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Synthesis and application of new sizing and finishing additives based on carboxymethyl cellulose

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ABSTRACT

Ammonium persulfate $(NH_4)_2S_2O_8$ was used to initiate the polymerization of vinyl acetate (VAc) monomer in presence of carboxymethyl cellulose (CMC) to produce (CMC-g-PVAc) adduct under different conditions including, initiator concentration, temperature and time of polymerization, as well as VAc to CMC ratio. The produced adduct was further saponified to produce the adduct CMC-g-poly vinyl alcohol (CMC-g-PVA). Saponification was conducted in ethanol using 40% aqueous sodium hydroxide solution. IR spectra of CMC, CMC-g-PVAc adduct and CMC-g-PVA adduct were investigated. CMC and CMC-g-PVA adduct in comparison with a physical mixture of CMC and PVA (Vinarol STH) were utilized as a sizing or finishing agent for 100% cotton and 50/50% cotton/polyester blend. It was found that samples finished using the produced CMC-g-PVA adduct acquired better mechanical properties such as wrinkle recovery angle, tensile strength, dyeability and oily stain release than CMC alone or physical mixture with PVA. On the other hand, it appears that (CMC-g-PVA) adduct is a promising easily removals sizing agents.

1. Introduction

Polymerization of some functional monomers in presence of water soluble polymers and gums gives useful adducts of superior properties than those of the starting materials, such as polyacrylamide/guar gum adduct as a new thickener for reactive printing on wool and nylon 6 (Ibrahim, Rashad, & Abo-Shosha, 2003), polyacrylic acid/pyrodextrin adduct as cotton sizing agent (El-Sayed, Famy, Ibrahim, & Abo-Shosha, 2004), polyacrylic acid/polyvinyl alcohol adducts as cotton sizes (Hebeish, Fahmy, Abo-Shosha, & Ibrahim, 2006), polyacrylamide/polyvinyl alcohol as finishing additives (Ibrahim, Hebeish, Fahmy, & Abo-Shosha, 2006), polyacrylic acid/gum arabic as thickeners for reactive printing of cellulosic fabrics (Ibrahim et al., 2006b) and polyacrylic acid/karaya or tamarind gums as thickeners for testing of protein fabric (Abo-Shosha, Ibrahim, Allam, & El-Zairy, 2008).

This stimulates the present work, where VAc is polymerized in presence of CMC followed by saponification inorder to convert the acetate groups to hydroxyl groups to produce CMC-g-PVA adduct. Accordingly a polyblend of CMC and PVA is produced, i.e., a mixture containing mainly CMC, CMC-g-PVA and PVA. Accordingly, the aim of this work is to: (a) prepare polyblend of CMC and PVA, (b) utilize the obtained poly blend in sizing and finishing in comparison with their physical mixtures and (c) investigate the impact of using these poly blends as finishing additives on post basic dyeing.

2. Experimental

2.1. Materials and chemicals

100% cotton fabric (145 g/m) and (50/50%) cotton/PET were used. Sodium carboxymethyl cellulose (CMC C-30 under commercial name Taylose) was purchased from Hoechst. Vinyl acetate monomer contaning 14 ppm hydroquinone as inhibitor was provided by Aldrich. Ammonium persulfate, as initiator, ethyl acetate, magnesium chloride, as a catalyst, sodium carbonate, sodium chloride, sodium hydroxide, ethanol, acetic acid and hydrochloric acid were all of laboratory grade chemicals.

Arkofix NG-ET of Clariant (dimethylol dihydroxy ethylene urea), was used as a crosslinking agent. Hostapal CV, non-ionic wetting agent and Basic red 18 (Dyestar) and Vinoral STH (Hoechst Orient S.A.A.) were of commercial grade.

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2.2. Methods

2.2.1. Prewashing

The used fabrics were boiled in aqueous solution containing 2 g/L non-ionic detergent for 30 min, thoroughly rinsed and dried at ambient condition.

