Graft Copolymerization onto Wool Fibers: Grafting of Acrylamide onto Wool Fibers Initiated by Potassium Monopersulphate/Fe(II) Redox System

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Synopsis

Graft copolymerization of acrylamide (AM) onto wool fibers has been studied in aqueous solution with a new redox initiating system, $KHSO_5/Fe(II)$. For estimation of comparative influence of salts and selection of reaction medium, grafting has also been studied in the presence of a multitude of inorganic salts and some organic solvents. It was observed that the graft percentage was influenced by the reaction time, temperature, concentration of monomer initiator, $FeSO_4$, and the base polymer. A maximum graft percentage of 120.5% was obtained at 35°C with the concentration of AM (0.8 *M*), $KHSO_5$ (0.0195 *M*) and Fe(II) (2.5×10^{-3} *M*) for reaction time of 2 h. From the experimental results, a suitable reaction mechanism for graft initiation and termination has been suggested. The water retention of the grafts and their behavior towards mineral acids and alkalis have been tested. The tensile strength and the thermal stability of the grafts have also been determined and compared with the base.

INTRODUCTION

Wool, a natural protein called α-keratin, has significant characteristics and has long since been used for making luxurious warm garments. With a view to enhance the durability of the woolen garments and to add improved properties such as improved dyeability, prevention of shrinkage and pilling, improved bacterial resistance, hygroscopicity, tensile strength, thermal stability, etc., attempts have been made since 1945 to chemically modify wool fibers. This involves functionality changes: via etherification, esterification, urethanation, amidation, etc.[1-5] by interfacial graft condensation of polyamides,[6-8] polyurethanes,[9] polyureas, polyesters, and polycarbonates,[10] via radical grafting of vinyl monomers involving high energy radiation, photochemical, and chemical method of initiation involving metal and nonmetal ion initiators,[11-31] and through chemical treatments.[32-39] Among these, the chemical method of initiation of grafting to improve wool properties has attracted attention during the recent years and in this regard quite a good number of initiators like Ce^{+4}, V^{+5}, Mn(III), $S_2O_8^{--}$, $P_2O_8^{--}$, H_2O_2, BPO, AIBN, etc. have been successfully used. However, no report seems to be available on graft copolymerization of wool fibers with potassium monopersulfate as initiator. Potassium monopersulfate

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is an acidic peroxo salt of recent origin. The author and his co-workers (Samal et al.) have recently studied the chemistry of $KHSO_5$ in detail and have seen that $KHSO_5$ under the influence of some salts, complexing agents, and metal salts/complexing agent couples effectively initiates vinyl polymerization and graft copolymerization onto cellulose and jute fibers,[40-56] where insignificant formation of homopolymers were noticed without causing damage to the basic properties of the fibers. We have therefore been interested to study graft copolymerization of wool fibers with this new initiation where the formation of homopolymer is minimized with simultaneous improvement in properties.

EXPERIMENTAL

Materials. Wool fibers were purified by continuous soxhelation in petroleum ether. They were then washed well with warm acetone followed by distilled water and air dried. Acrylamide (AM) monomer (E. Merck) was purified by recrystallisation from acetone and dried at room temperature under vacuum. A 4 (M) stock solution of the monomer in triple distilled water was used. Potassium monopersulphate ($KHSO_5$) was a gift sample from DuPont and was used without purification. A stock solution of 12.9×10^{-2} M of the initiator was used for all experiments and the strength of the stock solution was determined by iodometry. All other reagents were of BDH (AR) grade and used after purification by standard methods.

Graft copolymerization was carried out in a specially designed reaction vessel with an outlet and inlet system for deaeration. Defatted wool fibers (0.2–1 g) were immersed in a mixture containing water, required amounts of acrylamide (AM) and salt solution. The reaction systems were deaerated by passing oxygen free nitrogen for 1 h and sealed air tight. The vessels were then kept in a shaking constant temperature bath till thermal equilibrium followed by injecting required amount of $KHSO_5$ solution through the rubber seal. The grafting reaction was carried out for the desired time. The homopolymers were extracted by repeated washings with warm water, till the extract gave no precipitate with methanol.

