

Gamma Ray-Induced Graft Copolymerization of Acrylamide and Acrylic Acid to Nylon 6 Fabric

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Synopsis

Kinetics of radiation-induced grafting of acrylamide (Aam) and acrylic acid (Aa) to nylon 6 fabric were investigated employing a mutual radiation technique. Copper sulfate was used as the radical scavenger to reduce homopolymer formation. Formic acid was used for swelling, and its effect on grafting was studied. Maximum amount of grafting was doubled when formic acid was used for swelling nylon prior to, but not during, irradiation. The rate of grafting was not significantly affected if it was carried out in an atmosphere of air instead of nitrogen. The effect of monomer concentration, dose rate, and total dose on grafting has been studied. Rate of grafting was significantly higher when lower dose rates and monomer concentrations were used. Saturation grafting was proportional to monomer concentration up to 2.1M. Initial rate of grafting was proportional to monomer concentration. The rate of grafting of Aam was proportional to the dose rate to the power 0.25-1.0. A synergistic effect was noticed during grafting with mixtures of Aam and Aa (80:20; 20:80). Grafted fabrics showed considerable increase in moisture regain. Dyeability and tensile properties of the grafted fabrics were not significantly affected by grafting. Aa-grafted fabrics did not melt up to 320°C, whereas untreated nylon melts at 215°C.

INTRODUCTION

Chemical modification of nylon by graft copolymerization has been studied by many authors.¹⁻¹² These studies have been aimed at modifying viscoelasticity, stereoregularity, hygroscopicity, antistatic properties, and thermal stability^{13,14} and have shown that the use of certain additives^{15,16} such as methanol, ethanol, benzyl alcohol, ethylene glycol, glycerol, formamide, and dimethylformamide give enhanced grafting during grafting with vinyl monomers. It has been reported that swelling of nylon by solvents such as formic acid, aqueous zinc chloride, and hydrochloric acid,¹⁷ and water-immiscible swelling agents¹⁸ such as tetrachloroethane, ethylene chloride, and 1,2,4-trichlorobenzene increases the grafting yield and that the grafting efficiency is related to the swelling of nylon. Calcium and sodium salts¹⁹ and nickel and/or cobalt acetate of the grafted copolymers²⁰ are also reported to have nonmelting properties. These studies have been made mainly on nylon fibers or films, and very few studies^{21,22} are reported for grafting onto nylon fabric. It has been reported²³ that

the rate and extent of grafting is in the order fiber > yarn > fabric. The differences are attributed to the restrictions imposed by yarn or fabric geometry during the chemical reaction.

Considerable amount of homopolymer is formed during grafting initiated either by chemical methods or by radiation. The use of certain transition metal salts in the polymerization of several vinyl monomers to reduce the homopolymer formation has been reported.²⁴⁻²⁶ Of the various metal ions, Cu^{2+} is the most effective to suppress homopolymerization.²⁷

In the present paper, grafting of water-soluble vinyl polymers such as acrylamide, acrylic acid, and their mixtures to nylon fabric by mutual radiation technique using copper sulfate as a scavenger is reported. Though the rate and extent of grafting with the fabric are moderate,²³ an attempt is made to graft-copolymerize nylon 6 fabric with the above monomers to study the changes in fabric properties brought about by grafting.

EXPERIMENTAL

Materials

Nylon Fabric. A commercial nylon fabric was used after scouring with 2 g/l. nonionic detergent for 40-45 min at 70°C in a jigger, followed by thorough washing with water and drying.

Swelling of Nylon. The scoured fabric was preswollen with formic acid (20%, v/v) at room temperature (ca. 27°C) for 2 hr. The fabric was washed thoroughly with plenty of water, treated with dilute ammonia, washed, and dried.

Monomer. Acrylamide (Aam) and acrylic acid (Aa), after analyzing them for purity (mp and carboxyl content), were used in the form of aqueous solution.

Chemicals. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and formic acid, both A.R. grade were used.

