

Synthesis and Characterization of Mica-Vinyl Graft Copolymers*

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Synopsis

Graft copolymerization of methyl methacrylate (MMA) and acrylonitrile (AN) onto mica was carried out by the ceric ion method. Experiments were carried out both in the presence and absence of oxygen; oxygen has some detrimental effect in the grafting of AN onto mica. Mica-vinyl graft copolymers were characterized using infrared spectra after purifying the crude graft copolymers for the removal of the occluded homopolymers. The percent grafting, grafting efficiency and the ratio of R_g/R_h were determined. Mica-graft copolymers were saponified by treating with aqueous alkali to convert the nitrile groups to carboxyl groups with a view to utilize these groups for coupling to collagen substrates. Since in a chrome-tanned leather there are available coordination sites due to fixed chromium, the mica-graft copolymer could get bound, thereby resulting in a well filled-up leather.

INTRODUCTION

A large number of minerals constituting the body of earth are characterized by a high polymeric nature; however, polymer chemists have paid very little attention to this potentially vast source of new polymeric materials. In the field of present day polymer technology, minerals including mica are used mostly as inert fillers in plastics, rubbers, and paints. Among the polymeric materials, the micas have a very appropriate structure to build up new composite polymeric materials. These sheetlike minerals of aluminum with varying proportions of alkalis, iron oxides, and magnesia are extremely complex and variable in chemical composition. The principal members of the mica group are (i) muscovite, (ii) phlogophite, and (iii) biotite. The common mica muscovite is the most valuable of all the micas because of its economical importance and technology significance stemming from combinations of the properties such as perfect cleavage, flexibility, elasticity, toughness, resilience, translucent to transparency, low electrical and heat conductivity, and a very high dielectric strength.

Muscovite occurs in igneous rocks of almost all kinds, and it is somewhat harder than phlogophite. Both contain water, present as water of constitutions, which is expelled only by heating to a very high temperature. Mica is virtually unaffected by heat, solvents, water, acids (except hydrofluoric and sulfuric), and alkalis. Mica is marketed in the form of block mica or film mica and only about 15% of the mica produced is available in the form of block mica and splittings. The rest is waste and scrap, and it is utilized after grinding to powder for a variety

* Paper presented at the International Symposium on New Frontiers in Polymer Science and Polymer Applications, 7-11 January 1980, Madras, India.

of purposes such as roofing composition, paints, etc. The world's chief muscovite mica deposits of commercial importance occur in three major states of India: Andhra Pradesh (Nellore District), Bihar, and Rajasthan. About 80% of the world's requirements for sheet mica are supplied by India.

Waste scrap mica is utilized after reducing to powders by dry and wet grinding. In the dry grinding process, mica is washed free of adhering grit and clay, dried, and ground in high-speed hammer mills or pulverizers of the disintegrator type. Dry ground mica of 20, 30, or 40 mesh is used for various purposes. One of the main uses of mica is its filling property. It is used as the filling agent for phonograph records, ingredient explosives, cleansers, plastics, and rubber. In order to enhance the usefulness of mica, we developed a method whereby polymer chains become chemically attached to mica surface. In this paper, we report the synthesis and characterization of mica-vinyl graft copolymers. The grafted products were then utilized at various stages of the manufacture of leather. These polymer-mica compositions may also find a top place as fillers in resins because of their compatibility with the resins.

EXPERIMENTAL

Mica

Mica powder (waste scrap mica of particle size $5\ \mu\text{m}$), an indigenously available commercial product, was used as obtained in all the experiments.

Monomers

Methyl methacrylate (MMA) and acrylonitrile (AN) were obtained from BDH. MMA and AN were purified by washing with 6–8% sodium hydroxide solution and AN was further washed with a 3% orthophosphoric acid solution to remove the inhibitor completely. After this treatment, the monomers were washed with distilled water to remove the alkali completely and dried over anhydrous calcium chloride overnight. The monomers were then distilled under vacuum and stored in a refrigerator.

Chemicals

Ceric ammonium nitrate [$\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$] (Puriss, Fluka) was used without further purification. Methanol, acetone, and *N,N*-dimethylformamide used were of Analar grade.

