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GRAFT COPOLYMERIZATION OF METHYL ZMETHACRYLATE ONTO WOOL FIBERS INITIATED BY $NaBO_3$/Fe(II) REDOX SYSTEM

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ABSTRACT

Grafting of methyl methacrylate onto wool fibers was carried out by using $NaBO_3$/Fe(II) redox system as initiator. The effect of M/P ratio, initiator and activator concentrations, and the reaction temperature on the degree of grafting has been studied. A reaction mechanism is proposed for the grafting of MMA on wool in this system. Various improved properties of the grafts were also studied and compared with those of virgin wool fibers.

Key Words: Wool fibers; Methyl methacrylate; Grafting; Redox system; Acid and alkali attack

INTRODUCTION

Modification of wool fibers through functionality changes, graft copolymerization, and chemical treatment to improve their properties such as durability, dyeability, acid and alkali resistance has been the goal of interested researchers.[1–5] A good number of initiators like peroxodiphosphate,[6] potassium monopersulphate,[7] potassium persulphate,[8,9] potassium bromate,[10] and hydrogen peroxide [11] have been successfully used for graft copolymerization of different vinyl monomers onto wool. However, no report seems to be available on graft copolymerization of wool fibers with

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sodium perborate as initiator. Sodium perborate is safe to handle, cheap, and has the oxidizing properties of hydrogen peroxide.[12–13] In addition, sodium perborate has the ability to produce primary radicals under the influence of some salts or complexing agents.[14–15] Thus, in the present work, sodium perborate/ferrous ion system has been used as a source of primary radicals for graft copolymerization of methyl methacrylate onto wool fibers.

EXPERIMENTAL

Materials

Australian merino wool fibers were extracted for 24 hours with acetone and 24 hours with petroleum ether in a soxhlet apparatus, then washed with running water and dried in air at room temperature.

Methyl methacrylate (Merck, Germany) was washed with 5% sodium hydroxide solution and distilled water and dried with anhydrous calcium chloride. Reagent-grade ferrous sulphate and sodium perborate tetrahydrate were used without further purification.

Mordant yellow 10 (C.I. 14010 and $\lambda_{max} = 354$ nm) and Mordant Orange 10 (C.I. 26560 and $\lambda_{max} = 386$ nm) dyes supplied by Aldrich were used as dyestuffs.

Graft Copolymerization

0.5 g of defatted wool fibers were immersed in a mixture containing water and required amounts of methyl methacrylate and ferrous sulphate solution. The pH of the mixture was adjusted to 6 using HCl solution. The reaction system was deaerated by passing oxygen-free nitrogen for 30 minutes and sealed air tight. The vessels were then kept in a shaking constant temperature bath until thermal equilibrium followed by injecting the required amount of perborate solution. The grafting reaction was carried out for the desired time. The grafted wool was filtered from the reaction mixture, washed several times with distilled water, and then dried at room temperature. The homopolymers were extracted with hot acetone repeatedly, until the extract gave no precipitate with methanol.

The degree of grafting was calculated as follow:

$$\text{Degree of Grafting (\%)} = \frac{\text{dry weight of grafted wool} - \text{dry weight of original wool}}{\text{dry weight of original wool}} \times 100$$

The extent of homopolymer formed during grafting was estimated from:

$$\text{Homopolymer Extent } (\%) = \frac{\text{dry weight of homopolymer}}{\text{weight of monomer used}} \times 100$$

Viscosity Average Molecular Weight of Grafted Polymer

Grafted wool samples were hydrolyzed with 6 N HCl at 115°C for 24 hours, all the wool went into solution as amino acids, while the grafted polymer that was left was washed and dried. The $\overline{M}_v$ of polymer isolated from the grafts was determined by the viscosity method using a Ubbelohde viscometer and was calculated by using the Mark-Houwink equation.

Average Number of Grafted Chains

The average number of grafted chains per wool chain ($\bar{n}$) was calculated using the average molecular weights of wool and grafted polymer as follows:

$$\bar{n} = \frac{\text{weight of grafts}}{\overline{\text{M}}\text{ of grafts}} \bigg/ \frac{\text{weight of wool}}{\overline{\text{M}}\text{ of wool}}$$

Acid Solubility

0.1 g of graft copolymer, as well as control samples, were treated with 0.1 M HCl at 65°C for 60 minutes using a wool-liquor ratio of 1:100. The fibers were filtered, washed with distilled water, then dried at 110°C until they reached a constant weight. The percentage loss in weight of the wool gave the acid solubility.

