

Thermal Behavior of Cotton Grafted with Vinyl Monomers Individually and in Mixture Compositions

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Synopsis

Thermal analysis of cotton samples grafted with acrylamide, acrylonitrile, methyl acrylate, and methyl methacrylate individually and in mixture compositions has been carried out. Additional endothermic peaks in the DTA curves characteristic of the polymers grafted were observed. Graft copolymerization of acrylamide and acrylonitrile makes cotton thermally more stable, while in the case of methyl acrylate- and methyl methacrylate-grafted cottons, the initial decomposition starts at higher temperatures, but subsequent decomposition is faster and the overall thermal stability is lowered. In the case of binary mixtures of acrylamide and acrylonitrile, inception of decomposition starts earlier, but subsequent decomposition takes place at much higher temperatures than for individual monomer-grafted cottons. Interaction between monomers during grafting is indicated. When fabric samples containing polyacrylamide grafts are methylolated and subsequently cross-linked, there is a reduction in the thermal stability of the treated cotton.

INTRODUCTION

The thermal behavior of cotton and modified cottons has been studied extensively in the last few years. Schwenker et al.¹ have reported thermogravimetric and differential thermal analysis data for various textile fibers. Chatterjee and Conrad² found that decomposition of cellulose took place via depolymerization through the breakdown of glucosidic linkages. Tang and Neill,³ employing DTA and TGA methods, came to the conclusion that thermal decomposition of cellulose took place in two stages where the first stage (up to about 15% loss in weight) followed a zero-order reaction with an activation energy of 33-35 kcal/mole while the second stage (up to 85% decomposition) obeyed first-order kinetics with an activation energy of 53-55.7 kcal/mole. In general, it has been found that thermal decomposition of cotton takes place in three different stages.⁴⁻⁸ The first stage consists mainly in loss in adsorbed water. The second stage, in the temperature range of 240-450°C, constitutes decomposition of cellulose where more than 70-80% decomposition of the total material takes place. During the third stage, at temperatures >450°C, there is a loss in weight of the sample of about 15-20%.

Chemical modification of cotton by way of graft copolymerization with various vinyl monomers has been studied very extensively.⁹⁻¹⁶ However, only limited information is available on the thermal behavior of grafted cottons. Hurduc

et al.¹⁷ found that the thermal stability of cellulose grafted with acrylic monomers was lower than that of the unmodified cellulose. On the other hand, Varma and Narsimhan¹⁸ observed higher stability for cotton grafted with methyl or ethyl acrylate. With methyl methacrylate- or *n*-butyl acrylate-grafted cottons, stability was lower than that of untreated cotton. Simionescu and Mihailescu¹⁹ reported that during grafting cellulose esters with acrylic acid, a change in the supramolecular structure of cotton took place which was responsible for increased thermal stability at higher temperatures. No information, at present, is available with respect to the thermal behavior of cotton grafted with binary mixtures of vinyl monomers. The present investigation was, therefore, undertaken to examine thermal stability of cotton grafted with various vinyl monomers and their mixtures by studying the corresponding primary thermograms and calculating various thermal parameters. This study has also been extended to cottons containing polyacrylamide grafts subsequently methylolated and crosslinked.

EXPERIMENTAL

Materials and Methods

Chemicals. Pure acrylamide (E. Merck) and freshly distilled acrylonitrile (BDH) were used. Methyl acrylate and methyl methacrylate were purified before use by addition of 8% sodium hydroxide solution, shaking well, and separating out pure acrylate monomer in a separating funnel. The monomer was further washed several times with distilled water, dried, and distilled. Other reagents used were reagent-grade chemicals.

Yarn. Well-scoured and bleached single yarn (80 s) was used.

Fabric. Fabric employed was singed, desized, scoured, mercerized, and bleached cotton medium poplin.

Grafting Procedure. Grafting of acrylamide and acrylonitrile individually and as mixtures of various compositions onto cotton yarn was carried out in a bath thermostatically controlled and having a stirring arrangement. Liquor-to-material ratio was maintained at 30:1. Ceric ammonium nitrate was used as a catalyst. Graft copolymerization of methyl acrylate or methyl methacrylate was carried out employing the emulsion polymerization technique. Fabric was padded with monomers emulsified in the bath using 0.5% oleyl sulfate along with ceric ammonium nitrate as a catalyst at pH 1.5. Fabric was then batched on a roller for 30 min. Grafted materials were washed, dried, and extracted for 90 hr in a Soxhlet apparatus with appropriate solvents for the polymers to remove the homopolymers formed.

