

Mechanical and Some Other Properties of Acrylic-Monomer-Grafted Nylon 6 Fiber

A. K. MUKHERJEE and H. R. GOEL, *Department of Textile Technology, Indian Institute of Technology, New Delhi—110016, India*

Synopsis

Nylon 6 fiber, grafted with various vinyl monomers, viz., methyl methacrylate (MMA), ethyl methacrylate (EMA), and *n*-butyl methacrylate (*n*-BMA) were evaluated for their tensile, dye uptake, moisture regain, and solubility characteristics and compared to those of the parent nylon 6 fiber. The tensile properties (tenacity and initial modules) of the grafted samples show a decreasing trend and the percentage breaking elongation an increasing trend with the increase in the graft level in the case of all the three monomers compared to parent nylon 6 fiber. Disperse dye uptake also shows a decrease with the increase in the graft level in all the three monomers grafted only onto nylon 6 fiber. With the introduction of hydrophobic groups in the polymer backbone the moisture regain values decrease. This is true for all the samples and follows the order MMA-*g*-nylon > EMA-*g*-nylon > *n*-BMA-*g*-nylon. Solubility of the polymer in the solvent orthochlorophenol (OCP) and metacresol (MC) also decreases with the increase in the graft level for all the three monomers used in the following manner: OCP: EMA-*g*-nylon > *n*-BMA-*g*-nylon > MMA-*g*-nylon; MC: *n*-BMA-*g*-nylon > EMA-*g*-nylon > MMA-*g*-nylon.

INTRODUCTION

Nylon 6 is used extensively in the form of fiber. Being a highly polar polymer due to the presence of polyamide linkages and to its aliphatic nature, nylon 6 is capable of developing excellent orientation and crystallinity. As a consequence, nylon 6 fiber has excellent mechanical properties, low solubility (only soluble in highly polar solvents), low moisture absorption, and similar other properties which are manifestation of the above-mentioned characteristics of the structure. Depending upon the nature of the end group, it is either receptive to acid dyes or basic dyes. Disperse dyeability is restricted by the degree of architectural symmetry.

Attempts have been made to modify nylon 6 fiber¹⁻⁷ to improve its characteristics. Vinyl monomers grafted onto nylon 6 fiber constitute a major group in such modified nylon 6 fiber. This procedure of modification via graft copolymerisation has been able to produce modified nylon 6 fiber possessing some specific characteristics. However, during such conversion of a linear polymer into a branched (graft) copolymer with the help of a different chemical moiety nylon 6 fiber undergoes a change both in chemical as well as structural properties. The degree of change will obviously be dependent upon the graft level, graft sequence length, and associated structural changes.

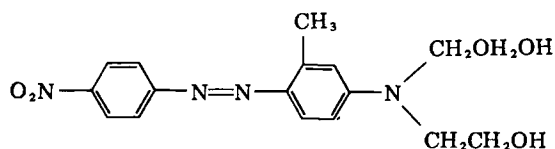
In the present study three vinyl monomers belonging to the acrylate group, viz., MMA, EMA, and *n*-BMA have been grafted onto nylon 6 fiber. The effect of graft level on the properties of the modified nylon 6 fiber thus obtained have been evaluated.

EXPERIMENTAL

The procedure for grafting nylon 6 fiber with various vinyl monomers is the same as described in our previous paper.⁸

Load elongation behaviour of the parent and grafted samples were studied in the dry state using Instron Tensile Tester Model 1112. The experiments were conducted in air under standard conditions, i.e., $65 \pm 2\%$ RH and 25°C . The load elongation curves obtained from Instron machine were converted to stress strain curves. The method given by Meredith⁹ was followed. The stress-strain curves were analyzed to get different parameters, such as breaking strength, elongation at break, and initial modulus, etc.

The dye up-take of parent and grafted samples was measured using disperse dye Cibacet Red 2G (C.I. Disperse Red-17) of the following chemical structure.



The purified dye was pasted with hot water and continuously stirred. After properly dispersing, distilled water was added to make up the dye bath (0.1% dye solution). 50 mg of the material was immersed in 40 cc of the dye solution at 40°C and the temperature of the dye bath liquor was raised to 95°C and the dyeing was carried out for 90 min at this temperature. The samples were then washed with acetone-water mixture (1:1) repeatedly and finally soaped with Sandozine NTS for 30 min.

The optical densities of parent and grafted dyed samples were measured using UNICAM SP 600 Series 2 Spectrophotometer. An indirect method was applied for calculating dye uptake considering 100% dye uptake for the parent sample; in other words, a relative study was made.

Moisture regain of the fiber samples was determined by vacuum desiccator method¹⁰ and calculated by the formula

$$R = 100W/b$$

where R = moisture regain, W = weight of the moisture, and b = dry weight of the sample.

