

# Characterization of Cotton–Polystyrene Graft Copolymers

N. THEJAPPA and S. N. PANDEY, *Cotton Technological Research Laboratory (Indian Council of Agricultural Research), Adenwala Road, Matunga, Bombay 400 019, India*

## Synopsis

Characterization of cotton–polystyrene graft copolymers prepared by ceric ion initiation is reported. Various techniques studied include moisture sorption, solubility in cupriethylenediamine (CED), infrared spectra, differential thermal analysis (DTA), electron micrographs and X-ray diffractograms, which point to the existence of true grafting. The graft copolymers showed a slight fall in breaking load and improved resistance to wetting.

## INTRODUCTION

Modification of cellulose fibers through graft copolymerization of vinyl monomers has evoked considerable interest in recent years.<sup>1,2</sup> Grafting, in general, is expected to add new properties associated with the side chains without drastically affecting the properties of cotton. One of the most important problems in the characterization of cellulose graft copolymers is the fundamental question whether the polymer formed is grafted onto cellulose chains or just distributed throughout the cellulose matrix without being chemically attached.

Solvent extraction is one of the methods used to characterize graft copolymers.<sup>3–5</sup> This is based on the difference in solubility between the graft copolymer and nongrafted homopolymer. Cellulose is insoluble in almost all organic solvents, whereas most synthetic polymers are soluble in some organic solvents. Extraction of the reaction product with an organic solvent should therefore remove all nongrafted homopolymers. Unextractable polymer add-on is evidence of grafting. Proof of grafting was also obtained by comparing the solubility behavior of the reaction product with a physical mixture of cellulose and the homopolymer.<sup>4</sup> Chromatographic analysis to demonstrate the existence of grafting has been used by Guthrie in an extensive investigation of cellulose grafted with vinyl chloride.<sup>6</sup>

Differential thermal analysis has been successfully used by Schwenker and Pacsu<sup>7</sup> to prove whether grafting has taken place. The sharp exothermic peak at 278°C, characteristic of polyacrylonitrile homopolymer observed with a physical mixture of polyacrylonitrile and cotton, was absent in the case of acrylonitrile-grafted cotton. Infrared spectra also help in showing the existence of grafts. Arthur and Demint found that the hydroxyl band intensity of grafted cotton was considerably less than the hydroxyl band intensity of control cotton.<sup>4</sup> Huang and Rapson<sup>8</sup> observed new bands characteristic of grafted side chains in the infrared spectra of styrene-grafted cotton. The presence of grafted

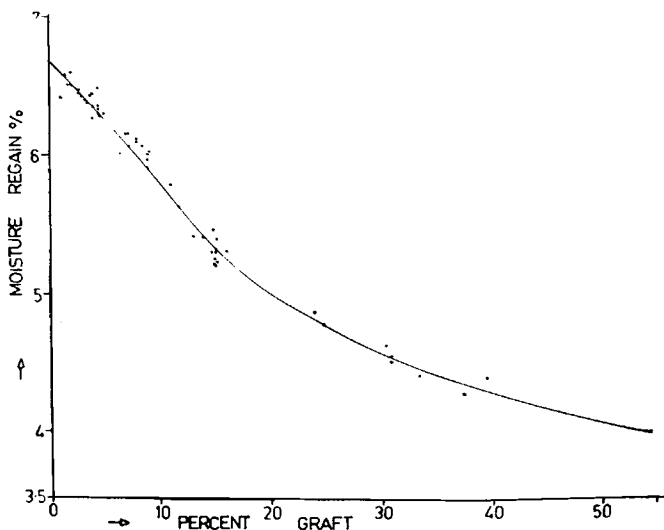


Fig. 1. Moisture regain of cotton-polystyrene graft copolymers.

polymer within the cotton fiber was demonstrated by Rollins et al.<sup>9</sup> by a series of electron micrographs of cotton grafted with acrylonitrile, styrene, methyl methacrylate, and vinyl acetate. The present study deals with the characterization of cotton-polystyrene graft copolymers by various techniques.

### EXPERIMENTAL

Cotton-polystyrene graft copolymers prepared by the ceric ion initiation method<sup>10</sup> were used for the study.

