Effect of Chemical Crosslinking on Film and Fiber Properties of Some Amorphous Vinyl Polymers

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INTRODUCTION

It has long been known that crosslinking imparts insolubility and infusibility to polymeric films or fibers.[1] Crosslinking may be brought about by several methods, including irradiation and heating techniques. In this work, chemical crosslinking of amorphous vinyl copolymers containing acryloyl chloride units was obtained by treatment with diamines. The effects of such crosslinking on film and fiber properties were determined.

DISCUSSION

The acryloyl chloride copolymers[2–5] investigated in our work were made by slow bulk polymerization. Crosslinking was effected by reacting the carboxylic acid chloride groups with diamine to form amide linkages between polymer chains. Care was taken to avoid premature crosslinking or hydrolysis of the acid chloride groups.

Estimation of Crosslinks

In estimating the degree of crosslinking in acryloyl chloride copolymers, it was assumed that the acid chloride groups were randomly distributed along the polymer chain, that none were lost by hydrolysis, and that the primary chains were infinitely long, that is, that the terminal chain ends could be neglected.

The total per cent nitrogen minus two times the titratable per cent nitrogen (to take account of diamine reacted at only one end) equals the per cent crosslinked nitrogen. The average molecular weight per crosslink M_c is, then, $2 \times 14 \times 100$ or 2800, divided by the per cent crosslinked nitrogen. Examination of results in Table I reveals that, in crosslinking methyl acrylate/acryloyl chloride fibers with aqueous ethylenediamine, the calculated degree of crosslinking increased as the per cent acryloyl chloride in the polymer increased.

TABLE I
Analysis of Diamine-Crosslinked Methyl Acrylate/Acryloyl Chloride Copolymers

Ratio MA/AC[a]	Crosslinking diamine	Total nitrogen, %	Titratable nitrogen, %	M_c[b]
95/5	Ethylene	1.12	0.04	2690
90/10	Hexamethylene	1.13	0.19	3730
90/10	Ethylene	1.90	0.05	1550
70/30	Ethylene	5.58	0.58	637

[a] Ratio by weight of methyl acrylate (MA)/acryloyl chloride (AC) as charged in polymerization.
[b] Molecular weight per crosslink.

Tensile Properties

All the polymers investigated in our work had low softening points and low moduli and were highly elastic and completely amorphous. Fibers and films of these polymers were not dimensionally stable, especially at temperatures above room temperature. It was expected that crosslinking would raise the softening point and modulus, reduce elongation, and increase the form stability of the crosslinked fibers and films. These predicted property changes upon crosslinking were observed in our experimental results.

Increasing amounts of acryloyl chloride in the copolymer led to increased crosslinking, as shown by values of M_c. In turn, the observed changes in physical properties of films and fibers were seen to vary in the predicted direction with acryloyl chloride content of the copolymers and with M_c (see Tables II–IV).

Tenacity and tensile strength at room temperature decreased slightly (based on tenacity at the break) on crosslinking compared to uncrosslinked controls. However, in all cases elongation drastically decreased, and initial modulus markedly increased with increased crosslinking. This also

TABLE II
Tensile Properties of Dry-Spun Fibers

		At 21°C.				At 80°C.			
		Tenacity, g./den., based on			Initial modulus M_i, g./den.	Tenacity, g./den., based on			Initial modulus M_i, g./den.
Fiber[a]	Draw, %	Original denier	Break denier	Elongation, %		Original denier	Break denier	Elongation, %	
EMA	Undrawn	0.4	0.4	4	14	0.1	0.75	643	0.35
	270	0.6	0.8	33	17	0.25	1.5	494	1.4
EMA/AC (83/17)									
Not crosslinked	Undrawn	0.2	0.5	177	7	0.02	0.06	189	0.01
	260	0.2	0.3	36	14	0.04	0.09	116	0.01
Crosslinked[b]	Undrawn	0.3	0.3	7	14	0.1	0.1	7	6.4
	260	0.4	0.4	8	17	0.3	0.35	15	10

[a] EMA = poly(ethyl methacrylate); EMA/AC = ethyl methacrylate/acryloyl chloride 83/17 copolymer.
[b] Crosslinked with ethylenediamine.