Thermal Analysis

The TG, DTG, and DTA analyses were carried out using a M-O-M (Budapest) Derivatograph. All analyses reported were done in floating air at atmospheric pressure at a heating rate of 8°C/min in a platinum crucible of special shape which had an indenture at the bottom so that the thermocouple placed in it measured the temperature at the center of the crucible. A similar platinum crucible filled with Al₂O₃ was used as the inert standard. Changes in weight of the sample and of the inert reference due to heating in a resistance furnace were

recorded on photosensitive paper by means of a light beam reflected from a mirror attached to the pointer of the balance. The instrument also measured at the same time the rate of weight change (TG) with the aid of a solenoid fixed on the balance beam and moving in the field of force of a permanent magnet.

Calculation of Thermal Data

The integral procedural decomposition temperature (IPDT) was calculated by the method given by Doyle.²⁰ Activation energy (E^*) for the decomposition reaction was calculated using the Horowitz and Metzger²¹ equation as modified by Dharwadkar and Karkhanawala.²² According to this equation,

$$\ln \ln (1 - \alpha)^{-1} = \frac{E^*}{RT_i^2} \cdot \frac{100}{T_f - T_i} \theta + C$$

where α = fraction reacted, E^* = activation energy, T_i = temperature of inception of decomposition, T_f = temperature of completion of decomposition, $\theta = T - T_s$, T = temperature under consideration, T_s = inflection temperature, C = constant, and R = gas constant.

RESULTS AND DISCUSSION

The results of thermal decomposition of cotton and grafted cottons are presented in Figures 1–6 and Tables I–IV. Thermal decomposition of cotton and grafted cottons takes place in three distinct stages. In the first stage, up to a temperature of about 150°C, only slight loss in weight is observed which can be attributed to the removal of adsorbed water. During the second stage, temperature range 240–450°C, most of the decomposition of cellulose takes place. During the third stage, temperatures >450°C, undecomposed cellulose and other impurities which amount to about 10–15% of the total weight are lost.

TABLE I
Temperature of Decomposition at Different Weight Losses
of Cotton Samples Grafted with Vinyl Monomers and Crosslinked Cotton

Sample	Graft add-on, %	Temperature of decomposition, °C, at weight loss of							
		10%	20%	30%	40%	50%	60%	70%	80%
Acrylamide-grafted cotton	5	290	320	325	335	350	365	440	500
	15	300	325	335	340	360	370	445	505
Acrylonitrile-grafted cotton	25	360	390	415	440	455	495	515	550
Methyl acrylate-grafted cotton	18	300	315	320	325	330	340	380	425
Methyl methacrylate- grafted cotton	23	300	320	325	330	340	355	385	450
Acrylamide-grafted cotton, methylolated and crosslinked	15	245	315	325	345	355	375	450	515
Cotton crosslinked through DMDHEU	(resin add- on 7%)	275	305	325	335	345	350	400	470
Untreated cotton	—	270	280	285	290	295	335	425	450

