# Ultraviolet-Radiation-Induced Graft Copolymerization of Styrene and Acrylonitrile onto Cotton Cellulose

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## SYNOPSIS

Photoinitiated graft copolymerization of the vinyl monomers, styrene and acrylonitrile, onto cotton cellulose was studied using uranyl nitrate and ceric ammonium nitrate as photoinitiators. Uranyl nitrate photoinitiation showed a higher level of grafting for styrene, whereas in the case of acrylonitrile ceric ammonium nitrate was found to be the better photoinitiator. Optimized conditions of grafting, when employed to cotton swollen with sodium hydroxide and zinc chloride, enhanced the graft levels for both monomers. Grafted samples were subjected to thermal analysis, as well as estimation of moisture regain and tenacity. Thermal stability increased, whereas, the moisture regain and tenacity decreased, with the increase in graft add-on in the case of both monomers. Acrylonitrile-grafted cotton showed dyeability with cationic dye that improved with the level of graft add-on. Possible explanations have been given.

## INTRODUCTION

Chemical modification of cotton by grafting reactions with various vinyl monomers provides the potential for significantly altering its physical and mechanical properties. Grafting synthetic polymers onto the cellulosic backbone reduces some of its inherent drawbacks and, in addition, the grafted fiber offers more advantages over those obtained by the physical blending of synthetic fibers with cotton fibers. The low-energy UV radiation process possesses certain advantages like less degradation of the backbone polymer and control over the grafting reaction.

Garnett et al.[1] studied the effect of radiation grafting of styrene onto cellulose in presence of methanol and also in the absence of alcoholic solvents using uranyl nitrate initiator.[2] Huang and Chandramouli[3] examined structure and properties of cellulose–styrene graft copolymer using ceric ion redox initiation. Similarly, use of inorganic salts has been found to enhance radiation grafting.[4] Davis et

al.[5] studied photoinduced graft copolymerization of styrene onto cellulose and low-molecular-weight alcohols were found to be effective as grafting bath solvents. Dramatic effect of alcohol chain length (alcohol–styrene–cellulose), on graft copolymerization, was observed. Demint and others,[6] by adding methanol or dimethyl formamide to the styrene grafting bath, observed that the rate of graft copolymerization onto cotton increased considerably. Dilli et al.[7] made extensive studies on grafting of styrene and vinyl pyridine onto cotton. Addition of methanol to the system gave maximum graft yield while, with higher alcohols, graft yield decreased in the order: ethanol > propanol > n-butanol.

Graft copolymerization reactions onto cotton cellulose with acrylonitrile have been studied using different initiation techniques, viz., manganese sulphate initiation,[8] ozonization,[9] plasma radiation,[10] Co-60-γ-ray radiation,[11] etc. Hebeish and Mehta[12] reported enhanced graft yield of acrylonitrile onto swollen cotton using ceric ion redox initiation. UV-radiation-induced vapor phase grafting of acrylonitrile onto cotton in the presence of biacetyl vapors has been studied by Seiber and Needles.[13] We have studied the use of low-energy UV radiation for the grafting of 2-hydroxyethyl methacrylate onto unswollen and swollen cotton.[14,15]

Thermal analysis enables understanding of the supramolecular structure of the fiber substance after chemical modification and determining its stability to thermal treatment. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) studies of cotton and mercerized cotton grafted with vinyl monomers are reported by Fernandez et al.[16] The effect on moisture regain and thermal degradation of styrene grafting onto cotton has been reported by Hanna et al.[17] Hurduc et al.[18] reported that acrylic monomers grafted onto cellulose showed lower thermal stability than that of unmodified cellulose. However, Varma and Narsimhan[19] observed that thermal stability increases with increase in the graft add-on and thermal stabilities of natural cotton and cotton grafted with different monomers are in the order: ethyl acrylate > methyl acrylate > natural > methyl methacrylate > n-butyl acrylate. We reported improvement in thermal stability of cotton on grafting with 2-hydroxyethyl methacrylate.[20] Thermal analysis of cotton samples grafted with acrylonitrile, acrylamide, etc. individually and in mixtures has been reported by Sharma and Daruwalla.[21]

In the present article, results of photoinitiated graft copolymerization of styrene and acrylonitrile monomers onto cotton cellulose using uranyl nitrate and ceric ammonium nitrate as photoinitiators have been reported. Effect of swelling the substrate on grafting was studied by using inorganic swelling agents, sodium hydroxide and zinc chloride, under optimum conditions. Estimation of moisture regain, tenacity and thermal behavior of the grafted samples has been carried out. In addition, acrylonitrile-grafted samples were estimated for dyeability with a cationic dyestuff.

## EXPERIMENTAL

### Materials

#### Substrates

Scoured and bleached 30 count cotton yarn was used as cellulose sample. Swollen samples of cotton were prepared by using 24% (w/w) sodium hydroxide and 70% (w/w) zinc chloride at 20°C for 1 h each, followed by thorough washing with water and then drying in air at room temperature.

#### Dye

A cationic dye, C. I. Basic Violet 16, supplied by Sandoz (India) Ltd., was used.

#### Chemicals

Acrylonitrile, supplied by S. D. Fine Chemicals Pvt. Ltd., and styrene, supplied by LOBA Chemie Indoaustranal Co., were vacuum distilled to make them free from the inhibitors. Uranyl nitrate (UN) and ceric ammonium nitrate (CAN) were used as photoinitiators.

### Graft Copolymerization

The technique of graft copolymerization onto cotton cellulose was similar to that reported earlier.[14] Aqueous grafting bath was used for acrylonitrile monomer, whereas for styrene monomer methanolic grafting bath was prepared. The grafting bath contained different amounts of the monomer, as well as those of the photoinitiators, along with the substrate. The temperature of reaction was varied between 20 and 60°C and the time of reaction increased up to 6 h. After completion of grafting, acrylonitrile-grafted samples were washed with dimethyl formamide to remove the homopolymer, boiled in water for 4 h, and then air dried. Styrene-grafted cotton samples were first washed with methanol, soxhlet extracted with benzene for 72 h, and then air dried. The graft add-on and graft yield were measured using standard formulae.[14]

### Moisture Regain

Moisture regain of control and grafted cotton samples was determined by the oven-drying method.[22]

### Tenacity

Control and grafted cotton samples of 1 cm length were tested for tenacity on an Instron Tensile Tester that recorded load–elongation curves. Stress–strain curves were recorded with a chart speed of 50 mm/min. The full scale of the recorder was adjusted for a load corresponding to 500 g.