Irradiation

Radiation Facilities. Radiation facilities were provided by the Bhabha Atomic Research Centre (BARC), Bombay. Radiation was effected by γ -rays from ^{60}Co γ -sources, AECL 200 and AECL 220, whose dose rates were 0.14 and 0.51 Mrad/hr, respectively. For the dose rate of 0.25 Mrad/hr, a γ -source fabricated in BARC was used, and for the dose rate of 0.074 Mrad/hr, a "AECL-200" γ -cell source with lead shielding was employed. The actual dose rates were measured by a Fricke dosimeter.²⁸

Irradiation. Glass tubes (50 ml) with standard joint stoppers were used for irradiation.

Procedure

About 1.5 g nylon fabric, accurately weighed, was placed in glass tubes to which 25 ml monomer solution containing 0.04M CuSO_4 was added. The tubes were then placed in a γ -source of predetermined dose rate and

lowered into the source by a mechanical device and irradiated for the required length of time at room temperature (ca. 30°C).

After irradiation, the sample was immediately washed to minimize post-irradiation effect and to remove homopolymer formed during the process. Since both the polymers (PAam and PAa) are water soluble, washing was done with plenty of water, boiling the sample several times in water, and finally drying under reduced pressure till constant weight was obtained. This appeared to remove all the homopolymer.

Per cent grafting was calculated from the difference in the dry weight of the sample before and after treatment. Reproducibility of the grafting yield was better than $\pm 5\%$.

RESULTS AND DISCUSSION

Preliminary experiments of grafting Aam and Aa to nylon fabric resulted in a crosslinked gel. The separation of the entrapped fabric from the gel for per cent graft determination was a difficult and lengthy procedure. This necessitated the use of a scavenger. Various metal salts have been used as scavenger in vinyl polymerization and grafting.²⁴⁻²⁶ In the present study, CuSO_4 was used as a scavenger to reduce the homopolymer formation.

The optimum CuSO_4 concentration for grafting was determined experimentally. The results are shown in Figure 1. It is seen that with in-

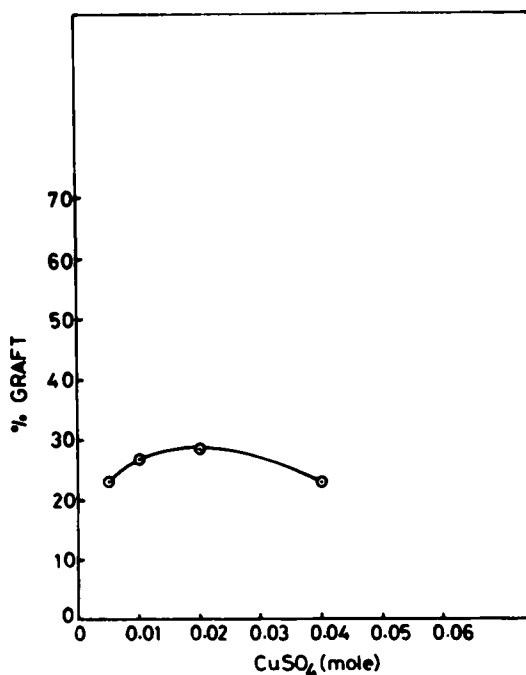


Fig. 1. Effect of copper sulfate on extent of graft copolymerization of Aam with irradiation nylon 6. Grafting in presence of formic acid, 20%; Aam, 3.56M; dose rate, 0.25 Mrad/hr, irradiation time, 2 hr.

creasing CuSO_4 concentration, grafting first increases and then decreases. Collinson et al.^{29,30} have shown that in radiation polymerization of acrylamide solution in the presence of ferric perchlorate, the overall polymerization rate decreases with increasing ferric ion concentration. A similar effect was also noticed by Huglin and Johnson³¹ in a study on grafting of acrylic acid to nylon 6. Though maximum graft yields were obtained at $0.02M$ CuSO_4 concentration, $0.04M$ CuSO_4 was selected for the entire study in order to provide sufficient CuSO_4 compared to monomer concentration, especially at high monomer concentrations.

