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Dyeing of Newly Synthesized Poly (Methacrylic Acid)-Carbamoylethylated Cotton Graft Copolymers

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Abstract: Unmodified cotton (substrate 1), carbamoylethylated cottons (CEC) having 0.21, 0.67 and 1.1% N (substrate II-IV) were graft copolymerized with methacrylic acid (MAA) at different initiator (PMPS) and monomer concentrations. This was done to tailor poly (MAA)-grafted carbamoylethylated cottons having different graft yields (expressed as meq-COOH/100 g sample). The resulted tailored cotton graft copolymers were dyed with two different dyes namely direct dye as well as basic dye (that has no or little affinity to cotton cellulose) to see their suitability towards dyeing. It was found from the data that; (a) the graft yield increases by increasing the initiator and monomer concentration within the range studied irrespective of the substrate used and follows the order: substrate IV>substrate III>substrate II>substrate I; (b) the introduction of carbamoylethylated groups ($CONH_2$) in the molecular structure of cotton cellulose offered extra additional sites for graft copolymerization reaction, that enhance the susceptibility of cotton towards grafting; (c) the colour strength K/S of carbamoylethylated cottons dyed with direct dye decreases after copolymerization with poly (methacrylic acid) prior to dyeing; (d) the resulted poly (MAA)-carbamoylethylated cottons graft copolymers show higher affinity for basic dye and bring about what we called perceptible shade and (e) dyeing of unmodified cotton and poly (MAA)-cotton graft copolymer were done just for comparison.

Key words: Cotton, Carbamoylethylated Cottons (CEC), Potassium Monopersulphate initiator (PMPS), Poly (MAA)-grafted carbamoylethylated cottons

INTRODUCTION

Since, 1950, various vinyl monomers have been grafted onto cellulosic materials, with the aim of tailoring new polymeric materials having particular properties[1]. It is well known that, free radical graft copolymerization of vinyl monomers onto cotton and modified cotton is the most common methods for initiating grafting. So, extensive studies on graft copolymerization of different monomers either hydrophilic or hydrophobic onto cyanoethylated and carboxymethylated cotton cellulose using ceric ion method[2-6]; nitrile monomers onto sulfonated Jute jute-cotton blended fabric using potassium permanganate/sulphuric acid redox system[7]; methacrylic acid onto DEAE-cotton using potassium permanganate/ citric acid system[8]; acrylic and acrylonitrile onto methyl and ethyl cellulose using potassium permanganate-P-xylene redox pair and ammonium per sulphate respectively[9,10] have been reported in the literature. While grafting onto acetylated cotton and cellulose bearing different substituents has also been reported[1]. On the other hand, improvement the dyeability of cotton fabrics as well as their dyeability with other dyes that has no or little affinity towards cotton via chemical modification has been also reported[11-15].
For simplicity the present study was discussed under the following objectives:

1. Carbamoylethylation of cotton
2. Graft copolymerization of methacrylic acid onto untreated cotton (substrate I) and carbamoylethylated cottons (substrate II-IV) using potassium monopersulphate/Fe^{2+} as a novel redox system and
3. Dyeing characteristics of the four substrate in question with particular attention for grafted one.

MATERIALS AND METHODS

Cotton fabric: Mill scoured bleached and mercerized plain weave (31 picks and 36 end/cm) was used.

Chemicals: Methacrylic acid stabilized with 0.01% hydroquinone was freshly distilled at 75°C and pressure of 100 mm Hg. They were stored at –10°C until used. Acrylamide, Sodium hydroxide, Potassium

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monopersulphate (Aldrich USA), ferrous sulphate (AR, BDH) and sulphuric acid were used as supplied.

Chemical modification of cotton:

Carbamoylethylation of cotton in aqueous medium: Aqueous carbamoylethylation involves padding the cotton fabric samples in aqueous solution containing acrylamide (5, 10 and 15%) and sodium hydroxide (4% based on weight of fabric). The fabric samples were then heated at 125°C for 6 min. At this end, the samples were thoroughly washed, neutralized with HCl (0.1 N), washed again and dried at ambient conditions.

N.B. Carbamoylethylated cotton having different degree of carbamoylethylation expressed as% N measured by Kjeldahal method[16] (substrate II-IV) was obtained by using different concentration of acrylamide 5,10 and 15% based on weight of substrate.

