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Preparation of polyethylene glycol/polyacrylamide adduct and utilization in cotton finishing

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ABSTRACT

Highly concentrated aqueous solutions of acrylamide (Am) were polymerized in presence of polyethylene glycol (PEG) using ammonium persulfate as initiator under different conditions including ammonium persulfate concentration (0.02–0.06 g/gAm) temperature (60–95 °C), Am/PEG400 ratio (1/1–1/5 g/g), PEG molecular weight (400–6000). At optimum reaction conditions a PEG 400/PAm adduct was prepared with a % total conversion of 99.7 in 2 min using ammonium persulfate (0.05 g/gAm), Am/PEG (1/2 g/g) at 70 °C. The structure of the adduct was confirmed by FT-IR spectra. The adduct was utilized as a finishing additive for cotton fabric in presence and absence of dimethyloldihydroxy ethylene urea (DMDHEU) by the bad – dry – cure method. In absence of DMDHEU, the adduct improves the fabric tensile strength, stiffness and oily stain release rating without affect the wettability along with decreasing the fabric resiliency compared to the blank sample. Inclusion DMDHEU the finishing bath (50 g/l) results in improving the fabric resiliency and stiffness as well as decreasing the strength, wettability and oily stain release compared to those of fabric treated with adduct in absence of DMDHEU. However, at an adduct concentration of 40 g/l and in presence of 50 g/l DMDHEU the fabric properties are in general, superior to those of blank fabric.

1. Introduction

Recently, free radical polymerization of vinyl monomers in presence of a substrate has resulted in the production of adducts that have useful applications. These adducts are formed in very high yield within a short time. They can be classified as water insoluble and water soluble. Water insoluble adducts are used as ion exchangers. Examples of the latter are, new cation exchange resins based on polyvinyl alcohol containing carboxyl groups for the removal of some textile contaminants from aqueous solutions (Fahmy & El-Sayed, 2002), sawdust/*N*-methylolacrylamide/methacrylic acid cation exchange composite (Ibrahim, Abo-Shosha, El-Sayed, & El-Alfy, 2002), crosslinked polyvinyl alcohol containing tertiary amino group (Ibrahim, Abo-Shosha, & Gaffar, 1997), cellulose/glycidyl methacrylate/*N*-methylolamide/methacrylacrylic acid cation exchange composite, a variety of water soluble adducts were prepared. Examples are polyacrylic acid/pyrodextrins adducts (Fahmy & El-Sayed, 2002), poly(acrylamide)/poly(vinyl alcohol) polyblends as size additives for cotton fabrics (Ibrahim, Hebeish, Fahmy, & Abo-Shosha, 2005) and polyclone of acrylic acid with polyvinyl alcohol as cotton sizes(Hebeish, Fahmy, Abo-Shosha, & Ibrahim, 2006).

The present work is undertaken to prepare water soluble polyethylene glycol/polyacrylamide (PEG/PAm) adducts via free radical polymerization of highly concentrated aqueous solutions of Am in presence of PEG of different molecular weight. Selected adduct is utilized as cotton finish in presence and absence of DMDHEU crosslinking agent.

2. Experimental

2.1. Materials

2.1.1. Fabric

Mill scoured and bleached cotton fabric (110 gm/m^2) was used, supplied by Miser Spinning and Weaving Company was used.

2.1.2. Chemicals

Acrylamid (Am) (Merck-Schuchardi), polyethylene glycol (PEG) with different molecular weights (400, 600, 2000, 4000, 6000) (Fluka), ammonium persulfate as initiator and magnesium chloride as a catalyst were all of laboratory grade chemicals.

The following specialty chemicals of Clariant Egypt were used: Arkofix, NG-ET, 45% aqueous solution of dimethyloldihydroxy ethylene urea (DMDHEU) as a crosslinker, leomin® NI, a non-ionic softener, and Hostpal CV, non-ionic wetting agent, were used.

