

Graft Copolymers of Cellulose and Vinylic Ketones.

I. Preparation of Poly(methyl Vinyl Ketone)-Cotton Cellulose Copolymers

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Synopsis

The graft copolymerization reaction of methyl vinyl ketone from several solvents with fibrous cotton cellulose, preirradiated to a dosage of 5.2×10^{19} eV/g with γ -radiation from ^{60}Co , was investigated. Solvents included water, methanol, N,N-dimethylformamide, and several combinations of these solvents. From water a maximum yield of copolymer product was obtained after 2 hr at 25°C. The addition of methanol to aqueous solutions of methyl vinyl ketone, in all concentrations, inhibited the graft copolymerization reaction. The addition of a small amount of N,N-dimethylformamide to aqueous solutions of the monomer increased the rate of the copolymerization reaction; however, the addition of large amounts of N,N-dimethylformamide to these solutions also inhibited the reaction. From solutions of methanol or N,N-dimethylformamide and monomer, little or no copolymerization of monomer with irradiated cellulose occurred. The copolymer products exhibited a strong infrared absorption band at 5.85μ which is characteristic of the $-\text{C}=\text{O}$ group of the grafted poly(methyl vinyl ketone). Fibrous copolymer yarns exhibited increased yarn number and decreased breaking strength and average stiffness, as compared with unmodified cotton yarns.

INTRODUCTION

Graft copolymerization of vinyl monomers with cellulose to yield copolymer products with desired properties has been reported extensively.¹ However, very little work with vinyl monomers containing α,β -unsaturated carbonyl moieties has been reported. Kern et al. reported the graft copolymerization of acrolein with cotton cellulose, using $\text{K}_2\text{S}_2\text{O}_8$ as initiator for the reaction.² Rowland and Brannan reacted various activated vinyl monomers, including methyl vinyl ketone, with cotton cellulose in which internal catalysis was provided by quaternary ammonium substituents on the cellulose.³ Ishanov et al. recently reported radiation-initiated crosslinking of cellulose with an α,β -unsaturated aldehyde.⁴

In view of the chemical reactivity of ketonic carbonyl groups, the preparation of fibrous cellulose copolymer products by reaction of α,β -unsaturated ketonic monomers with radiation-activated fibrous cotton cellulose was investigated. The graft copolymerization reaction of

methyl vinyl ketone with radiation-activated cotton cellulose is reported here. The effects of aqueous solvents containing methanol or *N,N*-dimethylformamide on the copolymerization reaction and some of the mechanical properties of the fibrous cellulose-poly(methyl vinyl ketone) products are also given.

EXPERIMENTAL

Materials

Cotton cellulose of Deltapine variety, spun into 7s/3 yarns, was purified in the usual manner.⁵ The fabric used was a cotton printcloth, 80 × 80, 3.12 oz/yd², that had been desized, scoured, and bleached. Methyl vinyl ketone, obtained from a commercial source, was purified by distillation under reduced pressure at 35°C/130 mm immediately before use. *N,N*-Dimethylformamide, obtained from a commercial source, was purified by heating over BaO at 100°C and then distilling over BaO. Methanol, certified A.C.S., was dried and distilled at atmospheric pressure prior to use. Deoxygenated distilled water was used to prepare the solutions.

Methods

The SRRL ⁶⁰Co radiation source was used.⁶ The dose rate, determined by ferrous-ferric dosimetry,⁷ was about 5.4×10^{19} eV/g-hr. Samples of cotton yarn or fabric were dried overnight under vacuum at 50°C and then sealed in glass tubes under nitrogen atmosphere. The samples were irradiated to a dosage of 5.2×10^{19} eV/g at ambient temperature, about 23°C. At this dosage, only minor losses in tensile strength of the fibrous cellulose were observed.⁸

Within 2 hr after irradiation, the samples were transferred to reaction vessels by using a dry-box under nitrogen atmosphere. The irradiated cellulose was then immersed in deoxygenated solutions containing methyl vinyl ketone and solvents. The system was evacuated and flushed with nitrogen several times. The irradiated cellulose was allowed to react under nitrogen atmosphere at 25°C for the desired reaction time. The copolymer product was washed free of unreacted monomer with methanol; homopolymer was removed by extracting the product with *N,N*-dimethylformamide at 55°C for 48 hr. The product was then successively washed with *N,N*-dimethylformamide and distilled water and dried under vacuum at 50°C. After equilibrating the cellulose-poly(methyl vinyl ketone) product at 25°C and 50% R.H., the extent of graft copolymerization was determined as the increase in weight of the reacted yarn or fabric, polymer add-on, over that of a control sample.