### Dyeing with Basic Dye

Dyeing with a basic dye (C. I. Basic Violet 16) was carried out in an open bath at a pH of about 5 for 3% shade. Total time of dyeing was 90 min and liquor ratio 50. Optical density of extracted dye was determined using Pye-Unicam SP 8 −400 UV/VIS Spectrophotometer and the dye content of the sample was found using the calibration curve.

## Thermal Analysis of Grafted Cotton

DTA and TGA were carried out using a Stanton Redcroft Thermal Analyser STA-780. The cotton sample was cut to approximately 1-2 mm length and 20 ± 5 mg were taken for each analysis. Analysis was carried out from room temperature (30°C) to 500°C at a heating rate of 10°C/min and a chart speed of 200 mm/h.

## RESULTS AND DISCUSSION

The parameters of grafting reaction of styrene and acrylonitrile onto cotton, viz., concentration of the photoinitiators and the monomer and time and temperature of reaction, were optimized and the same were applied to graft copolymerization of the swollen substrate.

### Effect of Photoinitiator Concentration

Photoinitiator concentrations of both UN and CAN were varied in the range of 0.05–0.35% (w/v) in the grafting baths. Figures 1 and 2 show that graft add-on increased with increase in initiator concentration up to a certain level in the case of acrylonitrile, as well as styrene, grafting. Further increase in initiator concentration, however, brought about a decrease in graft add-on due to fast termination of growing

polymer chains owing to the presence of excess initiator. Similar observation was made earlier by Cumberbirch and Holker[23] for other cellulosic systems.

### Effect of Reaction Time

Figures 3 and 4 show the effect of changing the time of reaction from 1 to 6 h on acrylonitrile and styrene graft add-on, respectively. Graft add-on was found to increase with the increase in time up to 4 h for both monomers using the two photoinitiators. This would be due to the increasing extent of initiation and propagation stages of the graft copolymerization reaction with time. Beyond 4 h, however, graft add-on showed a decrease, presumably due to the detrimental effect of UV radiation onto the grafted side chains at longer irradiation times in the presence of initiators. Irradiation of grafted cotton samples alone in absence of any photoinitiator did not show such detrimental effect. Fouassier and Herdol[24] noted similar behavior earlier during grafting of methyl methacrylate onto cellulose.

### Effect of Reaction Temperature

The temperature of reaction was varied between 20 and 60°C. Figures 5 and 6 show that the effect of
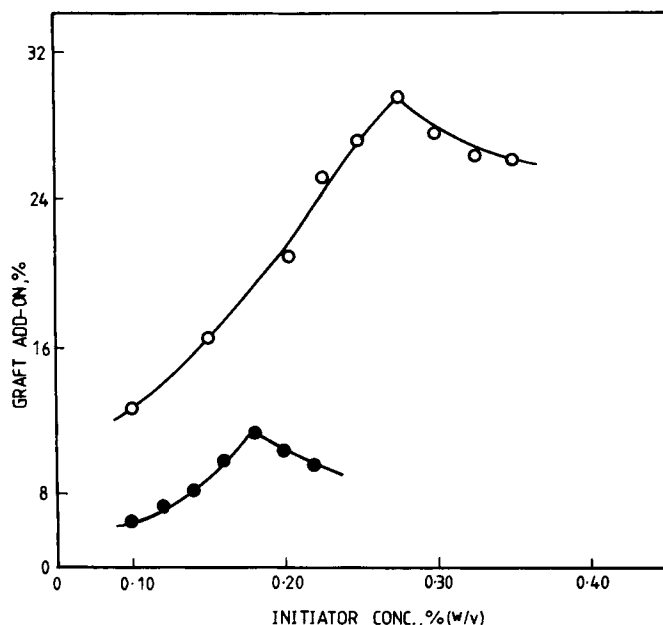


**Figure 1** Effect of initiator concentration on graft add-on. (●), UN photoinitiator, 5% (w/v) acrylonitrile, 40°C, 4 h; (○), CAN photoinitiator, 5% (w/v) acrylonitrile, 40°C, 4 h.
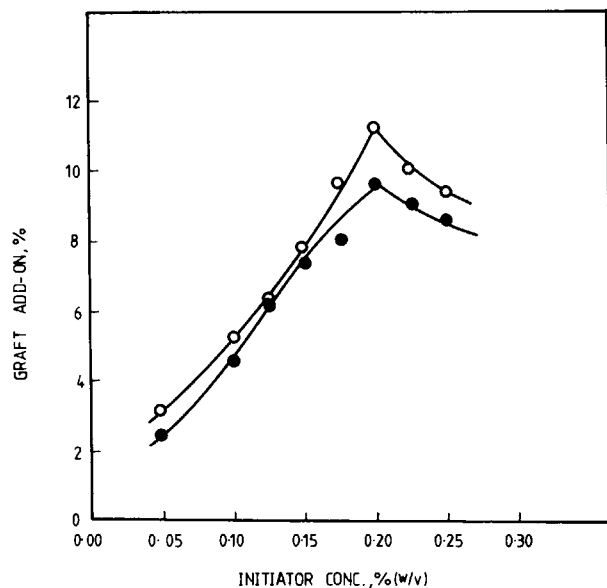
Figure 2 Effect of initiator concentration on graft add-on. (●), UN photoinitiator, 10% (w/v) styrene, 45°C, 4 h; (O), CAN photoinitiator, 30% (w/v) styrene, 50°C, 4 h.

rise in reaction temperature is to increase the graft add-on up to a certain level in the case of both monomer systems with the two photoinitiators used. For each system, the temperatures at which maximum graft add-on was obtained were different depending upon the monomer and the photoinitiator involved in the grafting reaction. Any further increase in the temperature of reaction beyond these specific values showed adverse effect on the graft add-on, presumably due to the increasing extent of radical termination at higher temperatures.