Effect of Formic Acid During Irradiation

During grafting of nylon fabric with Aam in the presence of formic acid (20%), which was used as a swelling agent (one-bath swelling and grafting method), maximum grafting of 34% was obtained (Table I) in the range of monomer concentrations used. It is seen from the table that with increase in monomer concentration from $1.4M$ to $8.4M$, grafting increased from 17% to about 35%, that is, a sixfold increase in monomer concentration yields only a twofold increase in per cent grafting. Mertvichanko et al.,³² from a study on the effect of solvents on grafting acrylonitrile to Kapron fibers, have reported that formic acid and propionic acid when used as solvents decreased the yield of graft copolymer. This indicates that, along with CuSO_4 , formic acid might also be scavenging the growing radicals. Hence, in all subsequent experiments, the fabric was swollen in formic acid in a separate treatment and washed free from it prior to grafting. The results in Table I show that in the absence of formic acid, grafting is almost doubled.

Preliminary study on grafting with Aa indicated that with Aa concentrations above $3.5M$, the fabric is damaged due to increased swelling. Hence, in these experiments, Aa concentrations lower than $3.5M$ were used. As in the case of Aam, preswelling and grafting gave higher graft yields compared to simultaneous swelling and grafting. However, for Aa, the difference is much smaller than for Aam (Table II).

The effect of air and nitrogen atmosphere on grafting was also studied. A very limited number of experiments both with Aam and Aa were carried

TABLE I
Effect of Formic Acid During Irradiation on Grafting of Aam on Nylon Fabric^a

No.	Monomer concentration, mole/l.	Per cent graft, %	
		With formic acid ^b	Without formic acid ^c
1	1.41	17.2	29.6
2	3.56	24.5	46.6
3	5.63	26.5	55.6
4	8.44	34.5	72.0

^a (CuSO_4 , $0.04M$; dose rate, 0.25 Mrad; irradiation time, 2 hr).

^b Simultaneous swelling and grafting.

^c Preswelling.

TABLE II
Effect of Formic Acid During Irradiation on Grafting of Aa on Nylon Fabric^a

No.	Monomer concentration, mole/l.	Per cent graft, %	
		With formic acid ^b	Without formic acid ^c
1	1.40	20.9	23.8
2	2.10	21.8	27.2
3	2.80	25.1	29.4
4	3.50	31.2	33.2

^a (CuSO₄, 0.04M; dose rate, 0.25 Mrad; irradiation time, 2 hr).

^b Simultaneous swelling and grafting.

^c Preswelling.

TABLE III
Effect of Air on Grafting^a

No.	Monomer		Per cent graft, %	
	Type	Concentration, mole/l.	Air atmosphere	Nitrogen atmosphere
1	Aam	2.11	36.80	38.53
2	Aam	3.56	48.10	49.67
3	Aa	2.10	27.20	28.28
4	Aa	3.50	32.60	33.25

^a CuSO₄, 0.04M; dose rate, 0.25 Mrad; irradiation time, 2 hr.

out for this study. The results are shown in Table III. No significant difference in grafting was noticed when irradiation and grafting were carried out in air instead of nitrogen. Presence of air usually affects grafting. In our experiments, however, the fabric throughout the irradiation grafting was well immersed in monomer solution, and therefore it is likely that the effect of air on grafting may not be significant. Further, in solution under irradiation, H atoms and hydrated electrons are produced which react with oxygen and also the scavenger. Thus, the oxygen in solution will be used up faster than it can affect grafting, and it was not replenished as the system was closed and the fabric was submerged. Hence, for kinetic studies, experiments were confined to irradiations in air atmosphere only.

Dose Rate and Dose Effect

The dose rate effect was studied for four dose rate levels, viz., 0.074, 0.14, 0.25, and 0.51 Mrad. The effect was found to be related to monomer concentration. A pronounced acceleration effect was observed during grafting of Aam, after some induction period (2 to 12 min), particularly when lower dose rates were used. In grafting experiments at the doses studied, there was an induction period which was inversely proportional to the dose rate (Fig. 2). This clearly indicates that there would be no induction period at an infinitely high dose rate. However, taking 1 min as an

