

Chemically Induced Graft Copolymerization of Vinyl Monomers onto Cotton Fibers

Mehlika Pulat, Ceyhan Isakoca

Gazi Üniversitesi Fen-Edebiyat Fakültesi, Kimya Bölümü, Teknikokullar, Ankara, Türkiye

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ABSTRACT: We investigated the chemically induced graft copolymerizations of acrylic acid (AA), acrylamide, crotonic acid, and itaconic acid (IA) onto cotton fibers. Benzoyl peroxide was used as an initiator. The effects of grafting temperature, grafting time, and monomer and initiator concentrations on the grafting yields were studied, and optimum grafting conditions were determined for the sample material. The maximum grafting yield value obtained was

23.8% for AA. Swelling tests, Fourier transform infrared spectroscopy, and scanning electron microscopy analyses of grafted and ungrafted fibers were also performed to characterize fiber properties. IA-grafted fibers were measured as the most swollen fibers, with a swelling value of 510%. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2343–2347, 2006

Key words: graft copolymers; swelling; fibers

INTRODUCTION

Cotton is a widely used natural, healthy, hygroscopic, and cheap textile material. Nearly 94% of its chemical structure consists of cellulose molecules. The textile industry has a high demand for cotton with improved physical and chemical properties. As the modification of synthetic and natural polymers via graft copolymerization is a commonly used method, several reports already exist on the modification of cotton in the literature.^{1–9}

Vinyl monomers are easily purchased chemicals that can be used in many reactions, such as polymerization and copolymerization. Some physical properties of natural and synthetic products can be improved by their modification with these kinds of monomers.^{10–12} Vinyl monomers such as acrylonitrile and methyl methacrylate are convenient monomers for the graft copolymerization of cellulose fibers and fabrics. The same special properties of cotton products, such as hygroscopic and dyeability, can be arranged by this modification method. Radical sites on the backbone of cellulose usually propagate reactions. In addition to potassium persulfate, ceric ions, azobisisobutyronitrile, and benzoyl peroxide (BPO) are rather frequently used as initiators, some studies have included induction by UV irradiation and γ -radiation.^{13–15}

In this study, we aimed to investigate the graft copolymerizations of acrylic acid (AA), acrylamide

(AAM), crotonic acid (CA), and itaconic acid (IA) onto cotton fibers with BPO as an initiator. The effects of grafting temperature, grafting time, and monomer and initiator concentrations on the grafting percentages were studied, and optimum grafting conditions were determined. Swelling tests, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM) analyses of grafted and ungrafted cotton fibers were also carried out.

EXPERIMENTAL

Materials

Combed cotton fibers (20/1) were obtained from the Turkish textile company Floksel Textile Co. BPO (Aldrich) was precipitated twice from a chloroform solution in methanol and dried in a vacuum oven for 2 days. AA, AAm, CA, and IA were also procured from Aldrich (Darmstadt, Germany).

Fiber preparation

Cotton fibers were used after the following treatment.^{16,17} Hanks of fiber samples about 300 cm in total length were boiled briskly in 500 mL of a NaOH solution (0.08%) containing 0.1 g of the nonionic surfactant Triton X (Merck) for 3 min. The sample was then washed successively with hot water, cold water, a 1.0% HCl solution, and finally, cold water until it was acid-free. The scoured cellulose thus obtained was dried at room temperature in a current of dust-free air.

Correspondence to: M. Pulat (mpulat@gazi.edu.tr)

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Grafting procedure

The graft polymerization procedure was performed according to the literature.^{5,6,18,19} To determine the effect of the polymerization temperature (T) on grafting yield, we investigated the polymerization reaction by changing the temperature between 40 and 80°C while we held the polymerization time ($t = 1$ h) and monomer and initiator concentrations ($[BPO]$) constant. Appropriate amounts of fabric were placed into round-bottom polymerization tubes containing 5.0 mL of BPO–acetone solution ($8.0 \times 10^{-2} M$). The tubes were put into a water bath at a constant temperature. After thermal equilibrium was reached, 45.0 mL of a vinyl monomer–water solution (1.5M) was added into the polymerization tubes, and the polymerization procedure was performed for 1 h. After polymerization, the treated fabrics were taken out. The residual solvent, monomer, and homopolymer were removed from the fabrics by extreme washing with hot and cold water. The treated fabrics were dried at 40°C in a vacuum oven for 48 h and weighed. The grafting yields (%) were calculated from the following equation:

$$\text{Grafting yield(\%)} = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

where m_0 and m are the masses of the ungrafted and grafted fabrics, respectively.²⁰

To determine the effect of t and the monomer and initiator concentrations on the grafting yield, we repeated the procedure, varying t (30–240 min) and the concentrations of monomer (0.5–3.0M) and initiator (2.0×10^{-2} to $12.0 \times 10^{-2} M$). The grafting yields were calculated with eq. (1).