Preparation of Initiator Solution

The required quantity of ceric ammonium nitrate (CAN) dissolved in 1*N* nitric acid was used. Fresh solutions were prepared for each experiment.

Procedure

Graft copolymerization reactions were carried out in a round-bottomed, three-necked flask of 100-mL capacity fitted with a water-sealed glass stirrer,

TABLE I
Grafting of Vinyl Monomers to Mica^a

Sample No.	Graft copolymer	Monomer	Atmosphere	Conversion of monomer, %		
				To graft	To homo-polymer	Total
1	Mi-g-PMMA	MMA	Air	5.505	14.848	20.353
2	Mi-g-PMMA	MMA	N ₂	10.345	28.690	39.035
3	Mi-g-PMMA	MMA	Air	5.896	5.552	11.448
4	Mi-g-PMMA	MMA	N ₂	11.082	8.446	19.528
5	Mi-g-PAN	AN	Air	3.097	47.555	50.652
6	Mi-g-PAN	AN	N ₂	11.600	27.047	38.647
7	Mi-g-PAN	AN	Air	2.640	46.143	48.783
8	Mi-g-PAN	AN	N ₂	12.180	41.073	53.253

^a (Reaction Time: 3 h) Temperature of grafting for serial numbers 1, 2, 5, and 6 is 30° C and for 3, 4, 7, and 8, 40° C. Monomer concentration: MMA = 2.4 mol/L; AN = 4.5 mol/L. Initiator concentration: CAN = 0.04 mol/L.

a gas inlet tube, and a thermometer. All grafting experiments were carried out while stirring at required temperatures. In a typical experiment, 2 g of mica powder was dispersed in 25 mL of distilled water, and the polymerization was carried out in both the presence and absence of oxygen. In the case of an oxygen-free atmosphere, nitrogen gas was bubbled through the reaction mixture to expel the air inside the flask for 30 min; then the required amount of initiator solution was added, followed by the desired amount of monomer. The reaction was allowed to proceed for 3 h, at the fixed temperature. The graft copolymers were separated by filtration, using weighed sintered crucibles. The grafted products were washed and dried. The experimental conditions of the graft copolymerization are summarized in Table I.

Analysis of the Grafted Products

The dried grafted products were extracted for 72 h, with two changes of fresh solvents for the homopolymers at room temperature using the tumbled bottle method. The extraction was continued until no precipitate was obtained from the extracted solution with methanol. The percent grafting in the final products were determined gravimetrically. The percent grafting, the efficiency of grafting, the percent conversion of monomer, and rate of grafting, etc., were calculated using the following equations:

$$\text{Grafting, \%} = \frac{(\text{wt of graft copolymer}) - (\text{wt of mica})}{\text{wt of mica}} \times 100 \quad (1)$$

$$\text{Grafting efficiency, \%} = \frac{\text{wt of grafted polymer}}{\text{wts of grafted polymer and homopolymer}} \times 100 \quad (2)$$

Conversion of monomer, %:

$$\text{To graft, \%} = \frac{\text{wt of grafted polymer}}{\text{wt of monomer charged}} \times 100 \quad (3a)$$

$$\text{To homopolymer, \%} = \frac{\text{wt of occluded homopolymer}}{\text{wt of monomer charged}} \times 100 \quad (3b)$$

$$\text{Total conversion, \%} = \frac{\text{wts of polymer grafted and homopolymer}}{\text{wt of monomer charged}} \times 100 \quad (3c)$$

R_p = rate of polymerization

$$= \frac{(\text{wt of total yield}) - \text{wt of backbone}}{\text{mol wt of monomer} \times \text{reaction period (in s)} \times \text{vol of reaction system}} \times 1000 \quad (4a)$$

R_h = rate of homopolymerization

$$= \frac{\text{wt of homopolymer extracted from the crude graft copolymer}}{\text{mol wt of monomer} \times \text{reaction period (in s)} \times \text{vol of reaction system}} \times 1000 \quad (4b)$$

$$\begin{aligned} R_g &= \text{rate of grafting} \\ &= R_p - R_h \end{aligned} \quad (4c)$$

Viscosity of the Extracted Homopolymers

The homopolymers were extracted with suitable solvents from the mica-vinyl grafted products, dried *in vacuo*, and powdered. Poly(MMA) (PMMA) and poly(AN) (PAN) (known weights) were dissolved in benzene and dimethylformamide, respectively. The reduced viscosities at several concentrations were measured using an Ubbelohde dilution viscometer at 30° C for PMMA and at 25° C for PAN. The intrinsic viscosity $[\eta]$ (in dL/g) was then obtained by extrapolation of a plot of η_{sp}/C vs C to infinite dilution.

