Effects of Chitosan Addition to DMEU-Processed Cotton Fabrics for Adsorbing Metallic Ions in Waste Water

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ABSTRACT: This study examines the effects of adding chitosan to the curing treatment of cotton fabrics, using dimethylolethyleneurea as a crosslinking reagent; in particular, how the adsorption of the processed cotton fabrics for metallic ions is influenced. Different concentrations of added chitosan, different curing temperatures and time, as well as different adsorption times and temperatures were examined. The cotton fabrics studied were compared with other adsorptive materials, and also, were examined by Fourier Transform Infrared Analysis (FTIR), Scanning Electronic Microscope (SEM), and Thermal Gravity Analysis (TGA) to study the crosslinkage reaction. The experimental results were as follows: the adsorption of copper and zinc ions increases as chitosan concentration increases, with the best adsorption when chitosan concentration is 0.5%; the adsorption of copper and zinc ions increases as the curing temperature rises, with the best adsorption at 140°C; the adsorption increases with longer curing time, with the best adsorption at 6 min after the processing begins. For adsorption of zinc ions, the cotton fabrics containing chitosan have better adsorption than pure chitosan, but worse adsorption than activated carbon. For the adsorption of copper ions, chitosan is the best, processed cotton fabrics are the second, and activated carbon is the poorest. The adsorption of these two kinds of ions increases with the longer time and higher temperature. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4440–4445, 2006

Key words: crosslinking; FTIR; fiber; waste

INTRODUCTION

When dimethylolethyleneurea (DMEU), dimethyloldihydroxyethyleneurea (DMDHEU), and dihydroxydimethylimidazolidinone (DHDMI) as a crosslinking reagent, are crosslinked to cotton fabrics, excellent results such as antiwrinkle, color-improving, and other physical properties of finishing can be achieved.[1–6]

Chitin, a polymer extracted from the waste exoskeletons of shrimps and crabs and its derivative, chitosan, are potentially important for environmental protection in handling toxic heavy metals in waste water.[7–10] Chitosan powder has been used in studies, mostly focusing on the adsorption of heavy metals, but it is difficult to recycle and clean up. Moreover, although chitosan can be processed into fibers for further application, its strength is very low and it is difficult to handle.[11–13]

Cellulose is a kind of polymer adsorptive agent characterized by large holes and many hydroxyl groups in its molecular structure. Chitosan also has these characteristics, and so crosslinking chitosan to cotton fabrics essentially can improve the adsorptive capacity and help to solve the recycling problem. Hence, this adds chitosan to DMEU, which is used in the processing of cotton fabrics by curing treatment, and then studies chitosan concentration, temperature, and time of curing treatment, as well as adsorptive temperature and time.[14,15] A comparison with other adsorptive materials for zinc and copper ions is also included.

EXPERIMENTAL

Materials

Fine-made and bleached cotton fabrics with size of 144 $\times$ 72/32^s $\times$ 34^s were used in this research. Chitosan of 85% deacetylation was purchased from OHKA Enterprises Co., Ltd. (Japan). Active carbon was a product of Taipei Chemical Industry Co., Ltd (Taiwan). Paraformaldehyde (96%) and Ethylene Urea (99%) were purchased from ACROS ORGANICS Co., Ltd Spectroquant 300, a color developer, was manufactured by Merck Co., Ltd (Germany). Other chemicals used in this research, including sodium hypophosphite (SHP), cupric sulfate, zinc sulfate, sodium hydroxide, acetic acid, and methyl alcohol were all of research grade.