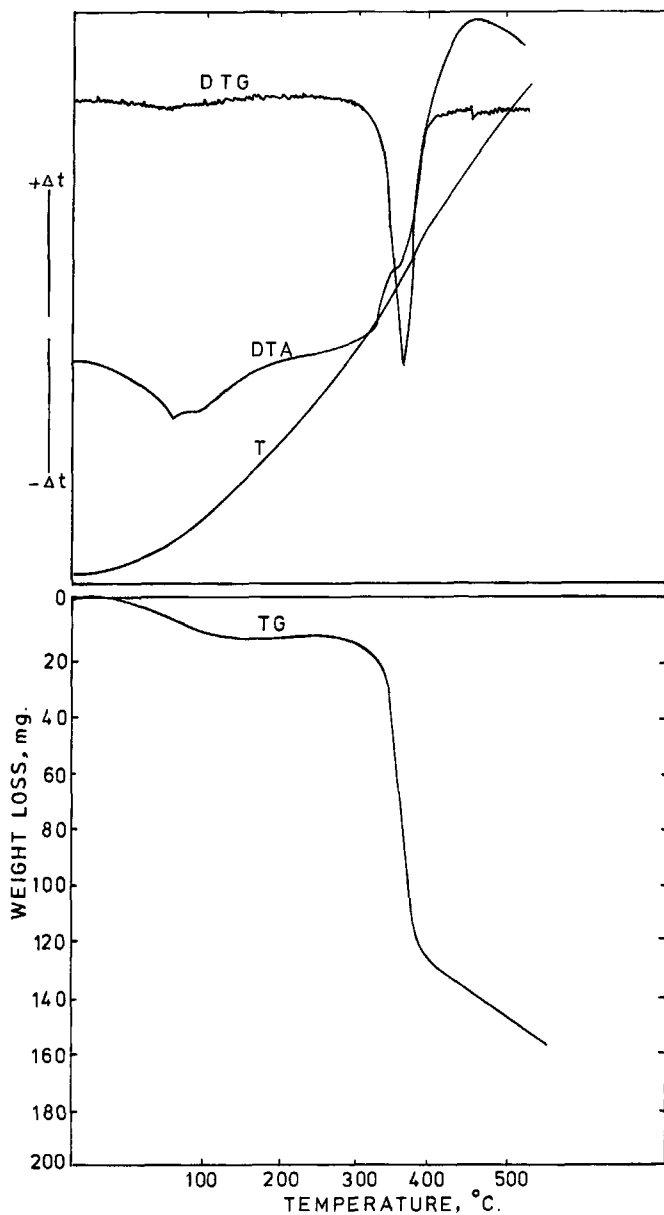


Fig. 1. Thermogram of cotton grafted with polyacrylamide (add-on 15%).

Samples grafted with acrylamide, acrylonitrile, methyl acrylate, and methyl methacrylate show characteristic thermal behavior as compared with untreated cotton. In the DTA curve of cotton, an endothermic peak at about 300°C is characteristic of cellulose decomposition. On grafting with acrylamide, a new peak at about 340°C in the thermogram appears. Similarly, in cotton grafted with acrylonitrile, methyl acrylate, and methyl methacrylate, new peaks appear at 460°, 360°, and 370°C, respectively (Figs. 1-4).