Relationships used for the evaluation of molecular weights (M) were those due to Fox et al.¹ for PMMA at 30° C in benzene:

$$[\eta] = 8.69 \times 10^{-5} \overline{M}_v^{0.76} \quad (5)$$

and due to Cleland and Stockmayer² for PAN at 25° C in dimethylformamide:

$$[\eta] = 2.43 \times 10^{-4} \overline{M}_v^{0.75} \quad (6)$$

Infrared Spectra

To provide the proof of grafting, the infrared (IR) spectra of the pure mica and the grafted mica were measured with a Perkin-Elmer model 337 grating infrared spectrophotometer, using potassium bromide (KBr) pellets (500 mg) containing 2–6 mg of the powdered polymers. The IR spectra of the saponified samples of the acrylonitrile-grafted mica was also taken to provide the evidence for the conversion of CN groups to carboxyl and carboxamide groups.

Saponification of Mica-Polyacrylonitrile Graft Copolymers

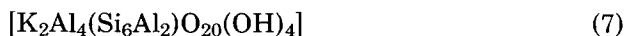
Gugliemelli and co-workers³⁻⁶ have shown that the polyacrylonitrile portion of starch polyacrylonitrile graft copolymers can be saponified with alkali to give

carboxylate- and carboxyamide-containing starch graft copolymers. Using a similar procedure, we have saponified 1 g of mica-polyacrylonitrile graft copolymer with 20 mL of 1*N* sodium hydroxide solution for 1½ h at 80° C. The resulting product was filtered, washed with distilled water, and dried. The powdered dried product was then incorporated into leather.

DISCUSSION

Structure of Mica

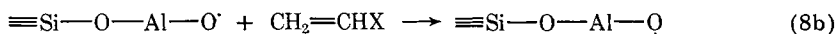
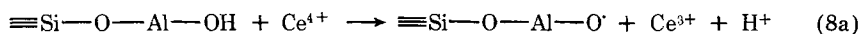
Mica is marketed in the form of film mica. Only about 15% of mica produced is available in the form of block mica and splittings. The rest is waste and scrap and is utilized after grinding to powder. The mica structure is based on sheet-linked (Si,Al)O₄ tetrahedrons (polysilicates) (Fig. 1), which accounts for the characteristic cleavage into sheets. Optically, most micas are biaxial and levorotatory with moderate birefringence. The mica group is structurally complex. The chemical formula of the muscovite is given by



The muscovite mica group has been used in our studies for grafting of vinyl monomers using ceric ion initiation technique.

Mechanism of Graft Copolymerization: Grafting onto Mica

Ceric salts are capable of oxidizing a large number of organic compounds such as alcohols, aldehydes, amines, and thiols and producing free radicals which may initiate polymerization. The redox method with ceric salts particularly ceric ion-alcohol systems has been used for initiation of polymerization and grafting of vinyl monomers by a number of investigators. It has been shown that ceric ion complexes reversibly with alcohols and glycols and the dissociation of the complexes is the rate-determining step. It was presumed by a similar mechanism that the hydroxyl group present in the mica may react with the ceric ion and liberate a free radical on the mica structure and graft polymerization will take place on these free radicals giving vinyl branches on the mica backbone as given in the following equation:



The experimental data indicated that the presence of mica in the polymerization system leads not only to grafting but also to the initiation of homopolymerization. In the ceric ion mica-MMA or AN-water systems, homopolym-

