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Modification of Tussah Silk by Methyl Methacrylate. Part II

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ABSTRACT

The physical properties of methyl methacrylate grafted tussah silk fiber (9.6 to 36.9% graft) were studied using standard methods. Properties of textile interest such as thermal conductivity and shrinkage; tensile properties such as breaking load, tenacity, tensile strength, and Young's modulus; and electrical properties such as electrical resistance were found to decrease with an increase in percentage of grafting. Possible explanations for such changes in properties are advanced and suitable end uses for the grafted fiber identified.

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INTRODUCTION

Tussah silk, an excellent textile fiber, is produced in many parts of Asia. It is different from and superior to cultivated mulberry silk in many respects. Compared to mulberry silk, tussah silk contains more alanine than glycine, greater amount of dicarboxylic and diamino acids, and also is more resistant to oxidizing agents than mulberry silk [1]. Tussah silk is scarcely affected by various salt solutions such as alkaline solutions of copper hydrate in glycerol, $ZnCl_2$, $CaCl_2$, LiCl, and $MgCl_2$, whereas ordinary silk is readily soluble in these reagents [2].

Because of its gloss, dyeability, eye appeal, and drape characteristics, tussah silk is the fabric of choice for ceremonial use. But its ease of soiling, laundering resistance, creasability, and staining qualities makes it unsuitable for daily use. To improve the textile properties of silk, blending [3] with other synthetic fibers has been attempted. However, the chemical modification of silk has not been investigated much. In a previous communication some physical properties showing an increasing trend with grafting have been reported [4]. This communication presents a few other textile properties of tussah silk which show decreasing trends with grafting.

The observed increase in thermal insulating capacity but decrease in shrinkage and electrical resistance of grafted tussah fiber suggests its end use of furnishing fabrics, fabric insulator, draperies, and in automative applications. The decrease in electrical resistance of the fiber with grafting implies a built up of a smaller amount of static charges on the fiber surface and thus makes the fiber more suitable for processing with textile machinery.

MATERIALS AND METHODS

Tussah silk fibers were collected from Orissa Co-operative Handicrafts Corporation Ltd., Bhubaneswar, India. They were degummed by the method of Mohanty et al. [5]. Then the fibers were grafted with methyl methacrylate in an aqueous solution of Ce(IV) (0.005 to 0.05 $\underline{M}$) at 50°C for 1 to 8 h using known methods [5, 6]. The grafted fibers were Soxhlet extracted with acetone until completely free from homopolymers and then oven dried at 60°C for 6 h followed by cooling to room temperature. The grafted silk so prepared was used to study the following physical properties.

Thermal Conductivity

Thermal conductivity (k) of ungrafted and grafted tussah fibers was studied by using the disk method [7]. The thermal insulating capacity of the fiber (k^{-1}) is given by the expression [8, 9]

$$k^{-1} = \frac{A\,(t_1 - t_2)}{msd\left(\frac{d\theta}{dt}\right)_{t_2}} \quad cal^{-1} \cdot s \cdot cm \cdot degree$$

where m = mass of the disk
s = specific heat of the material of the disk
d = thickness of the sample
$\left(\frac{d\theta}{dt}\right)_{t_2}$ = average rate of cooling of the disk
A = area of the sample
$t_1 - t_2$ = temperature difference in °C

The results of thermal insulating capacity measurements are presented in Fig. 1. It is seen that the thermal insulating capacity (k^{-1}) increases with an increase in the percentage of grafting. Since k^{-1} depends on the nature of the fiber as well as on the size and number of