From the weight of the graft copolymer and base polymer, the percent grafting was calculated using the following formula:

$$\text{Percent grafting} = \frac{X - Y}{Y} \times 100$$

where X = weight of graft copolymer and Y = weight of original base polymer.

Thermogravimetric Analysis. Thermogravimetric analysis was carried out with Netzsch Gembtt West Germany Model-409 thermobalances in air. The samples, cut into small pieces of weight 100 mg, were taken in each case for TGA. The temperature was varied from the room temperature to 800°C in case of a base polymer and 1000°C in case of the grafted samples and a heating rate of 5°C/min was maintained. Primary thermograms were derived by plotting percent residual weight against temperature.

Tensile Strength. The tensile strength of the grafted wool fibers were determined through determination of stiffness at break following the method of

Haque and Habibuddowla.[57] The stiffness at break was determined from the value of tenacity and elongation at break using the following relationship:

$$\text{Stiffness at break} = \frac{\text{tenacity at break}}{\text{elongation at break}} \times 100$$

The tenacity was expressed as g/den. After conditioning the wool samples, they were combed and the fiber aggregates of uniform length were taken and weight and length determined. The tensile strength was determined by means of a "Dutrons" tensile tester, Brand-20 Kgf capacity.

The procedures for determination of absorptions of water and water vapors, and the alkali and acid solubility, are described in the properties section of the grafts.

RESULTS AND DISCUSSION

Acrylamide was graft copolymerized with defatted wool fibers initiated by potassium monopersulfate, either alone or in the presence of metal salts under identical reaction conditions. The results of such polymerizations are presented in Table I. From Table I it is observed that the presence of salts like Na_2SO_3, KBr, $MgSO_4$, $MnSO_4$, $CdCl_2$, Na_2SO_4, K_2SO_4, $ZnSO_4$, NaBr, $ZnCl_2$, and NaCl in the reaction mixtures retards the percent grafting, whereas the presence of salts like $CoSO_4$, $CuSO_4$, $Cr_2(SO_4)_3$, $FeSO_4$, and $NiSO_4$ increases the percent grafting in the order $FeSO_4 > CoSO_4 > CuSO_4 > Cr_2(SO_4)_3 > NiSO_4$.

TABLE I

Results of Graft Percent in the $KHSO_5$-Initiated Graft Copolymerization of Acrylamide onto Wool Fibers in the Presence of Various Metals and Nonmetal Salts[a]

Salts	Percent grafting
—	1.7
$CuSO_4$	4.5
$Cr_2(SO_4)_3$	3.75
Na_2SO_3	0.5
KBr	0.2
$MgSO_4$	1
$MnSO_4$	0.3
$FeSO_4$	40.5
$CdCl_2$	0.75
Na_2SO_4	0.7
$NiSO_4$	2.4
K_2SO_4	0.2
$ZnSO_4$	0
NaBr	0.05
$ZnCl_2$	0
NaCl	0.7
$CoSO_4$	8.7

[a] Wool = 0.2 g; [AM] = 0.5*M*; [$KHSO_5$] = 0.013*M*; [salts] = 2.5×10^{-4} *M*; temp 40°C; time 2 h).

The enhancement of percent grafting in the presence of salts cited above may be attributed to their effectiveness in causing fast decomposition through redox reaction with $KHSO_5$ to form free radicals which attack the wool fiber and enhance the number of free radical sites on its backbone. Chain initiation by these free radical sites with monomer molecules at the immediate vicinity leads to high percent grafting.

The retardation of percent grafting in the presence of $ZnCl_2$, $CdCl_2$, and NaCl may be due to following oxidation reaction:

$$Cl^- + HSO_5^- \rightarrow Cl^\bullet + \bar{O}H + S\bar{O}_4^\bullet$$

or

$$\rightarrow Cl^- + S\bar{O}_4^2 + \dot{O}H$$

which decreases the number of free radical sites on the wool backbone due to (i) excess of free radicals causing homopolymerization that predominates over grafting, (ii) the $Cl^\bullet$ radical so formed may also combined with wool free radical preventing monomer addition onto them, and (iii) the $Cl^\bullet$ radical and the primary radicals from the initiators, i.e., $\dot{O}H$ and $S\bar{O}_4^\bullet$ cause premature termination of the growing grafted chains. All these factors are combinedly responsible for low percent grafting. Oxidation of Cl^- to $Cl^\bullet$ by $\dot{O}H$ radical has been noticed by Palit and Saha.[58] This is in agreement with our verification of liberation of Cl_2 through dimerization of $Cl^\bullet$ radicals. Explanations identical to these may hold good for KBr and NaBr. The retarding effect with Na_2SO_3 may be due to deactivation of the acidic peroxygen initiator through liberation of SO_2. With rest of the salts the adversity may be due to: (i) interference of SO_4^{-2} ion in the propagation step and (ii) partially due to redox potentials of Mn^{+2}, Mg^{+2}, and Zn^{+2} back driving the decomposition of $KHSO_5$ to $\dot{O}H$ and $S\bar{O}_4^\bullet$ radicals, thereby decreasing the percent grafting.

Effects of Monomer/Polymer Ratios

The effects of the monomer/polymer ratio on the grafting of acrylamide onto wool fibers were studied in a series of monomer concentration between 0.05 and 0.8 *M* at six initiator concentrations from 1.625×10^{-3} *M* to 32.5×10^{-3} *M* at a fixed weight of wool fiber (0.2 g), at a fixed time of 2 h and temperature of 35°C. The percent grafting was found to increase steadily with increase of monomer concentration (Fig. 1). This enhancement of percent grafting here may be interpreted in terms of AM concentration and its reactivity. Increase of m/p ratio increases monomer (AM) concentration at close proximity of the fiber backbone, where some of the AM molecules form a donor–acceptor complex, through interaction of their amide functions with —OH groups on wool backbone. Out of the uncomplexed monomers, those which are at the immediate vicinity of reaction sites become acceptors of the wool radicals resulting in chain initiation and thereafter themselves become free-radical donors predominantly for the complexed monomers converted to strong acceptors and neighbors to them than the remaining uncomplexed ones a little far away. These factors result in an increase in the reactivity of the monomers, thereby