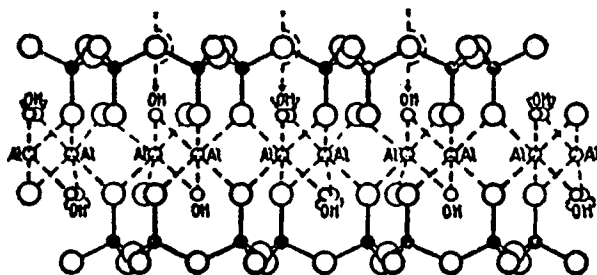


Fig. 1. Schematic structure of mica. (○) oxygen; (●) silicon; (○) aluminum.

erization may probably be taking place through a hydrogen atom transfer between the monomer and the mica-free radicals involving water in the system. However, another mechanism of formation of homopolymer could not be ruled out. There is a good possibility of termination of growing free radicals during grafting to take place through conversion of Ce^{4+} to Ce^{3+} . Since no studies have been carried out on the kinetics of the grafting reaction, terminations by coupling and disproportionation could not be eliminated.

Nitrogen Atmosphere versus Air during Grafting of Vinyl Monomers to Mica

In Table I, the percent monomer conversions to graft, to homopolymer, and to total conversion are given. From the table, it can be seen that in the case of MMA, the rate of conversion is higher in the presence of nitrogen as compared with the values in the presence of air. However, the rate of conversion to homopolymer is higher at 30° C in the presence of both air and nitrogen. At 40° C, the total conversion is lower as compared to 30° C and the rate of conversion to homopolymer is almost equal to that of the graft copolymer.

In the case of acrylonitrile, the effect of oxygen is very predominant. The formation of homopolymer is very much higher than grafting in the presence of oxygen on the contrary; in the presence of nitrogen the rate of conversion to grafting is higher even though a substantial homopolymer has also been formed. The effect of temperature could not have much influence on the total conversion of monomer to polymer.

Characterization of Mica-Vinyl Graft Copolymers

Composition of Mica-Vinyl Graft Copolymers

The analysis of crude mica-vinyl graft copolymers are given in Table II. From the table it can be seen that the amount of grafted polymers were lower than that of the occluded homopolymers. The presence of nitrogen has altered the amount of grafted polymer more in the case of acrylonitrile than methyl methacrylate. In the case of acrylonitrile, there was a substantial decrease in the grafted polymer due to the presence of oxygen. Since it could not be possible to separate unreacted mica from the crude graft copolymer, the percent mica given in Table II indicates the amount of mica present in the crude graft copolymer.

TABLE II
Analysis of Crude Mica-Vinyl Graft Copolymers

Sample No.	Graft copolymer	Total yield, g	Composition of the crude mica graft copolymers		
			Homopolymer, %	Grafted polymer, %	Mica, %
1	Mi-g-PMMA	3.221	27.657	10.254	62.089
2	Mi-g-PMMA	4.342	39.644	14.295	46.061
3	Mi-g-PMMA	2.687	12.397	13.168	74.435
4	Mi-g-PMMA	3.172	15.988	20.964	63.048
5	Mi-g-PAN	5.039	56.623	3.687	39.690
6	Mi-g-PAN	4.319	37.575	16.116	46.309
7	Mi-g-PAN	4.927	56.182	3.215	40.603
8	Mi-g-PAN	5.195	47.436	14.067	38.497

Grafting Efficiency and Ratio of R_g/R_h of Mica-Vinyl Graft Copolymers

The percent grafting was found to be higher in the presence of nitrogen than in the presence of air for both monomers, i.e., methyl methacrylate and acrylonitrile. This can be attributed to the higher conversion of monomer in the presence of nitrogen. However, the efficiency of grafting and the ratio of R_g/R_h were found to be the same for MMA in both the presence and absence of oxygen (Table III). The efficiency of grafting and the ratio of R_g/R_h are considerably decreased in the presence of oxygen for acrylonitrile grafting.

Molecular Weight and Intrinsic Viscosity Data of Extracted Homopolymers from Mica-Vinyl Graft Copolymers

Since it was not possible to digest the inorganic polymer backbone such as mica, the molecular weight of the occluded homopolymer was estimated with an assumption that the chain lengths of the homopolymer are equal to the grafted branches. Previous investigators⁷⁻⁹ working with different grafting systems have also suggested such a possibility. The molecular weights of PMMA was found to be on the order of $(50-100) \times 10^4$ and in the case of PAN it was found to be $(15-22) \times 10^4$ (Table IV).