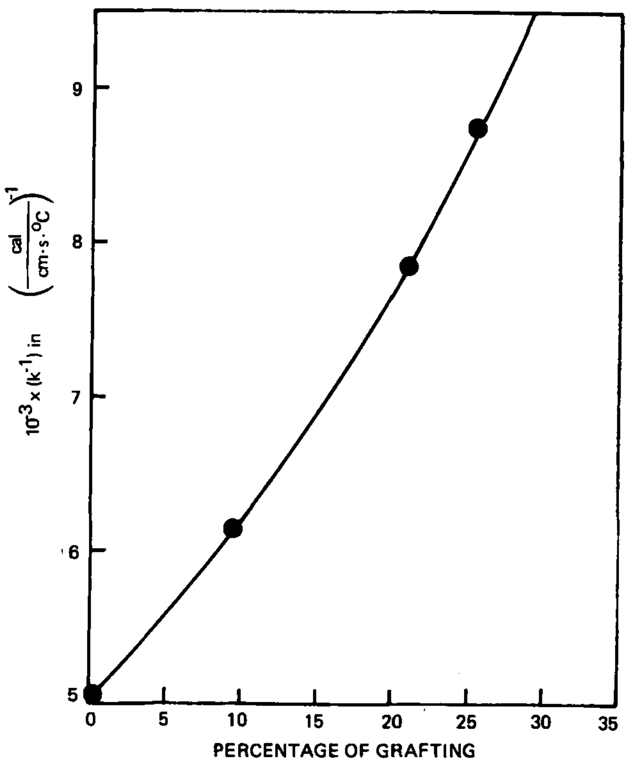

FIG. 1. Thermal insulating capacity (k^{-1}) vs percentage of grafting.

air spaces present in it, the increase of k^{-1} value with grafting can be explained as due to increased porosity of the grafted fiber as observed earlier by the authors [4].

Shrinkage

Shrinkage is a measure of the linear contraction of the fiber when laundered. The shrinkage of ungrafted and grafted fibers was determined by the Launderometer method according to ASTM standards on textile materials [10].

The results of these measurements are presented in Fig. 2. It is observed that shrinkage of grafted fiber linearly decreases with increased grafting. Such behavior of the fiber is explained as due to a loss in flexibility of the fiber as a result of an increase in the number of cross-linking knots [11, 12] on the surface of the fiber.

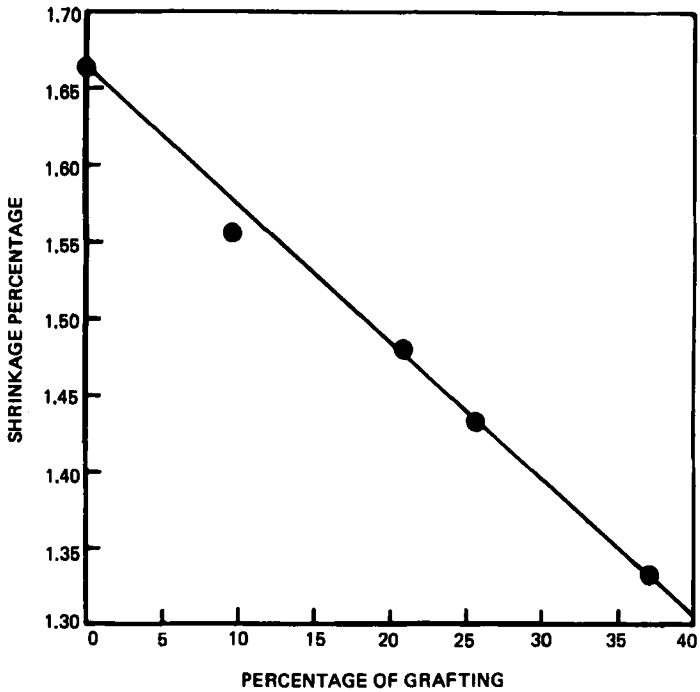

FIG. 2. Shrinkage percentage vs percentage of grafting.

Tensile Properties

The tensile properties [13] of both grafted and ungrafted fibers were measured by using an Instron Tensile Tester [14] at 35°C and constant relative humidity (65%).

The results of breaking load measurement are shown in Fig. 3. It is seen that the breaking load is a maximum for the ungrafted fiber and gradually decreases with grafting.

The results of tenacity measurements are shown in Fig. 4. It is observed that the tenacity of the fiber decreases with grafting.

The results of tensile strength measurements of ungrafted and grafted fibers vs percentage of grafting and moisture regain are shown in Figs. 5a and 5b, respectively. It is observed that the tensile strength of the grafted fibers decreases with a rise of grafting percentage (Fig. 5a). In a previous communication [4] we showed that grafted tussah fiber exhibits increasing regain with grafting. As increasing regain of animal fiber is associated with a decrease of tensile strength [15], the fall in tensile strength of tussah fiber with grafting is reconciled.