Alkali Solubility

0.1 g of graft copolymer, as well as control samples, were treated with 0.1 N NaOH at 65°C for 60 minutes using a wool-liquor ratio of 1:100. The fibers were filtered, washed with distilled water, aqueous acetic acid, and finally with distilled water again, then dried at 110°C until they reached a constant weight. The percentage loss in weight of the wool gave the alkali solubility.

Moisture Sorption

Moisture sorption of pure and grafted wool fibers was determined by the vacuum desiccator method. The wool samples were placed in a small weighting bottle and dried in a vacuum oven over 70°C to a constant weight (W_d). The dried samples were then placed in a desiccator containing saturated solution of potassium bromide (to give a relative humidity of 70% at $20°C \pm 1$) for 24 hours. The moisturized samples were weighed again (W_m), and the moisture sorption is given by:

$$\text{Moisture sorption } \% = \frac{W_m - W_d}{W_d} \times 100$$

Dyeing Procedure

Dyeing of the grafted and controlled wool fibers using Mordant Yellow 10 and Mordant Orange 10 was carried out for 60 minutes at 60°C using 1% of the dye, 15% Glauber's salt, and 10% acetic acid; the liquor-to-wool ratio was maintained at 100:1. The wool sample was filtered, and the optical absorbance of the filtrate was measured using a Unicam α-Helios UV vis spectrophotometer. From these results, the dye uptake by the wool fibers was computed.

Mechanical Properties

The tensile strength and elongation at break for the grafted and pure wool fibers having 23 μm average diameter and 4 cm average length were tested at room temperature using Spinlabe Sletometer Device at a crosshead speed of 0.5 cm/min.

Evidence of Grafting

An increase in the weight of the wool fibers after extraction.

By comparing the IR spectra, a strong absorption band at 1725 cm^{-1} appears in case of grafted samples that is characteristic for C=O group of poly(methyl methacrylate), while this band is absent in the spectrum of pure wool.

RESULTS AND DISCUSSION

Effect of Monomer/Polymer Ratio

The effect of M/P ratio on the degree of grafting has been studied at different perborate concentrations ($2.0 \times 10^{-3} - 25.0 \times 10^{-3}$ M) with a fixed concentration of ferrous ion (1.25×10^{-4} M) for a reaction time of 4 hours