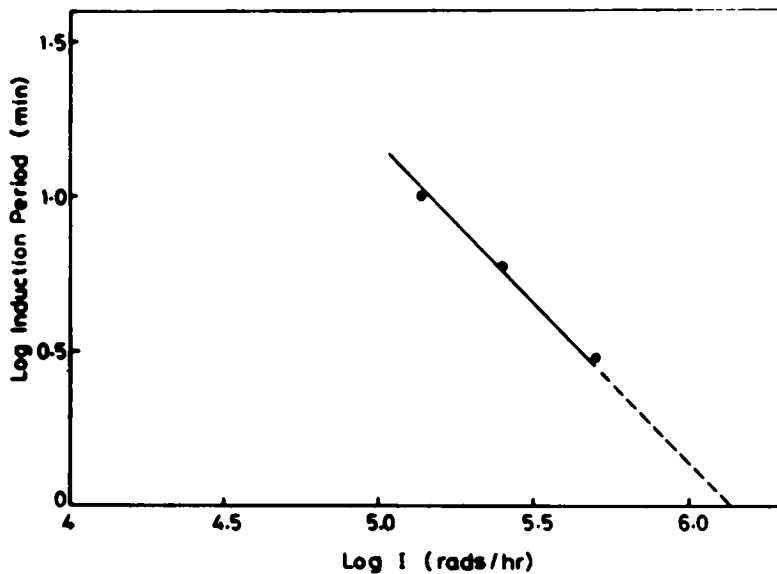


Fig. 2. Dependence of induction period on dose rate for radiation induced graft copolymerization of aqueous acrylamide on nylon 6.

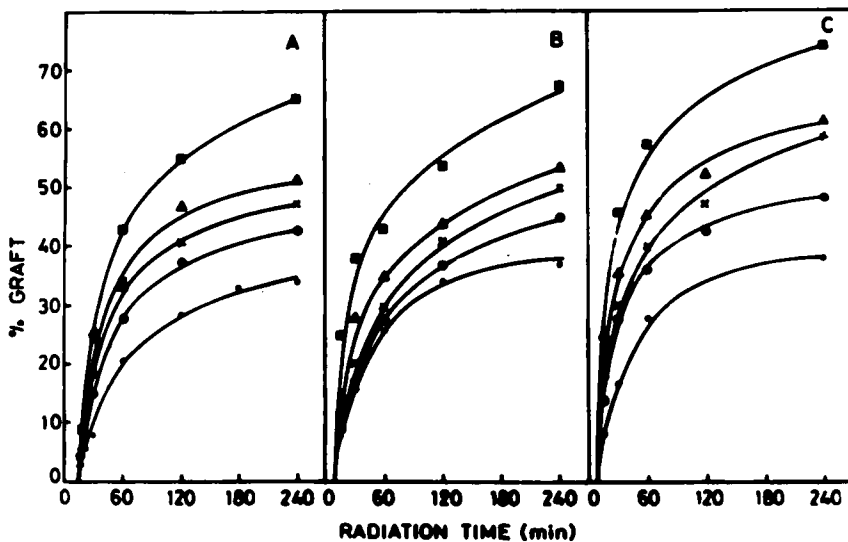


Fig. 3. Per cent Aam grafted vs. time of irradiation at different dose rates: (A) 0.14 Mrad; (B) 0.25 Mrad; (C) 0.51 Mrad. (●) 1.41M; (○) 2.11 M; (×) 2.80M; (△) 3.56M; (◻) 5.63M.

effectively negligible time, extrapolation of the line shows this to correspond to a dose rate of 1.35×10^6 rad/hr. The minimum dose for commencement of grafting is thus $1.35 \times 10^6 / 60 = 22500$ rad.

During grafting with Aa, no induction period was noticed. This could possibly be due to either the faster diffusion of Aa solution into the fabric