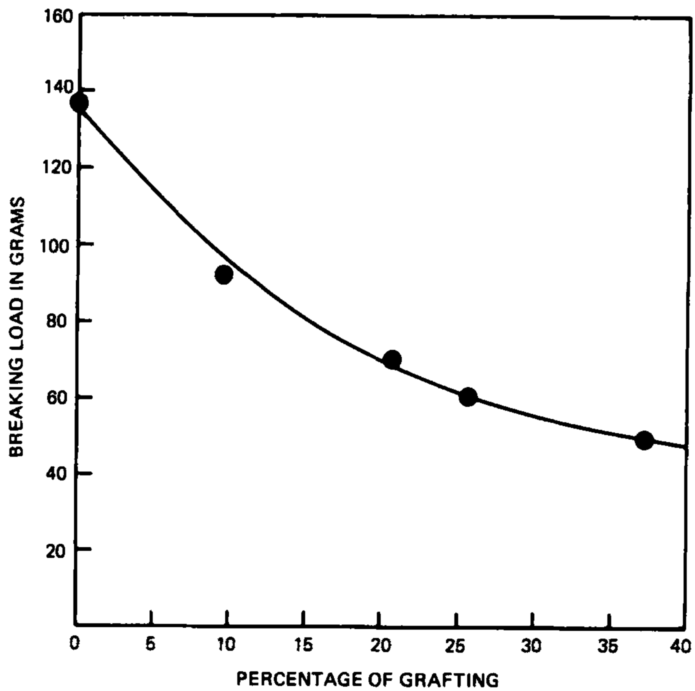

FIG. 3. Breaking load vs percentage of grafting.

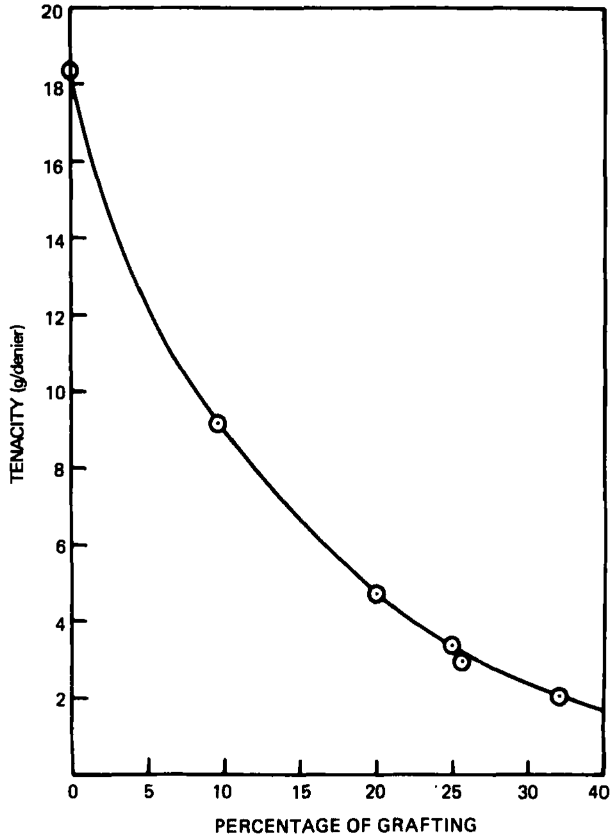

FIG. 4. Tenacity vs percentage of grafting.

The values of Young's modulus (y) vs grafting percentage are shown in Fig. 6a. It is noticed that Young's modulus of grafted fiber decreases with a rise in grafting percentage. The variations of load with elongation for ungrafted and grafted fibers are shown in Fig. 6b. The values of yield point, total stretch, elasticity and elastic limit, etc. were calculated from plots of load vs elongation (Fig. 6b) and are presented in Table 1.

The general decrease of tensile properties with grafting may be explained by supposing a marked relaxation of the intermolecular hydrogen bonds [16] formed between the amide and hydroxyl groups of the silk material, causing easy diffusion of water molecules [17] into the internal structure of the fiber. Again, the loss of tensile properties of the fiber can be ascribed to the loss of orientation of the silk fibroin due to cross-links [11, 18] developed during grafting.