Single yarn strength was measured on an Uster Automatic Single Yarn Tester.<sup>11</sup> Moisture regain of the graft copolymers at 65% RH were determined as per the ISI method.<sup>12</sup> Moisture regain at relative humidities of 25, 45, 85, and

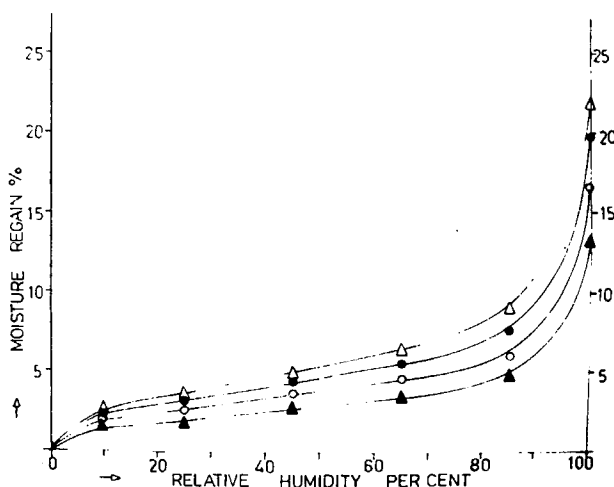


Fig. 2. Water sorption isotherms of cotton-polystyrene graft copolymers. (Δ) Ungrafted cotton, (●) percent graft 9.04, (○) percent graft 39.01, (▲) percent graft 54.15.

TABLE I  
Physicochemical Properties of Cotton-Polystyrene Copolymers

Sample no.	Percent graft	Initiator concentration (mol/L)	Reaction time (h)	Temperature (°C)	Breaking load (g)	Strength retention (%)	Elongation (%)	Moisture regain (%)	Percent solubility in		Water repellency time (min)
									0.5 M CED	72% H <sub>2</sub> SO <sub>4</sub>	
1	2	3	4	5	6	7	8	9	10	11	12
Control	—	—	—	—	253	100.0	7.0	6.67	100.0	100.0	2
S 4	4.54	0.004	4	65	225	88.9	7.0	6.33	98.3	99.6	35
S 17	9.04	0.004	4	65	203	80.2	7.3	5.96	91.3	96.0	150
S 31	15.12	0.005	4	90	152	60.1	5.9	5.23	83.9	91.0	160
S 42	24.48	0.003	4	90	174	68.8	6.7	4.78	73.1	82.6	180
S 47	31.67	0.010	4	90	—	—	—	4.61	67.1	78.0	180
S 44	39.01	0.005	4	90	140	55.3	7.7	4.40	63.6	76.1	180
S 46	45.42	0.008	4	90	99	39.1	5.0	4.22	57.2	73.3	180
S 45	54.15	0.006	4	90	144	56.9	8.8	3.92	51.2	69.1	180

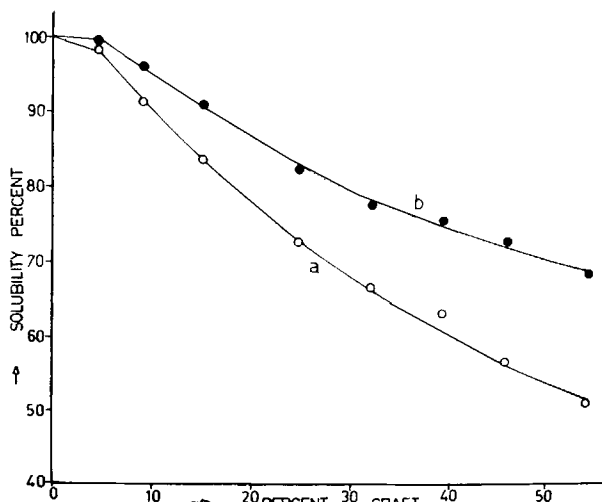


Fig. 3. Solubility of cotton-polystyrene graft copolymers: (a) in 0.5M CED; (b) in 72% H<sub>2</sub>SO<sub>4</sub>.