2.2.2. Graft copolymerization

VAc and ammonium persulfate mixture were poured into a conical flask, followed by posting CMC with that mixture. The temperature was raised to a specific value (30–80 °C). Polymerization reaction proceeded for a certain period from 20 to 180 min. PVAc homopolymer and unreacted monomer were removed from the obtained polymerization products by Soxhlet extraction with ethyl acetate for 2 h. The final polymer was then dried to a constant weight under vacuum.

2.2.3. Saponification of CMC-g-P VAc adduct

The Saponification process was carried out in absolute ethanol, according to the method described by Samaha et al. (2005). In a typical experiment, 5 g of the CMC-g-PVAc adduct were dispersed in 65 ml absolute ethanol, the obtained dispersion was placed in a round flask equipped with a condenser and mechanical stirrer. The temperature was adjusted to 40 °C. 1.25 ml of aqueous 40% NaOH was added to the mixture. The saponification took place, with precipitation of CMC-g-PVA adduct, in 3 min. After standing at room temperature for about an hour, the mixture was filtered, and then washed several times with methanol. The saponified adduct was also washed with ethanol/H_2O mixture (80/20) under mechanical stirring to extract VC-ONa and NaOH. Finally, CMC-g-PVA adduct (mixture of CMC and CMC-g-PVA and PVA homopolymer) was allowed to dry in air.

2.2.4. Sizing

Certain weight of the chemical mixture (CMC, CMC-g-PVA and PVA), CMC and physical mixture CMC/PVA were independently added to an agitated cold water bath and stirring was continued for 20 min to wet the granules, then the temperature was raised to 80 °C at a rate of 2 °C/min, where the cooking was continued for 30 min. After cooking, the samples of 100% cotton and 50/50% cotton/PET fabrics were fed into a pad box containing the size solution (5%) at a temperature of (80 °C), then run through pad rolls to squeeze out excess size to a wet pick up of ca. 100% and followed by drying at ambient condition for 24 h before testing.

2.2.5. Size removal

The reweighed-sized samples (W1) were subjected to washing with hot water by three methods: first method at 90 °C for 20 min, second method at 50 °C for 20 min and third method washing of other samples with aqueous solution containing 1 g/L sodium carbonate (Na_2CO_3) at 50 °C for 20 min. Using a material to liquor ratio 1:30. After the desired duration of treatment, the samples were thoroughly washed with water and dried to a constant weight (W2). The percent size removal was calculated as follows:

$$\text{The percent size removal}\,(\%) = \left[\frac{W1 - W2}{W1 - W0}\right] \times 100.$$

Residual size can be calculated as follows:

$$\text{Residual size}\,(\%) = \left[\frac{W1 - W0}{W0}\right] \times 100$$

where $W0$, $W1$ and $W2$ are the weights of samples before sizing, weights of samples after sizing and weights of samples after desizing then drying.

2.2.6. Finishing

100% cotton and 50/50% cotton/PET fabric samples were padded in a solution containing the polyblend, CMC or CMC/PVA, 50 g/L, DMDHEU, 50 g/L and magnesium chloride (5 g/L) to a wet pick up of ca. 80%, drying was achieved at 100 °C/5 min followed by curing at 160 °C/3 min. Finishing formulations used were detailed in the text. Finished fabric samples were then after-washed at 50 °C/15 min in presence of nonionic wetting agent (2 g/L) to remove unused reactants along with soluble by-products followed by rinsing and drying before testing.

2.2.7. Post dyeing

Portions of the treated fabric and control samples were post-dyed using Basic Red 18, according to a reported method (Abo-Shosha, Ibrahim, Fahmy, & Hebeish, 1995).

2.3. Chemical analysis and testing

IR Spectroscopy was carried out using BRUKER IR Spectrometer.