To 3% grafted polymer sample solution in orthochlorophenol (OCP)/and or metacresol (MC) methanol was added drop wise at 25°C until haziness appears. The volume of methanol required to bring haziness was taken as a measure of solubility. As methanol is a nonsolvent, hence, if the OCP/MC solution is capable of tolerating a transfer of methanol without polymer precipitation, the solubility of the grafted polymer in OCP/MC may be taken as more as compared to where methanol tolerance is less.

RESULTS AND DISCUSSION

Mechanical Properties. Mechanical properties (initial modulus, tenacity, and breaking elongation) of nylon 6 fiber, grafted with various vinyl monomers, viz., MMA, EMA, and *n*-BMA to various graft levels have been investigated. The results of this study have been presented in Table I.

TABLE I
Effect of Grafting on Tensile Properties of Nylon 6 Fiber

Sample	% GAO	Tenacity (g/d)	Breaking elongation (%)	Initial modulus (g/d)
Nylon 6	0	5.7	43.5	19.3
	23.0	5.4	46.1	15.2
	39.5	5.2	53.4	11.3
MMA- <i>g</i> -nylon	50.0	5.2	56.3	10.4
	74.8	4.3	57.4	9.7
	124.0	3.7	66.7	7.4
	17.9	5.5	53.0	11.4
	28.0	4.2	59.5	11.5
EMA- <i>g</i> -nylon	49.5	3.5	63.5	12.1
	66.6	3.3	70.0	15.1
	97.3	2.7	50.0	11.6
	116.0	2.5	53.0	10.8
	18.0	5.6	50.1	16.4
<i>n</i> -BMA- <i>g</i> -nylon	36.2	4.1	53.9	13.5
	51.2	3.6	58.0	9.7
	73.0	3.1	59.0	9.3
	95.9	3.0	61.2	8.7
	139.0	2.9	65.5	7.9

It is seen from the results that tenacity and initial modulus values in the case of all the three monomers grafted onto nylon 6 fiber decrease continuously and as a consequence breaking elongation increases. In the case of MMA-grafted samples, the decrease is continuous with increasing amount of grafting. For EMA grafted samples tenacity decreases and breaking elongation increases continuously as the graft level increases. However, initial modulus initially shows a decrease, then an increase and subsequently again a falling trend. *n*-BMA-grafted samples show similar results as that of MMA-grafted samples.

Initial modulus is a property of any material which mainly depends upon crystallinity amorphous ratio. In the case of nylon 6, a linear and polar polymer, grafting by nonpolar vinyl monomers (viz., MMA, EMA, and *n*-BMA) will lead to a decrease in polarity and structural irregularity (due to branching). As a consequence, the secondary valence forces between the chains will decrease. The lower mechanical properties in the case of all the samples is a reflection of these. Similar results have been obtained by several other workers.^{11,12}

Dye Uptake. The results of the dyeing behavior of nylon 6 and the grafted samples grafted with various vinyl monomers, viz., MMA, EMA, and *n*-BMA using a disperse dye (C-I Disperse Red 17) have been presented in Figure 1 and discussed. However, the dye uptake is maximum for MMA-grafted samples followed by EMA and then by *n*-BMA-grafted samples at a comparable graft level.

It has been found by several workers^{6,13,14} that the disperse dye uptake is not dependent on the nature of the functional groups of grafted polymers but is dependent on the structural characteristics. Grafting mostly takes place in the amorphous zone, an area on which disperse dye uptake depends, so with the increase in the graft level the dyeability decreases.

Moreover, with the increase in the graft level of various vinyl monomers grafted onto nylon 6, the mole fraction of nylon in the grafted polymer decreases. Since

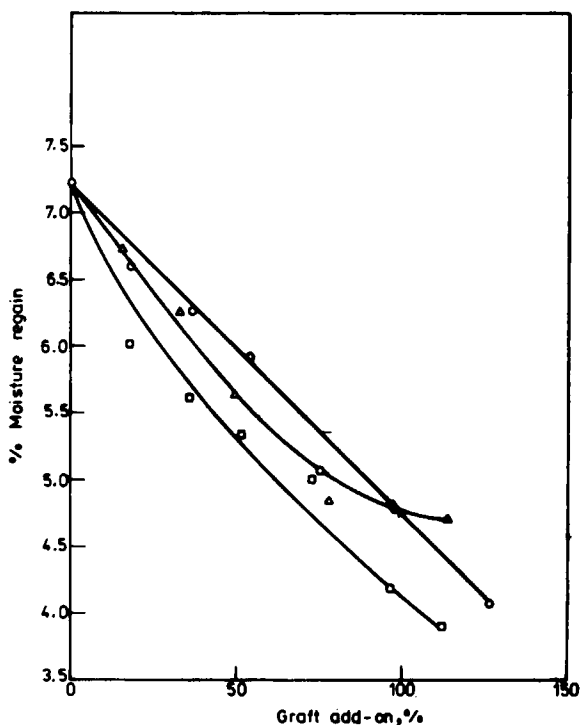


Fig. 1. Plot of dye uptake of parent and grafted samples of nylon 6 vs. graft add-on: (O) MMA-g-nylon; (Δ) EMA-g-nylon; (\square) *n*-BMA-g-nylon.

the dye uptake is dependent on the percentage of nylon in the grafted polymer, so it follows that as the amount of nylon in the grafted samples decreases (with increase in % GAO) the dye uptake also decreases irrespective of the monomer used.