100% was determined by conditioning the samples at these relative humidities using suitable mixtures of sulfuric acid and water.<sup>13</sup> Water sorption isotherms were obtained from the plot of moisture regain at different humidities. Resistance to wetting of the graft copolymers was determined according to the AATCC method.<sup>14</sup>

Solubility in cupriethylenediamine (CED) was determined as follows: 0.15 g of the grafted yarn was treated with 30 ml 0.5M CED solvent in a conical flask. The flask was covered with black cloth and shaken for an hour on a shaker. The contents were then filtered through a sintered glass crucible. The residue was washed with distilled water, 1% solution of acetic acid, and again with distilled water, and dried. From the weight ( $W$ ) of the residue, solubility was calculated using the formula

$$\text{solubility} = \frac{0.15 - W}{0.15} \times 100$$

Similarly, the solubility of the graft copolymers in 72% sulfuric acid was determined by treating 0.15 g of the grafted yarn with 30 ml 72% sulfuric acid for 1 h and then finding the weight of the undissolved material.

DTA of the graft copolymers was carried out on an AMINCO differential thermal analyzer under nitrogen.<sup>15</sup> Radial X-ray diffractograms of the powdered samples were obtained with the help of a Philips X-ray generator. Infrared spectra of the graft copolymers were studied by the KBr pellet technique of O'Connor et al.<sup>16</sup> Electron micrographs of the graft copolymers were obtained by the technique of Rollins et al.<sup>9</sup>

## RESULTS AND DISCUSSIONS

*Breaking load.* The breaking load of styrene-grafted yarn was slightly lower than that of the control. Strength retention was above 80% at initiator concentrations lower than 0.004M and reaction time less than 4 h. However, at higher initiator concentrations and longer reaction periods, strength decreased

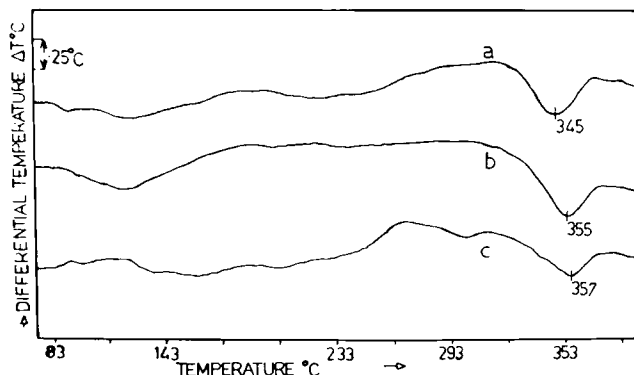


Fig. 4. Thermograms of cotton-polystyrene graft copolymers under nitrogen: (a) ungrafted cotton; (b) percent graft 9.04; (c) percent graft 39.01.

continuously.<sup>17</sup> This fall in strength might be due to the degradative action of the acid at higher initiator concentrations. These findings were in agreement with those of the earlier workers who have reported a fall in breaking strength of cotton fibers due to radiation grafting of styrene<sup>18</sup> and ceric ion grafting of acrylic monomers.<sup>19</sup>

**Moisture regain.** Moisture regain of styrene-grafted cotton was lower than that of control cotton. It decreased gradually with the increase in percent graft (Fig. 1). In cotton cellulose, the free hydroxyl groups in the amorphous region are mainly responsible for the absorption of water, since the crystalline regions are inaccessible. It is in these amorphous regions and on the surface of crystallites that graft copolymerization takes place. Hence, the grafting of polymers that are hydrophobic in nature is expected to decrease the moisture regain. These results are in agreement with earlier reports<sup>3,19,20</sup> that moisture regain decreases with increase in percent graft.

**Water sorption.** Equilibrium water sorption isotherms for cotton-polystyrene copolymers are given in Figure 2. Water sorption decreased with the increase in percent graft. Poutre et al.<sup>21</sup> also reported that styrene grafting reduces the equilibrium water content of wood pulp and cellulose.

**Water repellency.** Cotton-polystyrene graft copolymers having more than 4% graft showed improved resistance to wetting. These samples took more than 2 h to be wetted as compared with the instantaneous wetting of untreated yarn (Table I). Negeshi et al.<sup>22</sup> also reported that water repellency acquired by grafting was found to be retained by the fabric far better than the resin-treated fabrics.