In the analysis of TGA curves, the second stage, which is characteristic of

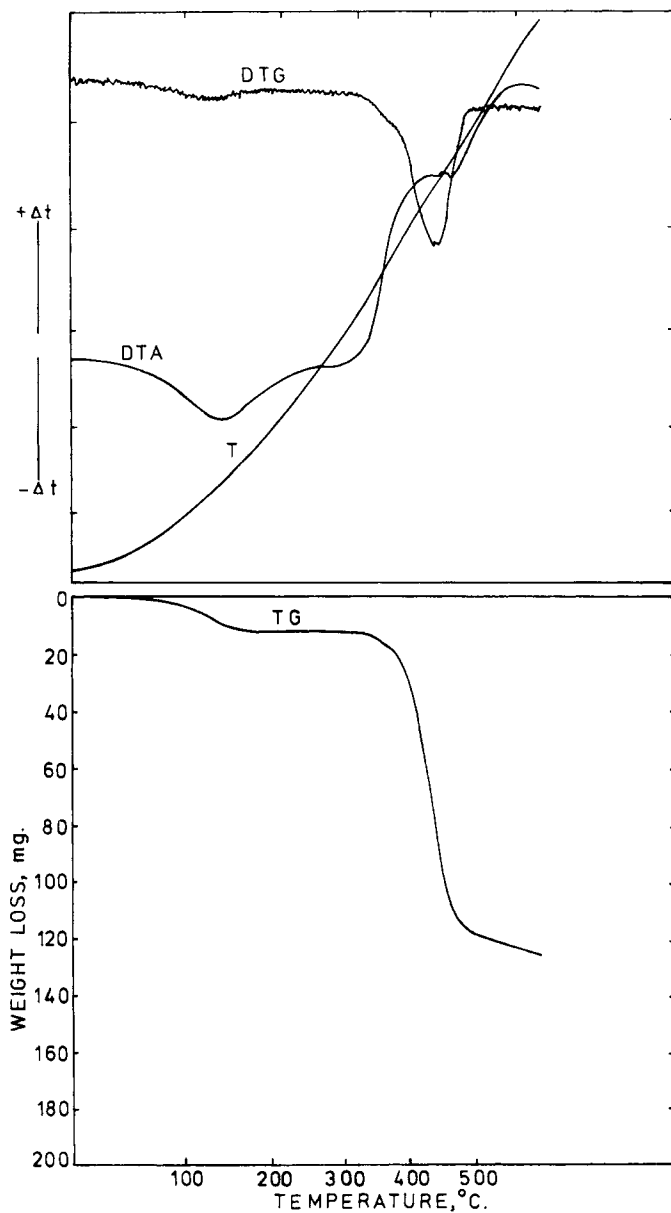


Fig. 2. Thermogram of cotton grafted with polyacrylonitrile (add-on 25%).

cellulose decomposition, was analyzed for all calculations of thermal data. The shapes of the TGA thermograms for untreated cotton and cotton grafted with different monomers are very similar (Fig. 5). However, thermal stability of the grafted cottons depends on the type of polymer grafted and the extent of grafting. As far as thermal stability is concerned, a fair idea can be obtained from the decomposition temperatures at various weight losses. Results of Table I show that decomposition temperature (T_D) at 10% decomposition for untreated cotton is 270°C, while for cotton grafted with acrylamide at 5% and 15% add-on, the

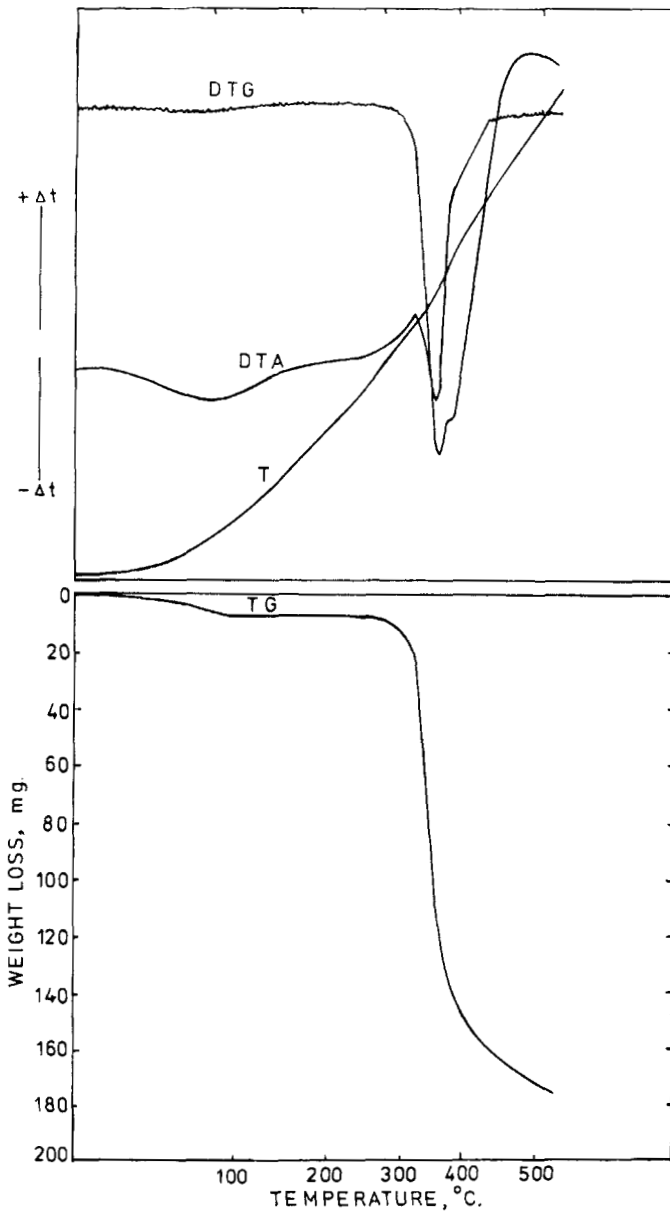


Fig. 3. Thermogram of cotton grafted with poly(methyl acrylate) (add-on 18%).