Moisture Regain. Moisture regain values of nylon 6 fiber grafted with vinyl monomers, viz., MMA, EMA, and *n*-BMA with various graft levels, observed under different relative humidity conditions have been reported. The results are presented in Figures 2 and 3.

From the results it is evident that the moisture regain values decrease with the increase in the graft level in all the three monomers grafted samples. However, the moisture regain values maintain the following order and are in agreement with increasing hydrophobic nature of the monomers (see Table II):

$$\text{MMA-g-nylon} > \text{EMA-g-nylon} > \text{n-BMA-g-nylon}$$

TABLE II
Moisture Regain at Comparable Graft Level

No.	Sample	% GAO	MR at 25°C	
			RH 65 \pm 2%	RH 95 \pm 2%
1	Nylon 6	0	4.10	7.2
2	MMA-g-nylon	54.4	2.97	5.93
3	EMA-g-nylon	49.5	2.97	5.68
4	<i>n</i> -BMA-g-nylon	51.2	2.84	5.34

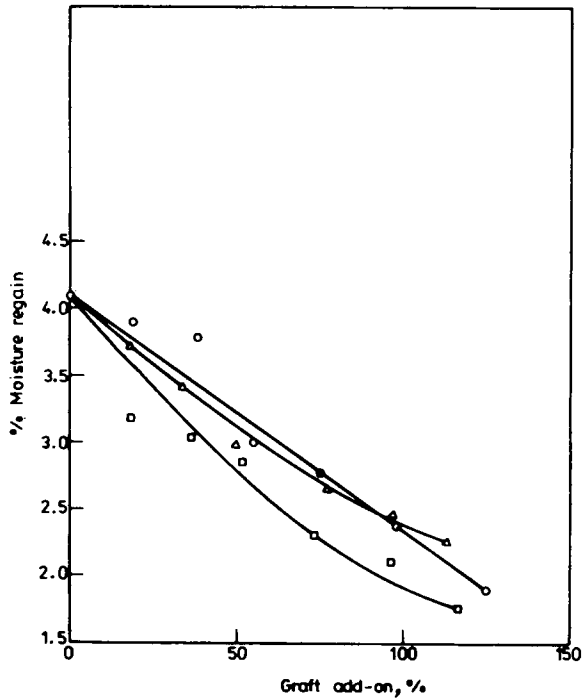


Fig. 2. Plot of moisture regain (RH $65 \pm 2\%$) vs. graft add-on: (O) MMA-g-nylon; (Δ) EMA-g-nylon; (\square) n-BMA-g-nylon.

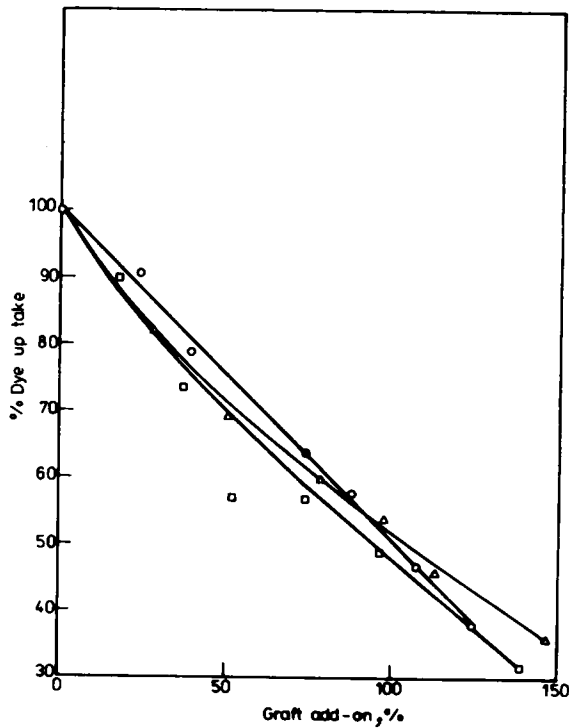


Fig. 3. Plot of moisture regain (RH $95 \pm 2\%$) vs. graft add-on: (O) MMA-g-nylon; (Δ) EMA-g-nylon; (\square) n-BMA-g-nylon.