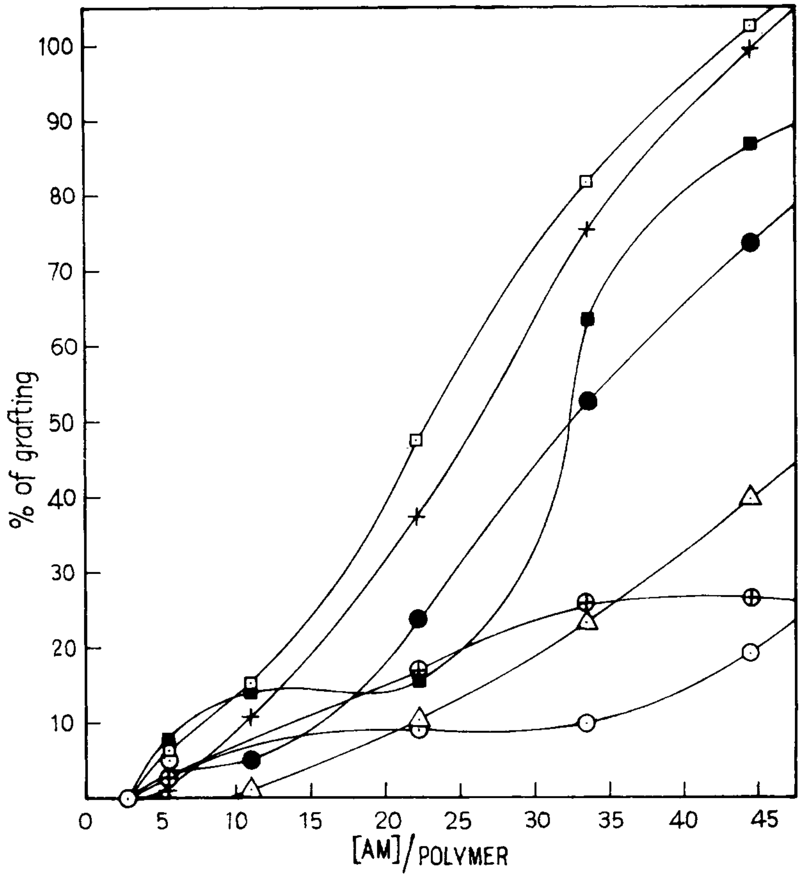

Fig. 1. Variation of percent grafting at fixed times: effects of [monomer]/polymer ratio at various initiator [$KHSO_5$] concentrations: wool, 0.2 g; [$FeSO_4$] = 1.25 × 10^{-3} M; temp 35°C; time 2 h. [$KHSO_5$] (○) 1.625 × 10^{-3} M; (⊕) 3.25 × 10^{-3} M; (●) 6.5 × 10^{-3} M; (+) 13.0 × 10^{-3} M; (□) 19.5 × 10^{-3} M; (■) 26.0 × 10^{-3} M; (△) 32.5 × 10^{-3} M.

enhancing percent grafting. Similar explanations for enhancement of percent grafting has been suggested by Gaylord[59] and Hebeish et al.[60]

Effects of Initiator Concentration

Graft copolymerization was studied at a number of initiator concentrations (1.625 × 10^{-3}–32.5 × 10^{-3} M) at different monomer/polymer ratios, varying from 2.8 to 44.88 (Fig. 2). It has been observed that the percent grafting increases on increasing the initiator concentration up to 19.5 × 10^{-3} M, beyond which it decreases. The increase of percent grafting with increasing initiator concentration may be ascribed to the increase of active sites on the backbone of the wool fibers arising from the attack of diffused $KHSO_5$ on polymer matrix.

The retardation of percent grafting with initiator concentration beyond 19.5 × 10^{-3} M may be due to (i) predominancy of homopolymerization over grafting, (ii) termination of growing grafted chains by excess of primary radicals formed from the initiator, (iii) premature termination of polymer chains by Fe(III)

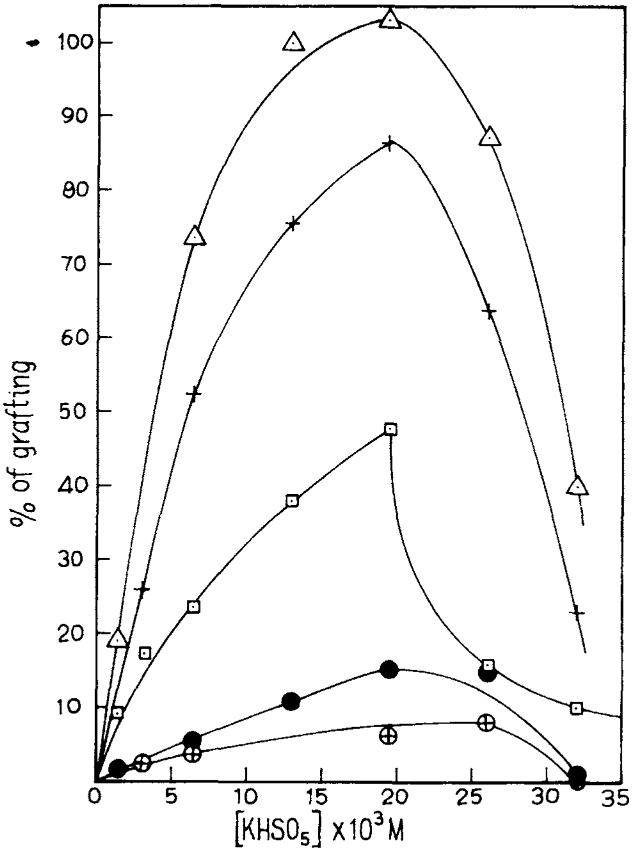

Fig. 2. Variation of percent grafting at fixed times: effects of $[KHSO_5]$ at various monomer (m)/polymer (p) ratios. Wool, 0.2 g; $[FeSO_4] = 1.25 \times 10^{-3}$ *M*; temp 35°C; time 2 h. m/p: (⊙) 2.81; (⊕) 5.61; (●) 11.22; (⊡) 22.44; (+) 33.66; (▲) 44.88.

ions produced during the disproportionation of Fe(II)/$KHSO_5$ redox pair (Fe(III) ion was proved to be an ideal retarder of radical polymerization),[61] (iv) a decrease in molecular weight (MW) of grafted PAM chains from 10^5 to 10^4 orders has been noticed; and (v) overall oxidation of the wool fibers retarding monomer addition onto them.