TABLE III
Grafting Efficiency and Ratio of R_g/R_h of Mica-Vinyl Graft Copolymers^a

Sample No.	Graft copolymer	Grafting, %	Grafting efficiency, %	R_g/R_h^a
1	Mi-g-PMMA	16.500	27.047	0.371
2	Mi-g-PMMA	31.036	26.502	0.361
3	Mi-g-PMMA	17.690	51.507	1.062
4	Mi-g-PMMA	33.245	56.747	1.312
5	Mi-g-PAN	9.290	6.114	0.065
6	Mi-g-PAN	34.800	30.016	0.429
7	Mi-g-PAN	7.920	5.412	0.057
8	Mi-g-PAN	36.540	22.872	0.297

^a R_g = rate of grafting; R_h = rate of homopolymerization.

TABLE IV
Molecular Weight and Intrinsic Viscosity Data of Extracted Homopolymers from Mica-Vinyl Graft Copolymers

Sample No.	Graft copolymer	PMMA extracted by benzene		Sample No.	Graft copolymer	PAN extracted by DMF	
		$[\eta]$ in benzene dL/g	$\bar{M}_n \times 10^{-4}$			$[\eta]$ in DMF, dL/g	$\bar{M}_n \times 10^{-4}$
1	Mi-g-PMMA	2.5	73.79	5	Mi-g-PAN	1.925	15.78
2	Mi-g-PMMA	3.15	99.77	6	Mi-g-PAN	2.2	18.88
3	Mi-g-PMMA	—	—	7	Mi-g-PAN	2.5	22.28
4	Mi-g-PMMA	1.85	49.66	8	Mi-g-PAN	2.40	21.18

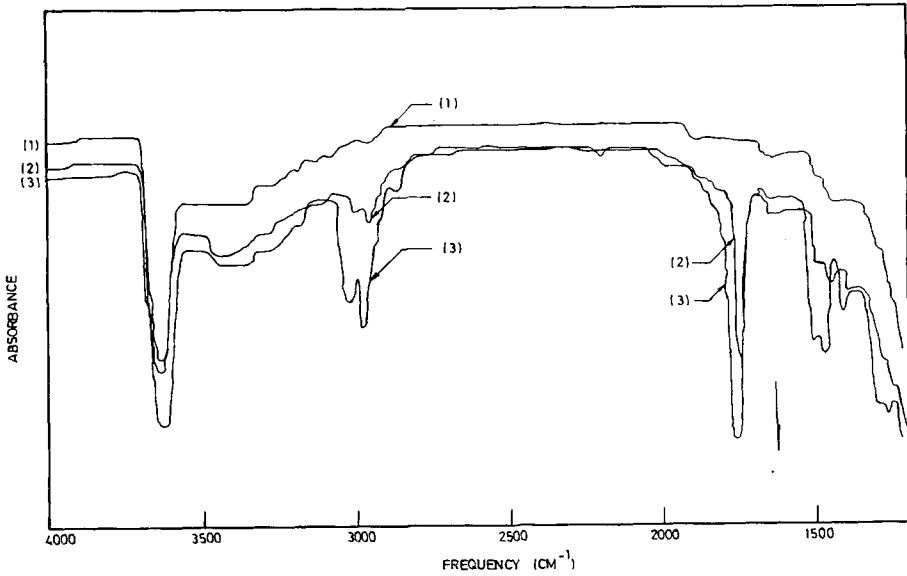


Fig. 2. Infrared spectra of untreated mica and poly(methyl methacrylate)-grafted mica: (1) untreated mica; (2) grafted mica (air); (3) grafted mica (N₂).