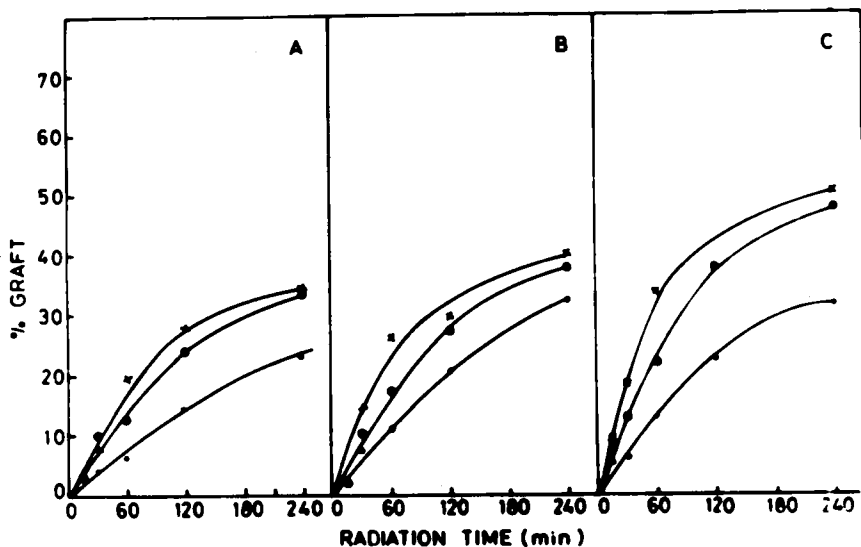


Fig. 4. Per cent Aa grafted vs. time of irradiation at different dose rates: (A) 0.14 Mrad; (B) 0.25 Mrad; (C) 0.51 Mrad. (●) 1.07M; (⊙) 2.1M; (×) 3.5M.

which is swollen by the monomer or due to the absence of any trace impurities in acrylic acid which could react with the radicals initially produced by radiation.

Grafting increases with the total dose applied (Figs. 3 and 4) when the dose rate and monomer concentration are kept constant.

Monomer Concentration

The effect of Aam concentration on per cent grafting was studied at different monomer concentrations, viz., 1.41, 2.11, 2.80, 3.56, and 5.63M. The results are shown in Figure 3. The rate curves show that grafting first increases steadily with time and finally tends to level off with further increase in time of irradiation. It is also seen from Figure 3 that a four-fold increase in concentration yields only a 75–100% increase in grafting. Monomer can be consumed in propagating the branch with the base polymer (grafting) and in self-polymerization (homopolymer). Graft copolymerization, when carried out with insufficient monomer, gives poor yield both of graft and homopolymer. This was corroborated by the fact that when the fabric was briefly immersed in the monomer solution and then irradiated, it showed a lower amount of grafting. This could possibly be due to poor water absorption of nylon which would retain little monomer solution.

A few experiments were carried out on grafting nylon fabric without preswelling. Unlike cellulose, swelling of nylon did not result in a significant increase in graft yield.

Figure 4 shows the relationship between the extent of Aa grafting and radiation time. Increasing graft yields are observed when the total dose,

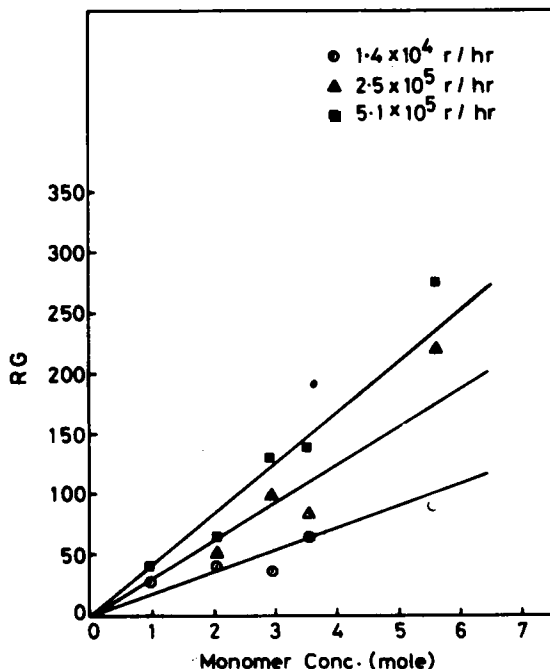


Fig. 5. Dependence of the rate of grafting of acrylamide on monomer concentration at different dose rates: (○) 1.4×10^4 r/hr; (△) 2.5×10^5 r/hr; (◻) 5.1×10^5 r/hr.

dose intensity, or monomer concentration are increased. Aa grafted samples were slightly bluish in color. This may be due to the complex formation of CuSO_4 with poly(acrylic acid).

The initial rate of reaction, graft/hr (RG), was calculated by taking the linear part of the curve in the plot of per cent graft versus time (Figs. 3 and 4). In order to check RG values mathematically, the values at points 6, 12, 18, and 24 were read from the smooth curve to facilitate simple numerical differentiation. Newton's forward interpolation formula was used for the numerical differentiation.