### Effect of Monomer Concentrations

The results plotted in Figures 7 and 8 for acrylonitrile and styrene grafting, respectively, show that graft add-on increased with increase in the monomer concentration for both the photoinitiators used. In the case of acrylonitrile grafting, rate of increase of graft add-on in the range of 20–30% (w/v) concentration was much lower than that in the range of 5–20% (w/v) concentration. Also, CAN appears to be the better photoinitiator, giving higher graft add-on values than UN at each concentration of acrylonitrile used. On the other hand, in the case of styrene grafting UN appears to be the more efficient photoinitiator, giving higher graft add-on values as compared to CAN. After attaining a maximum value at 30% (w/v) styrene concentration, graft add-on decreased slightly with further increase in monomer
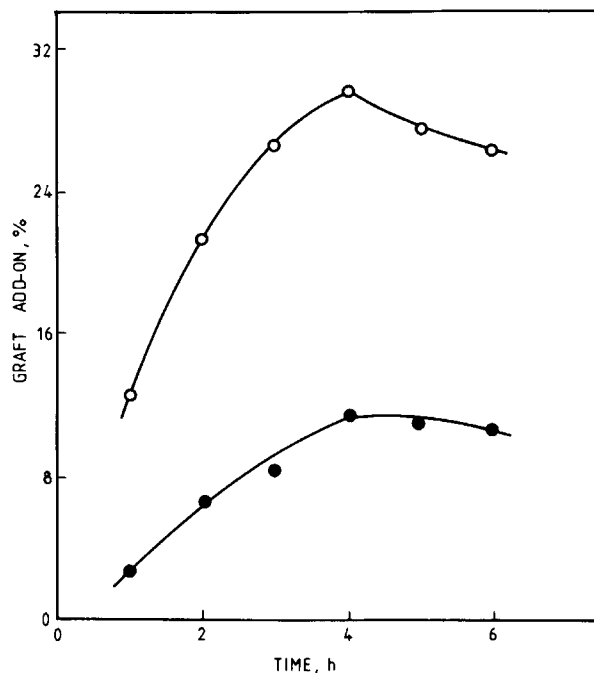


Figure 3 Effect of time of reaction on graft add-on. (●), 0.18% (w/v) UN photoinitiator, 5% (w/v) acrylonitrile, 40°C; (O), 0.275% (w/v) CAN photoinitiator, 5% (w/v) acrylonitrile, 40°C.

concentration. This is because of the depletion of methanol in the grafting bath, which should be in sufficient quantity to permit efficient swelling of the
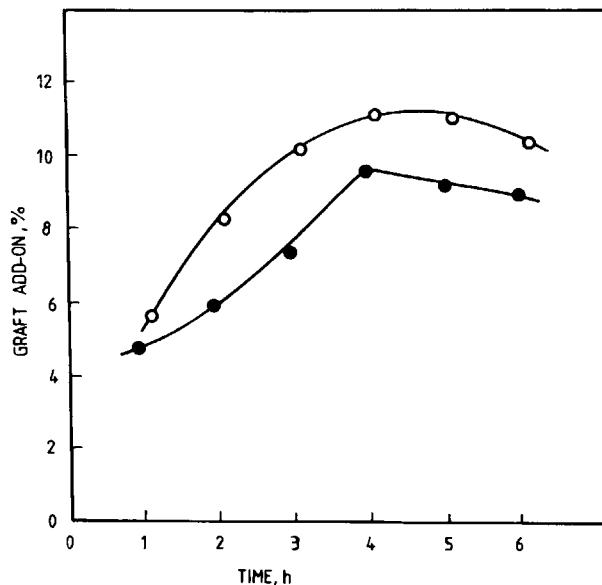


Figure 4 Effect of time of reaction on graft add-on. (●), 0.20% (w/v) UN photoinitiator, 10% (w/v) styrene, 45°C; (O), 0.20% (w/v) CAN photoinitiator, 30% (w/v) styrene, 50°C.
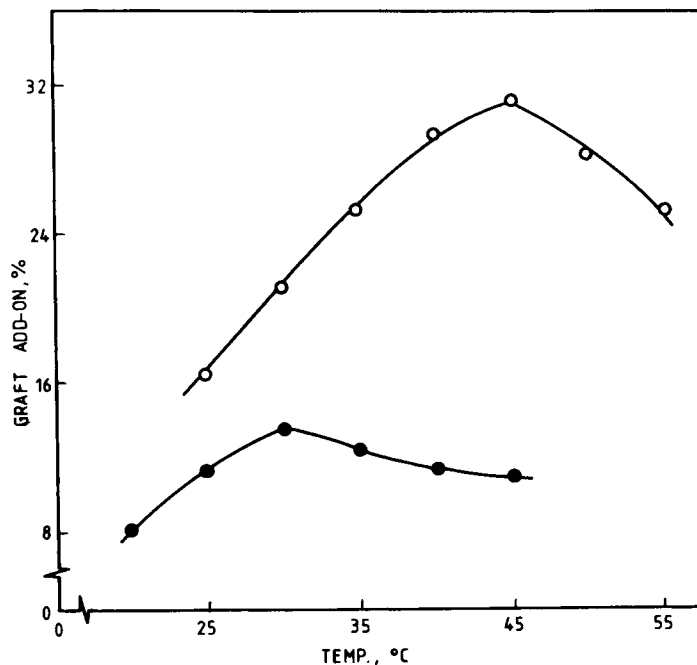
**Figure 5**  Effect of temperature of reaction on graft add-on. (●), 0.18% (w/v) UN photoinitiator, 5% (w/v) acrylonitrile, 4 h; (○), 0.275% (w/v) CAN photoinitiator, 5% (w/v) acrylonitrile, 4 h.

fiber and allow grafting reaction to proceed. Thus, as styrene concentration increases methanol concentration decreases in the grafting bath, leading to a decrease in the styrene graft add-on.

When the effect of acrylonitrile concentration on graft yield was studied, it was found that the values for acrylonitrile concentration at which maximum graft yield was observed were dependent upon the
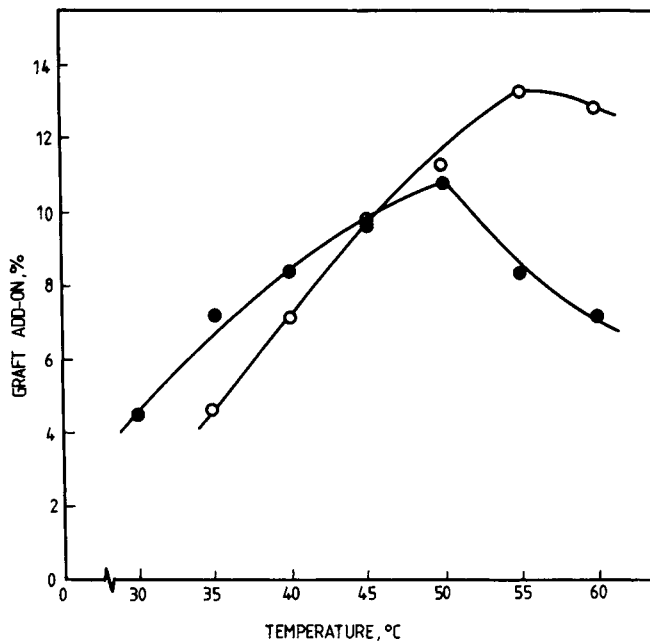