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2.2. Method

2.2.1. Preparation of PEG/PAm adducts

PEG/PAm adducts were prepared by free radical polymerization of highly concentrated solution of Am in presence of PEG as follows: polymerization was carried out under atmospheric oxygen in 30 ml polypropylene beaker containing a mixture of known concentration of PEG, Am and ammonium persulfate. The beaker was kept in a thermostatic water bath and after an induction period, an exothermic reaction started with the evolution of water vapour, followed by solidification of the product. The time elapsed between keeping the beaker in bath and complete solidification will be called the solidification time (ST). The solid product, or adduct was then cooled at ambient condition, disintegrated, ground and taken to analysis.

2.2.2. Fabric treatment

The fabric was passed to a wet pick-up of 80% of aqueous solutions of different concentrations (10–60 g/l) of PEG/PAm adduct, either separately or in presence of a crosslinking formulation containing DMDHEU (50 g/l), $MgCl_2{\cdot}6H_2O$ (5 g/l), acetic acid (2 g/l), Leomin®NI (20 g/l) and Hostapal CV (2 g/l). Fabrics treated in absence of DMDHEU were dried at 100 °C for 3 min, whereas those treated in presence of DMDHEU were dried at 100 °C for 3 min and then cured at 160 °C for 3 min. After treatment, wash was given to the fabrics at 50 °C for 15 min using a non-ionic detergent, followed by rinsing and drying at ambient conditions.

2.3. Analysis and testing

The extent of polymerization, expressed as percentage total conversation, %TC, was determined by assessing the instauration (double bond) content before and after polymerization (Welcher, 1963). The nitrogen content was determined according to Kjeldhal method (Vogel, 1975). Dry wrinkle crease recovery angle (WRA) was determined according to ASTM method S-1296-98. Stiffness of the treated and untreated samples was determined by DIN 53362. The tensile strength (TS) of the finished fabric samples was tested, in the warp direction, according to ASTM procedure D-2256-98. Oil soily release rating (OSR) was assessed according to the AATCC test method 130-1974. Wettability of finished fabric samples were tested according to AATCC test method 39-1980. A scanning electron microscope (SEM) examination was carried out for treated and untreated samples by mounting the samples on stub with double stick adhesive tape and coated with gold in a S150A sputler coater unit (Edwards, UK). The gold film thickness was 150 A°. The samples were then viewed in a JEAOL JXA-840A electron probe microanalyser. The infra spectra of the fabric samples were recorded by KBr pellet technique, using Nexus 670 FT-IR Spectrometer from Nicolet USA. The FT-IR spectra were recorded between the ranges from 4000 cm^{-1} to 1000 cm^{-1}.

3. Results and discussion

3.1. Tentative mechanism

In aqueous medium, $SO_4^{\cdot -}$ and $HO^{\cdot}$ free radical are generated as the result of decomposition of ammonium persulfate (El-Sayed, Fahmy, Ibrahim, & Abo-Shosha, 2004). These radical species, R can result in the following polymerization reactions:

$$\dot{R} + Am \rightarrow \underset{\text{(Activated molecule)}}{\dot{Am}} \quad (1)$$

$$\dot{Am} + n\dot{Am} \rightarrow \text{polyacrylamide homopolymer} \quad (2)$$

$$PEG + \dot{R} \rightarrow \underset{\text{(polyethylene glycol macromolecule)}}{P\dot{E}G} + RH \quad (3)$$

$$P\dot{E}G + mAm \rightarrow \underset{\text{(PAm-grafted-PEG)}}{PAm\text{-}g\text{-}PEG} \quad (4)$$

The blend obtained from these polymerization reactions is called PEG/PAm adduct. It contains PAm homopolymer, PEG-g-PAm, Am and ungrafted PEG in a state of entanglement. Factors affecting the formation of adduct are studied. The results obtained with appropriate discussion follow.

3.2. Ammonium persulfate concentration

The effect of ammonium persulfate concentration on the formation of adduct is shown in Table 1. It is observed that %TC increases and ST decreases on increasing the initiator concentration up to 0.05 g/g Am after which %TC decreases. Increasing the concentration of ammonium persulfate beyond 0.05 g/g can result in the generation of more free radicals capable of initiating, propagating and terminating polymerization reactions (El-Sayed et al., 2004). Current data suggest that initiation and propagation dominate termination up to a concentration of 0.05 g/g Am, beyond which the opposite holds true.