A plot of RG versus monomer concentration (Fig. 5) is linear. It is seen from the figure that initial rate is proportional to monomer concentration at all dose intensities, with straight lines passing through zero.

Figure 6 shows that the log time for 20% grafting is linearly related to the log dose intensity. Extrapolation of the line gives the same dose intensity (refer to Fig. 2) at which the time required for 20% grafting would be 1 min.

Intensity Dependence of Grafting

The intensity dependence of grafting was investigated for the whole dose rate range (0.074–0.51 Mrad). The log-log plot of rate of grafting versus intensity (Fig. 7) gives a straight line whose slope is the intensity exponent. It is seen from the figure that intensity exponent values are 0.25,

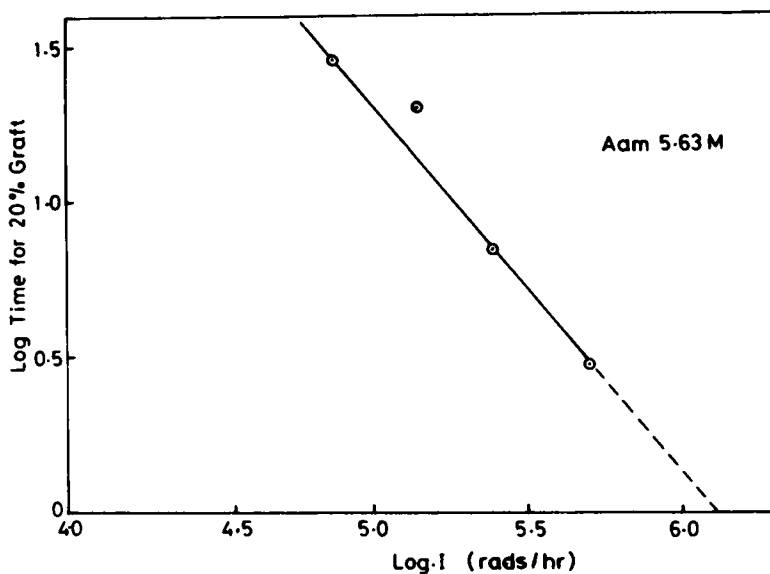


Fig. 6. Dependence of time for 20% Aam graft on dose rates.

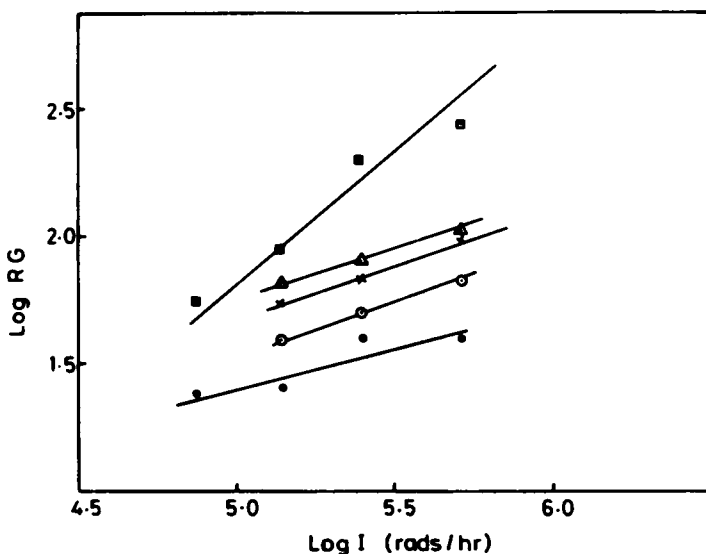


Fig. 7. Dependence of rate of grafting aqueous acrylamide on dose rate at different monomer concentrations: (●) 1.41M; (○) 2.11M; (×) 2.80M; (Δ) 3.56M; (□) 5.63M.