decomposition temperatures are 290° and 300°C, respectively. At 50% weight loss, T_D for untreated cotton is 295°C, while for 5% and 15% acrylamide-grafted cottons, the values are 350° to 360°C, respectively. The main decomposition of cotton takes place in the range of 270° to 450°C, while for cotton grafted with acrylamide the decomposition range lies between 280° and 500°C. In case of cotton grafted with acrylonitrile, the T_D value at 10% decomposition is 360°C, and 50% decomposition takes place at 455°C. In this case, up to a temperature of 500°C, only about 60% loss in weight of the grafted samples takes place. For

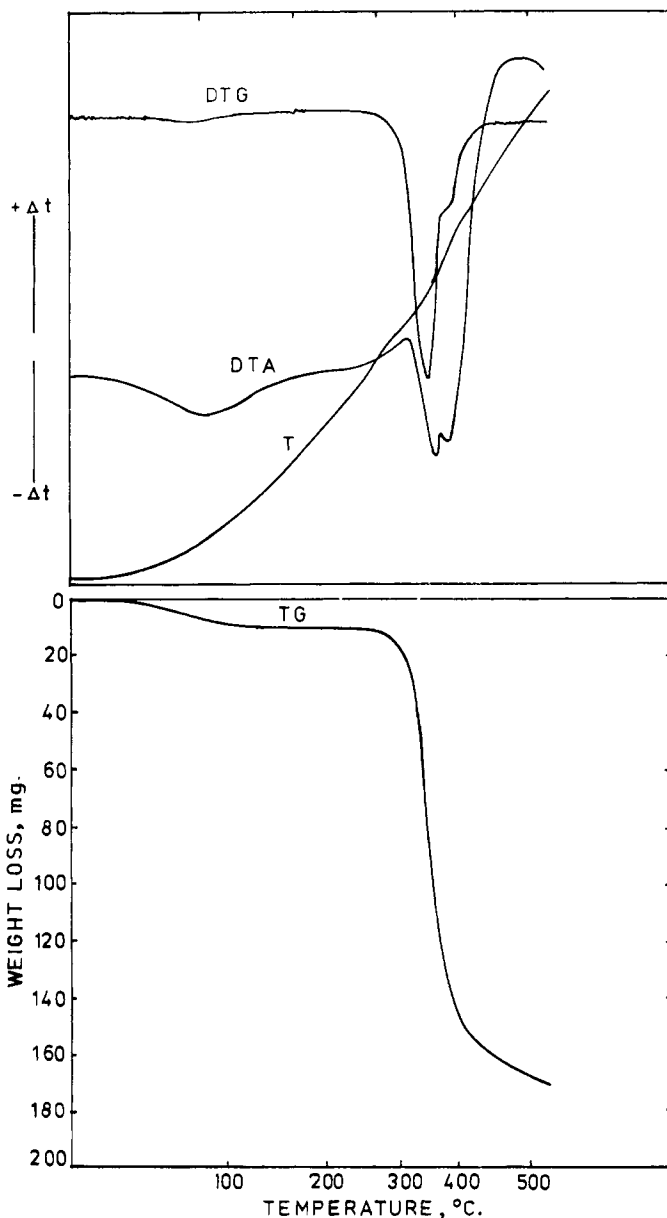


Fig. 4. Thermogram of cotton grafted with poly(methyl methacrylate) (add-on 23%).

cotton grafted with methyl acrylate (add-on 18%) at 10% and 50% decomposition, the temperatures of decomposition are 300° and 330°C, respectively. Most of the decomposition of cotton grafted with methyl acrylate takes place in the range of 300° and 400°C. Similarly, in case of methyl methacrylate-grafted cottons, the decomposition temperatures at 10% and 50% weight loss are 300° and 340°C, and more than 80% loss in weight takes place below 450°C.

