid onto collagen hydrolysate was carried out by free radical polymerization using $K_2S_2O_8/Na_2S_2O_5$ redox system at 70°C for 3 h to get complete conversion of the monomer to polymer (Table 1-3).

3.1 Effect of initiator concentration

The change in percentage grafting and grafting efficiency at varying concentrations of the initiator, $K_2S_2O_8$ at fixed concentration of acrylic acid and collagen hydrolysate at 70°C is given in the Table 1. The increase in percent grafting and grafting efficiency with persulphate concentration is due to generation of more primary radicals. The number of propagating radicals thereby increased the number of grafted sites on the backbone of collagen hydrolysate. At higher concentration, the efficiency decreases

since more number of monomer radicals formed, which gets terminated by coupling. At maximum grafting and grafting efficiency, the optimum initiator concentration is 18.49 $x10^{-3}$ mol/l.

Tab 1. Effect of initiator concentration

Sample	PPS Conc. x 10^{-3} (mol/L)	Wt. of grafted polymer (g)	Wt. of total polymer (g)	Percent grafting (PG)	Grafting efficiency (%)
1	3.699	3.2	3.7	38	90.04
2	9.247	4.8	5.32	44	89.43
3	18.49	5.6	6.14	56	91.20
4	27.74	5.4	5.96	50	76.21

AA (1.302 mol/L), $Na_2S_2O_5$ (0.00350 mol/L), Ch (10 g), time (3 h), temp(70ºC), vol (80 ml).

Tab 2. Effect of monomer concentration

Sample	Monomer concentration (mol/L)	Wt. of grafted polymer (g)	Wt. of total polymer (g)	Percent grafting (PG)	Grafting efficiency (%)
1	0.6938	3.2	3.70	32	86.48
2	1.0408	4.8	5.32	48	90.22
3	1.3877	5.6	6.14	56	91.20
4	1.7346	5.4	5.96	54	90.60

$Na_2S_2O_5$ (0.00350 mol/L), Ch (10 g), Time (3 h), Temp (70ºC), Vol (80 ml).

Tab 3. Effect of temperature

sample	Temperature (˚C)	Wt of grafted polymer (g)	Wt of total polymer (g)	Percent grafting	Grafting efficiency (%)
1	50	3.9	4.48	39	87.05
2	60	4.6	5.17	46	88.97
3	70	5.6	6.14	56	91.20
4	80	5.3	5.88	53	90.13
5	90	4.8	5.45	48	88.07

3.2 Effect of monomer concentration

The initial rate of grafting was found to increase with an increase in initial concentration of the monomer in the range of 0.6938 to 2.08515 mol/L keeping other parameter like backbone concentration, initiator concentration and temperature constant. The increase in the rate of grafting with increase in acrylic acid concentration may be due to the formation of more primary radicals which in turn may generate more grafting sites on collagen hydrolysate by abstraction of hydrogen atoms. But at higher concentration of monomer, the grafting efficiency decreases due to homopolymerization.

3.3 Effect of temperature

The percent grafting and grafting efficiency have been found to increase with increase in temperature from 50 to 70°C at constant concentration of monomer, initiator and backbone. The increase in grafting percentage and efficiency at higher temperature may due to increased number of collisions between the monomer and collagen hydrolysate molecules that results due to decrease in the viscosity of the medium. Formation and propagation of active sites on backbone polymer due to higher rate of generation of primary radicals. Enhancement in the activity of the monomer.

3.4 FT-IR spectroscopy

The FT-IR spectra of Ch and Ch-g- acrylic acid copolymer were recorded using Neicolet 20X spectrophotometer using KBr pellets. The FTIR spectrum of Ch (Figure 1a) shows a strong absorption band at 3342cm$^{-1,}$, 2958cm^{-1}, 1651cm^{-1} ,1450cm^{-1} ,and 1332cm^{-1} could be attributed to -NH stretching, asymmetric stretching of -CH, amide I, amide II and amide III respectively. The FTIR spectrum of Ch-g-PAA (Figure 1b) showed the presence of additional characteristic peak at 1720cm^{-1} show that the -COOH group of acrylic acid have grafted onto the backbone of collagen hydrolysate. It is a proof that grafting has taken place.

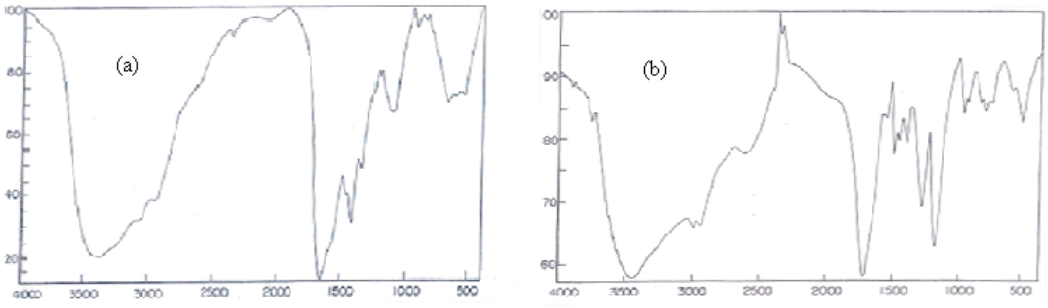

Fig1. FT-IR Spectra of (a) Collagen hydrolysate (b) Collagen hydrolysate-g-PAA

3.5 Solid state NMR spectroscopy

Figure 2 shows the ^{13}C high-resolution solid state CP MAS NMR spectra of collagen hydrolysate. These spectra shows high intense peak at 174.75ppm, which is due to amide carbonyl carbon. Many signals are seen in the range of 72.26-11.13ppm with varying intensities. It is known from earlier literature that collagen consists of glycine, proline, glutamic acid and aspartic acid predominantly this signals appreared in the region 72.26-11.13ppm supports the presence of these amino acid carbons. In the region 61.42-44.43ppm many carbons are resonating and in view of residual broadening of these signals are not well resolved however the overall spectral feature are in consistence in the structure of the collagen.

