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Surface modification of cotton fabric by grafting of polyurethane

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Abstract

Chemical modification of cotton was investigated using blocked isocyanates prepared from reaction of 4,4-diphenylmethane diisocyanate (MDI) with Poly(propylene glyols) followed by addition of methyl ethyl ketoxime (MEKO). The products were characterized by Fourier transform infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS). Evidences of grafting were obtained by IR from the appearance of CO bands absorbance and the reducing of relative intensity of OH, with respect to cotton. The results of XPS and SEM also give the same evidences that polyurethane has been grafted onto the surface of cotton.

Keywords: Polyurethane; Grafting; Cotton

1. Introduction

The nature of the cotton fibre has been extensively investigated. It has been found to consist of a primary wall containing cellulosic and non-cellulosic substances, a secondary wall and a tertiary wall. The cell wall polymers is very easy to form a crystalline composite due to their numerous hydroxyl groups, which help cotton changes dimensions with changing outside force inducing crease to the material. Chemical modification of cotton has been extensively studied for the past years in order to improve its wrinkle resistance, shrinkage resistance and dimensional stability (Andrews, Morris, Donaldson, & Welch; Cirino & Rowland, 1974; Cirino & Rowland, 1976; Hofreiter, 1977; Miller & Wild; Mostafa, El-Sanabary & Youssef, 1997; Mostafa & Morsy, 2004; Schramm, Rinderer, & Bobleter, 1997; Welch, 1992; Welch & Peters, 1997).

Formaldehyde addition products with urea, cyclic ureas, carbarnate ester or with other amides are widely used to produce cross-linking of the cotton cellulose molecules, as the above wrinkle resistance, smooth drying treatment are called. These products are effective and inexpensive, but have serious disadvantages in respect of relatively poor tenacity retention, abrasion resistance and lowering in whiteness index. They are associated with the disadvantage of formaldehyde splitting during processing and use endangering the health of processors and users (Miller & Wild; Welch, 1992). The use of polycarboxylic acids with or without catalysts appears to be much more safety than formaldehyde-based products in view of their environment friendly and non-toxic character. But large cotton fabric strength losses are often obtained with these polycarboxylic acid cross-linking agents (Andrews et al.; Schramm et al., 1997; Welch & Peters, 1997). A significant research work has been directed towards modifying hydrophilic characteristics of easy-care cotton fabrics by adding polyacrylate to the cross-linking formulation (Cirino & Rowland, 1974, 1976; Hofreiter, 1977). The tailored chemically modified starch products also have been used to minimize the expected great loss in the tensile strength of the finished (Mostafa et al., 1997; Mostafa and Morsy, 2004).

Polyurethane has been used to modify cotton and hence to improve their resistance to creasing and shrinking and/or to improve handle. But the crease-anti of the modification products is not endured and its washability is also not so good (Heywood, 1994). It is therefore considered that grafting cotton with polyurethane chains to produce chemical bonding between cotton cellulose and polyurethane in respect of all-round property improvement or improved property balance.

Blocked polyurethane are widely used and patented for a variety of applications including coating adhesives and

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cross-linkings of solid propellants. Stable at room temperature in the presence of polyols, they dissociate at different temperatures, depending upon the chemical nature of the group adjacent to the urethane linkage, to generate free isocyanates which react with the hydroxyl groups to give high molecular weight polyurethanes (Kothandaraman & Sultan Nasar, 1993; Kothandaraman & Sultan Nasar, 1995; Mohanty & Krishnamurti, 1998). This work is undertaken with a view of studying the chemical modification of cotton with blocked polyurethane prepared from successive additions of PPG and methyl ethyl ketoxime (MEKO) chosen as blocking agent to MDI. Under extra treated temperature, blocked polyurethane could generate free isocyanates and further react with the hydroxyl group of cotton fabrics. PU could also get cross-linking structure during the grafting process. By this way, high washability and endure crease-anti of treated cotton would be got.

2. Experimental

2.1. Materials

4,4′-Diphenylmethane diisocyanate was purchased from Aldrich with no further purification, and methyl ethyl ketoxime from Lancaster. Poly(propylene glyols) with molecular weight of 2000(PPG2000) were supplied by Elf Atochem and were continously stirred and degassed overnight at 70 °C in the flask before they were used. The 100% cotton used in this work was purchased from Victor Onward Textile Industrial Co. Ltd (3rd).