Swelling tests

Swelling percentage ($S\%$) values were determined from eq. (2), where m_w is the mass of the swollen fibers in distilled water at room temperature to a constant weight and m_d is the mass of the same fibers dried eventually at 40°C for 48 h.^{20–23}

$$S\% = \frac{m_w - m_d}{m_d} \times 100 \quad (2)$$

FTIR and SEM analysis

The FTIR spectra of the sheared fiber samples were recorded with a PerkinElmer model 1710 spectrophotometer (England).

With a Jeol model JSM 840A scanning electron microscope (Japan), we performed SEM analysis of 200-Å gold-palladium-coated fibers.

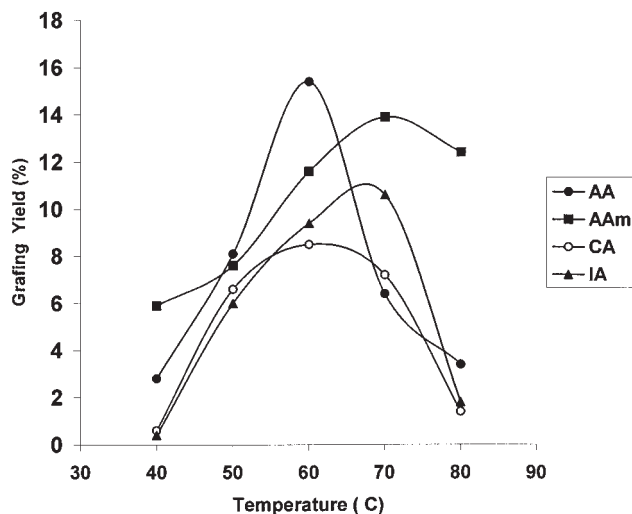


Figure 1 Effect of the temperature on grafting yields of the AA, AAm, CA, and IA monomers ($t = 1$ h, monomer concentration = 1.5M, $[BPO] = 8.0 \times 10^{-2} M$).

RESULTS AND DISCUSSION

Effect of the temperature

The effect of temperature on the graft polymerization of the cotton fibers was studied within the range 40–80°C. As the temperature was increased, the yields also gradually increased, reached a maximum value, and then decreased (Fig. 1). The initial increase in the grafting yield may have been due to the increase in the mobility and diffusion rate of the monomer and initiator molecules. Maximum grafting yields were observed for the AA and CA monomers at 60°C and at 70°C for the AAm and IA monomers. The grafting yield of AA was higher than the others. The decrease in grafting yield at higher temperatures was due to the favored chain-termination reactions and the increase in homopolymer formation. Similar results were also reported in the chemically initiated graft copolymerizations of various vinyl monomers on natural and synthetic fibers.^{5,6,7,11,17,24}

Effect of t

The effect of t on the grafting yield was investigated by changing t (from 30 to 240 min) at a constant temperature and constant monomer–initiator concentrations. As shown in Figure 2, the grafting yields initially increased with time and then reached a saturation grafting value after nearly 1 h. The following maximum grafting values were obtained: 15.4% for AA, 13.9% for AAm, 10.6% for IA, and 8.5% for CA.

Effect of the monomer and initiator concentrations

We studied the effect of monomer concentration on the grafting yield by varying its concentration be-

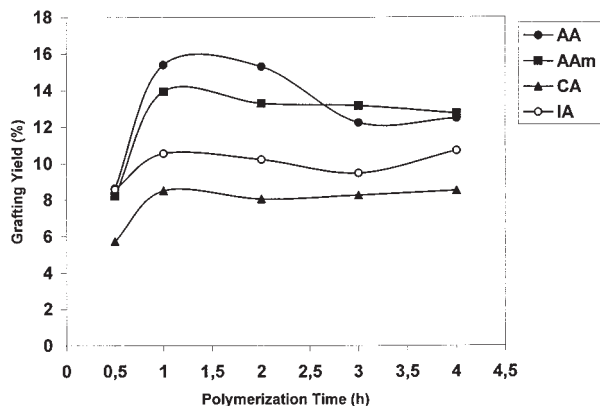


Figure 2 Variation of grafting yield with t (at 60°C for AA and CA and at 70°C for AAm and IA; monomer concentration = 1.5M , $[\text{BPO}] = 8.0 \times 10^{-2}\text{M}$).