Graft copolymerization procedure:

The graft copolymerization reaction was carried out as follows: It was carried out in 100 flasks containing an aqueous solution of monomer (20-100% based on weight of substrate). The flasks were stoppered and placed in a thermostatic water bath at 45°C. Nitrogen gas was purged through this solution to remove the dissolved oxygen. The cotton or modified cottons and calculated amounts of sulphuric acid (0.003 mol L^{-1}) and ferrous sulphate (0.005 mol L^{-1}) were added and the reaction mixture was mixed thoroughly. To initiate the reaction a known amount of initiator potassium monopersulphate solution (0.002, 0.004 and 0.006 mol L^{-1}) were added using a material to liquor ratio of 1:50. The content were shaken occasionally during polymerization. After the desired reaction time (2 h), the unreacted monomer was removed by washing with water. The samples were then extracted with hot water to remove the homopolymer (poly methacrylic acid) followed by drying. Extraction and drying were repeated till constant carboxyl content.

Evidence of grafting: This was done via measuring carboxyl content[17] of grafted samples three times for each samples, as well as their standard deviation. On other words, both the carboxyl content and the standard deviation for each sample were taken as an evidence of grafting onto cotton and modified cotton.

Dyestuffs: Two types of dyes of different classes namely basic and direct dyes were used. These dyes were:

1. Sandocryl Orange B-3RLE, basic dye, was supplied by Sandoz, Switzerland (C.I., Basic Orange 38).
2. Diamine Supra Turquoise Blue Gl, Direct dye, was supplied by Cassella, Italy.

Dyeing: Cotton or modified cottons were dyed with direct and basic dyes according to a reported method[18].

Colour strength measurement (K/S): Color strength, expressed as (K/S values) was measured according to a reported method[19].

RESULTS AND DISCUSSION

Copolymerization with methacrylic acid:

Carbamoylethyl content: Table 1 shows the graft yield (expressed as meq-COOH/100 g sample) of MAA onto unmodified cotton and carbamoylethylated cottons (substrate I-IV).

It is seen from Table 1 that:

a) The graft yield increases by increasing the carbamoylethyl content (expressed as % N) at given initiator and monomer concentration.
b) The graft yields for carbamoylethylated cottons are much higher than that unmodified cotton and follows the order: substrate IV>substrate III>substrate II>substrate I.

This can be explain in the manner of, presence of the $CONH_2$ groups on the cellulose backbone offer what we called extra additional sites for grafting[5] as well as opens up the cellulose structure that facilitate the diffusion and mobility of MAA as carboxylic monomer that leads to increase grafting.

Potassium monopersulphate concentration (initiator): Table 1 represents also that, the effect of potassium monopersulphate concentration on the graft yield of unmodified cotton and carbamoylethylated cottons (substrate I-IV).

It is seen from Table 1 that:

a) The graft yield increases by increasing the initiator concentrations within the range studied irrespective of the substrate used.
b) The graft yields for carbamoylethylated cottons are much higher than unmodified cotton and follows the order: substrate IV>substrate III>substrate II>substrate I.

This can be explained as mentioned above, in addition, the increase in graft yield may be also duo to the progressive reduction of potassium monopersuphate by

Table 1: Grafting of MAA onto unmodified cotton and carbamoylethylated cottons (substrate I-IV) having different initiator and monomer concentrations

MAA conc. (BOWS)	Graft yield (expressed as meq-COOH/ 100 g sample)											
	Substrate I			Substrate II			Substrate III			Substrate IV		
	A	B	C	A	B	C	A	B	C	A	B	C
0	01.92	02.30	05.50	02.30	04.00	04.30	03.00	04.30	04.50	03.20	04.50	04.72
20	50.20	61.40	68.00	53.90	64.00	72.50	60.00	72.00	77.00	76.50	85.00	90.20
40	57.90	68.00	74.90	62.00	73.00	80.00	70.20	81.90	86.50	88.00	100.00	104.00
60	64.00	75.00	81.00	70.00	79.00	86.00	76.10	85.90	91.30	92.00	111.00	114.00
80	70.50	79.00	86.00	76.50	85.00	90.50	81.90	92.00	94.00	99.00	121.00	126.00
100	73.50	83.00	90.00	80.00	89.00	94.00	85.10	96.90	101.00	104.00	126.00	130.00

Grafting reaction conditions: Cotton fabric, 2 g; [Fe^{2+}, 0.005 mol L^{-1}; time, 2 h; Temperature, 45°C; material to liquor ratio, 1:30

N.B. A = 0.002 mol L^{-1} PMPS, B = 0.004 mol L^{-1} PMPS, C = 0.004 mol L^{-1} PMPS

Where, PMPS = Potassium monopersulphate concentration; Substrate I, represent unmodified cotton; Substrate II-IV, represent carbamoylethylated cottons having 0.21, 0.76 and 1.0% N, respectively; BOWS = (based on weight of substrate)

Table 2: Dyeing of cotton, carbamoylethylated cotton, poly (MAA)- grafted cotton and poly (MAA)- grafted carbamoylethylated cottons with direct dye