Extend of grafting (i.e., grafting yield (%GY) and grafting efficiency (%GE)) was determined according to the following equations:

$$\text{GY}\,(\%) = \left[\frac{\text{Wp} - \text{Wo}}{\text{Wo}}\right] \times 100$$

$$\text{GE}\,(\%) = \left[\frac{\text{Wp} - \text{Wo}}{W1}\right] \times 100$$

where Wp, Wo are the weights of purified grafted polymer (CMC-g-PVAc) and CMC and $W1$ is the weight VAc monomer, respectively.

The extent of polymerization, expressed as percentage total conversion, %TC, was determined by assessing the unsaturation (double bonds) content before and after polymerization (Welcher, 1963). The nitrogen content was determined according to Kjeldhal method (Vogel, 1975).

Dry wrinkle recovery angle (WRA) was determined according to ASTM method D-1296-98.

The oily stain release (OSR) was assessed according to the AATCC test method 130-1993.

Carboxyl content, as meq/100 g was determined according to a reported method (Hashem, Refaie, & Hebeish, 2005).

The whiteness and yellowness index were evaluated by using Colour-Eye® 3100 spectrophotometer supplied by SDL Inter, England (Welch & Peters, 1997).

Dyeability of treated and untreated fabric samples was determined by measuring K/S values (K is the absorption coefficient, S is the scattering coefficient) at wave length of maximum absorbance for the used dyes, with Color-Eye® 3100 Spectrophotometer supplied by SDL Inter. England (Duff and Sinclair).

Tensile strength (kg) and elongation at break (%) were determined according to ASTM procedure D-2296-66T.

Wettability of finished fabric samples were tested according to AATCC test method 39-1980.

Roughness for the finished samples was measured using a Surfacoder 1700a.

3. Results and discussion

3.1. Graft polymerization of CMC with VAc

3.1.1. Tentative mechanism

Grafting of CMC with Vac in presences of $(NH_4)_2S_2O_8$, as initiator, comprises the following steps (Ibrahim, Abo-Shosha, Fahmy, El-sayed, & Hebeish, 2008):

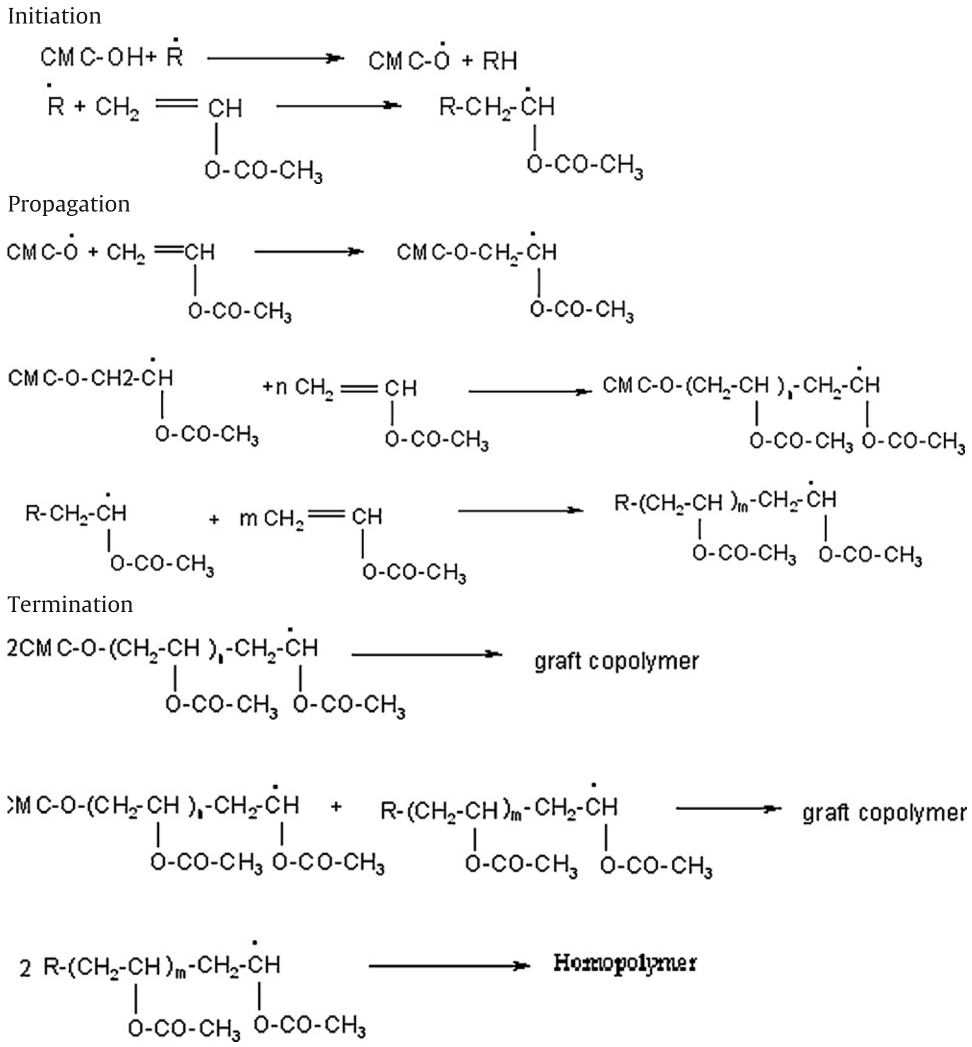
Table 1
Effect of init iator concentration on %TC, %GY, and% GE.