In the case of PAA, the ^{13}C Cross Polarized Magic Angle Spinning (CP-MAS) NMR, an intense broad signal is noticed at 170.30ppm and it is attributed to carbonyl of carboxyl group and another broaden and intense peak 40.4ppm is noticed due to backbone carbons. A shoulder signal at 37ppm is seen after the close examination of peak at 49.4ppm, this spectrum is very much in consistence with the structure of the polymer. The solid state ^{13}C NMR, Ch-g-PAA is shown in the Figure 2c. Interestingly this spectrum shows signal that are characteristic to PAA. Though the sample is blend of collagen hydrolysate and PAA, the appearance of signals pertaining to PAA alone indicated that the amount of Ch in the

sample is low in concentration. .This indicated that by increasing the appropriate amount of Ch in PAA mixture may show peaks related to Ch.

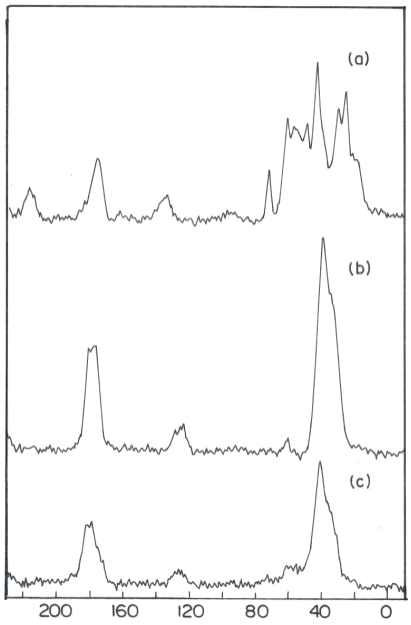

Fig. 2 Solid state NMR of (a) Collagen hydrolysate (b) PAA and (c) Collagen hydrolysate-g-PAA.

3.6 SEM

The control leather sample shows clear holes on the surface (Figure 3a). The Polymer treated experimental leather sample shows deposition of Ch-g-PAA, which indicated the size of the holes and thus increased the fullness of the leather. Control leather sample cross section shows very loose fibers whereas in the experimental leather sample, we can see solid block, collagen fiber bundles are interspersed with polymer particles. This clearly indicates that Ch-g-PAA copolymer has filled the pores of the leather to a greater extent.

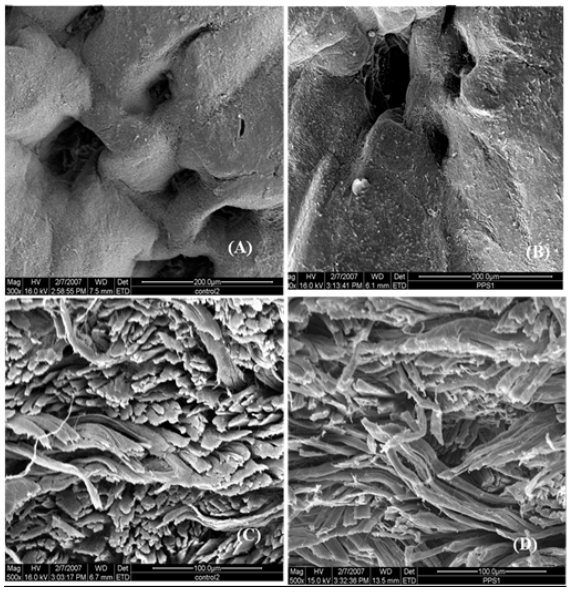

Fig.3 SEM of (A) Control Leather (Surface) (B) Ch-g-PAA (Surface) (C) Control Leather (Cross sectional view) (D) Ch-g-PAA (Cross sectional view).

3.7 Physical testing of leathers treated with collagen hydrolysate-g-PAA

Treated leathers showed an outstanding performance with respect to control. The results (Table 4) reveal number of interesting features. The collagen hydrolysate-g-poly (acrylic acid) graft polymer treated leather exhibit higher tensile strength, maximum load, grain crack strength and distension than those treated with market product.

Tab 4. Evaluation of physical properties of leathers

S.No.	Tensile strength (kg/cm^2)	% Elongation	Tear strength (N/mm)	Load for crack (kg)	Distension
1	201.85	67.92	60.46	24	9.77
2	208.59	71.92	50.51	32	13.36
3	221.53	65.17	54.43	39	13.74
4	280.23	67.83	49.36	32	12.64
5	198.95	68.42	78.38	21	10.67
6	272.08	85.83	56.97	26	10.58

Samples 1, 3 & 5 are marked product treated leather. Samples 2, 4 & 6 are Ch-g-(PMAA) treated leathers.

Conclusion

Graft copolymerization of acrylic acid onto collagen hydrolysate was carried out by free radical polymerization technique. The yield was better when it is separated from the ungrafted homopolymer by selective solvent extraction method. This work resulted in utilization of waste into useful products and recycling the wastes and wealth from waste. The collagen hydrolysate–g–poly(methacrylic acid) treated leather exhibit higher tensile strength. The extent of percentage grafting and grafting efficiency within the range examined seems to play a key role in this investigation.

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