TABLE III
Tensile Properties of Wet-Spun Crosslinked Fibers[a]

MA/AC Fiber[b]	Crosslinking agent	Tenacity, g./den., based on		Elongation, %	Initial modulus M_i, g./den.	Work recovery,[c] %	Tensile recovery,[c] %	Zero strength temp., °C.
		Original denier	Break denier					
95/5	Ethylenediamine	0.09	0.45	438	0.04	3	5	111
90/10	Hexamethylenediamine	0.11	0.45	359	0.13	3	5	140
90/10	Ethylenediamine	0.14	0.33	138	1.2	3	5	162
70/30	Ethylenediamine	0.22	0.33	49	6.3	21	55	250

[a] All yarns were spun from acetone solution and were not drawn.
[b] MA/AC = methyl acrylate/acryloyl chloride copolymer of the stated compositions.
[c] From 3% elongation.

TABLE IV
Tensile Properties of Crosslinked Films[a]

MA/AC Film[b]	Tensile strength, psi	Tenacity, g./den., based on		Elongation, %	Initial Modulus,	
		Original denier	Break denier		psi	g./den.
95/5	883	—	—	674	764	—
92.5/7.5	1604	0.11	0.44	316	7,700	0.52
90/10	2172	0.14	0.33	129	19,590	1.3
87.5/12.5	4870	0.30	0.35	16	287,000	17.8
85/15			Too brittle to test			

[a] All films were crosslinked with ethylenediamine.
[b] MA/AC = methyl acrylate/acryloyl chloride copolymer of specified compositions.

was especially noticeable at 80°C. where uncrosslinked fibers were extremely weak, plastic, and of very low initial modulus. At this temperature, the tenacity of drawn crosslinked fibers was perceptibly higher than that of uncrosslinked controls (see Table II).

Work and tensile recoveries increased after a certain level of crosslinking was reached. Zero strength temperature, a measure of the highest temperature at which tensile properties of a fiber or film are detectable, increased markedly with an increase in crosslinking. These were further indications of the preparation of more useful and form-stable materials.

Shrinkage

The shrinkage (the original length minus the final length after boil-off, divided by the original length) of both drawn and undrawn films and fibers decreased with increased crosslinking. Uncrosslinked, drawn fibers and films have a shrinkage of 50–70% (see Table V). Fibers and films drawn to an equal degree, but well crosslinked in this stretched condition before boil-off shrank only 10%. The greater was the amount of acryloyl chloride in the copolymer, the more the crosslinking, the less the shrinkage, and the more the form stability.

TABLE V
Shrinkage Properties of Films and Fibers[a]

| | Draw, %[b] | Shrinkage, % | |
		Uncrosslinked	Crosslinked[c]
EMA/AC Film[d]			
94/6	300	70	66
89/11	200	51	23
67/33	300	64	22
60/40	200	52	10
EMA Fiber[d]			
	Undrawn	1	—
	270	49	—
EMA/AC Fiber[d]			
89/11	200	53	23
83/17	Undrawn	−33[e]	1
	260	30	10
S/AC Fiber[d]			
90/10	Undrawn	51	36

[a] Samples were boiled off in water for 5 min. with length before and after boil-off used to determine shrinkage.

[b] Amount of shrinkage and its stabilization depends partially on amount of draw. The more the draw, the more the shrinkage.

[c] Samples crosslinked in ethylenediamine after drawing.

[d] EMA = poly(ethyl methacrylate); EMA/AC = ethyl methacrylate/acryloyl chloride copolymer, composition derived from chlorine analysis on as-spun fibers and films; S/AC = styrene/acryloyl chloride copolymer.

[e] Yarn elongated on boil-off.

Conclusions

Experimental results show that the amorphous vinyl polymers containing acryloyl chloride, when made into films and fibers, have no form stability and little utility until after crosslinking. These crosslinked fibers and films have properties approaching those of fibers made from crystalline or rigid polymers. The use of homopolymer control yarns as well as uncrosslinked copolymer yarns showed that the observed effects on elongation and initial moduli result from crosslinking, and not from any copolymer effect. X-ray diffraction studies

of the drawn, crosslinked films showed them still to be completely amorphous and unoriented, so the reduction of shrinkage observed with them is due to the chemical crosslinking carried out.

The chemical crosslinking of amorphous polymers containing reactive sites has been shown to be a potent and straightforward means to attain improved physical properties. Copolymers containing acryloyl chloride in fiber and film form were essentially useless until after a simple chemical crosslinking reaction provided the necessary changes in modulus, elongation, and recovery to transform them into potentially useful materials. This was demonstrated in our work by the reaction of diamines with acid chloride groups in a polymer.

The magnitude of the changes in elongation, initial modulus, zero strength temperature, and shrinkage caused by crosslinking was not minimal, but quite appreciable. The magnitude of these changes was about what was expected.