0.37, 0.50, 0.57, and 1.0 for 1.41, 2.11, 2.80, 3.56, and 5.63M monomer concentration, respectively. Thus, the rate of grafting is proportional to the power 0.37 for dose intensities lower than 0.14 Mrad and for monomer concentrations lower than 2.11M. At higher monomer concentrations and dose intensities, the rate of grafting is proportional to the 1.0 power of

TABLE IV
Grafting with Mixtures of Aam and Aa^a

Monomer, concn., mole/l.	Radiation time, min	Aam, %	Aa, %	Per cent graft, %	
				Aam + Aa(80:20)	
				calculated	experimental
2.11	15	8.0	2.2	6.8	6.6
	30	16.9	9.5	15.6	12.6
	60	27.8	17.1	25.6	32.9
	120	36.8	27.2	34.8	43.0
	240	44.6	37.9	43.3	52.7
3.56	15	12.2	7.5	11.2 (8.4)	4.3 (7.7)
	30	28.0	14.1	25.2 (16.9)	15.6 (16.9)
	60	34.6	26.1	32.9 (29.8)	36.9 (27.6)
	120	43.6	29.4	40.7 (32.2)	51.3 (40.2)
	240	51.5	39.2	49.0 (41.7)	60.3 (48.6)

^a CuSO₄, 0.04M; dose rate, 0.25 Mrad. Values reported in brackets indicate per cent grafts for 20:80 mixture of Aam and Aa.

the dose rate, thus indicating that as the dose rate increases, the mechanism of termination shifts from bimolecular to unimolecular. At intermediate dose rates, both mechanisms are operative. The termination at the highest dose rate is probably by reaction with the scavenger. This clearly establishes a certain amount of bimolecular crosslinking between the chains of the backbone polymer.

Grafting with Mixtures of Aam and Aa

Mixtures of Aam and Aa (80:20; 20:80) were also used for grafting to investigate a possible synergistic effect. The results are shown in Table IV. The results of grafting of Aam and Aa as single monomer are also given. Theoretical values for grafting of mixtures (80:20 and 20:80) were calculated from the graft values of Aam and Aa. Mixtures of Aam and Aa show a synergistic effect during grafting.

Properties of the Grafted Fabric

Nylon fabrics of varying graft add-on, both with Aam and Aa, were prepared and evaluated for moisture regain, dyeability, tensile properties, abrasion resistance, and stiffness.

Moisture Regain. Nylon possesses low equilibrium moisture regain which makes it uncomfortable for wear. Moisture regain of the grafted fabrics was determined by allowing the samples to attain the equilibrium moisture at 25°C and 65% relative humidity. The grafted samples show considerable increase in moisture regain (Fig. 8). Moisture absorption is rapid in the beginning with lower add-on and approaches saturation with increasing add-on.

Dyeability. The grafted fabrics were dyed with an acid dye, Ciba Keton Blue R, by a standard method. It was observed that the depth of shade

TABLE V
Dye Exhaustion by Nylon Fabric during Dyeing with Acid Dye Ciba Keton Blue R^a

No.	Sample particulars	Exhaustion, %
1	Aam grafted, 10%	94.0
2	Aam grafted, 20%	92.9
3	Aam grafted, 30%	88.8
4	Aam grafted, 40%	86.7
5	Aa grafted, 10%	91.8
6	Ungrafted control	90.0

^a 1% Shade, m: 1-1: 30.

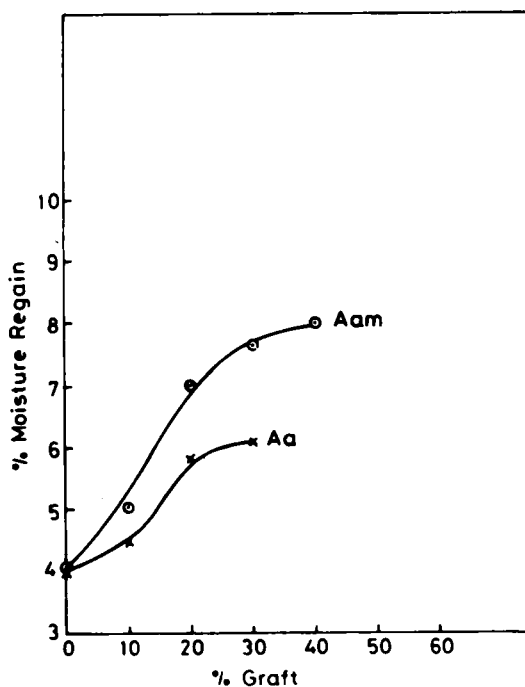


Fig. 8. Moisture regain vs. per cent graft: (○) Aam-grafted fabric; (×) Aa-grafted fabric.