**Solubility in CED.** Cotton-polystyrene graft copolymers could not be dissolved completely in 0.5 M CED, a solvent for cotton. This is due to the change in the basic nature of cotton brought about by grafting and hence is a proof of grafting. Solubility of the graft copolymers decreased with increase in percent graft (Fig. 3). These results corroborated the findings of Huang et al.<sup>3</sup> and Demint et al.<sup>20</sup> who reported that the solubility of styrene-grafted cotton linters in 0.5 M CED decreased with increase in percent graft.

**Solubility in 72% sulfuric acid.** Cotton-polystyrene graft copolymers could not be dissolved completely in 72% sulfuric acid, while ungrafted cotton was completely soluble (Table I). This change in solubility is due to grafting. Sol-

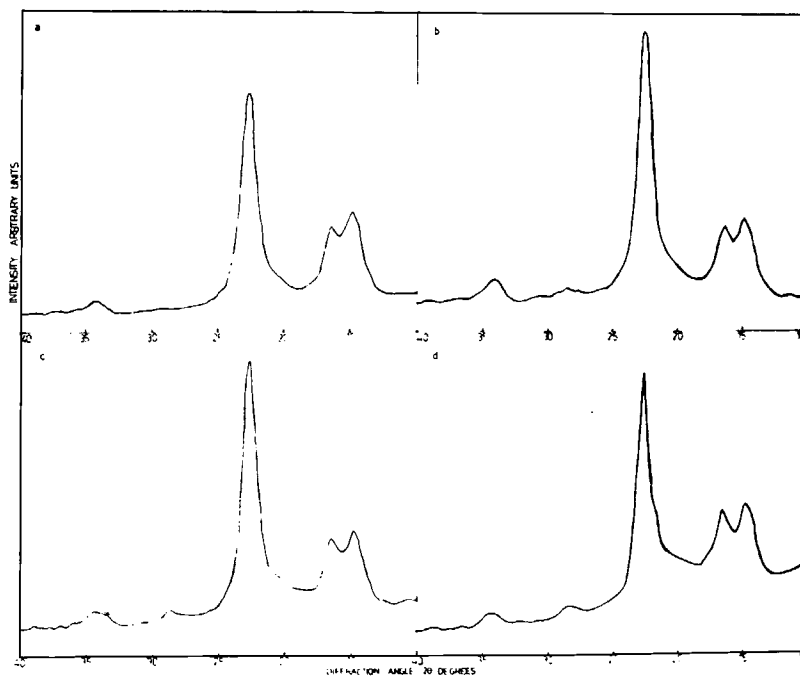


Fig. 5. X-Ray diffractograms of cotton-polystyrene graft copolymers: (a) ungrafted cotton; (b) percent graft 9.04; (c) percent graft 31.67; (d) percent graft 54.15.

ability of the graft copolymers in 72% sulfuric acid decreased with increase in percent graft (Fig. 3). These results corroborated the findings of Dasgupta,<sup>23</sup> who reported improvement in resistance of cotton fabrics to the action of acids and corrosive chemicals as a result of grafting.

*Differential thermal analysis (DTA).* DTA curves for cotton-polystyrene graft copolymers obtained under nitrogen atmosphere are shown in Figure 4. Ungrafted cotton showed a single sharp endothermic peak at 345°C. The graft copolymer with 9% graft showed a single endothermic peak at 355°C, and that with 39% graft showed a single endothermic peak at 357°C. The absence of a separate peak for polystyrene is an additional proof of grafting. Schwenker and Pacsu<sup>7</sup> observed a single endothermic peak at 370°C in the DTA curve of cotton-polyacrylonitrile graft copolymer, while the curve for the physical mixture of 70% cotton and 30% polyacrylonitrile had an additional exothermic peak at 278°C, which is unique for homopolymer polyacrylonitrile.

*X-ray diffractograms.* The basic X-ray diffraction pattern of cotton-polystyrene graft copolymers remained almost the same as that of cotton (Fig. 5). This is to be expected as the grafted polymer chains do not form a part of the cellulose crystalline structure. However, these side chains add to the background intensity which increases with percent graft [Figs. 5(b), 5(c), 5(d)]. Iwakura et al.<sup>24</sup> also reported that the crystallinity and orientation of cotton cellulose did not change due to grafting.