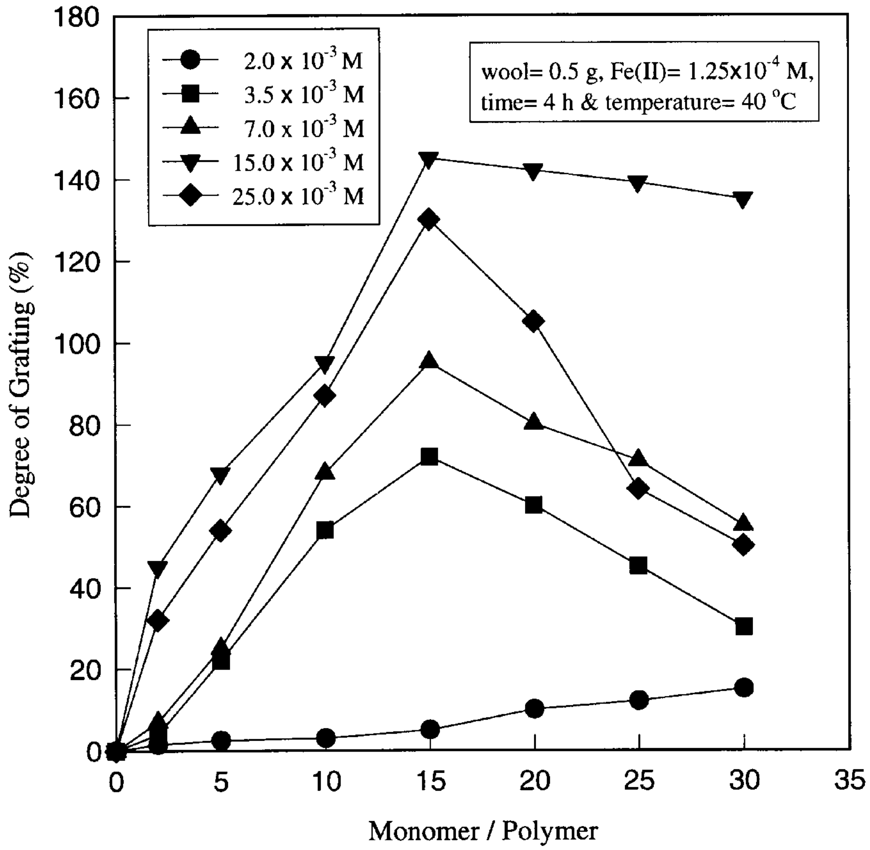

Figure 1. Effect of monomer/polymer ratio on the degree of grafting at various initiator concentration.

at 40°C (Fig. 1). As shown, the degree of grafting increases as the M/P ratio increases up to 15. Further increase in the M/P ratio is accompanied by a lowering in the degree of grafting.

By calculating the viscosity average molecular weight of PMMA isolated from the grafts and also the average number of grafted chains as a function of M/P ratios at constant concentrations of perborate and ferrous ions, Table 1, we get:

As the grafting percent increases the viscosity, average molecular weight increased while the average chain numbers remained nearly constant. This indicates that, under these conditions of grafting, a constant number of active sites has been formed on the wool backbone.

At higher M/P ratio, the grafting percent decreased while the homopolymer extent increased. This could be attributed to the fact that at higher monomer concentration, homopolymer formation, as well as wastage reactions due to monomer transfer, are accelerated.[16]

Table 1. Effect of M/P Ratio on the Viscosity Average Molecular Weight of PMMA Isolated from the Grafts, Number of Grafted Chains per Wool Chain, and the Homopolymer Extent (Wool = 0.5 g, $[NaBO_3] = 7 \times 10^{-3}$ M, $[FeSO_4] = 1.25 \times 10^{-4}$ M, Time = 4 Hours, and Temperature = 40°C)

M/P Ratio	Grafting (%)	$\overline{M}_v$ [a]	$\bar{n}$ [b]	Homopolymer Extent (%)
2	7	10,770	0.65	22
5	25	35,710	0.70	27
10	68	94,440	0.72	31
15	95	133,800	0.71	37
20	81	110,960	0.73	58
25	71	102,900	0.69	71
30	55	78,570	0.70	84

[a] $\overline{M}_v$ viscosity average molecular weight of grafted polymer.
[b] $\bar{n}$ Average number of grafted chains per wool chain.

Effect of Initiator Concentration

The effect of perborate concentration on the degree of grafting was studied with a series of M/P ratios (2–30) with a constant ferrous ion concentration (1.25×10^{-4} M) for a reaction time of 4 hours at 40°C (Fig. 2). It has been observed that the degree of grafting increases as the perborate concentration increased up to 15.0×10^{-3} M, beyond which it decreases. By calculating the viscosity average molecular weight of PMMA graft and its average number of chains as a function of perborate concentrations at constant values of M/P ratio and ferrous sulphate concentrations (Table 2), we found that:

There is an increase in the average number of grafted chains with perborate concentration. This indicates that as the perborate concentration increased, the number of active sites on wool backbone increased.

At higher perborate concentration, the viscosity average molecular weight of PMMA isolated from the grafts become lower. This can be attributed to the enhancement of the number of the primary radicals formed and then an increase in the rate of the termination steps.

An increase in the number of the primary radicals accelerates the homopolymer formation on the contrary of grafting.

Effect of Activator Concentration

The degree of grafting of MMA onto wool fibers at different ferrous ion concentrations has been studied over a range of reaction temperatures (30–50°C) at a constant M/P ratio and perborate concentration for a reaction