It may be noted from the above results that thermal decomposition of grafted cottons generally starts at relatively higher temperatures as compared with that

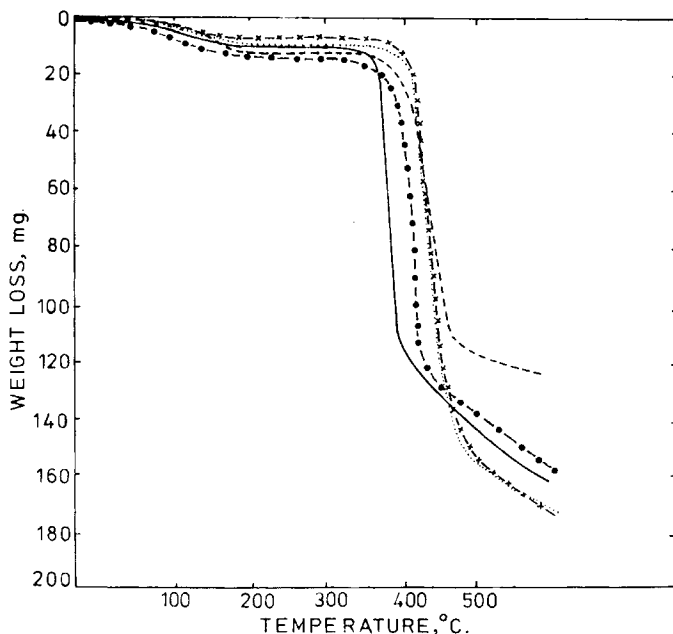


Fig. 5. Thermogravimetric analysis curves of cotton grafted with different vinyl monomers: (—) untreated cotton; (-●-) polyacrylamide (add-on 15%); (-×-) polyacrylonitrile (add-on 25%); (-·-·-) poly(methyl acrylate) (add-on 18%); (-·-·-) poly(methyl methacrylate) (add-on 23%).

for ungrafted cotton. For instance, in case of acrylonitrile-grafted cotton, initiation of decomposition commences at a later stage as compared with cotton. Similarly, with methyl acrylate- and methyl methacrylate-grafted cottons, decomposition commences at comparatively higher temperatures as compared with cotton, but this is followed by rapid decomposition. Similar behavior has been also observed by Varma and Narsimhan.¹⁸ However, with these grafted samples, decomposition is complete at an earlier stage ($\sim 425^{\circ}\text{C}$) as compared with ungrafted sample (Table I). Thus, grafting of acrylamide or acrylonitrile imparts

TABLE II
Thermal Data for Cotton Grafted with Vinyl Monomers and Crosslinked Cotton

Sample	Graft add-on, %	IDT, °C	FDT, °C	IPDT, °C	E^* , kcal/mole
Acrylamide-grafted cotton	5	210	380	341	24.9
	15	240	400	354	23.8
Acrylonitrile-grafted cotton	25	330	465	404	31.2
Methyl acrylate-grafted cotton	18	255	390	388	32.7
Methyl methacrylate-grafted cotton	23	245	400	356	46.8
Acrylamide-grafted cotton, methylolated and crosslinked	15	191	365	350	22.2
Cotton crosslinked through DMDHEU	(resin add-on 7%)	170	360	346	24.1
Untreated cotton	—	235	360	331	26.2