*Infrared spectra.* Infrared spectra of cotton-polystyrene graft copolymers showed new peaks characteristic of polystyrene at 3080, 3060, 3020, 1600, 1490, 1450, 750, and 694  $\text{cm}^{-1}$  (Fig. 6). From the spectra it is seen that the intensity of the new peaks increased with percent graft, while the intensity of the OH group

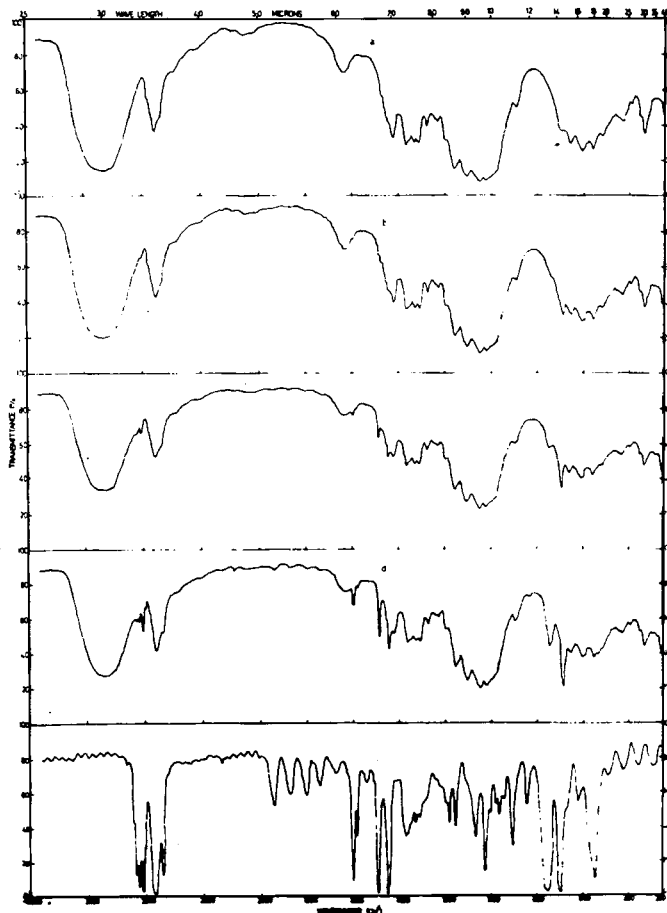


Fig. 6. Infrared spectra of cotton-polystyrene graft copolymers: (a) ungrafted cotton; (b) percent graft 9.04; (c) percent graft 24.48; (d) percent graft 54.15; (e) polystyrene.

decreased. This is an additional proof of grafting. The intensity of the new peaks can be used to estimate the styrene content of the graft copolymers. Several new bands characteristic of polystyrene in the infrared spectra of cotton-polystyrene graft copolymers obtained by radiation grafting have been reported by earlier workers also.<sup>8,25</sup>

*Electron micrograph.* Transmission electron micrographs of the graft copolymers show that the grafts are uniformly distributed throughout the cross section of the fiber [Figs. 7(b), 7(d)], and layering is completely masked by the graft when compared with untreated control samples [Fig. 7(a)]. This confirms the observations of the earlier workers.<sup>9</sup>

Though there was slight dissolution after treatment with 0.5M CED for 30 min, the cross-sectional shape of the grafted cotton remained almost the same [Fig. 7(c)]. At higher percent grafts, the fiber sections were unaffected by CED [Figs. 7(e), 7(f)]. No layering was observed in these cases. These facts again point to the existence of the true grafts.