tween 0.5 and 3.0M at a constant temperature, time, and initiator concentration. As shown from the results graphed in Figure 3, the grafting yields first increased with increasing monomer concentration, reached a maximum, and then decreased. As the monomer concentration increased, the diffusion of the monomer molecules into the fiber structure also increased, which led to a higher grafting yield. The decrease in grafting yield can be explained by the enhancement of homopolymer formation at high monomer concentrations. For the AAm and IA monomers maximum, the grafting yields were obtained at a 1.0M concentration. The maximum grafting yield obtained was for the AA monomer at a 2.5M concentration.

Figure 4 represents the effect of initiator concentration on the grafting yield. Evidently, the grafting percentage increased significantly as the BPO concentration increased, and a further increase in the BPO concentration decreased the grafting yield. Free radicals occurred as a result of the decomposition of BPO taking place in various reactions in the polymerization

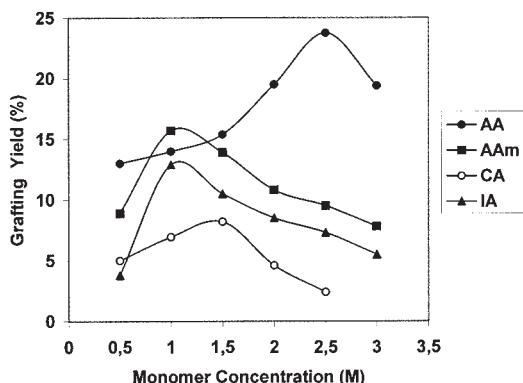


Figure 3 Variation of grafting yield with monomer concentration (at 60°C for AA and CA and at 70°C for AAm and IA; $t = 1\text{h}$, $[\text{BPO}] = 8.0 \times 10^{-2}\text{M}$).

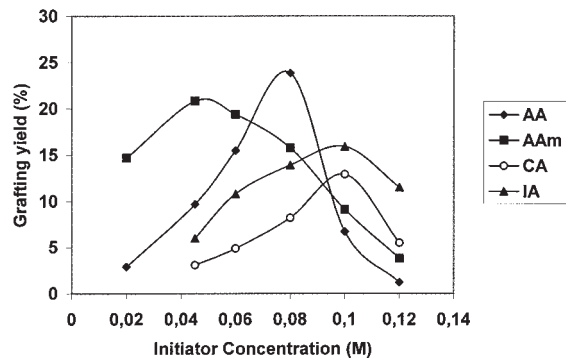


Figure 4 Variation of grafting yield with initiator concentration ($t = 1\text{h}$, $T = 60^{\circ}\text{C}$ for AA and CA and 70°C for AAm and IA; monomer concentrations = 2.5M for AA, 1.5M for CA, and 1.0M for AAm and IA).

media. The increase in BPO concentration increased the probability of both hydrogen abstraction from the cellulose backbone and chain-transfer reactions of polyacrylamide, poly(acrylic acid), poly(crotonic acid), and poly(itaconic acid) homopolymers with cellulose. So the grafting yield increased in both cases. However, the excessive increase in BPO concentration caused the formation of free-radical species via the decomposition of BPO ($\text{C}_6\text{H}_5\text{COO}\cdot$ and/or $\text{C}_6\text{H}_5\cdot$). These free radicals reacted with cellulose macroradicals and growing polymer chains, which resulted in termination or combination reactions; consequently, the grafting yield decreased.

The optimum grafting conditions and maximum grafting yields for different monomers are summarized as follows:

For the AA monomer; $T = 60^{\circ}\text{C}$, $t = 1\text{h}$, monomer concentration = 2.5M , initiator concentration = 0.08M , and grafting yield = 23.8% .

For AAm the monomer; $T = 70^{\circ}\text{C}$, $t = 1\text{h}$, monomer concentration = 1.0M , initiator concentration = 0.04M , and grafting yield = 20.8% .

For the CA monomer; $T = 60^{\circ}\text{C}$, $t = 1\text{h}$, monomer concentration = 1.5M , initiator concentration = 0.10M , and grafting yield = 12.9% .