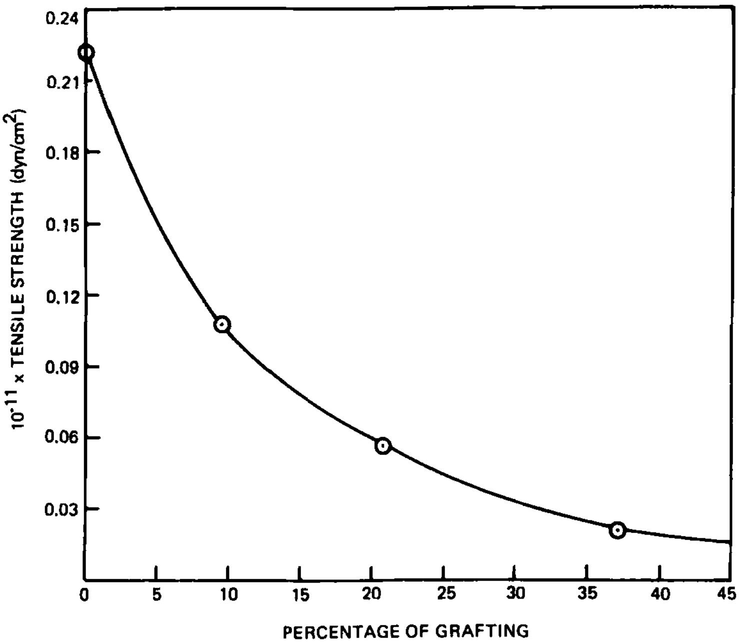

FIG. 5a. Tensile strength vs percentage of grafting.

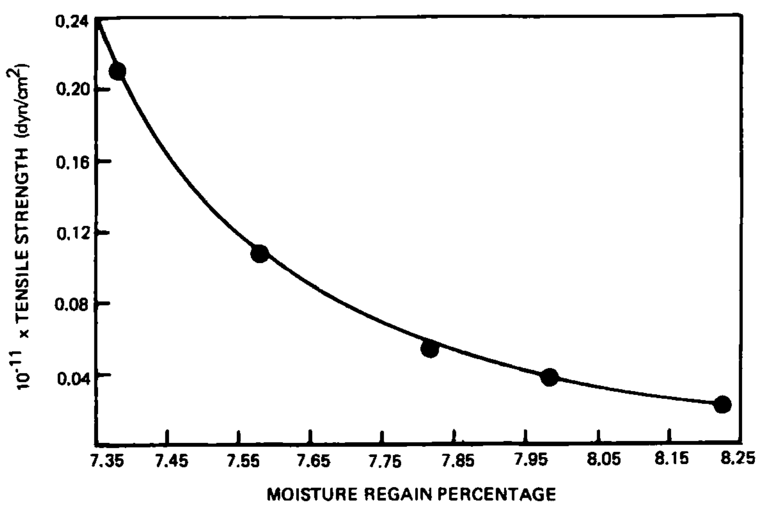

FIG. 5b. Tensile strength vs moisture regain percentage.

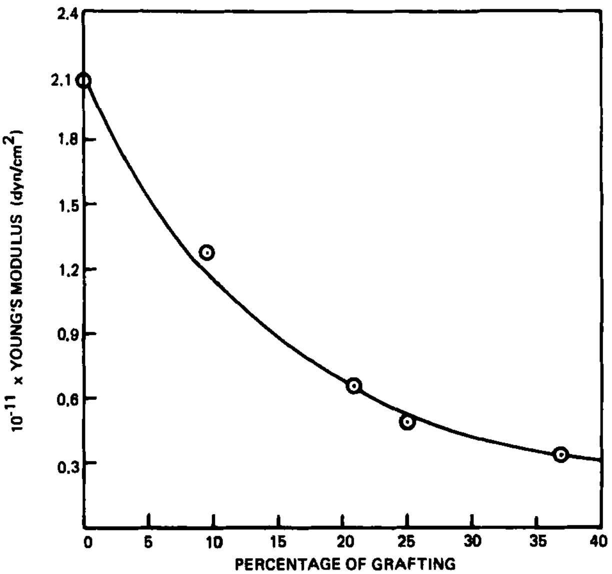

FIG. 6a. Young's modulus vs percentage of grafting.