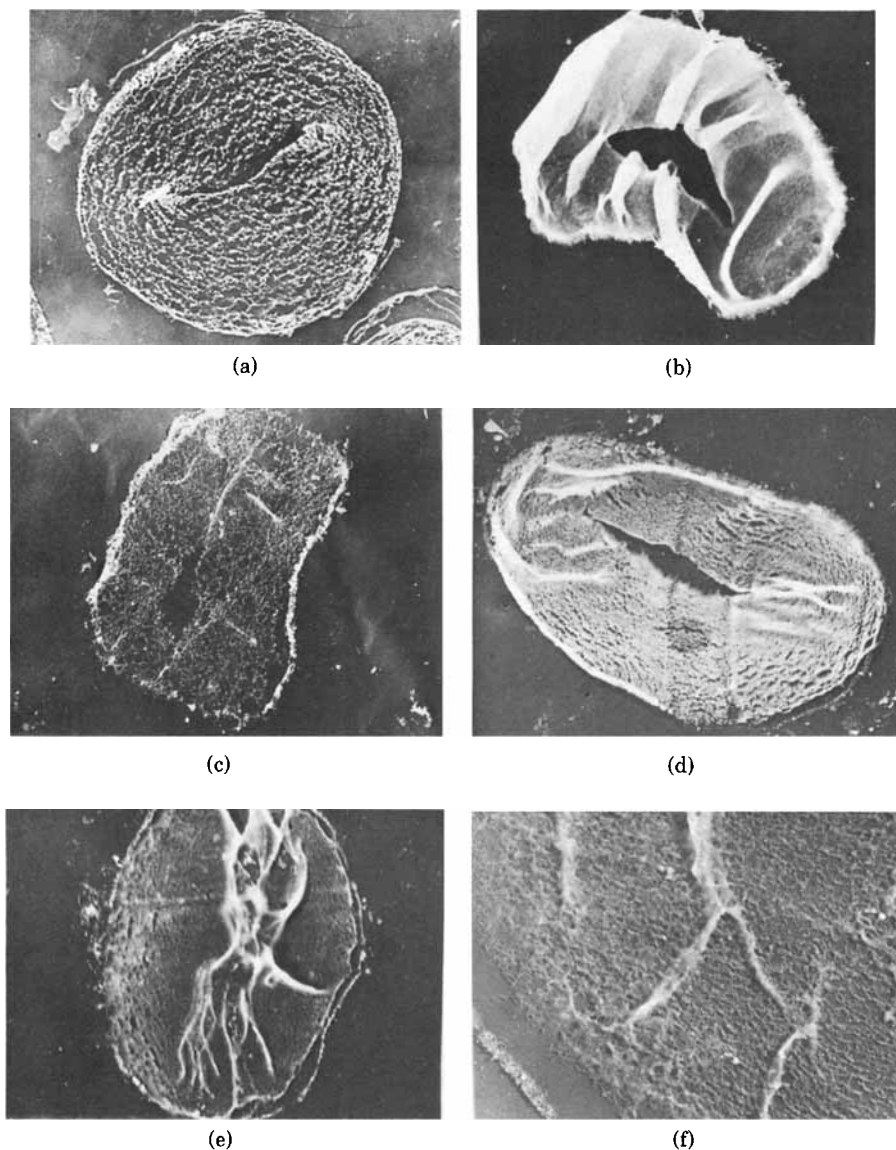


Fig. 7. Electron micrographs of cotton-polystyrene graft copolymers: (a) ungrafted cotton 2,050 $\times$ ; (b) percent graft 9.5 7380 $\times$ ; (c) percent graft 9.5, CED treated Magn. 6,050 (d) percent graft 54.15 6700 $\times$ ; (e) percent graft 54.15 CED treated 6500 $\times$ ; (f) percent graft 33.1 CED treated 21,300 $\times$ .

### CONCLUSIONS

Moisture regain, water sorption, solubility in CED, infrared spectra, DTA curves, X-ray diffractograms, and electron micrographs of cotton-polystyrene graft copolymers studied revealed distinct changes in cotton cellulose. The copolymers could not be completely dissolved in CED, a cellulose solvent. Infrared spectra of the copolymers showed new bands characteristic of the grafted polymer and decrease in OH band intensity, indicating that grafting has taken place. Electron micrographs revealed that the polymer was grafted uniformly throughout the cross section of the fiber. DTA curves showed a single endo-



thermic peak characteristic of the copolymer; the absence of a separate peak characteristic of polystyrene confirmed true grafting. The graft copolymers showed good water repellency and slight fall in breaking load.

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