TABLE I
Variation of S% Values of the Grafted Fibers with T

| Monomer | T ($^{\circ}\text{C}$) | | | | |
|---------|----------------------------|-----|-----|-----|-----|
| | 40 | 50 | 60 | 70 | 80 |
| AA | 350 | 375 | 465 | 350 | 345 |
| AAm | 118 | 195 | 234 | 253 | 198 |
| CA | 355 | 348 | 490 | 410 | 354 |
| IA | 330 | 368 | 396 | 448 | 342 |

$t = 1\text{h}$; monomer concentration = 1.5M ; $[\text{BPO}] = 8.0 \times 10^{-2}\text{M}$.

TABLE II
Variation of S% Values of the Grafted Fibers with t^a

| Monomer | t (h) | | | | |
|---------|---------|-----|-----|-----|-----|
| | 0.5 | 1.0 | 2.0 | 3.0 | 4.0 |
| AA | 344 | 465 | 450 | 413 | 449 |
| AAM | 153 | 253 | 245 | 240 | 230 |
| CA | 351 | 490 | 486 | 492 | 483 |
| IA | 381 | 448 | 429 | 459 | 415 |

^a At 60°C for AA and CA and 70°C for AAM and IA; monomer concentration = 1.5M, [BPO] = 8.0×10^{-2} M.

For the IA monomer; $T = 70^\circ\text{C}$, $t = 1$ h, monomer concentration = 1.0M, initiator concentration = 0.10M, and grafting yield = 15.9%.

Although some homopolymerization reaction occurred, these grafting yield values were higher than the values given in the literature. Maximum grafting yield values on cotton fibers have been reported by other researchers as 1.46–10.2% for AAM, 9.5% for IA, and 1.5% for AA.^{7,8,25}

Swelling values

S% values calculated from eq. (2) are presented in Tables I–IV. The S% value of the ungrafted cotton fibers was 155%. As shown by the results, the swelling values of the grafted fibers increased according to the grafting percentage. The most swollen fibers were the AA-grafted fibers. The AAM-grafted fibers were the least swollen fibers. A comparison of S% values shows that the swelling capacities of the grafted fibers were nearly three times higher than the capacity of the ungrafted cotton fibers.

FTIR spectra

The FTIR spectra of the grafted and ungrafted fibers are presented in Figure 5. As specific cellulose groups existed in the grafted and ungrafted fibers, similar absorption peaks were obtained for all of the samples. All of the spectra had the same absorption peaks at

TABLE III
Variation of S% Values of the Grafted Fibers with Monomer Concentration^a

| Monomer | Monomer concentration (M) | | | | | |
|---------|---------------------------|-----|-----|-----|-----|-----|
| | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
| AA | 386 | 374 | 465 | 470 | 502 | 460 |
| AAM | 211 | 280 | 253 | 190 | 205 | 193 |
| CA | 367 | 352 | 490 | 360 | 328 | — |
| IA | 360 | 469 | 448 | 385 | 372 | 378 |

^a At 60°C for AA and CA and 70°C for AAM and IA; $t = 1$ h; [BPO] = 8.0×10^{-2} M.

TABLE IV
Variation of S% Values of the Grafted Fibers with Initiator Concentration

| Monomer | Initiator concentration (M) | | | | | |
|---------|-----------------------------|------|------|------|------|------|
| | 0.02 | 0.04 | 0.06 | 0.08 | 0.10 | 0.12 |
| AA | 335 | 348 | 335 | 502 | 314 | 349 |
| AAM | 180 | 290 | 285 | 280 | 213 | 140 |
| CA | — | 330 | 398 | 490 | 499 | 366 |
| IA | — | 365 | 438 | 469 | 510 | 453 |

$t = 1$ h; $T = 60^\circ\text{C}$ for AA and CA and 70°C for AAM and IA; monomer concentration = 2.5M for AA, 1.5M for CA, and 1.0M for AAM and IA.

1070–1150 cm^{-1} (C—O stretching), 1260–1410 cm^{-1} (O—H bending), and 3600–3100 cm^{-1} (O—H stretching). The adsorption band appearing in the 2850–2810- cm^{-1} region in spectrum a corresponded to the aryl ether groups of cellulose molecules. The peaks at 1725–1700 cm^{-1} in spectra b, c, and d indicated that —CO₂H groups existed in the AA, CA, and IA molecules. The broad bands in the 1560–1650 and 3500- cm^{-1} regions in spectrum e belonged to primary amide groups (—NH₂ bending) and —CONH₂, respectively.²⁶

SEM analysis

Scanning electron micrographs of the ungrafted and grafted fibers are presented in Figure 6. As shown by the SEM results, the ungrafted fiber surfaces had a smoother and a more homogeneous appearance than the grafted fibers. As clearly shown in the micrographs, the rough and scaly tissue of the grafted fibers and bonded fibrils indicated the grafted copolymers.