3.3. Reaction temperature

The effect of reaction temperature on the %TC and ST is shown in Table 2. It can be noted that %TC reaches a maximum of 97.3% at a temperature of 70 °C, then decreases with further rise in temperature to reach as low as 77.03% at 95 °C. Raising the temperature up to 70 °C has the following positive effects (El-Sayed et al., 2004): (a) Enhancing the rate of decomposition of the initiator (formation of free radicals), (b) facilitating the mobility and collision of the free radicals and the reactant, i.e. formation of macro radicals, as well as of polymerization products and (c) overcoming the activation energy barriers of the process.

That the %TC decreases by raising the temperature beyond 70 °C can be attributed to high extent of termination at elevated temperature. It can be also noticed that ST decreases steadily by increasing the temperature in the range studied.

3.4. Am/PEG ratio

Table 3 shows that decreasing Am/PEG ratio from 1/1 to 1/2 slightly increases the %TC and shortens the ST. Further decrease in Am/PEG ratio up to 1/5 is accompanied by decreasing the %TC and increasing the ST. Keeping in mind that the initiator concentration is directly related to Am concentration, then decreasing the latter results in decreasing the initiator concentration. Accordingly, the highest Am and in turn initiator concentration is at an Am/PEG ratio 1/1. Current data suggest that the number of free radical species resulted from the initiator decomposition is at optimum concentration at a ratio 1/2, before it termination is effective and after it initiation and propagation are low. This can explain the highest %TC and the shortest ST observed at a ratio of 1/2.

3.5. PEG molecular weight

Table 4 shows that increasing PEG molecular weight is accompanied by decreasing the %TC without changing the ST. Increasing

Table 1
Effect of ammonium persulfate concentration on the solidification time (ST) and percent total conversion (%TC) of the formed adducts

Ammonium perslufate concentration (g/g Am)	TC (%)	ST (min)
0.02	75.67	3
0.03	82.24	2.5
0.04	87.84	2
0.05	89.20	1.5
0.06	77.03	1

Temperature 80 °C; PEG molecular weight 400; Am/PEG ratio, 1/5(wt/wt).

Table 2
Effect of reaction temperature on the solidification time (ST) and percent total conversion (%TC) of the formed adducts

Temperature (°C)	TC (%)	ST (min)
60	90.2	4
70	97.3	2.5
80	89.2	2
90	86.49	1.5
95	77.03	1

Ammonium persulfate concentration, 0.05 g/g Am; PEG molecular weight 400; Am/PEG ratio, 1/5 (wt/wt).

Table 3
Effect of acrylamid/polyethylene glycol ratio on the solidification time (ST) and percent total conversion (%TC) of the formed adduct

Am/PEG ratio (wt/wt)	TC (%)	ST (min)
1:1	97.94	2
1:2	99.7	2.5
1:3	96.3	3
1:4	90.78	4
1:5	87.5	5

Ammonium persulfate concentration, 0.05 g/g Am; reaction temperature, 70 °C; PEG molecular weight, 400.

Table 4
Effect of acrylamid/polyethylene glycol molecular weight on the solidification time (ST) and percent total conversion (%TC) of the formed adducts

PEG molecular weight	TC (%)	ST (min)
400	99.7	2
600	98.97	2
2000	88.30	2
4000	86.60	2
6000	84.54	2

Ammonium persulfate concentration, 0.05 g/g Am; reaction temperature, 70 °C; Am/PEG ratio 1/2.

PEG molecular weight is logically accompanied by diluting both Am and the initiator, and hence decreases the %TC. It seems that the heat of polymerization is high enough to cause solidification within 2 min, regardless of PEG molecular weight under the conditions employed.

3.6. Utilization of the adducts

Adduct based on PEG 400 was selected for utilization as a finishing additive in presence and absence of DMDHEU finishing formulation as it had maximum %TC. Before utilization its FT-IR spectra was investigated as shown in Fig. 1. It can be seen that characteristic absorption band for –C–O–C– spectra stretching vibration at 1115.84 cm^{-1} and from Fig. 2, CN stretching vibration is shown at 2238.83 cm^{-1}. Similar observations were noticed in the PEG400/PAm adduct. In the case of PEG400/PAm adduct the ester carbonyl stretching was observed at 1655.20 cm^{-1}. The FT-IR results confirm the formation of the PEG400/PAm copolymer.