**Figure 6**  Effect of temperature of reaction on graft add-on. (●), 0.20% (w/v) UN photoinitiator, 10% (w/v) styrene, 4 h; (○), 0.20% (w/v) CAN photoinitiator, 30% (w/v) styrene, 4 h.
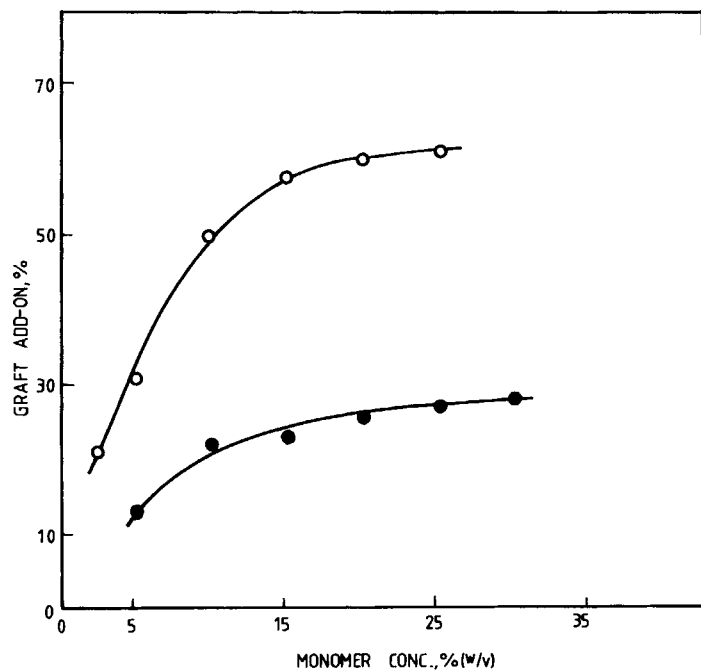
**Figure 7**    Effect of acrylonitrile concentration on graft add-on. (●), 0.18% (w/v) UN photoinitiator, 30°C, 4 h; (O), 0.275% (w/v) CAN photoinitiator, 45°C, 4 h.
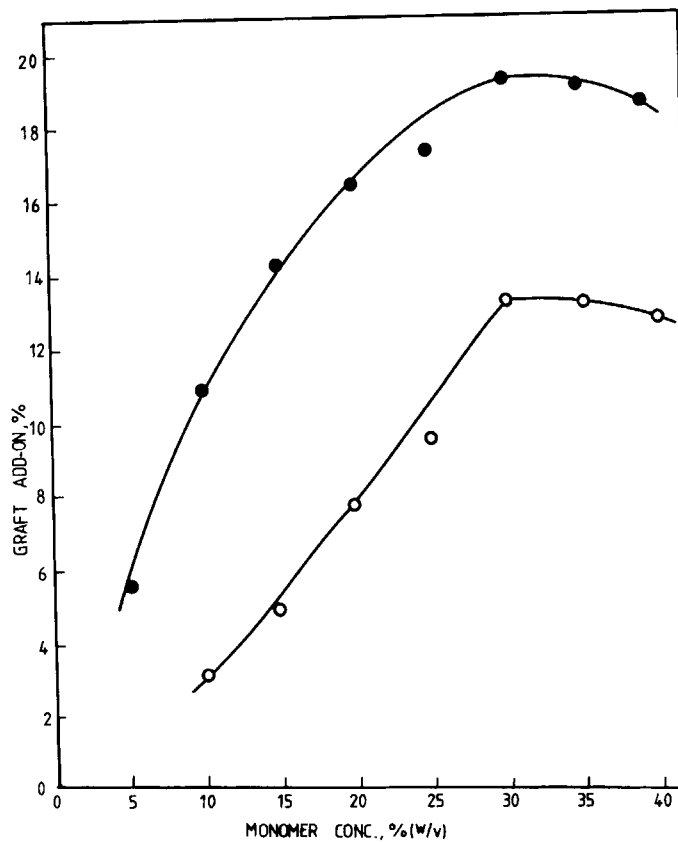


**Figure 8**    Effect of styrene concentration on graft add-on. (●), 0.20% (w/v) UN photoinitiator, 50°C, 4 h; (O), 0.20% (w/v) CAN photoinitiator, 55°C, 4 h.
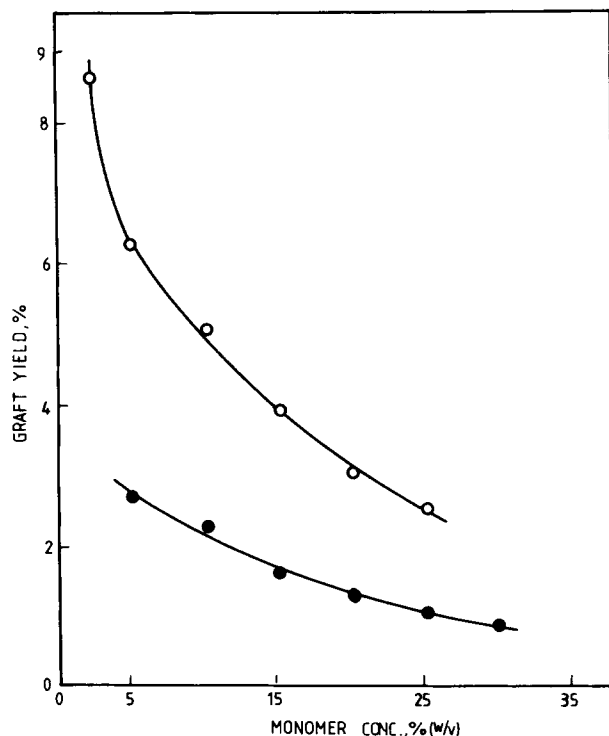
**Figure 9**   Effect of acrylonitrile concentration on graft yield. (●), 0.18% (w/v) UN photoinitiator, 30°C, 4 h; (○), 0.275% (w/v) CAN photoinitiator, 45°C, 4 h.

photoinitiator used, although for both initiators graft yield decreased gradually with increase in monomer concentration. This suggests that the utilization of acrylonitrile monomer is better at this specific con-

centration than that at any other concentration (Fig. 9). Although higher graft add-on values were obtained beyond this concentration, there was correspondingly higher homopolymer formation also, which has an effect of lowering graft yield.