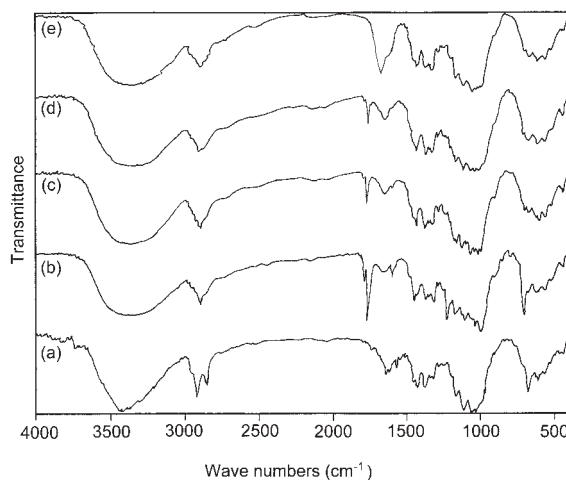


Figure 5 FTIR spectra of (a) ungrafted fibers and (b) AA-, (c) CA-, (d) IA-, and (e) AAM-grafted fibers.

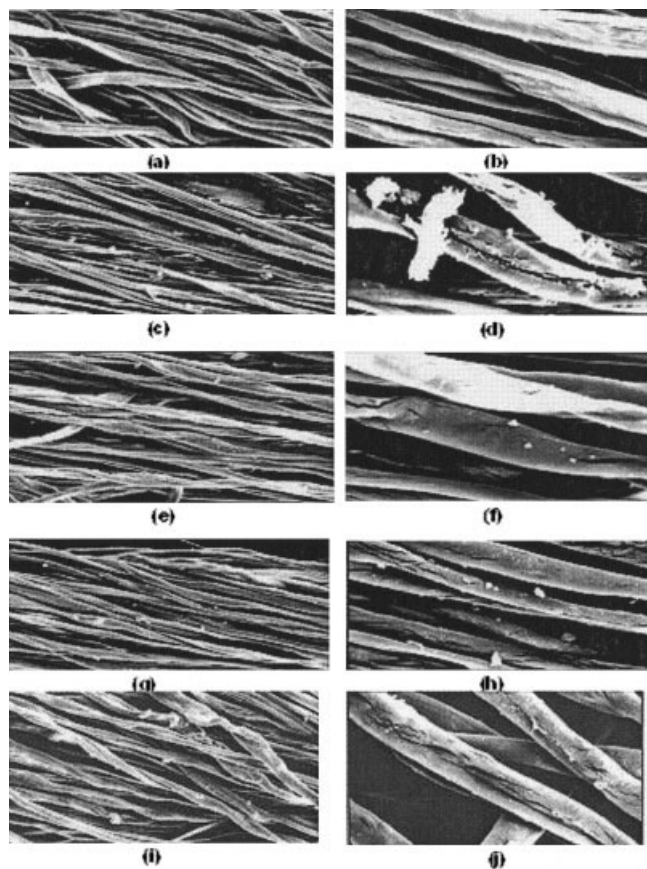


Figure 6 SEM micrographs of ungrafted cotton fibers at (a) 300 and (b) 1000 \times , AA-grafted fibers at (c) 300 and (d) 1000 \times , AAm-grafted fibers at (e) 300 and (f) 1000 \times , IA-grafted fibers at (g) 300 and (h) 1000 \times and, CA-grafted fibers and (i) 300 and (j) 1000 \times .

CONCLUSIONS

In this study, graft copolymerizations of AA, AAm, CA, and IA monomers onto cotton fibers with a BPO initiator were performed. The polymerization conditions were investigated, and the optimum grafting conditions were found to be 60–70°C and a 1.5M monomer concentration. Maximum grafting yield val-

ues were obtained as follows: 23.8% for AA, 20.8% for AAm, 12.9% for CA, and 15.9% for IA. The existence of graft polymerization was proven via FTIR spectra and SEM analysis. 5% values showed that the swelling capacities of the grafted fibers were nearly three times higher than the capacity of the ungrafted cotton fibers.

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