of grafted fabrics decreased with increasing grafting. Such a decreasing dyeability with increasing graft add-on was also reported by Sinohara and Mukoyama.¹⁰ The residual dye in the exhaust dye bath was determined by measuring the optical density at a wavelength of 635 $m\mu$. The results are shown in Table V. The results agree with the observation of decreasing depth of shade with increasing per cent graft.

Grafted nylon was also dyed with a basic dye, Rhodamine B. The results show that the depth of shade increases with increasing grafting. The dyed samples (Rhodamine B) were evaluated for fastness to washing and light. They showed poor fastness to both.

TABLE VI
Tensile and Stiffness Properties of Grafted Nylon*

No.	Sample particulars	Tensile strength, kg and extension, %				Stiffness/flexural rigidity, mg·cm		
		Warp		Weft		Warp	Weft	Over-all
		St.	Ext.	St.	Ext.			
1	Aam grafted, 10%	25.9	47.3	37.1	40.8	88.0	126.7	105.6
2	Aam grafted, 20%	27.4	52.3	41.4	47.8	122.5	223.5	165.4
3	Aam grafted, 30%	27.7	52.3	41.7	46.2	172.2	323.3	235.9
4	Aam grafted, 40%	28.2	50.3	38.8	43.0	209.5	566.9	344.6
5	Aa grafted, 10%	25.7	40.3	37.6	31.6	143.3	234.6	183.4
6	Aa grafted, 20%	28.0	44.1	39.4	43.7	249.7	564.3	375.3
7	Aa grafted, 30%	30.1	54.3	45.4	51.8	364.8	777.7	532.7
8	Irradiated for 30 min	25.0	47.2	35.4	39.5	53.8	77.5	64.6
9	Irradiated for 120 min	25.2	45.3	33.4	34.8	53.6	84.2	67.2
10	Untreated control	25.2	36.1	43.2	42.1	47.6	64.9	55.6

* Instron tensile tester. Specimen size 1 in. × 3 in.; rate of traverse, 10 cm/min.

TABLE VII
Abrasion Resistance of Grafted Nylon*

No.	Sample particulars	Abrasion cycles		Log abrasion cycles	
		Warp	Weft	Warp	Weft
		1	Aam grafted, 10%	5266	17027
2	Aam grafted, 20%	6061	5633	3.8	3.7
3	Aam grafted, 30%	2505	4977	3.4	3.7
4	Aam grafted, 40%	3731	8233	3.6	3.9
5	Aa grafted, 10%	2672	4673	3.4	3.7
6	Aa grafted, 20%	1318	3972	3.1	3.6
7	Aa grafted, 30%	1600	3598	3.2	3.5
8	Irradiated for 30 min	4954	4228	3.7	3.6
9	Irradiated for 120 min	4651	13255	3.7	4.1
10	Untreated control	5308	19863	3.7	4.3

* Stoll Flex Universal Abrasion Tester. Head wt, 1 $\frac{1}{4}$ lb; bar tension, 5 lb.

Tensile Properties. The grafted samples were tested for tensile strength, elongation, abrasion, and stiffness. Results are given in Tables VI and VII. It is clear that there is no loss either in strength or elongation by treatment. Stiffness increases with increased graft add-on. Aa-grafted samples show larger increases in stiffness. The effect appears to be more pronounced in the weft direction.

Nylon fabrics have excellent abrasion resistance. Grafted samples were tested for flex abrasion. From the log (abrasion cycle) values, it is seen that the maximum loss in abrasion is of the order of 10–15%.

Melting Property. Grafted nylon was found to be resistant to melting. Nylon grafted with Aa (30% add-on) retained its fibrous structure up to 320°C, the maximum temperature studied, whereas corresponding untreated nylon 6 melted at 215°C. A more detailed study of the effect of grafting on the melting point of nylon is being undertaken, and the results will be published in due course.

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