G E (%)	GY (%)	TC (%)	$(NH_4)_2S_2O_8$ (mmol/L)
10.5	5.5	60.3	17.54
14	7	65	26.37
18.2	9.1	69.2.	35.08
19	9.5	88.7	43.85
17.8	8.9	81.9	52.62

Reaction conditions: temperature, 70 °C: time, 120 min: (VAc/CMC) ratio, 0.5 w/w.

3.1.3. Grafting time

Grafting of VAc onto CMC was carried out by changing time of reaction from (20 to 180 min), keeping the other reaction conditions constant, as shown in Table 2. %TC, %GY and % GE increased rapidly in the first 60 min of the process. Further increase in grafting time up to is accompanied by a decrease in %GY and %GC due to the formation of homopolymer along with as an increase in %TC.



where R• is a $SO_4^{\bullet -}$.

3.1.2. Initiator concentration

Graft copolymerization of VAc onto CMC was studied using different concentration of $(NH_4)_2S_2O_8$ ranging from 17.54 to 52.62 mmol/L. It is clear that, increasing the concentration of $(NH_4)_2S_2O_8$, up to 43.85 mol/L, results in an enhancement in %TC, %GY and %GE (Table 1). This could be attributed to the formation of more active sites, i.e., free radicals on both CMC and VAc monomer thereby enhancing the extent of grafting, expressed as %TC, %GY and %GE. In addition, the initiating process for $(NH_4)_2S_2O_8$ in graft copolymerization is similar to that of common free-radical initiators, which first decompose and form free radicals; these free radicals react with the monomer and start the propagation of the chain. Further increase in $(NH_4)_2S_2O_8$ concentration, i.e., beyond (43.85 mmol/L) is accompanied by decrease in % TC, %GY and % GE, due to faster rate of termination reaction as a result of excessive radical concentrations in the polymerization medium.

3.1.4. Grafting temperature

The graft copolymerization of VAc onto CMC was studied by varying the reaction temperature from 40 to 80 °C at constant concentration of $(NH_4)_2S_2O_8$ 43.85 mmol/L, reaction time, 120 min, VAc/CMC ratio 0.5 (w/w). Data in Table 3 singfiy that increasing the grafting temperature up to 70 °C brings about an increase in %TC, %GY and %GE most probably due to the increase of the kinetic energy of monomer molecules thereby increasing the concentration of monomer molecules nearby to the active sites onto the CMC and the enhancing the extent of diffusion of monomer molecules from the reaction mixture to the CMC. Further in grafting temperature up to 80 °C has practically a negative impact on the aforementioned values may be due to the low boiling point of the VAc (72.4 °C).