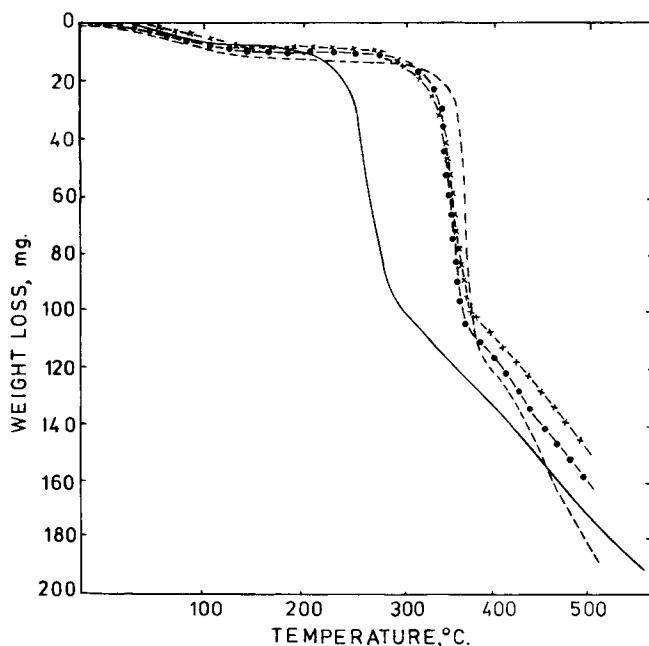


Fig. 6. Thermogravimetric analysis curves of cotton grafted with poly(acrylamide-acrylonitrile) mixtures at different compositions in bath: (—) acrylamide-acrylonitrile 80:20; (—●—) acrylamide-acrylonitrile 60:40; (—) acrylamide-acrylonitrile 40:60; (—×—) acrylamide-acrylonitrile 20:80.

to cotton greater thermal stability, while grafting with methyl acrylate or methyl methacrylate, although it results in a delay in the initiation of decomposition once decomposition commences subsequent reaction, is faster. These results are in agreement with those obtained by Hurdac et al.¹⁷ Thermal stability of cotton grafted with different vinyl monomers increases in the order acrylonitrile > acrylamide > cotton > methyl methacrylate > methyl acrylate.

In Table II values are given of initial decomposition temperature (IDT), final decomposition temperature (FDT), integral procedural decomposition temperature (IPDT), and activation energy (E^*) for different grafted cottons. IPDT as proposed by Doyle²⁰ represents the integral end of volatilization. It may be noted that these results are also in conformity with those of decomposition temperatures at various weight losses given in Table I. In general, values of activation energies obtained for different grafted samples are in conformity with

TABLE III
Temperature of Decomposition at Different Weight Losses of Cotton Samples Grafted with Acrylamide-Acrylonitrile Mixture at Different Compositions

Composition in bath, %		Graft add-on, %		Temperature of decomposition, C, at weight loss of							
Acrylamide	Acrylonitrile	Acrylamide	Acrylonitrile	10%	20%	30%	40%	50%	60%	70%	80%
100	00	5	—	290	320	325	335	350	365	440	500
80	20	7.5	1.5	295	310	325	325	345	375	425	490
60	40	16.4	3.0	290	305	330	340	365	410	470	550
40	60	15.5	8.5	275	295	310	320	345	405	520	550
20	80	16.4	7.5	270	300	320	330	350	510	530	550
00	100	—	25.0	360	390	415	440	455	495	515	550
Untreated cotton	—	—	—	270	280	285	290	290	335	425	450

their relative thermal stability as characterized by T_D , IDT, FDT, and IPDT, as compared with ungrafted cotton. However, in case of acrylamide-grafted samples, activation energy for decomposition is lower than that for ungrafted cotton although T_D , IDT, FDT, and IPDT values are slightly higher.

Mixed Monomers

In earlier studies, it was found that acrylamide-acrylonitrile mixtures when grafted onto cotton at different monomer compositions, keeping the total monomer concentration in the bath constant, show synergistic behavior in graft add-on at a specific monomer composition (40:60).²³

It was, therefore, thought interesting to examine the thermal behavior of samples grafted at different monomer compositions with a view to observe whether a similar behavior was also evident. Results of Table III indicate that in case of monomer mixtures, inception of decomposition reaction takes place at comparatively lower temperatures. At a composition of acrylamide-acrylonitrile of 40:60, where synergistic behavior has been observed in case of graft add-on,²³ decrease in the temperature at which degradation commences is more marked than at other compositions of the mixture (Fig. 6). Initial rapid decomposition is followed by a slower rate, which goes to show that initially (up to 60–70% decomposition), the cellulosic component of the grafted sample is decomposed followed by degradation of the grafted polymer. Temperatures at which inception of the latter stage of decomposition commences are higher than those in case of single monomer-grafted samples. This indicates that with mixed monomer grafting, polymers formed during grafting are likely to interact with the formation of a mixed polymer. A similar observation has also been recorded from solubility studies of grafted polymers.²³ However, activation energy data for the mixed monomer-grafted cotton samples lie between those obtained for the corresponding individual monomer-grafted samples (Table IV).