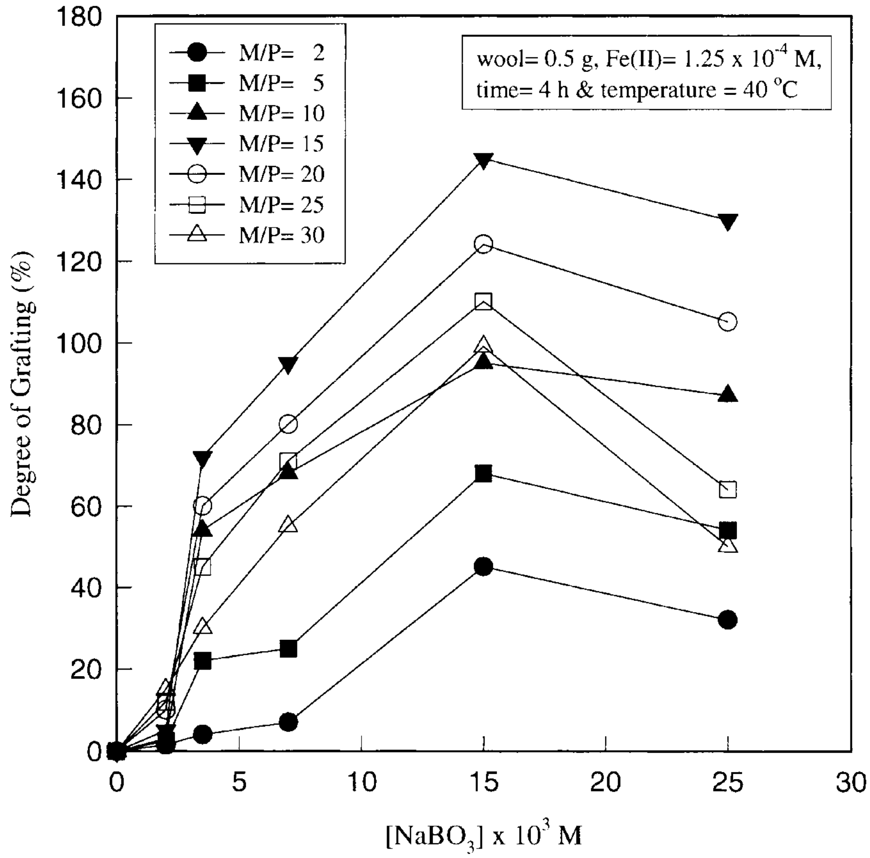

Figure 2. Effect of perborate concentration on the degree of grafting at various monomer concentrations.

time of 4 hours (Fig. 3). At zero ferrous ion concentration, no reaction takes place, which indicates that the primary radical is not formed in the absence of ferrous ions. Also, the degree of grafting increases as the ferrous ion concentration increases up to 2.5×10^{-4} M. A further increase in the activator concentration leads to a decrease in the degree of grafting again.

By calculating, the viscosity average molecular weight of the grafted polymer and its number of chains as a function of ferrous ion concentrations at constant values of M/P ratio and perborate concentrations (Table 3) we found that:

As the ferrous ions increased, the number of grafted chains increased. This indicates that the number of active sites on the wool macromolecule increased.

An increase in the viscosity average molecular weight of PMMA isolated from the grafts as the ferrous ions increased up to 2.5×10^{-4} M; above that, it decreased again. This could be attributed to an increase in the number

Table 2. Effect of Initiator Concentration on the Viscosity Average Molecular Weight of PMMA Isolated from the Grafts, Number of Grafted Chains Per Wool Chain, and the Homopolymer Extent (Wool = 0.5 g, M/P = 10, $[FeSO_4] = 1.25 \times 10^{-4}$ M, Time = 4 hours, and Temperature = 40°C)

$NaBO_3$ (M) × 10^3	Grafting (%)	$\overline{M}_v$	$\bar{n}$	Homopolymer Extent (%)
zero	—	—	—	—
2.0	3	12,000	0.40	21
3.5	45	88,230	0.51	24
7.0	68	94,450	0.72	31
15.0	95	100,000	0.95	44
25.0	87	77,680	1.12	69