Infrared Spectra of Graft Copolymers

Proof of grafting has been provided by IR spectra of representative samples of graft copolymers. In Figure 2, the IR spectra of untreated mica and poly-(methyl methacrylate)-grafted mica are given. The IR spectrum of pure mica shows the presence of hydroxyl groups at 3625 cm^{-1} , whereas the IR spectrum of mica-PMMA graft copolymer showed characteristic absorption bands of

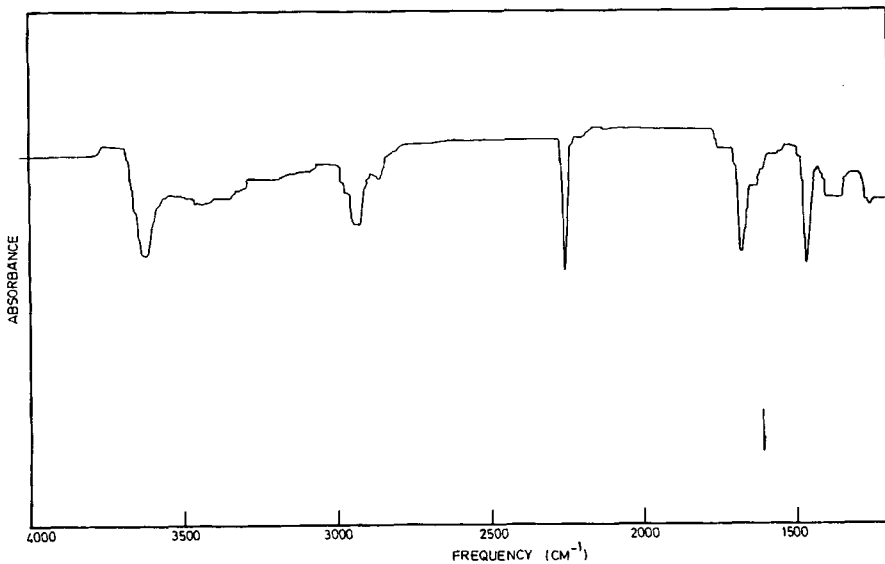


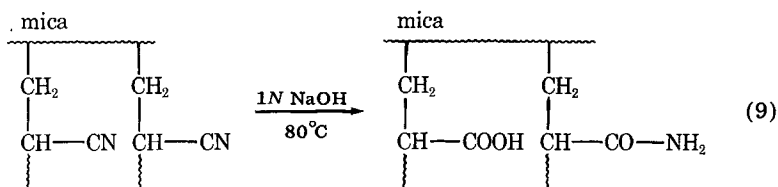
Fig. 3. Infrared spectrum of polyacrylonitrile-grafted mica.

PMMA at 3050, 1730, 1450, and 1240 cm^{-1} in addition to the hydroxyl groups of mica at 3625 cm^{-1} .

The IR spectra of mica-PAN graft copolymers (Fig. 3) shows the presence of the characteristic band for PAN (2250 cm^{-1}) and the hydroxyl groups due to mica (3625 cm^{-1}). The IR spectra clearly indicated the evidence for grafting of PMMA and PAN onto mica.

Saponification of Mica-PAN Graft Copolymers

Mica-PAN graft copolymers were saponified using sodium hydroxide solution using the method of Gugliemelli et al.³⁻⁶ to improve the usefulness of the grafted products in the manufacture of leather. The saponified grafted products with alkali is expected to give carboxylate- and carboxylamide-containing mica graft copolymers, as shown in the following:



The IR analysis of the saponified product actually (Fig. 4) showed the absence of nitrile absorption (2250 cm^{-1}) and the presence of carboxyl bands (1720 cm^{-1}) due to both amide and carboxylic acid.

Application of the Mica-Vinyl Graft Copolymers in the Manufacture of Leather

Mica-vinyl graft copolymers were saponified, as explained earlier, by treating with aqueous alkali to convert the nitrile groups to carboxyl groups for coupling