3.7. The adduct as cotton finish

Table 5 shows the effect of finishing cotton fabric with different concentration of adduct, in the presence and absence of DMDHEU on the performance properties of the fabric, via, %N, WRA, TS, stiffness, wettability and OSR.

In the absence of DMDHEU, Table 5 reveals that increasing the adduct concentration, in the range studied, is accompanied by: (a) Increasing the %N, (b) decrease in WRA along with an increase in both of TS and stiffness, which can be understood in terms of precipitating of the adduct on cotton fibers resulting in coating and encapsulating them as well as adhering them together (as illustrated by SEM shown in Figs. 3 and 4) giving rise to higher stiffness and strength (compared to the blank sample) as well as decreased ability to regain from wrinkling and (c) Enhancing the OSR of the treated sample (to reach a maximum even at the lowest concentration) compared to the black sample, probably due to shielding the fibers with a hydrophilic coating as is evident by the very low wettability time.

Increasing the adduct concentration in presence DMDUEU affect the fabric properties in a similar trend to that in its absence, but with different values. It can be said that the values of %N, WRA and stiffness are higher in presence than absence of DMDHEU. This can be associated with crosslinking of both cellulose and adduct chains as well as binding adduct to the fabric. Further were the TS, wettability and OSR are lower in presence than in absence of DMDHEU. Hindering cellulose chain mobility via crosslinking and damaging them under the effect of acidic catalyst ($NH_4Cl{\cdot}5H_2O$) are responsible for the lower TS. Consumption of

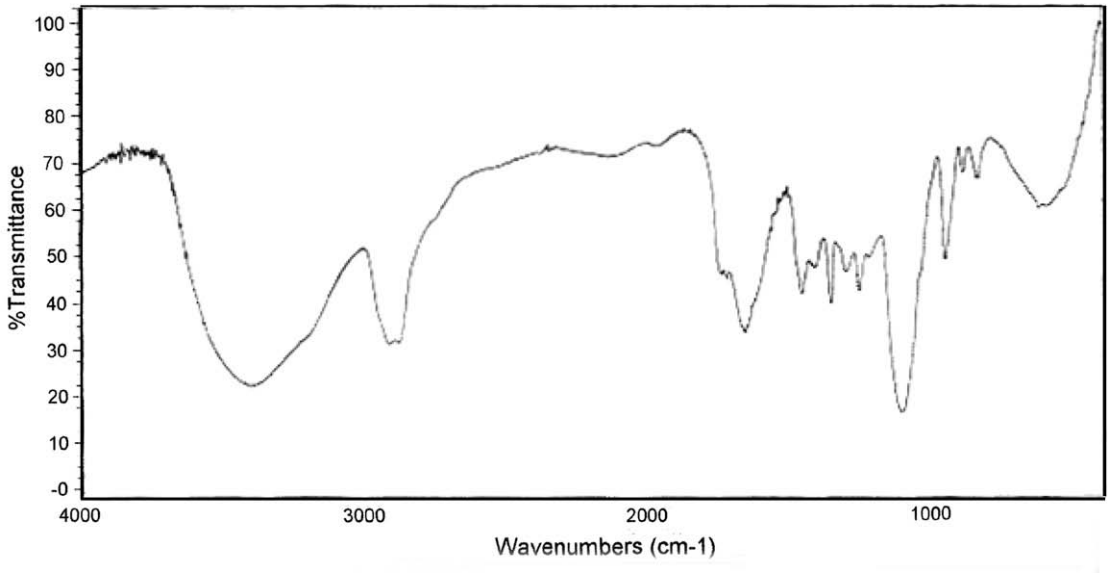

Fig. 1. FT-IR of PEG 400.