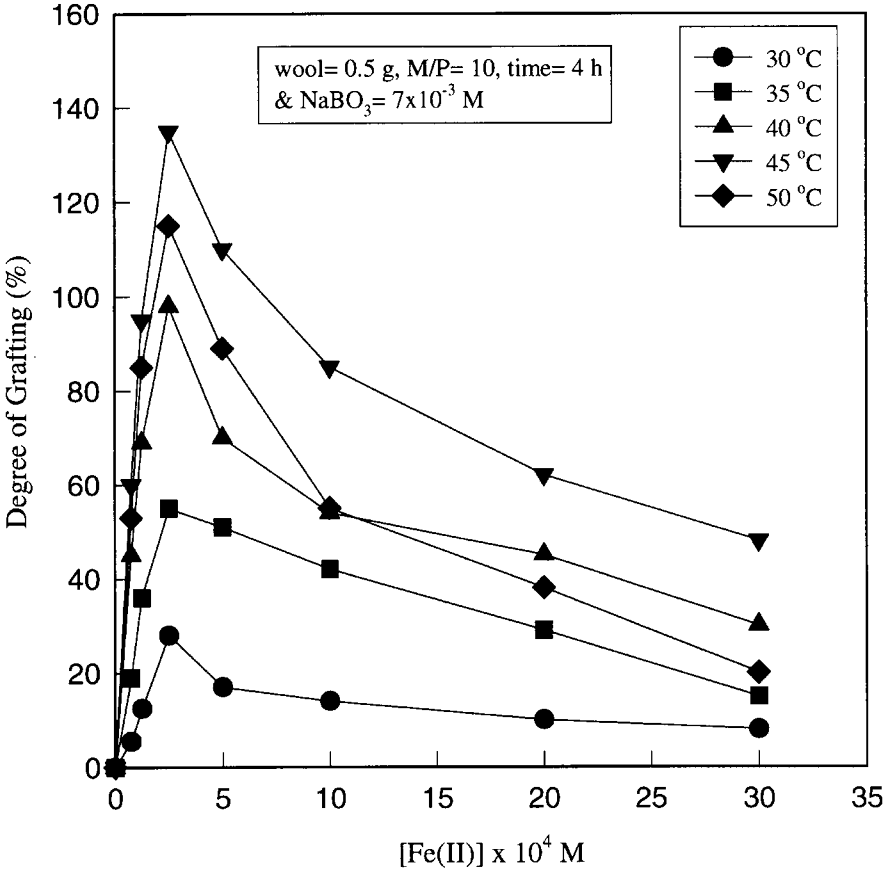

Figure 3. Effect of ferrous ion concentration on the degree of grafting at different temperatures.

Table 3. Effect of Activator Concentration on the Viscosity Average Molecular Weight of PMMA Isolated from the Grafts, Number of Grafted Chains per Wool Chain, and the Homopolymer Extent (Wool = 0.5 g, M/P = 10, [$NaBO_3$] = 7×10^{-3} M, Time = 4 hours, and Temperature = 40°C)

$FeSO_4$ (M) × 10^4	Grafting (%)	$\overline{M}_v$	$\bar{n}$	Homopolymer Extent (%)
zero	—	—	—	—
0.75	45	93,750	0.48	20
1.25	68	94,440	0.72	31
2.50	98	111,360	0.88	38
5.00	70	69,300	1.01	43
10.00	54	47,780	1.13	53
20.00	45	36,290	1.24	67
30.00	30	21,430	1.40	82

of primary radicals in the reaction medium, which increased the rate of termination step.

The extent of homopolymer formation increased due to a rise in the number of the primary radicals and then the rate of homopolymerization.

Effect of Reaction Temperature

The effect of the reaction temperature on the degree of grafting has been studied at a different activator concentration (0.75×10^{-4}– 30.00×10^{-4} M), using a constant M/P ratio and perborate concentration for a reaction time of 4 hours (Fig. 4). The degree of grafting initially increases as the temperature rises, reaches a maximum at 45°C, and finally decreases again. The initial increase is mainly due to an increase in the diffusion rate of the monomer onto the wool fibers, which is attributed to increased mobility of the monomers and enhanced swellability of wool. At a higher temperature, homopolymer formation in a solution is faster than the copolymerization onto the wool fibers.[8]

Based on the above results, a schematic representation for the graft copolymerization of MMA onto wool fibers initiated by perborate/ferrous ion as a redox system can be represented as shown below.

Formation of the primary radical species is generated from a sodium perborate/ferrous ion system [14]

$$BO_3^- + 2H_2O \longrightarrow [HOOB(OH)_3]^-$$

At pH = 6,

$$[HOOB(OH)_3]^- + Fe(II) \xrightarrow{H^+} H_3BO_3 + Fe(III) + OH^\bullet + OH^-$$