Substrate I		Substrate II		Substrate III		Substrate IV	
Graft yield	K/S	Graft yield	K/S	Graft yield	K/S	Graft yield	K/S
00.0	1.29	00.00	1.21	00.00	0.81	00.00	0.71
61.4	0.63	64.00	0.53	72.00	0.44	85.00	0.43
68.0	0.51	73.00	0.49	81.00	0.41	100.00	0.39
75.0	0.48	79.50	0.42	85.00	0.34	111.00	0.33
79.0	0.46	85.00	0.41	92.00	0.29	121.00	0.28
83.0	0.44	89.00	0.38	96.90	0.27	126.00	0.27

N.B. Graft yield (expressed as meq. - COOH group/100 g substrate) Dyeing reaction conditions: Direct dye;
Diamine Supra Turquoise Blue GL; [Dye concentration], 4% shade; Dyeing temperature; boiling; dyeing time, 100 min; liquor ratio, 1:30

Table 3: Dyeing of cotton, carbamoylethylated cotton, poly (MAA)- grafted cotton and poly (MAA)- grafted carbamoylethylated cottons with basic dye

Substrate I		Substrate II		Substrate III		Substrate IV	
Graft yield	K/S	Graft yield	K/S	Graft yield	K/S	Graft yield	K/S
00.00	0.11	00.00	0.16	00.00	0.25	00.00	0.36
61.40	1.35	64.00	1.43	72.00	1.76	85.00	1.18
68.00	1.82	73.00	2.10	81.00	2.23	100.00	2.34
75.00	2.23	79.50	2.43	85.00	2.61	111.00	2.74
79.00	2.40	85.00	2.65	92.00	2.79	121.00	2.82
83.00	2.51	89.00	2.76	96.90	2.83	126.00	2.99

N.B. Graft yield (expressed as meq. - COOH group/ 100 g substrate); Dyeing reaction conditions: Basic dye;
Sandocyl Orange B- 3RLE; [Dye concentration], 4% shade; Dyeing temperature; boiling; dyeing time, 60 min; liquor ratio, 1:30

ferrous ion producing sulphate ion radicals and hydroxyl free radicals that attack cellulose molecule creating more free radical species that participate mainly in graft initiation.

Methacrylic acid concentration: It is seen in Table I that, the graft yield increases by increasing the methacrylic acid concentration within the range studied irrespective of the substrate used. It is clear from the Table 1 that, there is a direct relation between the graft yield and monomer concentration. This is truly duo to greater availability of the monomer molecules at higher methacrylic concentration in the proximity of cotton fabric.

Dyeability:

Dyeing with direct dye: It is well known early from the literature that, the binding forces in case of dyeing cotton with direct dye were 100% physical duo to cotton has no polar groups that are responsible for formation what we called salt linkage. Beside, the main role of hydroxyl groups during dyeing process are well known duo to when cotton was acetylated its affinity to direct dyes was reduced or eliminated[20] according to the degree of acetylation.

It can be seen from Table 2 that, presence of $CONH_2$ groups as additional site onto cotton cellulose backbone reduces its affinity towards direct dye.

Beside, formation of carboxyethyl groups with a negative charge onto cotton surfaces as the result of hydrolysis of carbamoylethylated cottons[21] during their preparation that repels the similarly charged dye anion.

On the other hand, decrement of K/S in case of grafted substrate in question by introducing poly methacrylic acid grafted chins may be explained as mentioned above (Table 2).

Dyeing with basic dye: The main goal of this research was to dye the cotton cellulose in fabric form by basic dye that has no affinity to cotton fabric.

It is seen Table 3 that:

a) The unmodified cotton and carbamoylethylated cottons show perceptible shade to some extent.
b) The Color strength in case of carbamoylethylated cottons (substrate II-IV) are higher than that unmodified cotton (substrate I) and the higher the extent of carbamoylethylation expressed as % N of the modified cotton, the higher the color strength.

This could be explained in the manner of, formation of carboxyethyl groups that formed during hydrolysis of carbamoylethylated cotton.

c) K/S in case of grafted four substrates in question is much higher than that ungrafted substrates, which can be explained in the manner of introducing grafted chains containing poly methacrylic acid groups i.e. carboxylic groups onto the molecular structure of cotton or carbamoylethylated cottons permits cotton cellulose to react with basic dye in question via ionic bond and
d) The K/S in case of grafted carbamoylethylated cottons increases by increasing the carbamoylethyl contents and follows the order: Grafted onto substrate IV>Grafted onto substrate III>Grafted onto substrate II>Grafted onto substrate I.

CONCLUSIONS

Grafting of methacrylic acid onto cotton and carbamoylethylated cottons improves the affinity of cotton and modified cottons to basic dye via formation of ionic bond with basic dye. That was proven by higher color strength of grafted substrate.

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