Figure 10 shows infrared spectra obtained for ungrafted cotton, as well as for cotton grafted with acrylonitrile and styrene. The additional peak observed at 2249 $cm^{-1}$ wavelength in the spectrum for acrylonitrile-grafted cotton indicates introduction of —CN groups in the fiber structure due to acrylonitrile grafting,[25] whereas the peak observed at 1620 $cm^{-1}$ wavelength in the spectrum for styrene-grafted cotton indicates introduction of aromatic C—C stretch. This was also observed by Guthrie and Haq.[26]

## Effect of Preswelling

The graft copolymerization reaction conditions, thus optimized, viz., grafting time, temperature, and the photoinitiator concentration, were employed during grafting of zinc chloride-swollen and sodium hydroxide-swollen cotton substrates with acrylonitrile and styrene. Tables I and II give the results on graft add-on of the unswollen and swollen cotton with changes in concentrations of acrylonitrile and styrene, respectively, in the grafting bath under optimized conditions of reaction. Thus, swollen cotton showed very high graft add-on values as compared to those for unswollen cotton at each concentration of acrylonitrile and styrene used. The higher graft add-on values in the case of swollen cotton were
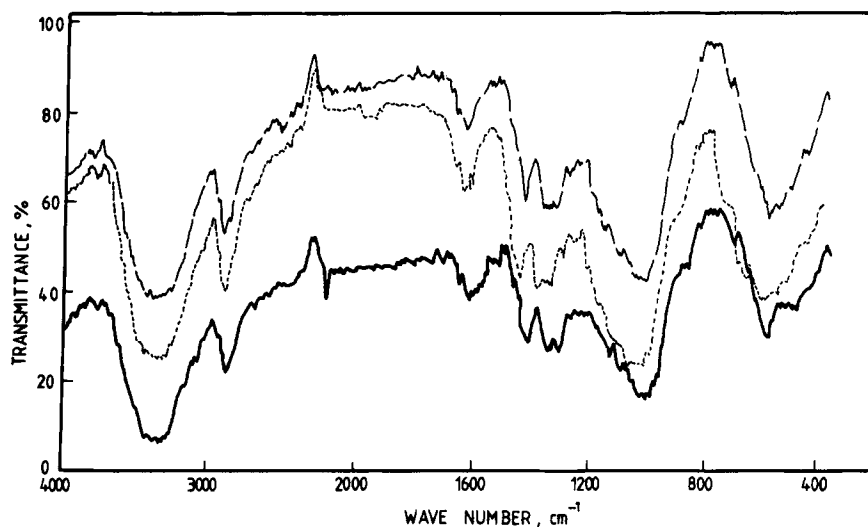


**Figure 10**   Infrared spectra of cotton samples. (– – –), control cotton; (– – – – – – –), styene-grafted cotton; (———), acrylonitrile-grafted cotton.

**Table I   Effect of Swelling on Grafting of Acrylonitrile onto Cotton Cellulose**

| Acrylonitrile Concentration (%) (w/v) | Cotton Sample | Graft Add-on (%) | |
| --- | --- | --- | --- |
| | | UN Initiation[a] | CAN Initiation[b] |
| 2.5 | Unswollen | — | 21.60 |
| | NaOH swollen | — | 38.15 |
| | ZnCl$_2$ swollen | — | 35.64 |
| 5.0 | Unswollen | 13.50 | 31.25 |
| | NaOH swollen | 22.64 | 47.80 |
| | ZnCl$_2$ swollen | 19.54 | 45.36 |
| 10.0 | Unswollen | 22.46 | 50.48 |
| | NaOH swollen | 35.36 | 58.32 |
| | ZnCl$_2$ swollen | 32.45 | 55.45 |
| 15.0 | Unswollen | 23.58 | — |
| | NaOH swollen | 38.12 | — |
| | ZnCl$_2$ swollen | 36.20 | — |

[a] UN initiation, 0.18% (w/v) UN, 30°C, 4 h.
[b] CAN initiation, 0.275% (w/v) CAN, 45°C, 4 h.

**Table II   Effect of Swelling on Grafting of Styrene onto Cotton Cellulose**

| Styrene Concentration (%) (w/v) | Cotton Sample | Graft Add-on (%) | |
| --- | --- | --- | --- |
| | | UN Initiation[a] | CAN Initiation[b] |
| 10.0 | Unswollen | 10.84 | 3.18 |
| | NaOH swollen | 19.23 | 10.45 |
| | ZnCl$_2$ swollen | 17.20 | 8.74 |
| 20.0 | Unswollen | 16.38 | 7.60 |
| | NaOH swollen | 24.50 | 16.55 |
| | ZnCl$_2$ swollen | 21.76 | 15.90 |
| 30.0 | Unswollen | 19.12 | 13.20 |
| | NaOH swollen | 26.46 | 17.42 |
| | ZnCl$_2$ swollen | 24.10 | 15.24 |

[a] UN initiation, 0.20% (w/v) UN, 50°C, 4 h.
[b] CAN initiation, 0.20% (w/v) CAN, 55°C, 4 h.

**Table III   Effect of Grafting of Acrylonitrile on Moisture Regain (MR) of Cotton**

| Acrylonitrile Concentration (%) (w/v) | Unswollen | | ZnCl$_2$ swollen | | NaOH swollen | |
| --- | --- | --- | --- | --- | --- | --- |
| | Graft Add-on (%) | MR (%) | Graft Add-on (%) | MR (%) | Graft Add-on (%) | MR (%) |
| 0.0 | 0.00 | 6.13 | 0.00 | 8.70 | 0.00 | 9.20 |
| 2.5 | 21.60 | 4.87 | 35.64 | 5.83 | 38.15 | 6.33 |
| 5.0 | 31.25 | 4.39 | 45.36 | 5.58 | 47.80 | 5.84 |
| 10.0 | 50.48 | 3.98 | 55.45 | 4.92 | 58.38 | 5.40 |
| 15.0 | 58.30 | 3.80 | — | — | — | — |
| 20.0 | 60.50 | 3.67 | — | — | — | — |
| 25.0 | 62.14 | 3.65 | — | — | — | — |

CAN initiation, 0.275% (w/v) CAN, 45°C, 4 h.

**Table IV   Effect of Grafting of Styrene on Moisture Regain (MR) of Cotton**

| Styrene Concentration (%) (w/v) | Unswollen | | ZnCl₂ swollen | | NaOH swollen | |
|---|---|---|---|---|---|---|
| | Graft Add-on (%) | MR (%) | Graft Add-on (%) | MR (%) | Graft Add-on (%) | MR (%) |
| 0 | 0.0 | 6.13 | 0.00 | 8.70 | 0.00 | 9.20 |
| 10 | 10.84 | 4.68 | 17.20 | 6.30 | 19.23 | 6.90 |
| 20 | 16.38 | 3.95 | 21.76 | 6.15 | 24.50 | 6.51 |
| 30 | 19.12 | 3.60 | 24.10 | 5.73 | 26.46 | 6.32 |

UN initiation, 0.20% (w/v) UN, 50°C, 4 h.

attributed to the higher accessibility and greater reactivity of the substrate than the unswollen one. Moreover, in the case of sodium hydroxide-swollen cotton graft add-on was found to be higher than that in the case of zinc chloride-swollen sample under equivalent conditions of grafting due to stronger swelling action exerted by sodium hydroxide than that by zinc chloride. Thus, the swelling of substrate prior to graft copolymerization helps obtaining higher graft levels under milder conditions of grafting. This is particularly relevant for UV-radiation-induced grafting as it is difficult to attain very high graft levels by this low-energy source.