Table 2
Effect of grafting time on %TC, %GY, and% GE.

GE (%)	GY (%)	TC (%)	Grafting time (min)
9.4	4.7	40	20
13	6.5	55	40
25.2	12.6	68.3.	60
21	10.5	89.1	120
21	10.5	88.3	180

Reaction conditions: temperature, 70 °C; [$(NH_4)_2S_2O_8$], 43.85 mmol/L: (VAc/CMC) ratio, 0.5 (w/w).

Table 3
Effect of grafting temperature on %TC, %GY, and% GE.

GE (%)	GY (%)	TC (%)	Grafting temperature (°C)
12.8	6.4	55	40
17.2	8.6	68.3	50
19	9.5	80.9	60
25.2	12.5	88.3	70
20.1	10.1	79.3	80

Reaction conditions: [$(NH_4)_2S_2O_8$], 43.85 mmol/L: (VAc/CMC) ratio, 0.5 (w/w): grafting time (120 min).

Table 4
Effect of VAc/CMC ratio on %TC, %GY, and % GE.

GE (%)	GY (%)	TC (%)	VAc/CMC ratio (w/w)
31.2	7.8	70.2	0.25
21.2	10.6	91.4	0.5
19.5	19.5	67	1

Reaction conditions: [$(NH_4)_2S_2O_8$], 43.85 mmol/L; grafting time (120 min): temperature (70 °C).

3.1.5. *VAc/CMC ratio*

The change in %TC, %GY and % GE as a function of VAc/CMC ratio at a fixed initiator concentration (43.85 mmol/L) is shown in Table 4. It is clear that a maximum %TC, %GY and %GE values were obtained.

4. Characterization

The IR spectra of CMC, CMC-g-PVAc and CMC-g-PVA are shown in Fig. 1A–C. The CMC-g-PVAc and CMC-g-PVA are confirmed by the difference between IR spectra of CMC and those of the grafted polymer. In Fig. 1A existence of a peak at 1617.74 cm^{-1} for CMC of carbonyl of carboxyl salt, presence of peak at 1725.67 cm^{-1} in Fig. 1B for CMC-g-PVA indicate the presence of carbonyl ester bond ($O–C{=}O–CH_3$) and in Fig. 1C presence of peak at 1737.22 cm^{-1} indicate that presence of carboxyl group ($O–C{=}O$) and disappearance of the peaks at 1326.36 and 1425.10 cm^{-1} indicate that the methyl group do not exist in saponified of CMC-g-PVA at the IR spectra of graft copolymers is a certain evidence of grafting. Most of the other peaks are related to the carbohydrate backbone.

Table 6
Effect of different methods on desizing of cotton and cotton/PET fabrics.

Type of fabrics	Substrate	Size removal (%)		
		First method	Second method	Third method
100% cotton fabric	CMC only	100	100	100
100% cotton fabric	CMC-g-PVA	100	100	100
100% cotton fabric	CMC/PVA	100	100	100
50/50% cotton/PET	CMC only	100	100	100
50/50% cotton/PET	CMC-g-PVA	100	100	100
50/50% cotton/PET	CMC/PVA	100	100	100

Conditions: First method: washing with hot water at 90 °C for 20 min. Second method: washing with hot water at 50 °C for 20 min. Third method: washing with 1 g/L of sodium carbonate at 50 °C for 20 min.