In another set of experiments, cotton was grafted with acrylamide, and these polyacrylamide chains were methylolated using alkaline formaldehyde and subsequently crosslinked with adjacent cellulose chains using an acid catalyst.²⁴ With these samples, a marginal reduction in thermal stability is noticed as compared with that for uncrosslinked grafted cottons, and there is also a re-

TABLE IV
Thermal Data for Cotton Grafted with
Acrylamide-Acrylonitrile Mixture of Different Compositions

Composition in bath, %		Graft add-on, %		IDT, °C	FDT, °C	IPDT, °C	E^* , kcal/mole
Acryl- amide	Acrylo- nitrile	Acryl- amide	Acrylo- nitrile				
100	00	5	—	210	380	341	24.9
80	20	7.5	1.5	225	395	392	28.3
60	40	16.4	3.0	205	395	383	27.6
40	60	15.5	8.5	205	330	346	26.5
20	80	16.4	7.5	205	360	367	19.9
00	100	—	25.0	330	465	404	31.2
Untreated cotton		—	—	235	360	331	26.2

duction in the activation energy of decomposition (Table II). Similar behavior is also observed in case of cotton crosslinked through dimethyloldihydroxyethyleneurea (DMDHEU).

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References

1. R. F. Schwenker, Jr., L. R. Beck, Jr., and R. K. Zuccarello, *Amer. Dyestuff Rep.*, **53**, 817 (1964).
2. P. K. Chatterjee and C. M. Conrad, *Text. Res. J.*, **36**, 487 (1966).
3. W. K. Tang and W. Neill, *J. Polym. Sci. C*, **6**, 65 (1964).
4. M. Košik, V. Luzakova, and V. Reiser, *Cell. Chem. Technol.*, **6**, 589 (1972).
5. C. M. Conrad and D. J. Stanosis, *Appl. Polym. Symp.*, **2**, 121 (1966).
6. L. E. A. Godfrey, *Text. Res. J.*, **40**, 116 (1970).
7. S. R. Hobart, R. J. Berni, and C. H. Mack, *Text. Res. J.*, **40**, 1079 (1970).
8. N. Hurduc, I. A. Schneider, and C. Simionescu, *Cell. Chem. Technol.*, **2**, 569 (1968).
9. S. Kaizerman, G. Mino, and L. F. Meinhold, *Text. Res. J.*, **32**, 136 (1962).
10. M. Negishi, Y. Nakamura, T. Kakinuma, and V. Iizuka, *J. Appl. Polym. Sci.*, **9**, 2227 (1965).
11. J. C. Arthur, Jr., R. J. Demint, W. F. McSherry, and J. F. Jurgens, *Text. Res. J.*, **29**, 759 (1959).
12. V. Stannett, J. D. Wellons, and H. Yasuda, *J. Polym. Sci. C*, **4**, 551 (1964).
13. W. H. Rapson, *J. Polym. Sci. A*, **1**, 257 (1963).
14. I. Sakurada, T. Okada, S. Hatakeyama, and F. Kimura, *J. Polym. Sci. C*, **4**, 1233 (1964).
15. Z. A. Rogovin, *J. Polym. Sci. C*, **37**, 221 (1972).
16. C. Simionescu and S. Oprea, *J. Polym. Sci. C*, **37**, 251 (1972).
17. N. Hurduc, C. Simionescu, and I. A. Schneider, *Cell. Chem. Technol.*, **5**, 37 (1971).
18. D. S. Varma and V. Narsimhan, *J. Appl. Polym. Sci.*, **16**, 3325 (1972).
19. C. Simionescu and S. Mihailescu, *Cell. Chem. Technol.*, **4**, 23 (1970).
20. C. D. Doyle, *Anal. Chem.*, **33**, 77 (1961).
21. H. H. Horowitz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
22. S. R. Dharwadkar and M. D. Karkhanawala, in *Inorganic Materials and Physical Chemistry*, Vol. 2, R. F. Schwenker and P. D. Garn, Eds., Academic Press, New York/London, 1969.
23. V. N. Sharma and E. H. Daruwalla, *Cell. Chem. Technol.*, in press.
24. V. N. Sharma and E. H. Daruwalla, *Text. Res. J.*, in press.

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