The physical properties of the fibrous cellulose copolymers were determined by standard procedures.^{9,10} Infrared spectra of the copolymers were determined by means of the KBr disc technique using a double-beam infrared spectrophotometer.

RESULTS AND DISCUSSION

Graft Copolymerization

The effects of composition of solution and reaction time on the extent of graft copolymerization of methyl vinyl ketone with irradiated cellulose are shown in Figures 1 and 2 and Table I. From aqueous solutions of methyl vinyl ketone, both the rate and extent of graft copolymerization of monomer with irradiated cellulose increased with increased concentration of monomer and reaction time (Fig. 1). For each concentration of monomer investigated (9, 15, and 25 vol-%), about 70% of the copolymerization reaction occurred within about 30 min, and the maximum extent of copolymerization occurred after about 2 hr with 16, 28, and 30% add-on of grafted poly(methyl vinyl ketone), respectively. Apparently, chain transfer reactions were factors in the termination of graft copolymerization reactions, since cloudy suspensions of poly(methyl vinyl ketone) homopolymer were noted after a reaction time of 1 hr in the case of initial concentration of monomer of 25 vol-% and after 2 hr in the case of 9 and 15 vol-%.

The addition of methanol to the aqueous solution of methyl vinyl ketone decreased the extent of graft copolymerization (Table I). The addition of *N,N*-dimethylformamide to these solutions to about 20 vol-% increased the extent of graft copolymerization; further addition of *N,N*-dimethylformamide decreased the extent of copolymerization. The rate of graft

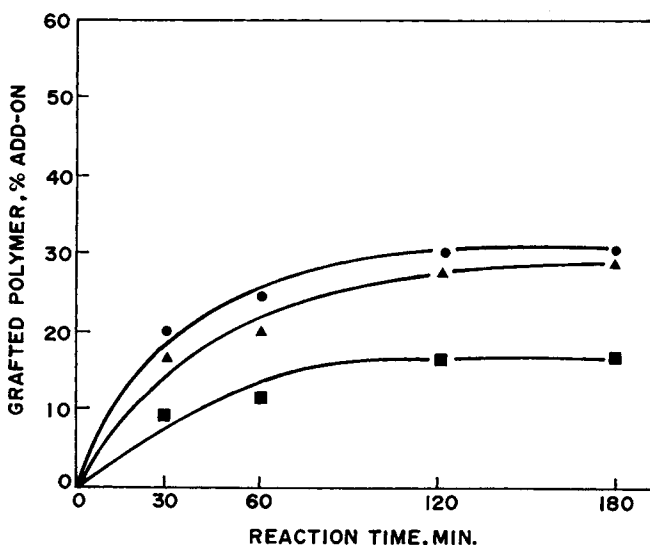


Fig. 1. Effects of composition of methyl vinyl ketone-water solution and reaction time on extent of graft copolymerization with irradiated cellulose yarn at 25°C. Dosage 5.2×10^{19} eV/g; cellulose solution ratio 1/50: (■) 9 vol-% methyl vinyl ketone; (▲) 15 vol-%; (●) 25 vol-%.

TABLE I
Effects of Composition of Solution and Type of Solvent on Extent of Graft
Copolymerization of Methyl Vinyl Ketone with Irradiated Cotton Yarn at 25°C^a

Composition of solution, vol-%		Polymer, % add-on	
Water	Solvent	Methanol	N,N-Dimethyl- formamide
100	0	30	30
90	10	25	48
80	20	21	43
60	40	15	33
50	50	14	20
40	60	9	18
20	80	8	5
0	100	3	4

^a Dried, purified cotton yarn irradiated in nitrogen atmosphere at 25°C to 5.2×10^{19} eV/g. Reaction conditions: cellulose solution ratio 1/50; cellulose immersed in methyl vinyl ketone, 25 vol-%, and water-solvent, 75 vol-%, for 120 min at 25°C.