EXPERIMENTAL

Reagents

Acryloyl chloride (Monomer-Polymer Laboratories, Borden Co., Chemical Division) was freshly distilled at atmospheric pressure under nitrogen just before use.

Acryloyl chloride is very sensitive to hydrolysis. Freshly distilled material allowed to stand in a stoppered flask in a refrigerator for several days underwent a slow hydrolysis. Vinyl copolymerization of this "hydrolyzed" monomer led to gelled, insoluble products. Infrared analysis indicated the presence of anhydride linkages in these copolymers. The anhydride disappeared on crosslinking with diamine and on hydrolysis.

Acrylic anhydride, an effective divinyl crosslinking agent,[6] would be formed by the reaction of acryloyl chloride and the acrylic acid formed from the hydrolysis of the acid chloride. Gelled, anhydride-crosslinked, insoluble polymers resulted from the polymerization of acryloyl chloride contaminated with even small quantities of acrylic anhydride.

All other monomers and solvents used were either reagent grade or commercial materials. All monomers contained inhibitors and were distilled under nitrogen from Drierite with the exception of acrylic acid, which was used as received. The distilled monomers were stored in glass stoppered flasks in a refrigerator. All solvents used were also distilled and stored over Drierite.

Polymerization Procedure

The high reactivity of acid chloride groups toward water required the exercising of extreme precautions to keep all materials anhydrous before, during, and after polymerization when acryloyl chloride or its copolymers were involved. All polymerizations were carried out in an atmosphere of dry nitrogen.

The best procedure for making acryloyl chloride copolymers was found to be the slow bulk polymerization illustrated below for the preparation of poly(ethyl methacrylate), a control polymer for our work.

A solution of distilled ethyl methacrylate (100 g.) and 0.2 g. of α,α'-azobis (α,γ-dimethylvaleronitrile), was placed in a large (400 $\times$ 50 mm.) test tube fitted with a capillary inlet going beneath the surface of the monomer and a Drierite drying tube outlet. The test tube was placed in a water bath at 47°C. Dry nitrogen was passed slowly through the capillary. After 1 hr., the capillary was raised to just above the surface of the polymerizing mass which had become quite viscous. The material was completely coverted to a hard, clear, colorless solid in 3 hr. The poly(ethyl methacrylate) was isolated in nearly quantitative yield (97.5 g., 97.5%) by breaking the glass tube. The inherent viscosity was 2.26 (0.5% solution in acetone at 30.0°C.).

In Table VI are listed the acryloyl chloride copolymers prepared by bulk polymerization. The acryloyl chloride copolymers were not as hard or brittle as the poly(ethyl methacrylate). After isolation, these gummy copolymers were immediately placed in a dry box containing phosphorus pentoxide as the desiccant.

TABLE VI
Bulk Polymerization of Acryloyl Chloride Copolymers

Comonomer	Acryloyl chloride, wt.-%	Inherent viscosity[a]	Yield, %
Ethyl methacrylate	5–50	1.10–2.42 (methylene chloride)	>90
Methyl acrylate	2.5–15	0.60–1.23 (chloroform)	>90
Styrene	7–11	0.30–1.28 (chloroform)	20–25

[a] Of 0.5% solution in the specified solvents at 30.0°C.

Although a methyl acrylate/acryloyl chloride 70/30 copolymer made in cyclohexane solution was of sufficiently high molecular weight for evaluation as films, generally solution polymerizations led to low molecular weight polymers with poor conversion.

An alternative route for making acryloyl chloride copolymers consisted in making the corresponding acrylic acid copolymers, followed by conversion of the carboxylic acid groups to acid chloride groups by treatment with thionyl chloride.[7] For example, styrene/acrylic acid 90/10 copolymers were made in an aqueous emulsion system at low pH (about 1.5) in high conversions (80 to 95%) and with moderately high inherent viscosities (1.07 to 1.61 in chloroform) by use of the well-known potassium persulfate–sodium bisulfite initiation system. Conversion of the styrene/acrylic acid 90/10 copolymers to the corresponding acryloyl chloride copolymers was accomplished by dissolving the dry polymer in chloroform and subsequent addition of a slight excess of thionyl chloride. The action of thionyl chloride on the acrylic acid copolymer apparently did not degrade it for a sample of styrene/acrylic acid 90/10 copolymer had an inherent viscosity of 1.16 after reaction with thionyl chloride; the inherent viscosity of the original polymer was 1.07.