## Moisture Regain

Moisture regain values for control, zinc chloride-swollen, and sodium hydroxide-swollen cotton samples were 6.13, 8.70, and 9.20%, respectively. Upon grafting acrylonitrile and styrene onto these samples, it was observed that moisture regain decreased gradually with increase in graft add-on. These results are given in Tables III and IV, respectively. This decrease in moisture regain was attributed to the introduction of hydrophobic groups, such as —CN from acrylonitrile, that reduce moisture sorption. Moreover, the drop in moisture regain is
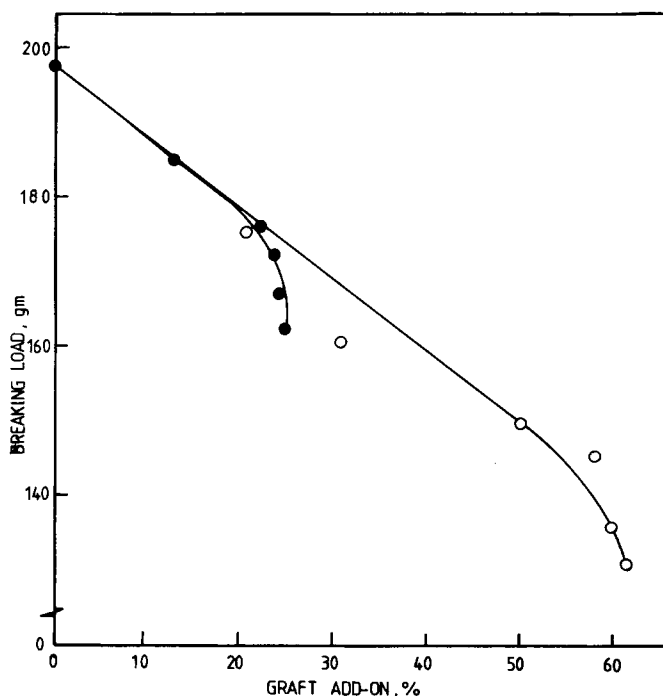


**Figure 11**   Effect of acrylonitrile graft add-on on breaking load. (●), UN photoinitiator; (○) CAN photoinitiator.
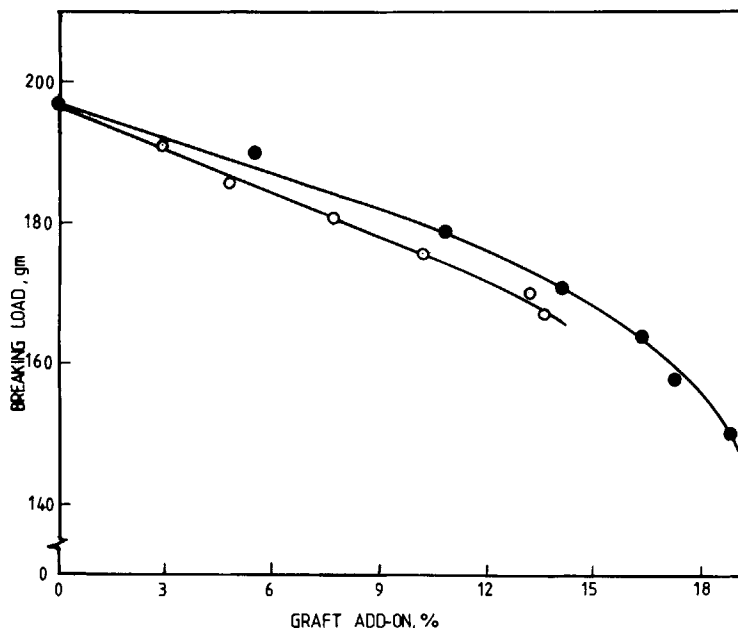
**Figure 12** Effect of styrene graft add-on on breaking load. (●), UN photoinitiator; (○) CAN photoinitiator.

higher for the styrene-grafted cotton than for acrylonitrile-grafted cotton due to the more hydrophobic nature of the former.

## Tenacity

Tensile strength of cotton yarn grafted with both acrylonitrile and styrene was found to decrease progressively with increase in graft add-on (Figs. 11 and 12). In the preliminary experiments, ungrafted samples, exposed to UV radiations up to 6 h, did not show any change in the breaking load, suggesting that grafting itself has a detrimental effect on tensile strength behavior. The increase in graft add-on having negative influence on tensile strength may be attributed to the increasing extent of crosslinking in the fiber structure as the graft add-on increases. Also, the grafted side chains act only as a dead load as far as the tensile properties are concerned and, hence, contribute toward the decrease in tenacity. The loss in tensile strength is more in the case of styrene-grafted samples than for acrylonitrile-grafted samples at equivalent levels of graft add-on, perhaps due to higher molecular weight of styrene monomer, which exerts more load on the backbone molecular chains. Appreciable amounts of graft levels, thus, can be obtained without any severe loss in tensile strength, a necessity for textile substrates.