5. Utilization

5.1. *As sizing agent*

Solutions of 5% solid CMC, and CMC-g-PVA adduct as well as mixture of CMC and PVA were independently cooked at 80 °C and used as sizing agents for 100% cotton and 50/50% cotton/PET blend fabrics. The sized fabric samples were then examined for tensile strength (TS, kg) and elongation at break (EB, %), as well as desizability under different conditions, i.e. by washing with hot water at 90 °C, 50 °C for 20 min or by using a solution containing 1 g/L of sodium carbonate at 50 °C/20 min. The results obtained are set out in Table 5.

It is seen (Table 5) that, sizing of the fabric samples results in an increase in tensile strength along with a decrease in elongation at break of 100% cotton fabrics compared with the untreated ones. However, the magnitude of improvement in the tensile strength is more pronounced for CMC-g-PVA adduct and CMC/PVA than for CMC. The variation of tensile strength and elongation at break with varying the sizing agent is rather expected because of the difference between these sizing agents with respect to, viscosity of the size formulation, film forming properties, degree of encapsulation, adhesion and cohesion forces as well as coatability of the sized fabric (Samaha, Nasr, & Hebeish, 2005). Also add-on depends on the type of treated material and the type of fabric.

Table 6 shows that, any of the used desizing conditions brings about a 100% size removal.

5.2. *As finishing additive*

Table 7 shows the effect of using 50 g/L of CMC, CMC-g-PVA adduct or CMC/PVA, separately as an additives in presence of DMDHEU, 50 g/L on the carboxyl content (meq/100 g), % nitrogen content, performance properties (WRA, TS, EB, wettability, yellowness, whiteness, roughness, OSR and dyeability of finished fabric samples, i.e., 100% cotton and 50/50% cotton/PET). It is clear that incorporation of CMC-g-PVA adduct, CMC, or CMC/PVA in the finishing formulation has a positive impact in post dyeing due to

Table 5
Effect of sizing materials on the properties of cotton and cotton/PET blend fabrics.

Type of fabrics	Substrate	Add on (%)	TS (kg)	EB (%)	Size removal (%)
Untreated 100% cotton fabric	–	–	65.02	17.08	100
100% cotton fabric	CMC only	3.47	67.04	11.12	100
100% cotton fabric	CMC-g-PVA	3.79	70.20	10.96	100
100% cotton fabric	CMC/PVA	3.02	71.25	10.75	100
Untreated 50/50% cotton/PET	–	–	52.89	10.58	100
50/50% cotton/PET	CMC only	3.77	57.77	11.83	100
50/50% cotton/PET	CMC-g-PVA	2.12	68.11	9.29	100
50/50% cotton/PET	CMC/PVA	3.56	65.18	9.25	100

Conditions: 5% solid CMC, CMC-g-PVA adduct or CMC/PVA mixture; temperature, (80 °C). Drying at ambient condition for 24 h.