Measurements

DMEU is synthesized by the Hoover method.[16] Paraformaldehyde and ethylene urea were prepared in

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1:2*M* ratios, and each was dissolved in 250 mL methyl alcohol. When paraformaldehyde was dissolved in methyl alcohol, an appropriate amount of sodium hydroxide was added. The prepared ethylene urea was placed in an oil bath reaction trough, and slowly dissolved at a gradual increase of temperature up to 40°C by a heating reactor, installed with a cooling tube. The paraformaldehyde solution was then slowly added into the oil bath reaction trough, and the reaction was maintained at 50°C for 1 h. The sample was incubated in a refrigerator for 24 h, and washed for the second time in methyl alcohol for subsequent purification. The sample was dissolved in methyl alcohol, left over night, and dried to obtain DMEU.[15]

First, 8% DMEU resin processing solutions were prepared containing different concentrations of chitosan hydrolyzed in acetic acid (0.25, 0.5, 0.75, and 1%) and an appropriate catalyst ($MgCl_2$.2%ows). Test fabrics in size 10 cm × 10 cm were soaked and pressed by a tenter machine(Rapid Labortex Co., Ltd.), by the 2 dips-2 nips process. The rate of pick-up was controlled at 80%. Without predrying, the fabrics were then cured at different temperatures (120–150°C) and time courses of curing treatment (2–8 min). The crosslinked-cotton fabrics described earlier were analyzed by Fourier Transform Infrared, installed with Microscope ATR (FTIR, Bio-Rad Digilab FTS-40), and observed under scanning electron microscope (SEM joel 5610). The thermal weight loss of the crosslinked cotton fabrics was estimated by a thermogravity analyzer (TGA, Du Pont 2200). The cotton fabrics mentioned earlier, processed in different conditions, were put into copper and zinc ion solutions to carry out an oscillating adsorption experiment in a thermostatic oscillating trough at different temperatures (30, 50, 70, and 90°C) and adsorption times (30, 60, 120, and 240 min). The concentration of metallic ion was tested using Spetroqant 300 reagent (Merck Co., Ltd., Germany). The absorbing ratio (%) can be derived through the following: the concentrations of the original solutions minus the concentrations of the residual solutions after absorbing treatment divided by the concentrations of the original solutions and multiplied by 100% was obtained by subtracting the concentration of remaining solution from that of original solution and multiplying by100%.

Spectroqant 300 testing was carried out by maintaining the pH of zinc ion solution after adsorption at 5–8, and when necessary, an acid or alkaline was gradually dropped into the solution until the pH reached an appropriate range. Five drops of Zn-1k reagent were added into Spectroqant 300 reagent, and mixed well, followed by an addition of 0.5 mL sample solution. Subsequently, five drops of Zn-2k reagent were added and mixed well with the sample solution, and it was left still for 15 min. The pH of the postadsorptive copper ion solution was maintained at 5–9 by adjusting the pH with an acid or alkaline dropped in, and 5 mL of the sample solution was added to the reagent and mixed well. Five drops of Cu-1k reagent was then added, mixed well, and it was left still for 5 min. When a color was developed, the sample solution was measured by UV light spectrophotometer for the concentration of metallic ion, from which the adsorptive capacity at different conditions of curing treatment were compared with that of pure chitosan and active carbon adsorptive materials. A standard curve was set up by weighing and dissolving 0.1, 0.5, and 0.8 g copper sulfate, and 0.1, 0.3, and 0.5 g zinc sulfate, each in 100 mL water, from which 10 mL solution was drawn out to prepare copper and zinc ion solutions in 0.001, 0.003, 0.005, and 0.008 concentrations (mg/L). A UV light spectrophotometer was used to measure the absorbance of the copper and zinc ion solutions to draw a standard curve.

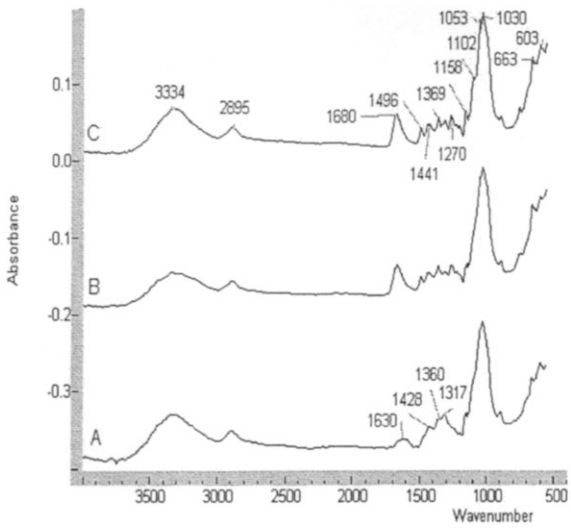
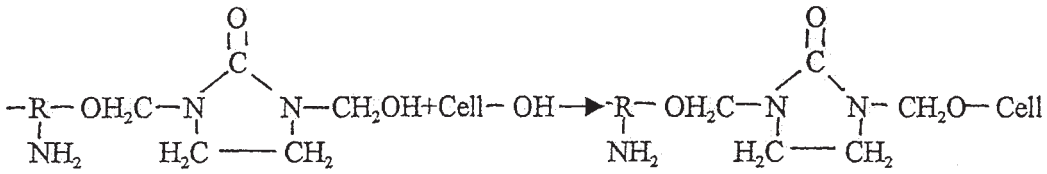