Effects of $FeSO_4$ Concentration

Graft copolymerization has been studied at various $FeSO_4$ concentration (1.25×10^{-3}–20×10^{-3} *M*) at a number of temperatures between 25 and 50°C and at fixed concentration of AM (0.8 *M*), $KHSO_5$ (0.0195 *M*) for 2 h (Fig. 3). The percent grafting increased with increase in the concentration of Fe(II) up to 2.5×10^{-3} *M*, beyond which it decreased. The increase in the percent grafting up to 2.5×10^{-3} *M* of Fe(II) concentration is mainly attributed to increase in the concentration of Fe(II)–$KHSO_5$ transient species, which undergoes forced decomposition at the fiber surface, resulting in the production of wool radicals at a faster rate. The decrease of percent grafting at higher

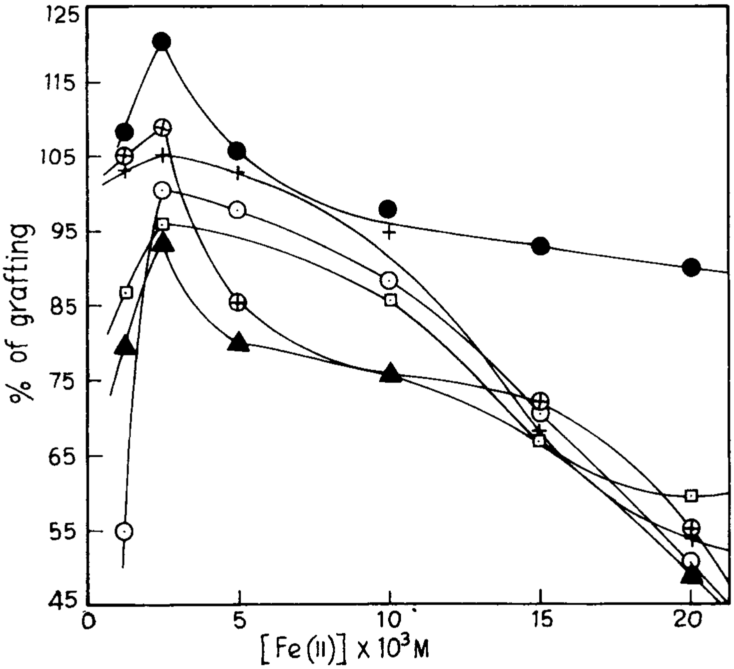

Fig. 3. Variation of percent grafting at fixed times: effects of [$FeSO_4$] at various temperatures. Wool, 0.2 g; [AM] = 0.8 *M;* [$KHSO_5$] = 19.5 × 10^{-3} *M;* time 2 h. *T* (°C): (⊙) 25°C; (⊗) 30°C; (●) 35°C; (+) 40°C; (⊡) 45°C; (△) 50°C.

concentrations ($> 2.5 \times 10^{-3}$ *M*) of Fe(II) may be attributed to the detrimental factor of excess of Fe(III) ions produced upon oxidation of Fe(II). That excess of Fe(III) ions are detrimental to grafting has been observed by Morin and Rogovin[62] and Mishra et al.[63] in H_2O_2/Fe(II) system initiated graft copolymerization.

Effect of Temperature

The effect of reaction temperature on percent grafting has been shown in Figure 4). It has been observed that the percent grafting increases up to 35°C and then decreases. The increase in the percent grafting may be attributed to (i) increase in the production rate of active free radicals which increase the number of grafting sites at a faster rate (thereby the rate of graft initiation by these radicals increases) and (ii) increase of temperature increases the rate of diffusion of AM into the fiber matrix, where grafting is also initiated at the complexed monomers. Samal and co-workers[51,64,65] had similar observations in the grafting of AM onto cellulose, nylon 6, and silk fibers. The decrease in the percent grafting beyond 35°C may be attributed to (i) activation of wool backbone and the initiator leading to overall oxidation of the former, (ii) increase in the rate of production of homopolymers, and (iii) premature termination of growing grafted chains by Fe(III) ions, a phenomenon similar to that put forward in the case of effect of initiator concentration.