## Dyeability

Cotton, as such, cannot be dyed with cationic dyes. When acrylonitrile-grafted samples were dyed with

a cationic dye (C. I. Basic Violet 16), dyeability was found to increase with the increase in the graft add-on, as shown in Figure 13. Dyeability, as well as increase in dye uptake with higher graft add-on, was due to the presence of anionic nitrile groups in acrylonitrile-grafted cotton samples.
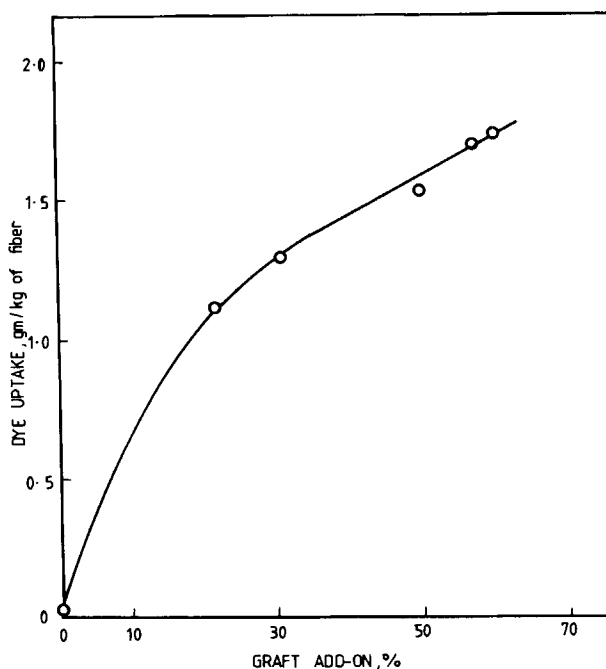


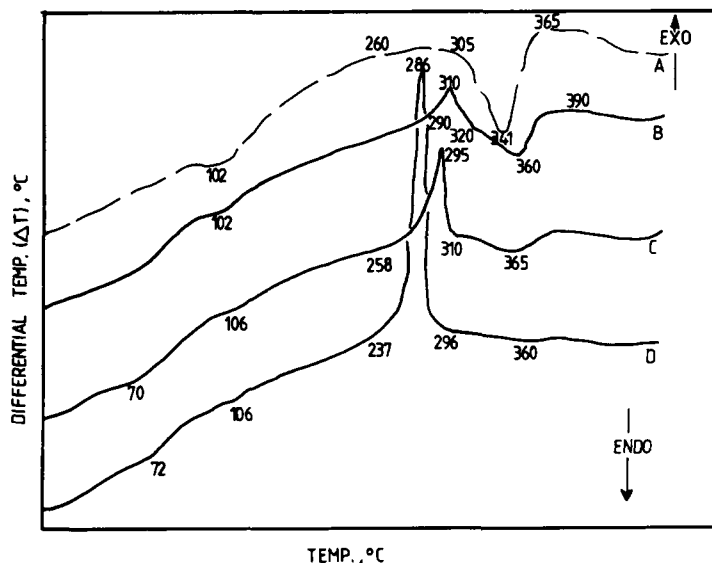**Figure 13** Effect of acrylonitrile graft add-on on basic dye uptake.

**Figure 14**   Effect of acrylonitrile graft add-on on differential temperature. (A), 0.00%; (B), 13.50%; (C), 31.25%; (D), 62.14%.

## DTA

Figures 14 and 15 show the DTA curves of natural cotton and cotton grafted at different levels with acrylonitrile and styrene. In the DTA curve of control cotton, an endotherm was observed at around 100°C due to moisture desorption, followed by an exothermic process starting at about 260°C due to oxidative attack at the carbonyl groups and the C — H bonds. The major endothermic reaction was

observed to start at 305°C with a peak at 341°C, which reflects the thermal depolymerization of cellulose.

DTA curves of cotton grafted with acrylonitrile, shown in Figure 14, reveal that grafting with acrylonitrile presents an altered DTA curve giving an exothermic peak around 310°C, occurring prior to the cellulose decomposition endotherm at 341°C, which reflects the presence of nitrile groups. As graft add-on increases, intensity of the new peak increases
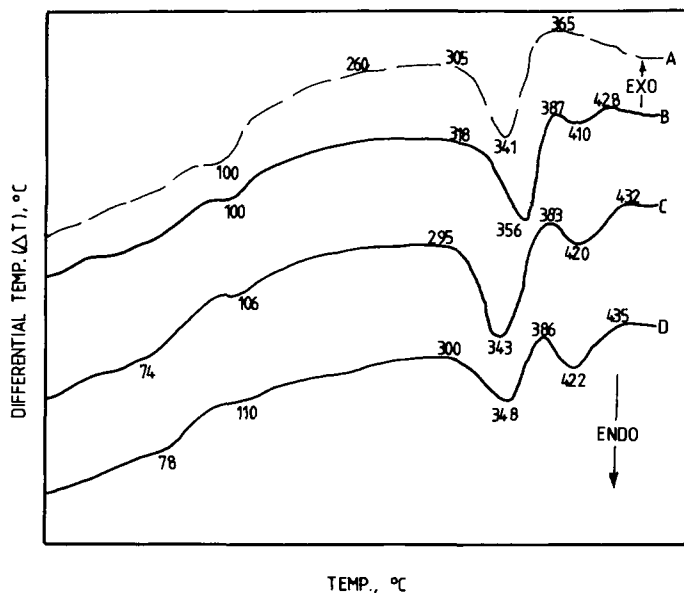


**Figure 15**   Effect of styrene graft add-on on differential temperature. (A), 0.00%; (B), 10.84%; (C), 19.12%; (D) 26.46%.
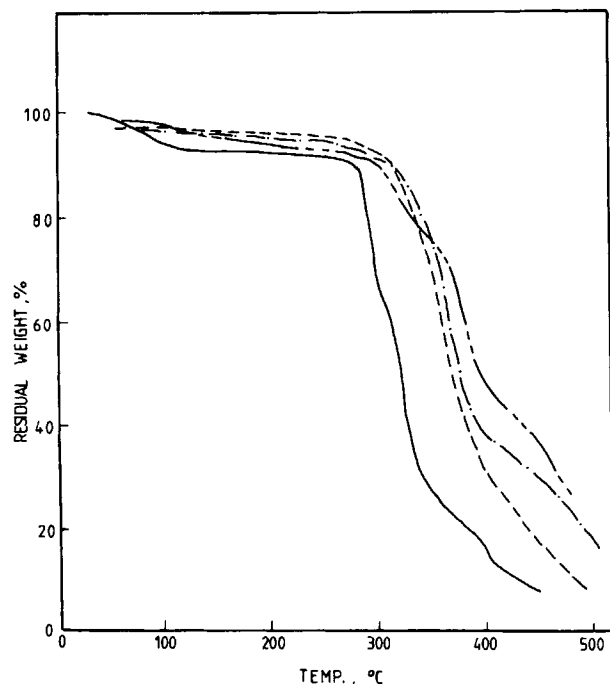
**Figure 16** Effect of temperature on residual weight of acrylonitrile-grafted cotton. (——), 0.00%; (-----), 13.50%; (- · - · -), 31.25%; (· · — · · — · ·), 62.14%.

sharply and the cellulose decomposition peak simultaneously becomes smaller and smaller, disappearing finally at 62.14% acrylonitrile graft add-on.