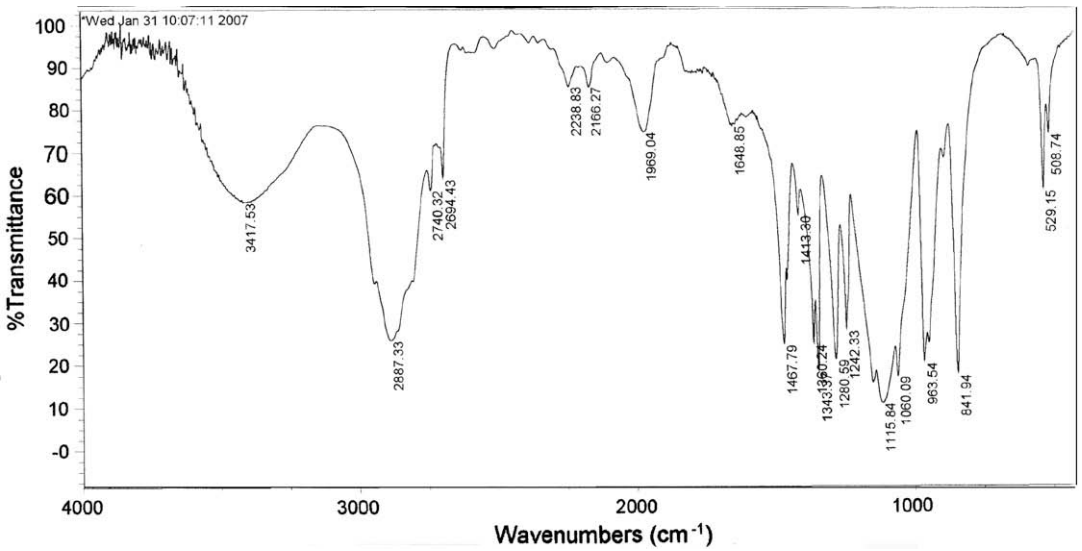

Fig. 2. FT-IR of PEG400/PAm.

Table 5
Effect of PEG400/PAm adducts concentration on the performance properties of the finished cotton fabric in presence (P) and absence (A) of DMDHEU formulation

Adduct conc. (g/l)	%N		WRA (W+F)		Stiffness (mg cm)		T.S (Kg)		Wettability (Sec)		OSR	
	P	A	P	A	P	A	P	A	P	A	P	A
Blank untreated	–		156		300		32		<1		3	
10	0.59	0.41	264	150	1085	516	27	37	3	<1	3–4	5
20	0.65	0.48	265	144	1299	1201	30	39	2	<1	4	5
40	0.69	0.58	238	138	1641	1500	35	43	1	<1	4	5
60	0.72	0.65	223	130	1851	1756	38	42	<1	<1	4	5

P: DMDHEU, 50 g/l; $MgCl_2{\cdot}6H_2O$, 5 g/l; acetic acid, 2 g/l; softener, 20 g/l; wetting agent, 2 g/l.
A: Acetic acid, 2 g/l; softener, 20 g/l; wetting agent, 2 g/l.
WRA: wrinkle recovery angle; T.S: tensile strength (warp); OSR: oily stain release rating.

some the hydroxyl and/or amide groups of cellulose and adduct is responsible for lower wettability and OSR.

However, the picture is not so dark and the bright side of it is as an adduct concentration of 40 g/l in presence of DMDHEU superior performance properties, in general, of finished fabric can be reached if compared to those of blank sample as shown in Table 5. Based on the above, the following mechanism can illustrate the reactions among cellulose, DMDHEU(R $(CH_2{-}OH)_2$) and adduct:

$$2\text{Cell}{-}\text{OH} + \text{R}{-}(\text{CH}_2{-}\text{OH})_2 \xrightarrow[\Delta]{\text{H}^+} \text{R}{-}\text{CH}_2{-}\text{O}{-}(\text{Cell})_2 + 2\text{H}_2\text{O(I)} \quad (5)$$

$$2\text{Adduct}{-}\text{OH} + \text{R}{-}(\text{CH}_2{-}\text{OH})_2 \xrightarrow[\Delta]{\text{H}^+} \text{R}{-}\text{CH}_2{-}\text{O(Adduct)}_2 + 2\text{H}_2\text{O(II)} \quad (6)$$