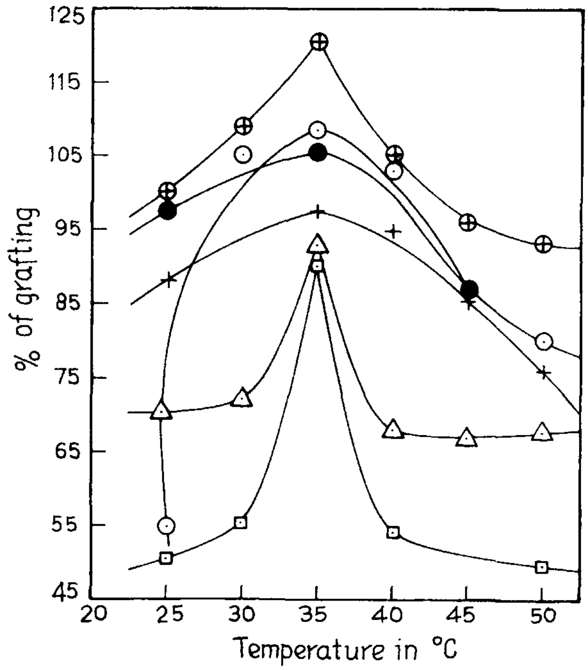

Fig. 4. Variation of percent grafting at fixed times: effects of temperature at various [$FeSO_4$]. Wool, 0.2 g; [AM] = 0.8 *M*; [$KHSO_5$] = 19.5 × 10^{-3} *M*; time 2 h. [$FeSO_4$]: (⊙) 1.25 × 10^{-3} *M*; (⊕) 2.5 × 10^{-3} *M*; (●) 5.0 × 10^{-3} *M*; (+) 10.0 × 10^{-3} *M*; (△) 15.0 × 10^{-3} *M*; (□) 20.0 × 10^{-3} *M*.

Effects of Solvent Composition

The effects of organic solvents on the extent of grafting has been studied at various solvent compositions of (5 : 95–50 : 50 v/v) at 35°C for fixed concentrations of AM (0.8 *M*), $KHSO_5$ (19.5 × 10^{-3} *M*) Fe(II) (1.25 × 10^{-3} *M*), and wool (0.2 g) for a reaction time of 2 h. The results of such studies with solvents like formic acid, acetic acid, and morpholine are listed in Table II. From Table II it is seen that the grafting reaction is completely inhibited in the presence of morpholine of all compositions, where as progressive retardation of graft percentage is noticed with acetic acid and formic acid with increase in solvent composition.

TABLE II
Variation of Percent Grafting at Fixed Times: Effects of Solvent Composition[a]

	% Grafting					
Solvent	5%	10%	20%	30%	40%	50%
Formic acid	40.45	29.6	28.9	22.9	17.5	15
Acetic acid	55.55	31.25	27	21.05	18	16.1
Morpholine	0	0	0	0	0	0

[a] Wool 0.2 g; [AM] = 0.8*M*; [$KHSO_5$] = 0.0195*M*; Fe(II) = 1.25 × 10^{-3} *M*; temp 35°C; time 2 h; controlled value = 108.6%.

TABLE III
Water Retention Values of Wool-*g*-PAM Samples with Various Percentage Grafting

Samples	Percent grafting	Water retention (g/g)
Parent fiber	0	3.0
Wool-*g*-PAM	15.0	7.6
	40.4	13.8
	68.1	22.6
	80.1	31.8
	120.5	38.6

The complete inhibition of grafting with morpholine may be due to (i) exhaustive oxidation of the additive predominating overgrafting and (ii) the inhibiting effect of morpholine *N*-oxides formed during the oxidation reaction. The ability of $KHSO_5$ in oxidizing cyclic amines to corresponding *N*-oxides has been recognized by Kennedy and Stock.[66] Further the retardation and/or inhibition of grafting by these *N*-oxides has been recognized by Samal et al.[55] and Kinoshata et al.[67] The progressive retardation in the percent grafting with increase in the composition of acetic acid and formic acid may be due to the chain transferring ability of these solvents which cause (i) premature termination of the growing grafted chains and (ii) predominancy of homopolymerization by excess of these solvent radicals. Both of these factors adversely contribute to grafting.