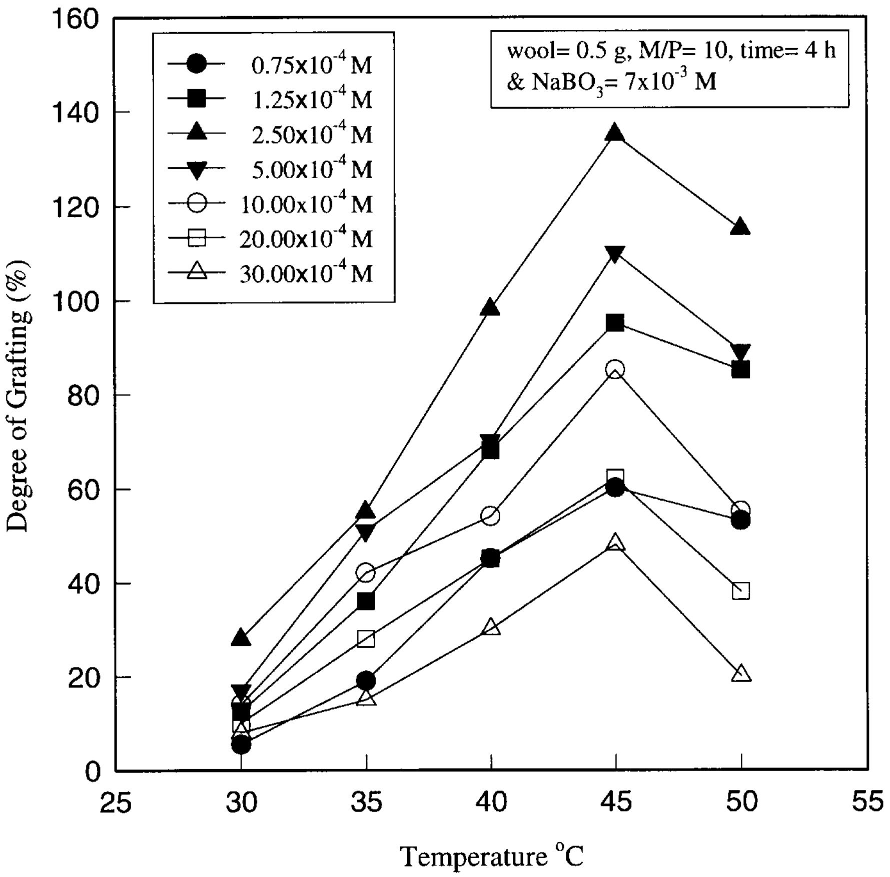

Figure 4. Effect of various temperatures at various activator concentrations on the degree of grafting.

The freshly produced ferric ions might react with OH$^-$ to reproduce ferrous ions and the primary radical species:[11,15]

$$\mathrm{OH^- + Fe(III) \longrightarrow Fe(II) + OH^\bullet}$$

This means that ferrous ions are not consumed during this process, and thus, only a low concentration of it was required for the graft copolymerization.

Formation of macrowool radicals, due to an attack of the primary radical species:

$$\mathrm{W + OH^\bullet \longrightarrow W^\bullet + H_2O}$$

Initiation with monomer (M):

$$\mathrm{W^\bullet + M \longrightarrow WM^\bullet}$$

Propagation:

$$\mathrm{WM}^{\bullet} + \mathrm{nM} \longrightarrow \mathrm{WM}^{\bullet}_{\mathrm{n}+1}$$

Termination may occur due to the interaction with Fe(III), mutual combination of growing grafted chains, or the presence of primary radicals in excess.

Properties of Grafted Wool Fibers

Acid and Alkali Solubility

The hydrolysis of wool molecules under the action of aqueous solutions of acids and alkalis is due to the hydrolytic fission at the polypeptide bonds. The nature of hydrolysis depends mainly on the nature of the hydrolyzing agent. Thus, acids and alkalis show characteristic differences.

The effect of hydrochloric acid on the wool grafted fibers are given in Table 4. The acid solubility increases at a low degree of grafting, while a further increase in the degree of grafting is accompanied by an improvement in the wool resistance against acid attack. This may be due to the fact that the polypeptide chains were protected to a smaller extent at a low degree of grafting when compared to high graft-on wool.