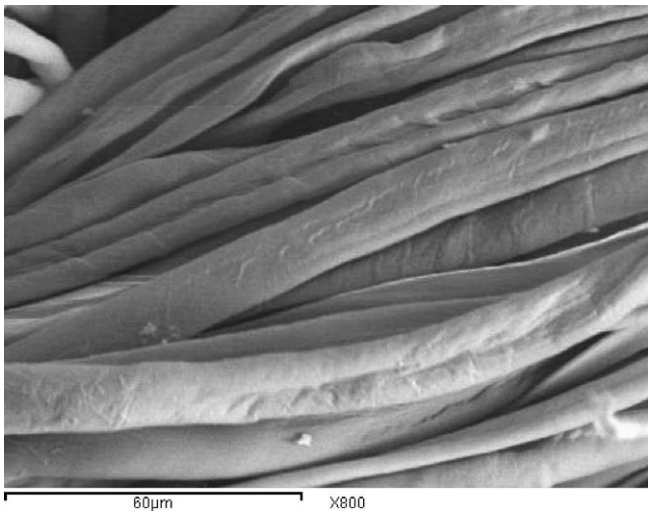

Fig. 3. Scanning electron microscopy of untreated cotton fabric.

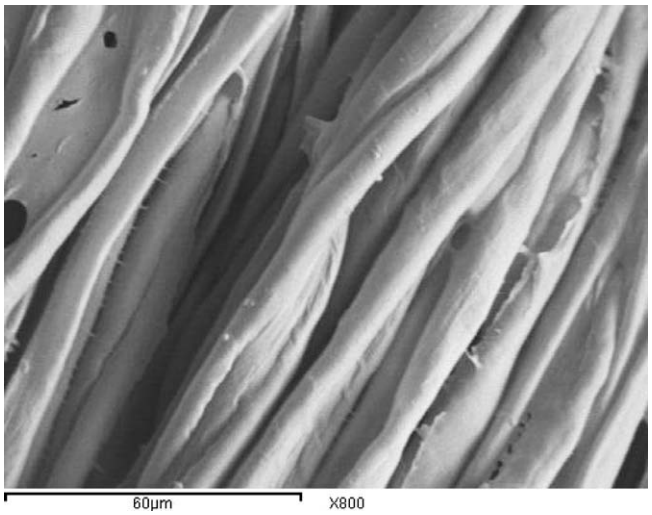

Fig. 4. Scanning electron microscopy of treated cotton fabric with PEG400/PAm.

$$2\text{Adduct—CONH}_2 + \text{R—(CH}_2\text{—OH)}_2 \xrightarrow[\Delta]{\text{H}^+} \underset{\text{(III)}}{\text{R—CH}_2\text{—O—(NHCO—Adduct)}_2} + 2\text{H}_2\text{O} \quad (7)$$

$$2\text{Adduct—OH} + \text{R—(CH}_2\text{—OH)}_2 + \text{Cell OH} \xrightarrow[\Delta]{\text{H}^+} \underset{\text{(IV)}}{\text{Adduct—O—CH}_2\text{R—CH}_2\text{—O—Cell}} \quad (8)$$

Crosslinked cellulose (I) is formed in reactions and adduct is either crosslinked through its hydroxyls (reaction 6) or amides (reaction 7) giving rise to crosslinked adduct II and III. Adduct is bound to cellulose (compound IV) as shown in reaction 8. It is to be noticed that any compound having a labile hydrogen can be crosslinked and/or bound to cellulose in similar fashion. Forever, adduct itself can be crosslinked through "amide- DMDHEU-hydroxyl reaction.

4. Conclusions

Optimum conditions of polymerization reaction were ammonium persulfate concentration of 0.05 g/gAm, Am/PEG ratio of 1/2 g/g a temperature of 70 °C. At these conditions PEG400/PAm adduct was prepared with a %TC of 99.7 within 2 min. FT-IR spectra proved the adduct structure. Adduct can be used in absence or presence of DMDHEU as a finishing additive to cotton fabric. At adduct concentration of 40 g/l and DMDHEU concentration of 50 g/l, the fabric properties (%N, WRA, stiffness, TS and OSR) were superior to those of blank fabric, however wettability increased from <1 to 3 s which is acceptable.

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