TABLE III
Effect of Grafting on Solubility of Nylon 6 Fiber

Sample	% GAO	Solubility [volume (mL) of methanol required to bring haziness]	
		Ortho-chlorophenol	Meta-cresol
Nylon 6	0	12.9	10.4
	14.3	10.1	9.7
	23.1	9.5	9.1
MMA- <i>g</i> -nylon	37.6	8.5	7.8
	50.4	8.1	7.6
	82.0	8.1	6.8
	124.0	7.4	6.2
	17.4	12.4	9.6
EMA- <i>g</i> -nylon	28.0	12.3	8.5
	49.5	10.4	8.1
	66.6	10.2	7.9
	97.5	9.9	7.6
	146.5	8.9	7.0
	18.7	9.6	9.6
<i>n</i> -BMA- <i>g</i> -nylon	37.6	9.1	9.1
	51.2	8.4	8.7
	67.7	8.4	8.4
	96.5	8.1	8.1
	151.8	8.0	8.0

Solubility. The results of solubility studies of the samples of nylon 6 grafted with monomers MMA, EMA, and *n*-BMA at various graft levels in different solvent, viz., ortho-chlorophenol and meta-cresol, have been presented in Table III.

TABLE IV
Variation of Dye Uptake and Moisture Regain with Grafting

Sample	% GAO	% Dye uptake (arbitrary units)	% Moisture regain at 25°C	
			RH 65 ± 2%	RH 95 ± 2%
Nylon	0	100	4.1	7.7
	18.6	92	3.9	6.6
MMA- <i>g</i> -nylon	37.6	80	3.7	6.6
	54.4	72.5	2.9	5.9
	74.6	65	2.8	5.1
	97.9	53	2.3	4.8
	124.0	45	1.9	4.1
	17.4	87.5	3.7	6.7
EMA- <i>g</i> -nylon	33.0	77.5	3.4	6.3
	49.5	72.4	2.9	5.7
	77.8	60	2.6	4.9
	97.3	52.4	2.5	4.8
	112.7	45	2.3	4.7
	18.3	90	3.2	6.0
<i>n</i> -BMA- <i>g</i> -nylon	36.3	76	3.0	5.6
	51.2	68.5	2.8	5.3
	73.0	58.5	2.3	5.0
	95.9	47.5	2.1	4.2
	116.5	41.0	1.7	3.9

From the results, it is seen that, as the graft level increases, the solubility of the polymer in the particular solvent decreases. This is true for all the three monomers, viz., MMA, EMA, and *n*-BMA grafted onto nylon 6 and for the solvent OCP and MC. However, at a comparable graft level, the solubility of these samples show the following trend:

OCP: EMA-*g*-nylon > *n*-BMA-*g*-nylon > MMA-*g*-nylon

MC: *n*-BMA-*g*-nylon > EMA-*g*-nylon > MMA-*g*-nylon

The overall solubility of the samples of nylon 6 grafted with the above monomers is more in OCP as compared to MC.

References

1. Y. Shinohara, M. Kashiwagi and K. Mukai, *Dai-Z-Kai Nippon Isotrope Kaigi Hobunshu*, **13**, 741 (1958).
2. Y. Shinohara, *Kobunshi Kagaku*, **17**, 197 (1960).
3. Y. Shinohara and E. Kukoyama, *Sen-i-Gakkaishi*, **18**, 480 (1962).
4. Y. Shinohara, Proceedings of the U. N. International Conference Peaceful Uses of Atomic Energy, Geneva, 1958.
5. G. J. Howarad, S. R. Kim, and R. H. Peters, *J. Soc. Dyers Colour.*, **85**, 468 (1959).
6. Nippon Rayon Co., Ltd., Japan Pat. 4250 (1961).
7. S. H. Abdel Fattah, E. Allam, and M. A. Moharram, *J. Appl. Polym. Sci.*, **20**, 1049 (1976).
8. A. K. Mukherjee and H. R. Goel, *J. Macromol. Sci., Chem.*, **A17**(4), 545 (1982).
9. R. J. Meredith, *Text. Inst.*, **36**, T-107 (1945).
10. A. R. Urganhart and A. M. Williams, *Text. Inst.*, **15**, T-138 (1924).
11. D. S. Varma and N. D. Ray, *Angew. Makromol. Chem.*, **32**, 81 (1973).
12. A. A. Armstrong, Jr., and H. A. Rutherford, *Text. Res. J.*, **33**, 264 (1963).
13. L. Jansco, *Magy Textiltech.*, **27**(7), 333 (1974).
14. M. O. Chantler, G. A. Patlett, and J. A. B. Whiteside, *J. Soc. Dyers Colours*, **85**, 621 (1969).

Received March 10, 1983

Accepted September 20, 1983