2.2. Synthesis

Polyurethane emulsion was prepared according to the following procedure. To prepare polyurethane prepolymer, 3 mmol of PPG(2000), 2 mmol of DMPA(2000), 60 g of ethyl acetate was added and mixed with 6 mmol of MDI in a reaction kettle. The mixture was vigorously agitated by a mechanical stirrer. The reaction took place under a dry nitrogen atmosphere at a temperature of approximately 60 °C. When the –NCO content reached the theoretical value, the reaction was stopped. Then 2.1 mmol of MEKO was added into the ethyl acetate solution of prepolyurethane and the reaction monitored by IR until total disappearance of the absorption band of isocyanate. The reaction mixture was cooled to 50 °C and 2 mmol of triethylamine was added to neutralize the free carboxylic groups. Then the mixture of acetone with water was dropped into the reactor until to obtain blocked polyurethane aqueous emulsions.

2.3. Reactions with cotton fabrics

Cotton fabric samples were padded through two dips and two nips in above blocked PU emulsion without further dilution to a wet pickup of ca 85%. The fabric samples were dried for 3 min at 100 °C and cured for 3 min at 150 °C. The samples were then washed several times with THF, and dried at vacuum till constant weight before being analyzed by IR and XPS.

2.4. Apparatus

FT-IR analysis was carried out with Perkin-Elmer System 2000 FT-IR analyzer.

The XPS analyses were performed with a Physical Electronics 5600 multi-technique XPS system. The X-ray source was operated at 13 kV, 20 mA using Al Kα radiation (1486.6 eV). Vacuum during analyses was in the 10 Pa range. All the experiments were carried out at the normal incidence relative to the plan film surface.

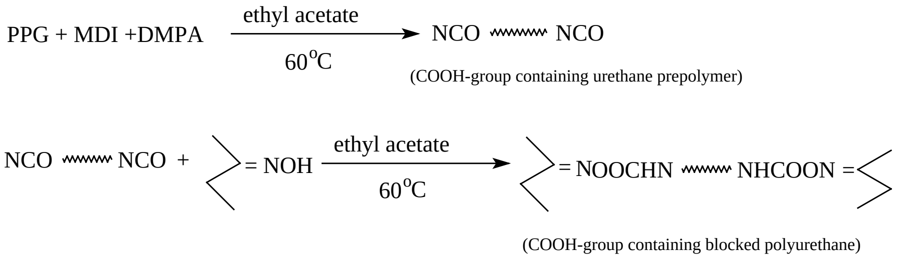
The surface morphology of cotton fabrics taken from treated and untreated cotton fabrics was studied in a Hitachi scanning electron microscope (Model S340).

3. Results and discussion

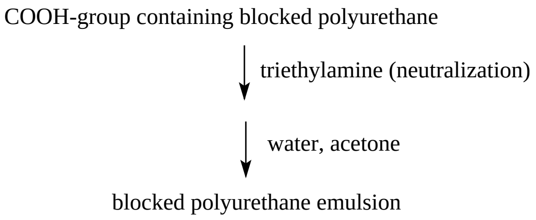
3.1. Synthesis of blocked polyurethane and its reaction with cotton fabric

The synthesis of blocked polyurethane was performed without catalyst in a one pot-two steps procedure (Scheme 1). Under these conditions, triethylamine was added to neutralize the free carboxylic groups. Then the mixture of acetone with water was dropped into the reactor until to obtain blocked polyurethane aqueous emulsions without further purification (Scheme 2).

Grafting of polyurethane on cotton was performed with different concentration of blocked polyurethane emulsion to



Scheme 1. Synthesis of COOH-group containing blocked polyurethane.



Scheme 2. Synthesis of blocked polyurethane emulsion.

finishing cotton fabrics. The reaction between cotton and blocked polyurethane will happen during curing process (Scheme 3).

Reaction between cotton and blocked polyurethane is proved by the weight increase obtained after reaction calculated according to the following formula

$$\text{the weight percent increase (WPI)} = \frac{G_1 - G_0}{G_0} \times 100\%$$

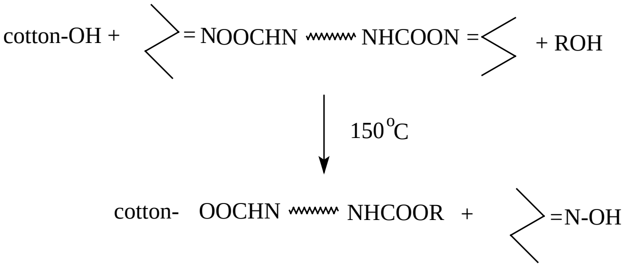
G_0 means the weight of untreated cotton, G_1 means the weight of cotton after reaction.