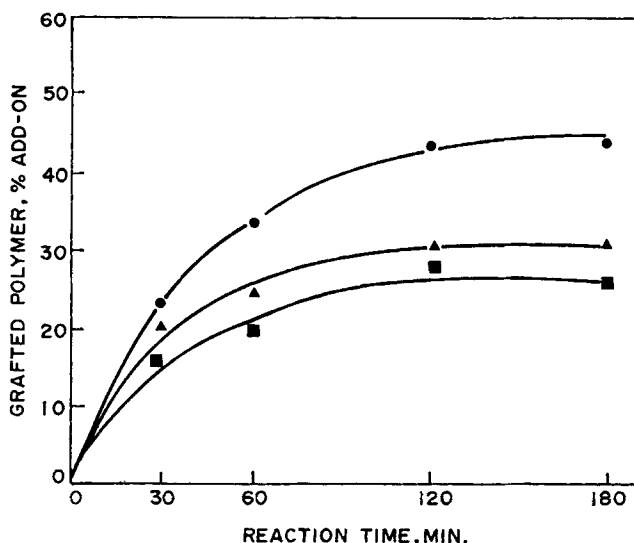


Fig. 2. Effects of solvent type and reaction time on extent of graft copolymerization of methyl vinyl ketone with irradiated cellulose yarn at 25°C. Dosage 5.2×10^{19} eV/g; cellulose solution ratio 1/50; methyl vinyl ketone concentration 25 vol-%; (■) methanol/water, 20/80 vol-%; (▲) water; (●) N,N-dimethylformamide/water, 20/80 vol-%.

copolymerization of methyl vinyl ketone with irradiated cellulose was also greater from water-N,N-dimethylformamide (80-20 vol-%) than from water or methanol-water (80-20 vol-%) (Fig. 2).

Methyl vinyl ketone is soluble in water; poly(methyl vinyl ketone) is insoluble in water.¹¹ Water also interacts readily with cellulose to cause swelling. The polymer is soluble in methanol. Consequently, a greater extent of copolymerization of methyl vinyl ketone with irradiated

cellulose would be expected from water than from water-methanol or methanol due to the Trommsdorff-type effect.¹²

Poly(methyl vinyl ketone) is also soluble in *N,N*-dimethylformamide. Therefore, the increased rate and extent of graft copolymerization from some *N,N*-dimethylformamide-water solutions cannot be explained on the basis of the Trommsdorff-type effect. The accelerative effect on graft copolymerization from solutions containing less than about 20 vol-% *N,N*-dimethylformamide may be due to a decreased rate of chain termination of the grafted polymer from these solutions, as compared with that from water. The accelerative effect of some *N,N*-dimethylformamide-water solutions on graft copolymerization could be due to a greater swelling effect on cotton cellulose, making radical sites more accessible to monomer, as compared with that from water. Different swelling abilities of these solutions would probably correlate with differences in the rate of scavenging of cellulosic free radicals by the solutions. This explanation is less likely, since we have shown that solutions of *N,N*-dimethylformamide-water (20-80 vol-%) are equally effective as water in scavenging cellulosic radicals in irradiated cotton.¹⁴ Addition of monomer to these solutions would probably not significantly affect their relative rates of free-radical scavenging.

Properties of Fibrous Cellulose Copolymers

Poly(methyl vinyl ketone) was apparently covalently linked, that is, grafted, to the cellulose in the copolymer product. Samples of the copolymer product were ground to pass 20-mesh and then extracted at reflux with pyridine, acetone, or *N,N*-dimethylformamide. Only very small amounts of poly(methyl vinyl ketone) were removed from the copolymer product. Attempts to remove cellulose sufficiently from the copolymer product by acid hydrolysis to yield poly(methyl vinyl ketone) that could be dissolved in solvents for the polymer were unsuccessful.¹⁵

The infrared spectra of purified cotton cellulose and of cellulose-poly(methyl vinyl ketone) copolymer are shown in Figure 3. The C=O stretch for poly(methyl vinyl ketone) is very intense and occurs at 5.85 μ .¹⁶ Subsequent chemical reactions of this ketonic carbonyl group of the copolymer can be readily monitored by recording changes in intensity of the C=O stretch.