On the other hand, the alkali solubility values of all grafted samples were decreased if compared with that of pure wool (Table 4). This may be

Table 4. Effect of Grafting Degree on the Moisture Sorption, Mechanical Properties, and Acid and Alkali Solubility of Wool-Graft Poly(methyl Methacrylate) Grafted Copolymer Fibers

Grafting (%)	Acid Solubility (%)	Alkali Solubility (%)	Moisture Sorption (%)	Tensile Strength (Pascal) × 10^{-5}	Elongation at Break (%)
0	20.0	14.8	15.0	2.5	17.5
5	23.0	14.7	14.6	2.7	18.7
15	24.2	14.2	13.5	3.0	21.3
30	18.5	13.5	12.8	3.4	27.5
45	16.2	12.8	10.3	4.1	34.7
62	15.4	11.2	8.5	4.9	49.4
85	13.7	10.9	7.2	5.8	57.0
99	12.1	9.5	6.0	6.4	48.3
115	10.9	8.1	5.1	6.9	40.4
130	10.4	7.5	4.0	7.2	36.2
145	10.2	6.8	3.5	7.3	33.1

attributed to the replacement of the disulphide bonds by a more stable link or entirely new crosslinks introduced by the grafting process.

Moisture Sorption

The effect of the degree of grafting on the moisture sorption of wool fiber has been studied, and the results are given in Table 4. The grafting process causes a slight decrease in the moisture sorption and as the degree of grafting increases, the moisture sorption decreases. This is due to the grafting process blocking the water attracting groups on the wool main chains causing a drop in the moisture sorption values.[17]

Mechanical Properties

The tensile strength and the elongation at break for grafted samples were measured and are given in Table 4. By comparing these values to

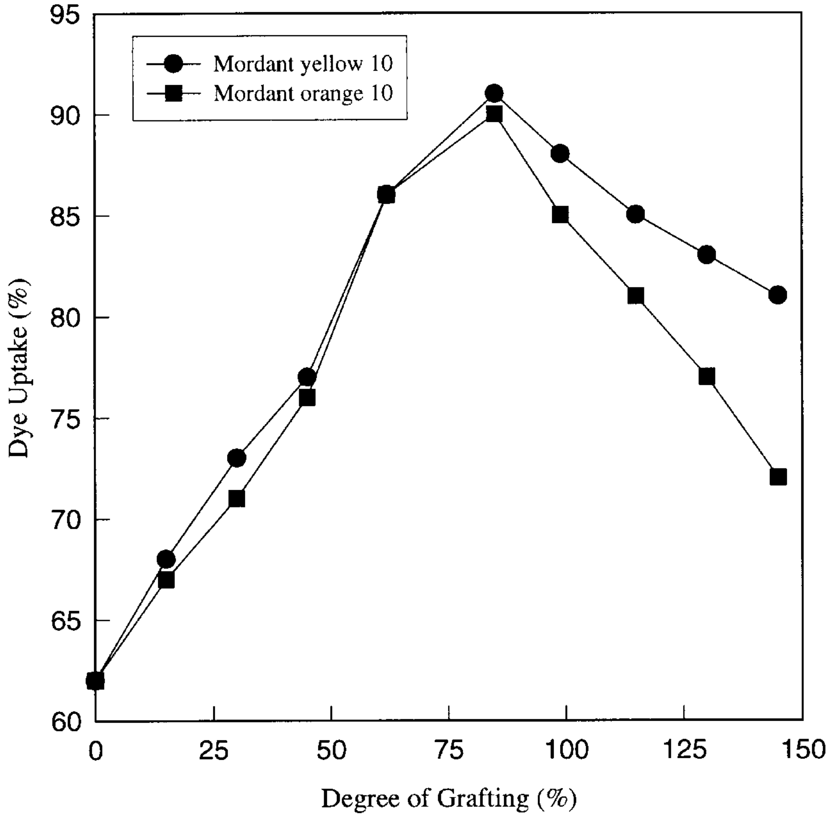

Figure 5. Effect of degree of grafting on the dye uptake for wool-g-PMMA fibers.

that of pure wool, we get the tensile strength increase with the degree of grafting, while the elongation at break decreases again at a high degree of grafting. This is due to the internal crosslinking formation through bimolecular combination of growing grafted chains, which may impart the elastic nature of the fibers.[9]

Dye Uptake

The effect of the degree of grafting on the dyeability of wool fibers was studied using different dyes (Fig. 5). Wool as a partially crystalline material has the ability to dye uptake due to its diffusion through the amorphous regions of the wool.

Also, the dye uptake increases as the degree of grafting increases up to 85%. This is due to the grafting process increases in the amorphous regions in the wool molecules in addition to opening its surface structure.[17] Further increase in the degree of grafting above 85% was accompanied by a decrease in the dye uptake values; this may be because at high grafting, the open structure of the wool starts to close again, which affects the diffusion process and then the dye uptake values.

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