PU grafted cottons with WPI of 2.2 and 5.3% were got by using 5 and 10% solid concentration of blocked polyurethane emulsion to finishing cotton fabrics. The untreated cotton and grafted cotton were investigated using XPS, FTIR and SEM.

3.2. XPS analyses

Fig. 1 shows the XPS wide scan spectra and the atomic ratios for cotton samples (a) untreated, PU grafted cotton with WPI of 2.2% (b) and 5.3% (c). All the fabric samples were washed in an acetone and dried during 3 h at 45 °C. The relative composition of PU grafted cotton samples surface by XPS analysis is listed in Table 1. The date revealed that the content of N_{1s} was increased after surface grafting, which indicated that PU chains has been grafted onto the surface of cotton. It can been seen that the content of C_{1s} in spectra (b) is lower than the content of C_{1s} in spectra (c). These differences can be attributed to the different WPI.

The details of the high resolution O_{1s} peak (Fig. 2) were used to further define the surface coverage of cotton fabrics. The O_{1s} spectra principally shows four components present in untreated cotton fabric molecule: OH at 533 eV, C–O–C and COOR at 533.5 eV, C=O at 532.1 eV and $CONH_2$ at 531.1 eV (Fig. 2(a)). This is consistent with previously reported XPS results for cellulose (Beamson & Briggs, 2001).



Scheme 3. Reaction blocked polyurethane with cotton.

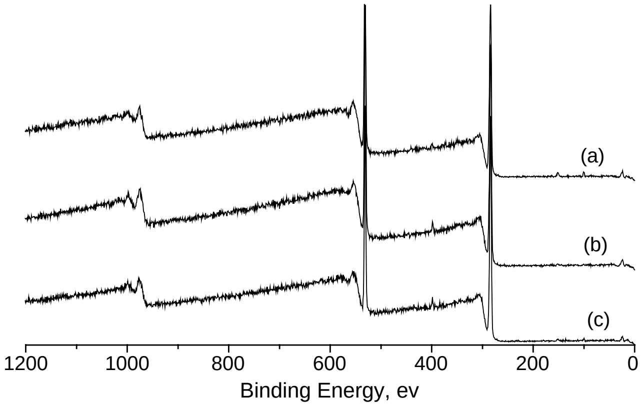


Fig. 1. The XPS spectra of (a) untreated cotton, (b)PU grafted cotton with WPI of 2.2% and (c)PU grafted cotton with WPI of 5.3%.

The similar components present in treated cotton fabric have been showed in the O_{1s} spectra (Fig. 2(b) and (c)). But it also showed a big change of the percentage intensities of the components peak, especially for the component at 533 eV, assigned mainly to OH in the O_{1s} envelope of cotton fabric. Untreated cotton, PU grafted cotton with WPI of 2.2% and PU grafted cotton with WPI of 5.3% has represented 27.68, 16.40 and 9.56% of the total area respectively, which give the evidence that PU has reacted with the OH group of cotton fabric and lead to decrease the content of OH group.

3.3. IR(ATR)

The presence of graft polyurethane on the surface of the treated cotton fabric samples has been also identified by IR(ATR) spectroscopy, as shown in Figs. 3 and 4.

A broad absorption band over 3500–3000 cm^{-1}, characteristic of hydrogen bonded O–H stretching vibration is common to all the three spectra in Fig. 3. However, it was observed from spectra(c) that there was a slight gradual decrease in the intensity of the OH stretching band indicating a gradual increasing of the extent of grafting degree. In heating condition, thermal dissociation of polyurethane could happed and generated

Table 1
The relative composition of PU grafted cotton samples surface by XPS analysis

Content (%)	C_{1s}	N_{1s}	O_{1s}
Untreated cotton	69.77	0.90	27.97
PU grafted cotton (2.2%)	70.17	1.21	27.23
PU grafted cotton (5.3%)	74.21	1.61	23.59