MECHANISM

The mechanism of graft copolymerization of AM onto wool fibers with a new redox initiating system $KHSO_5/Fe(II)$ may be pictured as involving the generation of macro wool radicals formed by the attack of the primary radical species on the fiber backbone. The wool radicals so formed subsequently attack the monomer at the immediate vicinity leading to graft initiation. The termination of the graft copolymerization may be due to the interaction with Fe(III), mutual combination of growing grafted chains on different backbones, may also be due to excess of primary radicals.

Properties of the Grafts

Acrylamide grafted wool fibers have the following properties.

Absorption of Water and Water Vapors: (Water Retention)

The extend of absorption of water and water vapor of both the virgin and grafted wool fibers was determined through measurement of water retention of the samples following the method of Ranby and Gadda[68] with slight modification. The water retention increased on increasing percent grafting. One gram of both virgin and the grafted fibers were separately immersed in 100 mL of distilled water for 12 h. The contents were then filtered in a sintered glass filter and sucked at 700 mm Hg pressure. The volume of the filtrate was mea-

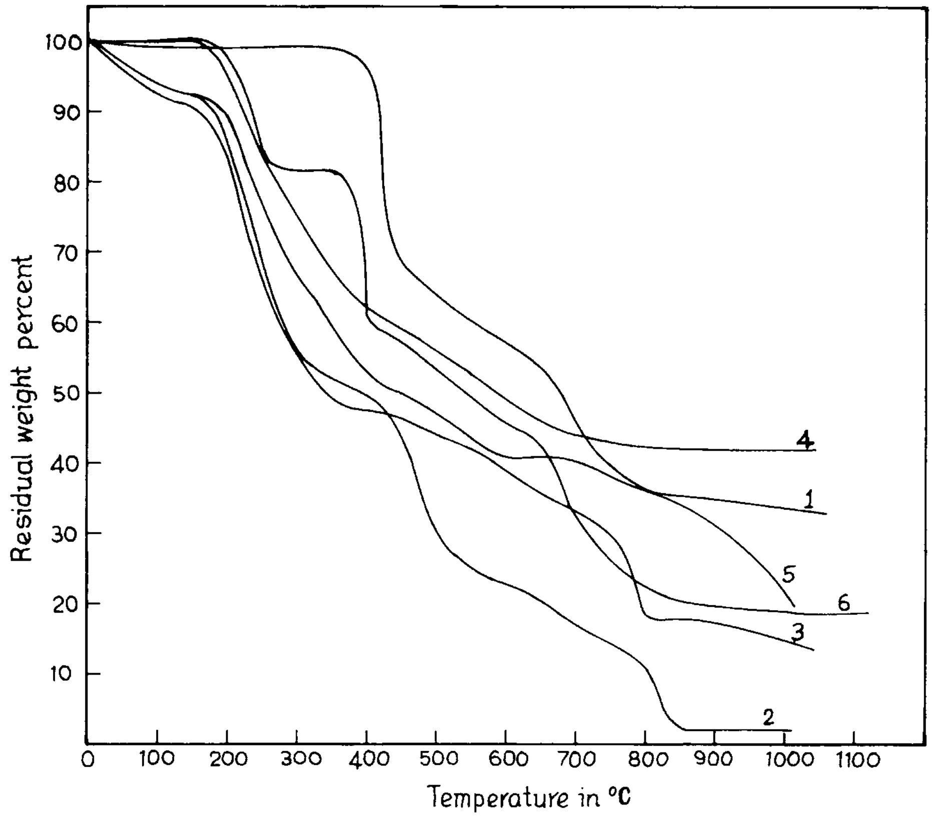

Fig. 5. Primary thermograms of parent wool fiber and wool fiber grafted with acrylamide. Graft-on %: (1) parent fiber; (2) 15.0; (3) 40.4; (4) 68.1; (5) 80.1; (6) 120.5.

sured and the water retention which is equal to the amount of water absorbed was calculated as grams of water per grams of dry material (Table III).