Some of the mechanical properties of copolymer yarns are shown in Table II. The breaking strengths of the copolymer yarns were less than those of untreated or irradiated cotton yarns; however, the breaking strengths of the copolymer yarns were relatively independent of polymer add-on. Similarly, after an initial decrease, elongation at break and breaking toughness of the copolymer yarns were less than those of untreated cotton yarns but were relatively independent of polymer add-on. The average stiffness of the yarns decreased with increasing polymer add-on. Cotton cellulose-poly(methyl vinyl ketone) copolymer fabrics, containing

TABLE II
Properties of Cotton Cellulose-Poly(methyl Vinyl Ketone) Copolymer Yarns^a

Property	Polymer, % add-on						
	0 ^b	0 ^c	13	23	38	45	53
Yarn number, tex	255	246	285	310	351	371	399
Breaking strength, lb	9.1	9.2	7.0	6.9	7.1	7.0	7.3
Elongation at break, %	16	15	15	12	12	15	15
Tenacity, g/tex	16	17	11	10	9.1	8.6	8.3
Breaking toughness, g/tex	0.72	0.74	0.41	0.35	0.35	0.35	0.35
Average stiffness, g/tex	99	111	75	81	74	57	56

^a Dried, purified cotton cellulose yarn irradiated in nitrogen atmosphere at 25°C to 5.2×10^{19} eV/g, then immersed in aqueous solution of methyl vinyl ketone (25 vol-%) at 25°C for 0.5 to 3 hr to obtain desired polymer add-on. Homopolymer extracted with N,N-dimethylformamide.

^b Purified cotton cellulose yarn.

^c Irradiated cotton cellulose yarn.

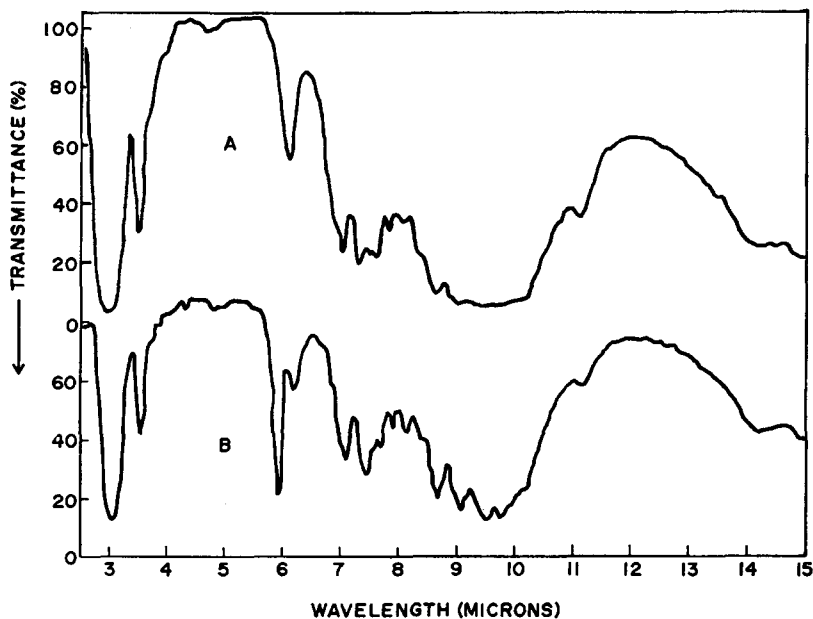


Fig. 3. Infrared spectra of purified cotton cellulose (A) and of cellulose-poly(methyl vinyl ketone) copolymer (B). Copolymer composition: cellulose, 100 parts; poly(methyl vinyl ketone), 45 parts.

9-16% polymer add-on, exhibited small decreases in breaking strength, increases in elongation at break, and small decreases in tearing strength and flex abrasion resistance, as compared with untreated cotton fabrics. The properties of both cotton yarn and fabric copolymer products were satisfactory for textile products.

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