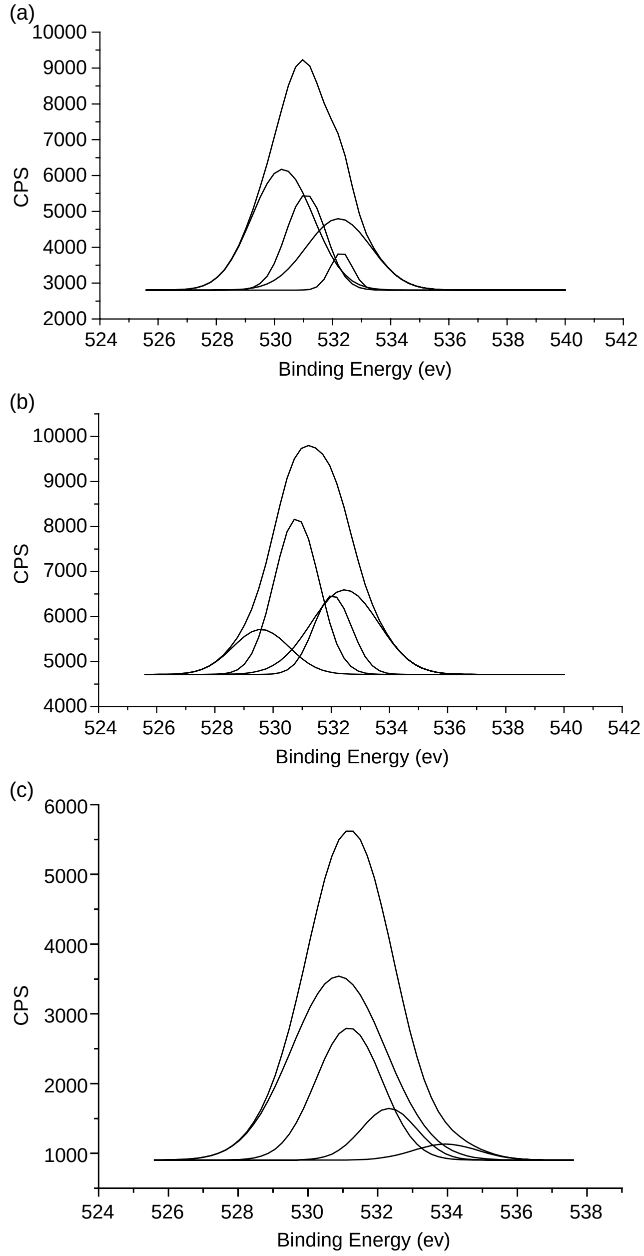


Fig. 2. High-resolution O_{1s} spectra for (a) untreated cotton, (b)PU grafted cotton with WPI of 2.2% and (c)PU grafted cotton with WPI of 5.3%.

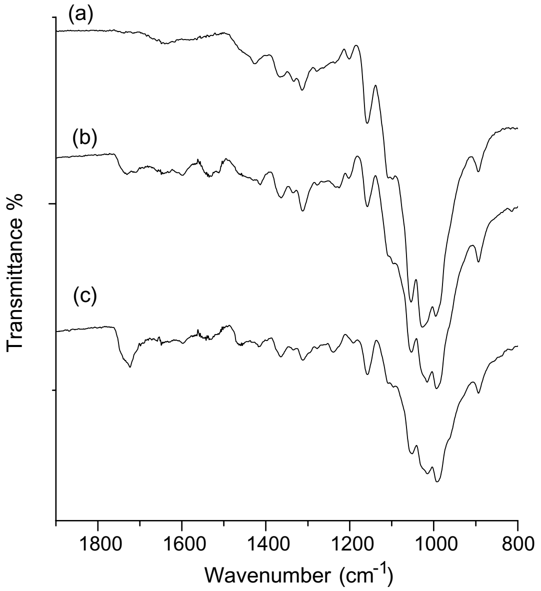


Fig. 3. FTIR spectra in the region 1900–500 cm^{-1} of untreated cotton (spectrum a) and PU grafted cotton with WPI of 2.2% (spectrum b) and 5.3% (spectrum c).

free isocyanate group which could react with the hydroxyl groups of cotton and result in grafted products. It is also proved that PU has been grafted on cotton by the appearance of two bonds at 1712–1731 cm^{-1} (carbonyl C=O stretching in –O(C=O)–NH group) and 1599 cm^{-1} (C=O stretching of carboxylic group) in the spectra of PU cheated cotton samples shown in Fig. 4. The lowering of the intensities of the OH in-plane bending bands at 1335, 1312 and 1201 cm^{-1} in the spectra of PU cheated cotton samples also indicated that PU has been grafted on cotton by reacting with its OH group. In the case of PU grafted cotton samples, the absorption band of C=O stretching in spectra(c) is more intense than which in spectra(b), due to higher degree of grafting.