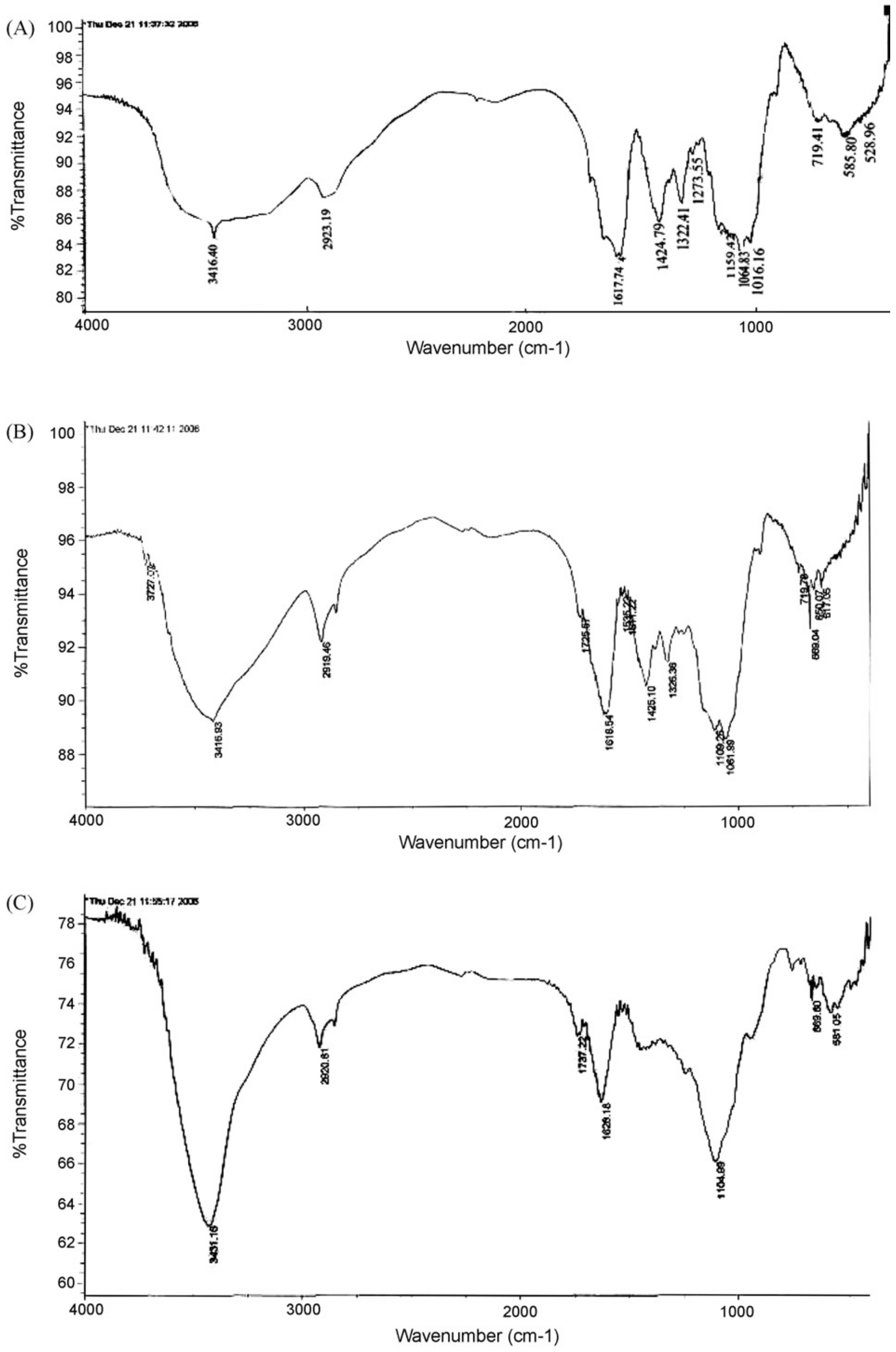


Fig. 1. The FTIR spectra of (A) pure CMC, (B) CMC-g-PVAc and (C) CMC-g-PVA.

presence of –COOH groups onto the finished fabric matrix. On the other hand, the variation in other performance and mechanical properties is governed by both the kind of additive as well as the type of substrate along with extent of modification substrates, according to the following tentative mechanism (Ibrahim, Abo-Shosha, Elnagdy, & Gaffar, 2002; Yang, 1993).

$$\text{Cell-OH} + \text{DMDHEU} + \text{Cell-OH} \xrightarrow[\text{heat}]{H^+} \text{Easy care finished cotton} \quad (1)$$

$$\text{Cell-OH} + \text{DMDHEU} + \text{CMC-h-PVA adduct} \xrightarrow[\text{heat}]{H^+} \text{crosslinked cotton with CMC-g-PVA graft} \quad (2)$$

$$\text{Cell-OH} + \text{DMDHEU} + \text{CMC} \xrightarrow[\text{heat}]{H^+} \text{Crosslinded cotton with CMCgraft} \quad (3)$$

$$\text{Cell-OH}+\text{DMDHEU}+\text{PVA-OH} \xrightarrow[\text{heat}]{H^+} \text{crosslinded cotton with PVA graft} \quad (4)$$

$$2\text{CMC-g-PVA} + \text{DMDHEU} \xrightarrow[\text{heat}]{H^+} \text{coating film or washable byproduct} \quad (5)$$

Table 7
Effect of incorporation of the prepared adduct on some properties of finished fabric samples.