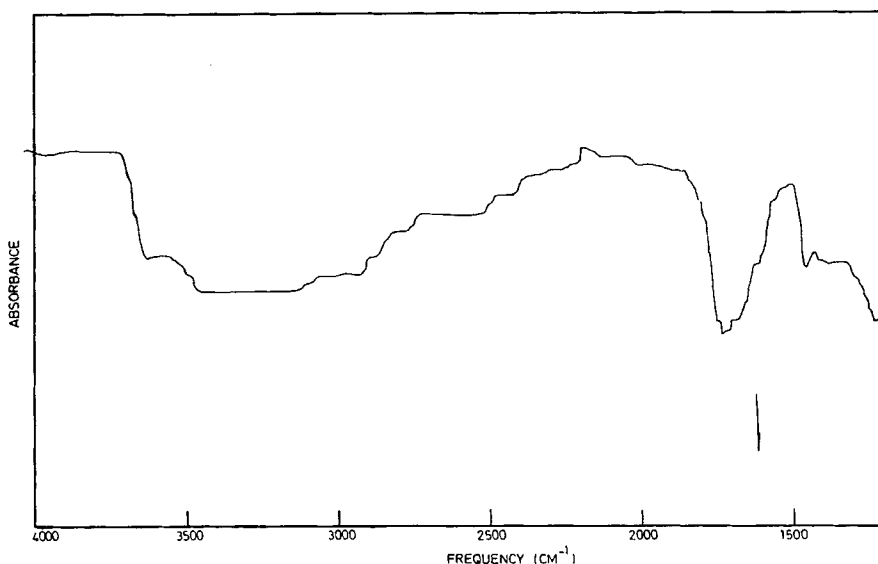


Fig. 4. Infrared spectrum of saponified mica-polyacrylonitrile graft copolymer.

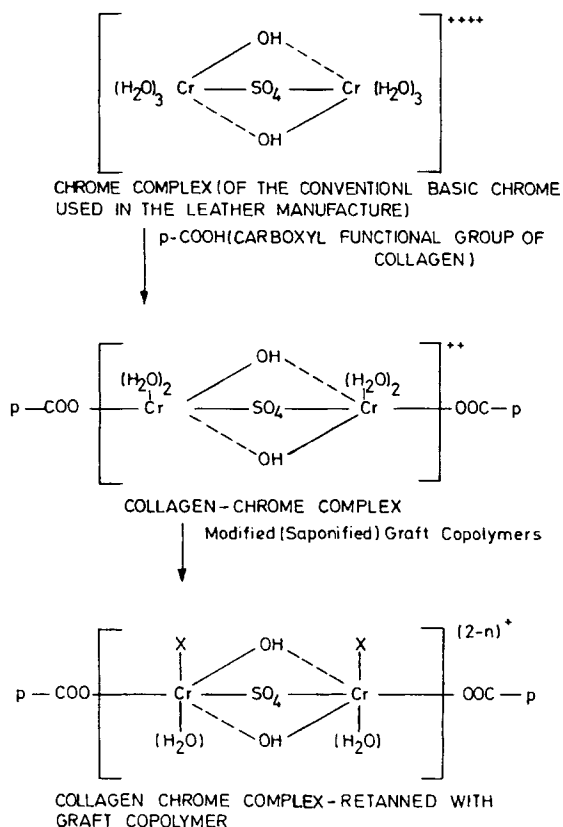


Fig. 5. Scheme for the complex formation of mica-graft copolymer with chrome-tanned collagen, where X^{n-} = modified mica-acrylonitrile polymer and $n = 1$ or > 1 .

to collagen substrates. The aqueous dispersion of saponified mica-vinyl graft copolymer was then used for incorporation at various stages in the manufacture of leather to improve the physicochemical and mechanical properties of leather.

The use of products based on polyacrylic and methacrylic acids for tanning and for improved filling of leathers is well known. The mica-vinyl graft copolymers, which have a structure as shown in eq. (9), possess a functional carboxyl group. It may be reasonably expected that such a compound can form coordination complexes with chrome. Since in a chrome-tanned leather there are available coordination sites due to fixed chromium, the mica-graft copolymer could get bound (Fig. 5), thereby resulting in a well-filled-up leather. It is also expected that such filling up by high-molecular-weight substances (polysilicates) effect a lubricating action also. Further, the treated leathers showed overall improvement in properties such as physical appearance, feel, fullness, softness, smoothness of grain surface, and a better nap on the flesh side of treated leather pieces. The results of the various chemical and physicochemical properties will be published elsewhere.

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Received July 18, 1980

Accepted March 18, 1981