Preparation of Films and Fibers

Once the acryloyl chloride copolymer was formed, it was immediately dissolved in an anhydrous solvent, all operations being carried out in a dry box. Any insoluble, gelled material was removed by filtration, and the final solution was stored in a glass-stoppered flask in the dry box. Dilute (10%) solutions were kept in this manner for long periods (several weeks), but upon concentration to 30–40% solids gelation occurred very readily (overnight).

The anhydrous solvents must be inert to all reactions with acid chloride groups. This limited the solvents at our disposal to methylene chloride, chloroform, benzene, acetone, and related materials. Dilute solutions of acryloyl chloride copolymers were concentrated in vacuo to about 20–25% prior to film casting or wet spinning and to about 35–40% solids for immediate dry spinning.

Films were dry-cast on glass plates in a dry box with the use of a standard 20- or 30-mil casting knife and stored in a desiccator containing phosphorus pentoxide.

Fibers were prepared from acryloyl chloride copolymers by conventional wet and dry-spinning techniques. Wet spun yarns were crosslinked as prepared by coagulation of the spinning solution

in a 15% aqueous ethylenediamine bath. Wet spinning led only to crosslinked, undrawn fibers.

Dry spinning permitted the preparation of uncrosslinked control yarns, both drawn and undrawn, with which the crosslinked fibers could be compared. Yarns were immediately stored after spinning in a desiccator over phosphorus pentoxide.

Crosslinking Procedure

Films and fibers of acryloyl chloride copolymers were crosslinked by converting the acid chloride groups to amide linkages by soaking the film or fiber under restraint (as taut on a bobbin or plate) in a 15–20% aqueous ethylenediamine solution for about 10 min. The excess diamine was then removed by a careful washing with water and the fiber or film was dried.

Infrared analysis was used to investigate the course of the reaction by following of the appearance of amide and disappearance of acid chloride absorption bands.

Acryloyl chloride copolymers were also observed to be rendered insoluble by any prolonged contact with certain metals, specifically metal stirrers and spinnerets. Such crosslinking was also effected by metallic ions, especially polyvalent ions such as calcium. This crosslinking was apparently of an ionic salt nature. It was not investigated in detail.

References

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Synopsis

Copolymers containing various amounts of acryloyl chloride were made with ethyl methacrylate, methyl acrylate, and styrene by bulk polymerization and by conversion of acrylic acid copolymers. Fibers and films of these polymers were crosslinked with ethylenediamine, and it was shown that increased crosslinking led to increased tenacity (at elevated temperature), modulus, zero strength temperature, and thermal stability and also greatly decreased elongation and shrinkage. The average molecular weight between crosslinks was calculated. The effect of crosslinking amorphous fibers and films was shown experimentally to produce materials with properties predicted for more rigid polymer structures.

Résumé

On a préparé des copolymères contenant différentes quantités de chlorure d'acryloyle avec le méthacrylate d'éthyle, l'acrylate de méthyle et le styrène par polymérisation en bloc et par conversion de copolymères d'acide acrylique. Des fibres et des films de ces polymères ont été pontés avec l'éthylène diamine et cela montre qu'un accroissement du pontage conduit à un accroissement de la tenacité (à température élevée), du module, de la résistance à la température 0, et de la stabilité thermique en même temps qu'une grande diminution dans l'élongation et la rétrécissement. Le poids moléculaire moyen entre les ponts a été calculé. L'expérience montre que l'effet du pontage sur des fibres et des films amorphes conduit à des matériaux ayant des propriétés prévues pour des structures polymériques plus rigides.

Zusammenfassung

Copolymere mit wechselndem Gehalt an Acryloylchlorid wurden mit Äthylmethacrylat, Methylacrylat und Styrol durch Massepolymerisation und durch Umwandlung von Acrylsäurecopolymeren dargestellt. Aus diesen Polymeren wurden Fasern und Filme erzeugt und mit Äthylendiamin vernetzt; es wurde gezeigt, dass eine erhöhte Vernetzung zu einer höheren Zähigkeit (bei höherer Temperatur), höherem Modul, höherer Temperatur für das Verschwinden der Festigkeit und besserer thermischer Stabilität, begleitet von einer starken Abnahme der Dehnung und Schrumpfung, führt. Das mittlere Molekulargewicht der Kette zwischen zwei Vernetzungsstellen wurde berechnet. Es wurde experimentell gezeigt, dass die Vernetzung bei amorphen Fasern und Filmen zu einer Bildung von Stoffen führt, deren Eigenschaften einer starreren Polymerstruktur entsprechen.