Figure 1 IR diagram of the cotton fabrics cured at different temperatures using DMEU as a crosslinking reagent with chitosan added.(A, original fabrics; B, 130°C; and C, 150°C).

RESULTS AND DISCUSSION

FTIR analysis

Cotton fabrics were processed by resin curing treatment, using a crosslinking reagent, DMEU with an addition of chitosan. The processed fabrics of different curing temperatures were analyzed by Fourier Transform Infrared, installed with Microscope ATR (FTIR, Bio-Rad Digilab FTS-40). The results are shown in Figure 1: the telescopic oscillation of —OH base appears in the range of 3300–3400 cm^{-1}, which overlaps with that of —NH base. At 1680 cm^{-1}, an overlapping area of C═O (carbonyl band) and C—N bond is observed. This is not seen in the original cotton fabrics, proving that the cotton fabrics contain DMEU resin as



Scheme 1

indicated in the following reaction formula of cotton fabrics, DMEU, and chitosan. A phenyl group appears at 1496 cm^{-1}, and at 1270 cm^{-1}, there are oscillations of C—O—C and C—N bonds, suggesting that the cotton fabrics have an ether group, which results from the reaction of the —OH base of DMEU and cotton fibers, or the etherification of the —OH base of chitosan (Scheme 1). None of these findings were deserved in the original cotton textiles. Furthermore, when the temperature of curing treatment is 150°C, there is an oscillation of —COH bond at 1102 cm^{-1}. This peak is not seen for the temperatures lower than 130°C, indicating that chitosan existed on the cotton fabrics, although the binding amount may be less.

SEM analysis

The surface of the processed cotton fabrics was observed under scanning electronic microscope (SEM joel 5610), and the results are as shown in Figure 2: Figure 2(b) shows the cotton fabrics cured with DMEU, with the addition of chitosan, and we can see a small amount of chitosan bound on the surface.

TGA analysis

Cotton fabrics were cured using DMEU as a crosslinking reagent, with the addition of chitosan at different curing temperatures, and analyzed by thermal-gravity analyzer (TGA, Du Pont 2200). The results are shown in Figure 3: as the curing temperature increases to 150°C, the pyrolytic temperature slightly increases from approximately 295°C to 310°C because the cotton fabrics are crosslinked to DMEU, which increases the heat resistance of the processed Fabrics. When the temperature of curing treatment rises to 170°C, the pyrolytic temperature is similar to that when the curing treatment is 150°C, suggesting that 170°C is the limit of the maximal temperature of curing treatment. Moreover, all processed cotton fabrics have lower pyrolytic temperature than original cotton fabrics (about 355°C) because the cotton fabrics are influenced and damaged during the curing treatment of high temperature.

Analysis of chitosan concentration

From Table I, the adsorption of the processed fabrics to copper and zinc ions increases as the chitosan concentration goes up, giving the best adsorption to copper and zinc ions when chitosan concentration is 0.5%. Chitosan adsorbs metallic ions because it contains an amine group, and DMEU contains nitrogen atoms, which can also adsorb metallic ions. When cotton fabrics are added with chitosan and crosslinked to DMEU, the cotton fabrics have a saturated value, whose adsorption to metallic ions reaches the highest peak of crosslinkage when chitosan concentration increases to 0.5%. Higher concentrations do not lead to greater adsorption, but the adsorption of copper ions is better than that of zinc ions.