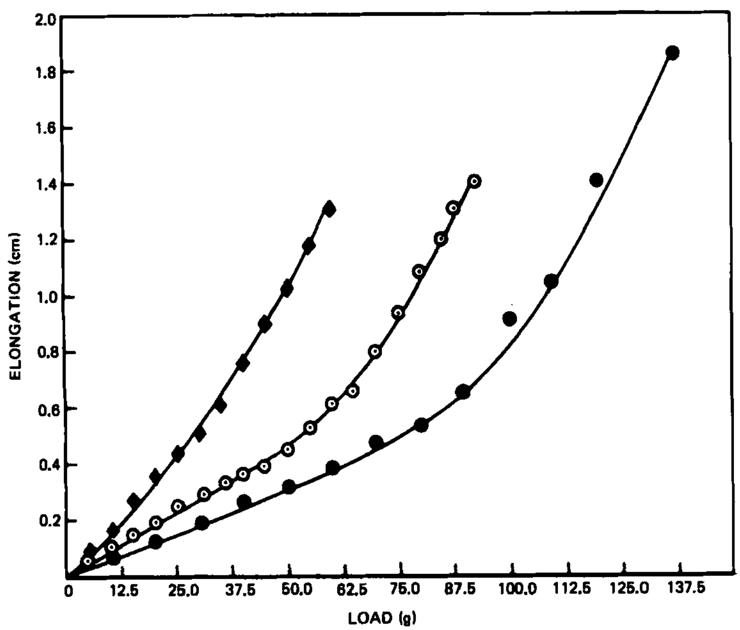

FIG. 6b. Elongation vs load. (●) Ungrafted, (○) 9.6% grafted, (■) 25.6% grafted.

TABLE 1

Tensile properties	Ungrafted	Grafted (9.6%)	Grafted (25.6%)
Yield point, g	76.25	45.00	13.75
Total stretch, cm	1.85	1.40	1.31
Elasticity, cm	0.49	0.40	0.19
Elastic limit, g	73.75	43.75	12.5

Electrical Property

The electrical resistance of ungrafted and grafted fibers was determined with the help of a Million Megohmmeter (BPL, Model RM 160 MK IIIA) and was also calculated by using the corrected empirical formula [19]

$$R = aM^{-n}$$

where R = resistance in megohms of a 4-cm length fiber
M = moisture content
a and n are constants

For silk, a = 16 and N = 23.

The experimental and calculated results of ungrafted and grafted fibers are shown in Fig. 7 (Table 2).

The grafted fibers were found to have reduced electrical resistance compared to the ungrafted one. We have noted [4] before that with an

TABLE 2. Observed and Calculated Electrical Resistance of Tussah Fibers

Nature of the fiber	Moisture content (%)	Resistance by million megohmmeter (MΩ)	Resistance calculated from empirical formula (MΩ)
Ungrafted	6.890	3.35×10^8	3.88×10^8
Grafted (9.6%)	7.063	2.30×10^8	2.61×10^8
Grafted (20.8%)	7.237	1.40×10^8	1.63×10^8
Grafted (36.9%)	7.580	0.65×10^8	0.85×10^8

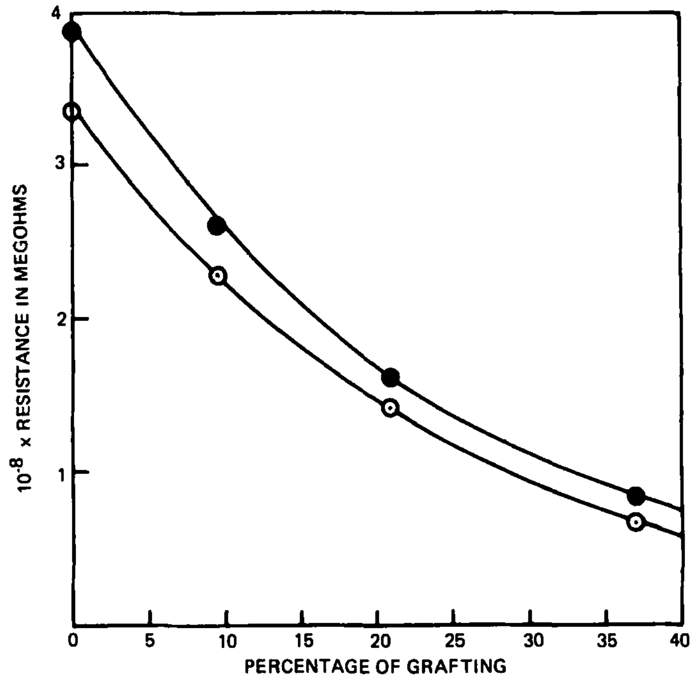

FIG. 7. Resistance vs percentage of grafting. (•) Resistance calculated from empirical formula. (o) Resistance measured experimentally.

increased percentage of grafting, there is a rise in moisture content, which implies incorporation of more water molecules in the pores of the fiber surface. Hence, the decrease in electrical resistance with an increase in grafting percentage is reconciled [20], and is explained as due to the formation of a continuous conducting film of moisture over the internal and external surfaces of the fiber.

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