It is interesting to note that the new exothermic peak appearing at the 310°C for a graft add-on of 13.50% acrylonitrile goes on shifting toward lower temperature, simultaneously with increase in the peak intensity, as graft add-on increases. Thus, the peak shifted to 286°C for a sample of 62.14% acrylonitrile graft add-on. It has been reported for pure acrylonitrile that this peak appears at 296°C.[27] It was also observed that with the increase in graft add-on the endothermic peak at 100–110°C, corresponding to moisture desorption, diminished, which must be due to the decrease in moisture regain of grafted samples. From DTA curves of samples containing 31.25 and 62.14% acrylonitrile graft add-on, it is interesting to note that a new endothermic peak at around 70–75°C appears. This would probably correspond to the glass transition temperature of polyacrylonitrile, which is around 75°C.

DTA curves of styrene-grafted cotton, shown in Figure 15, indicate that grafting with styrene gives an altered DTA curve showing a new endothermic peak at around 410–425°C. This new endothermic peak was appearing after the major cellulose decomposition endotherm at 341°C, representing the presence of polystyrene copolymer. This new endothermic peak becomes larger with increase in graft add-on and, simultaneously, the cellulose decomposition endothermic peak becomes smaller. The endothermic peak around 100–110°C corresponding
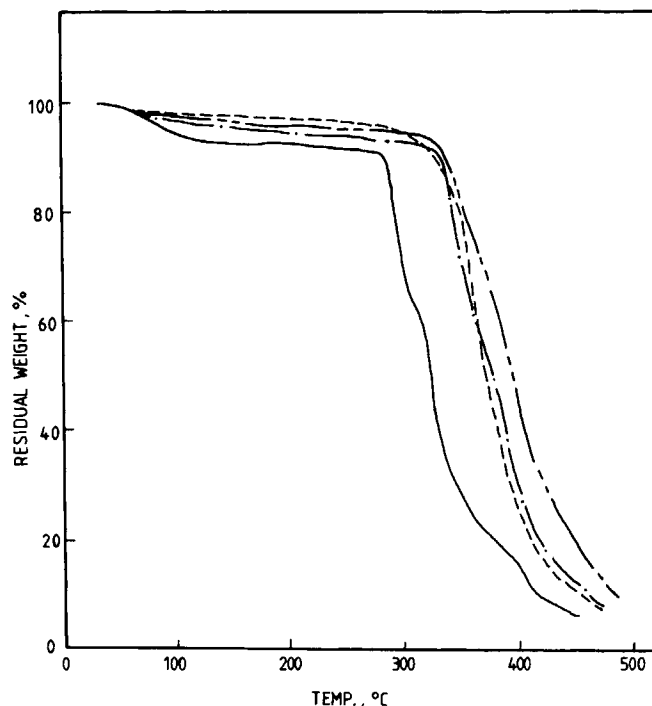


**Figure 17** Effect of temperature on residual weight of styrene-grafted cotton. (——), 0.00%; (-----), 10.84%; (- · - · -), 19.12%; (· · — · · — · ·), 26.46%.

to moisture desorption seems to be disappearing with increase in styrene graft add-on due to increased hydrophobicity of the grafted sample. It was also observed in this case that there was a small endothermic peak at 75–80°C in the DTA curves of samples of higher styrene graft amounts. This peak was probably representing the glass transition temperature of polystyrene.

## TGA

Thermograms of control cotton and cotton grafted with acrylonitrile and styrene are shown in Figures 16 and 17 and the decomposition temperature $(T_D)$ at different weight losses are presented in Tables V and VI, respectively. Shapes of thermograms of control cotton and grafted cotton samples do not differ from each other significantly. It is evident from the data that in the case of ungrafted cotton the $T_D$ at any weight loss level is considerably lower than that for cotton grafted with either acrylonitrile or styrene. At higher weight loss levels, it may be observed that the $T_D$ increases with increase in graft add-on. In control cotton, major weight loss of about 70% occurs between 270 and 345°C, whereas in the grafted samples it occurs between 310 and 405°C for a sample with 13.50% acrylonitrile graft add-on and between 325 and 392°C for a sample with 10.84% styrene graft add-on. This effect becomes more pronounced as graft add-on increases. Thus, for a sample with 62.14% acrylonitrile graft add-on, even up to a temperature of 470°C, only about 70% loss in weight of the grafted sample takes place. Similar behavior has been observed by Sharma and Daruwalla.[21]

**Table V    Temperature of Decomposition at Different Weight Losses of Cotton Grafted with Acrylonitrile**

| Weight Loss (%) | Temperature of Decomposition (°C) | | | |
| --- | --- | --- | --- | --- |
| | Graft Add-on (%) | | | |
| | 0.00 | 13.50 | 31.25 | 62.14 |
| 10 | 280 | 315 | 310 | 300 |
| 20 | 290 | 335 | 341 | 331 |
| 30 | 295 | 350 | 360 | 368 |
| 40 | 310 | 360 | 365 | 380 |
| 50 | 320 | 370 | 375 | 392 |
| 60 | 335 | 385 | 390 | 438 |
| 70 | 340 | 405 | 450 | 470 |
| 80 | 386 | 440 | 490 | — |
| 90 | 412 | 485 | — | — |

**Table VI    Temperature of Decomposition at Different Weight Losses of Cotton Grafted with Styrene**

| Weight Loss (%) | Temperature of Decomposition (°C) | | | |
| --- | --- | --- | --- | --- |
| | Graft Add-on (%) | | | |
| | 0.00 | 10.84 | 19.12 | 26.46 |
| 10 | 280 | 325 | 329 | 335 |
| 20 | 290 | 348 | 340 | 350 |
| 30 | 295 | 355 | 350 | 365 |
| 40 | 310 | 363 | 359 | 380 |
| 50 | 320 | 370 | 375 | 392 |
| 60 | 335 | 380 | 385 | 403 |
| 70 | 340 | 392 | 394 | 420 |
| 80 | 386 | 410 | 420 | 445 |
| 90 | 412 | 460 | 465 | 490 |

Thus, grafting of both acrylonitrile and styrene onto cotton was also found to be imparting better thermal stability to control cotton, even at considerably low graft add-on levels and, among the two, acrylonitrile grafting is better in this regard.

## CONCLUSION

In conclusion, the proper conditions of graft copolymerization reactions, including preswelling of substrate, have to be selected for getting an appreciable amount of graft add-on even with a low-energy source such as UV radiation. The nature and level of graft add-on determine the ultimate useful properties of the graft copolymer formed. Thermal decomposition of cotton starts at relatively higher temperatures on grafting with either acrylonitrile or styrene. Cotton grafted with acrylonitrile and styrene showed thermal stability in the order acrylonitrile > styrene > control cotton, which is also increased with increase in graft add-on.

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