Analysis of curing conditions

Cotton fabrics were cured for 4 min at different temperature, at 120, 130, 140 and 150°C. The results shown

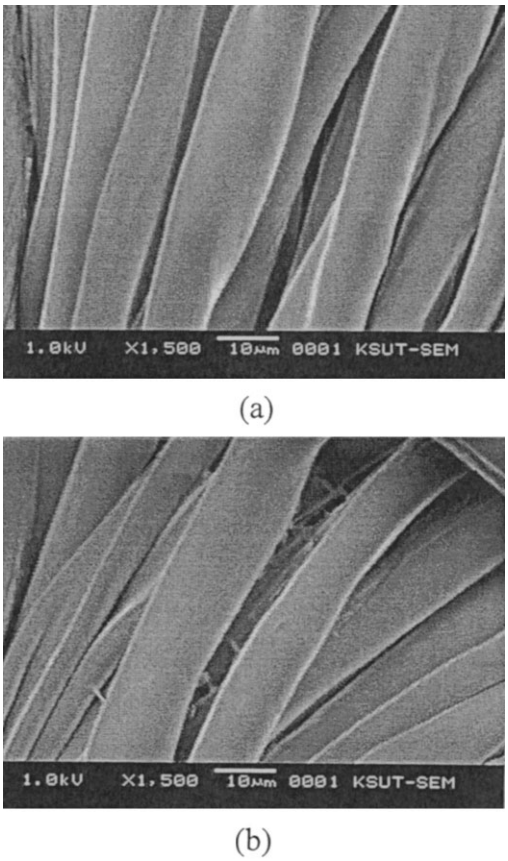


Figure 2 (a) SEM photograph of original cotton fabrics and (b) SEM photograph of cotton fabrics cured at 150°C, using DMEU as a crosslinking reagent with chitosan added.

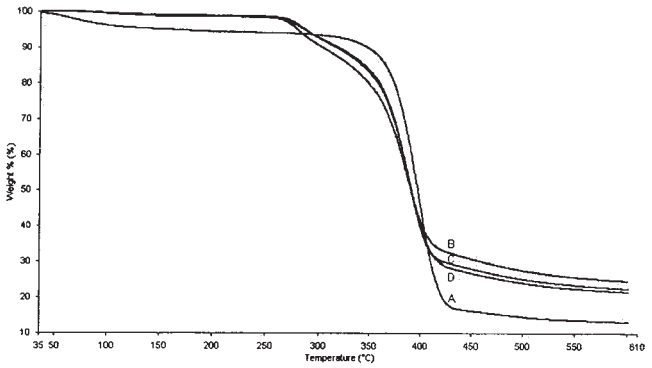


Figure 3 TGA diagram of the cotton fabrics cured at different temperatures, using DMEU as a crosslinking reagent with chitosan added.(A, original fabrics; B, 130°C; C, 150°C; and D, 170°C).

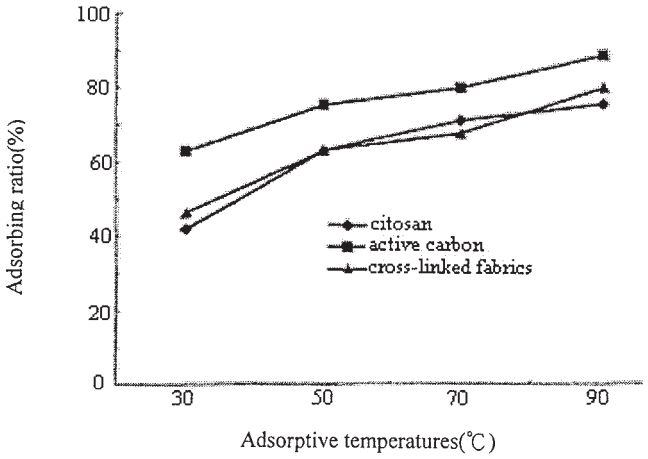


Figure 4 Relationship of three kinds of adsorptive materials at different temperatures for adsorbing zinc ions. (curing temperature, 140°C; curing time, 6 min; adsorption time, 60min; and chitosan concentration, 0.5%).