Type of fabric	Finishing formulation	Carboxyl content (meq/100 g)	%N	WRA (W + F)°	TS (kg)	*K*/*S*	Wettabilit (s)	YI	WI	EB (kg)	Roughness R_a (μm)	OSR
Untreated cotton fabric	–	0.0	–	158	65.02	5.48	<1	–19.	130.7	17.87	10.32	1
Ccotton fabric	DMDHEU only	0.0	0.46	220	46.10	4.87	<1	–19.	129.6	11.58	19.41	2
Cotton fabric	CMC + DMDHEU	68.102	0.38	180	50.00	7.13	<1	–20	130.7	8.04	14.30	3
Cotton fabric	CMC-g-PVA adduct + DMDHEU	44.462	0.41	195	52	6.3	<1	–19	129.9	8.13	12.60	4
100% cotton fabric	CMC/PVA + DMDHEU	48.163	0. 45	199	54	6.68	<1	–19	129.2	11.19	14.26	4
Untreated of blend	–	0.0	–	264	52.89	34.46	>120	–17	117.1	10.58	12.37	1
Blend	DMDHEU only	0.0	0.39	280	38.91	3.74	34	–17	117.6	8.58	15.18	2
Blend	CMC + DMDHEU	61.447	0.30	269	43	6.00	4	–16	116.9	9.87	16.20	3
Blend	CMC-g-PVA adduct + DMDHEU	42.737	0.36	273	47	4.98	7	–16	116.67	9.50	15.12	4
Blend	CMC/PVA + DMDHEU	46.25	0.36	270	49	5.12	8	–17.	117.83	10.96	15.86	4

Conditions: 50 g/L of treated material, 50 g/L of DMDHEU, 5 g/L of $MgCl_2{\cdot}6H_2O$ wet pick-up 80%, drying temperature at 100 °C/5 min; curing temperature at 160 °C/3 min.

$$2\mathrm{CMC} + \mathrm{DMDHEU} \xrightarrow[\text{heat}]{H^+} \text{coating film or washable byproduct} \qquad (6)$$

$$2\mathrm{PVA} + \mathrm{DMDHEU} \xrightarrow[\text{heat}]{H^+} \text{coating film or byproduct} \qquad (7)$$

In accordance with this tentative mechanism, the results of Table 7 signify that the tensile strength decreases from 65.02 to 45.28 kg for cotton fabric and from 52.89 to 49 kg for cotton/PET fabric, due to crosslinking of cotton and cotton/PET with DMDHEU in presence of CMC, CMC-g-PVA adduct and CMC/PVA $^{(15,16)}$.

6. Conclusion

CMC-g-PVA was prepared by using ammonium persulphate as initiator in graft polymerization of VAc onto CMC under different conditions. Under optimum conditions (temperature 70 °C; time of polymerization 120 min, VAc/CMC ratio 0.5 w/w, ammonium persulphate concentration, 43.85 mmol/LVAc). The %TC, %GY and% GE were achieved as 88.3%, 12.5%and 25.2% respectively. The appearance of the band at 1737.22 cm^{-1} (for CMC-g-PVAc) in the IR spectra indicates the grafting of VAc onto CMC. Also, the complete disappearance of such band in the CMC-g-PVA assures the saponification process. CMC, CMC-g-PVA or CMC/PVA was applied as sizing and finishing additives in the presence of DMDHEU. Using of the prepared adduct in sizing as will as in easy care finishing formulations results in a significant improvement in most of evaluated physico-mechanical, chemical and dyeing properties.

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