3.4. SEM

Fig. 5 are the SEM pictures of untreated cotton fabric and PU grafted cotton fabric samples. As shown on Fig. 5(a), the surface morphology along the fiber of the untreated cotton is rough and scaly. On the contrary,

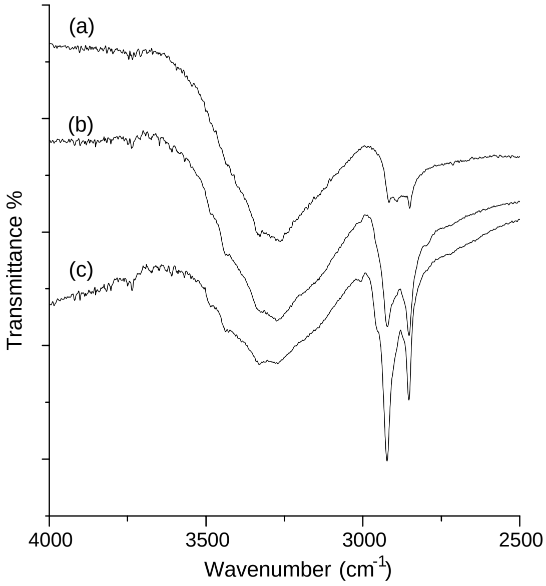


Fig. 4. FTIR spectra in the region 4000–2500 cm^{-1} of untreated cotton (spectrum a) and PU grafted cotton with WPI of 2.2% (spectrum b) and 5.3% (spectrum c).

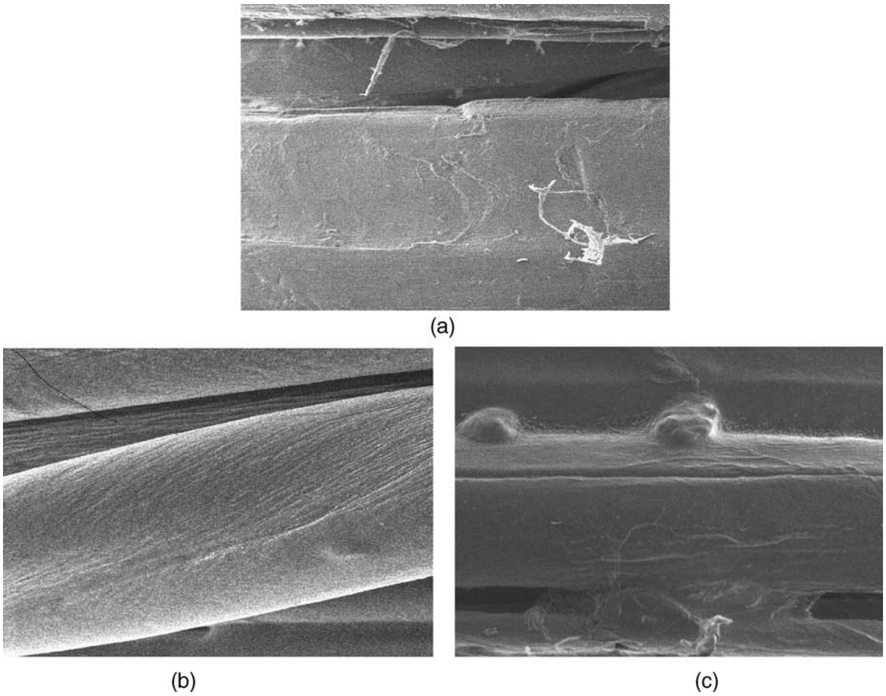


Fig. 5. The SEM pictures of (a) untreated cotton, (b)PU grafted cotton with WPI of 2.2% and (c)PU grafted cotton with WPI of 5.3%.

the surface of the PU-grafted cotton is completely surrounded by the grafted PU chain. In addition, they are some polymer layers exist between the fibers stays, which indicated some adhesion of PU occur during the grafting process.

4. Conclusion

The XPS measurement demonstrated that it is possible to graft polyurethane chains onto the surface of cotton after finishing process, and the FTIR(ATR) further illustrated that Polyurethane could react with the hydroxyl groups of cotton and result in grafted products. SEM analysis indicates that on the macro-scale the sheet surface is fairly uniformly distributed with polyurethane. The results has showed blocked polyurethane could generate free isocyanates and further react with the hydroxyl group of cotton fabrics. PU could also get cross-linking structure during the grafting process. By this way, high washability and endure crease-anti of treated cotton would be got.

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