in Table I indicate that the adsorption of processed fabrics to copper ions increases as the curing temperature rises, giving a better adsorption to copper and zinc ions when the curing temperature is 140°C, because it is suitable for every condition. Cotton fabrics were cured at 140°C for different lengths of time (2, 4, 6, and 8 min). The results shown in Table I indicate that the adsorptive capacity improves when the curing time is longer, and the best adsorptive capacity to copper and zinc ions is achieved when the curing time is 6 min. The saturated value comes later, indicating that a long processing time of curing treatment does not benefit the crosslinking effect because under a longer curing treatment, the reaction of fibers to DMEU resin and chitosan has sufficiently reached the saturated value.

Analysis of different adsorptive materials

Adsorption experiments were carried out on three kinds of adsorptive materials: cotton-processed fabrics, chitosan, and active carbon, at 30, 50, 70 and 90°C in a thermostatic oscillating trough for 60 min. The results shown in Figures 4 and 5 indicate that an increase of temperature is advantageous for adsorptive materials to adsorb metallic ions. Active carbon adsorbs more zinc ions, whereas the cotton-processed fabrics adsorb less zinc ions. Chitosan adsorbs more copper ions, whereas the cotton-processed fabrics adsorb less copper ions. The adsorption of three kinds of adsorptive materials to copper ions reaches equilib-

TABLE I
Relationship of Different Concentrations of Chitosan, Curing Conditions, and the Cotton-Processed Fabrics Adsorbing Copper and Zinc Ions

Curing conditions		Residual concentration of metal ions (ppm)		Adsorbing ratio (%)	
		Copper	Zinc	Copper	Zinc
Concentration of original metal ion	—	1.439	0.115	0	0
Concentration of chitosan (%)	0.25	1.085	0.096	24.6	16.5
	0.50	0.856	0.081	40.5	29.6
	0.75	0.840	0.080	41.6	30.5
	1.00	0.831	0.078	42.3	32.1
Curing temperature (°C)	120	0.959	0.101	33.4	12.2
	130	0.866	0.082	39.8	28.5
	140	0.856	0.081	40.5	29.6
	150	0.756	0.048	47.4	58.3
Curing time (min)	2	1.025	0.096	28.8	16.5
	4	0.856	0.081	40.5	29.6
	6	0.749	0.048	47.9	58.2
	8	0.782	0.057	45.6	50.4

Curing temperature, 140°C; curing time, 4 min; adsorption temperature, 50°C; adsorption time, 60min; and chitosan concentration, 0.5%.

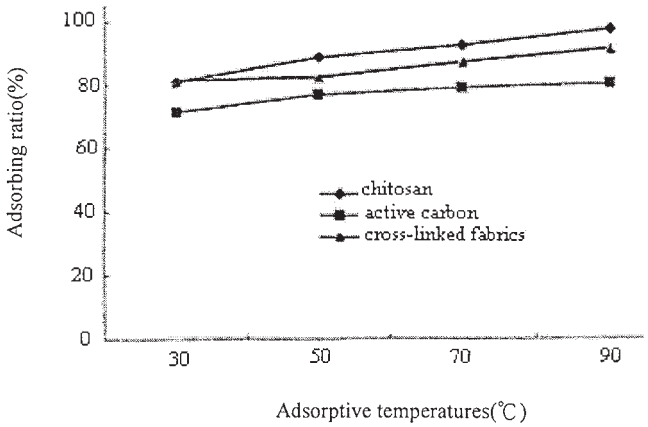


Figure 5 Relationship of three kinds of adsorptive materials at different temperatures for adsorbing cupper ions. (curing temperature, 140°C; curing time, 6 min; adsorption time, 60min; and chitosan concentration, 0.5%).

rium at 50°C. The adsorption of zinc ions is affected more by temperature. The adsorption ratio of cotton-processed fabrics for copper ions exceeds 80% at 50°C, and for zinc ions, it exceeds 60%. At 50°C, adsorptive experiments of these three kinds of adsorptive materials were carried out for 30, 60, 120, and 240 min. The results shown in Figures 6 and 7. Activated carbon is the best and the cotton-processed fabrics are worst in adsorbing zinc ions, while chitosan has excellent adsorption for copper ions. That is improves with longer adsorption time. These three kinds of adsorptive materials also have an increased amount of adsorbed metallic ions, and they are better in adsorbing copper ions than zinc ions.