Alkali and Acid Solubility

The behavior of the grafts and the virgin wool fibers towards alkali was tested by determining the percentage of alkali solubility with time. For this the

TABLE IV
Decomposition Temperatures (T_D) at Different Weight Losses

		T_D (°C) corresponding to the weight loss of the grafted sample							
Sample	Grafting (%)	10%	20%	30%	40%	50%	60%	70%	80%
Base polymer	Nil	415	422	442	550	675	740		
(wool)	15.0	155	210	238	282	390	464	501	655
Acrylamide-grafted	40.4	180	220	246	277	340	581	750	794
samples	68.1	220	270	330	438	585			
	80.1	200	238	280	348	445	705	916	1002
	120.5	235	370	405	544	665	715	880	

TABLE V

Effect of Graft Percent on Tensile Strength of Acrylamide-Grafted Wool Fibers

Grafted sample	Grafting (%)	Elongation at break (BL)%	Tenacity (g/den)	Tensile strength
Parent fiber	0	1.48	2.75	185.8
Wool-*g*-PAM	15.0	1.50	2.81	187.3
	40.4	1.54	2.98	193.5
	68.1	1.6	3.5	218.7
	80.1	1.62	3.68	227.1
	120.5	1.7	4.2	247.0

samples were immersed separately in acqueous solution of 0.1 *M* NaOH solution for various time intervals for 1 h at 65°C using a wool–liquor ratio of 1 : 100. The method adopted was similar to that of Leavean and co-workers.[69] The treatment showed that the grafted samples are least soluble in alkali, and about solubility less than about 10% was noticed with the grafted sample of percent grafting 40.0, which still decreases with the increase of percent grafting up to 120.5. The virgin fiber, on the other hand, was soluble up to nearly 80% under identical conditions. Further, the alkali-treated grafted fibers did not lose tensile strength to any appreciable extent.

A similar procedure was adopted with 0.1 *M* HCl using a wool–liquor ratio of 1 : 100. The results of acid treatment showed that the grafted fibers have greater tenacity towards acid than the virgin fiber.

Thermal Behavior. The thermal behavior of wool fibers grafted with acrylamide to various percentages of grafting (15.0–120.5%) was studied by comparing their primary thermograms. Primary thermograms of parent wool and wool grafted with acrylamide are shown in Figure 5. The temperature of the decomposition is very much influenced by the percent of grafting. The decomposition temperatures T_D at various degrees of grafting are presented in Table IV.

From Table III it is seen that the decomposition temperature of the graft copolymers is less than that of the base polymer. Further, among the grafted samples for a given percentage of weight loss the decomposition temperature increases with increasing grafting percent. For instance, at 60% weight loss the acrylamide grafted samples show decomposition temperatures of 464, 581, 705, and 715°C for grafting percentages of 15.0, 40.4, 80.1, and 120.5%, respectively. Further, 60% weight loss of the base polymer occurs at 740°C, indicating that the thermal stability of the graft copolymers at low percentage of grafting is less than that of the base polymer. However, the overall thermal stability increases at a higher percentage of grafting. From the residual weight as calculated from the above primary thermograms and applying the Freeman and Carroll equation,[70,71] the energy of activation (E) and order of the reaction (n) involved in such pyrolysis has been calculated. The E values are found to be 15.7, 16.6, 20.1, 21.0, and 24.3 kcal/mol and the n values are found to be 1.3, 1.25, 1.22, 1.31, and 1.06 for samples of 15.0, 40.4, 68.1, 80.1, and 120.5% grafting, respectively. Progressive increase in the value of E with increase in the graft percentage indicates that at much higher percentage of grafting the samples become moderately thermally stable.

Tensile Strength

The tensile strength of the grafted and the virgin wool fibers are presented in Table V. The result shows that the tensile strength of the samples increases with increase of percent grafting.

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