CONCLUSIONS

With an addition of chitosan, the cotton fabrics were cured with DMEU resin, and their adsorption to metallic ions can be concluded in the following points based on experimental results:

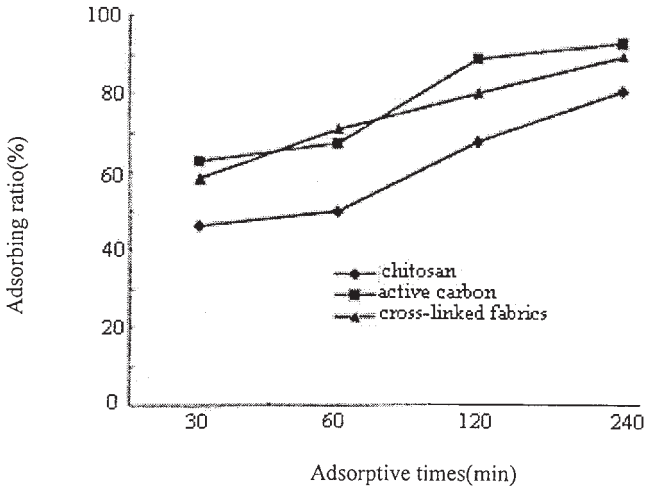


Figure 6 Relationship of three kinds of adsorptive materials at different times for adsorbing zinc ions. (curing temperature, 140°C; curing time, 6 min; adsorption temperature, 50°C; and chitosan concentration, 0.5%).

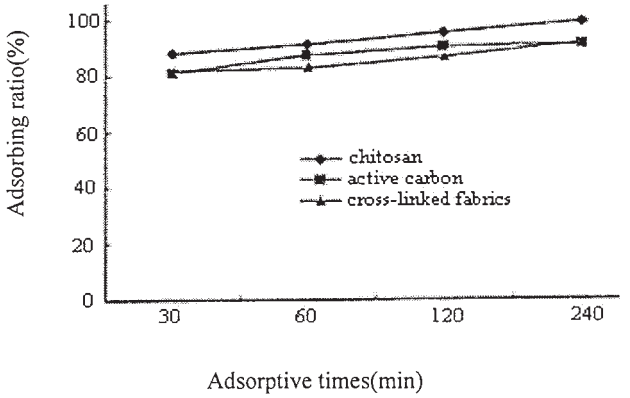


Figure 7 Relationship of three kinds of adsorptive materials at different times for adsorbing cupper ions. (curing temperature, 140°C; curing time, 6 min; adsorption temperature, 50°C; and chitosan concentration, 0.5%).

1. Using DMEU as a crosslinking reagent with chitosan added, the cotton fabrics were separately cured, and as indicated by IR, SEM, and TGA analyses, they can form an etherification reaction. Chitosan can bind to cotton textiles. All heat-processed cotton fabrics have lower pyrolytic temperature than the original cotton textiles.
2. The adsorption of copper and zinc ions increases as chitosan concentration increases, and the best adsorption occurs when chitosan concentration is 0.5%. The adsorption of these two kinds of metallic ions also increases as the curing temperature rises, and the best adsorption occurs at 140°C. The adsorption of these metallic ions increases as the curing treatment goes on, giving the best adsorption at 6 min.
3. Adsorptive materials adsorb more metallic ions as the adsorptive temperature goes up, so that equilibrium is reached at 50°C for adsorbing copper ions.
4. Adsorptive materials adsorb more metallic ions following an increase of adsorption time, and the adsorption of copper ions is better than that of zinc ions.
5. Chitosan is better for adsorbing copper ions than the processed fabrics. Activated carbon is also better than the cotton-processed fabrics in adsorbing zinc ions. The adsorption ratio of the cotton-processed fabrics for copper ions is above 80% at 50°C, and for zinc ions, it is above 60%.

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