Vacuum 91 (2013) 7–13

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Surface oxidation of cellulose by ozone-gas in a vacuum cylinder to improve the functionality of fluoromonomer

Mazeyar Parvinzadeh Gashti [a,*], Alireza Pournaserani [a], Hamed Ehsani [a], Mahyar Parvinzadeh Gashti [b]

[a] *Department of Textile, Islamic Azad University, Shahre Rey Branch, Tehran, Iran*
[b] *Faculty of Mechanical Engineering, Islamic Azad University, Parand Branch, Parand, Iran*

ARTICLE INFO

Article history:
Received 3 August 2012
Received in revised form
18 October 2012
Accepted 29 October 2012

Keywords:
Cotton
Water repellency
Ozone-gas

ABSTRACT

The influence of the ozone-gas treatment on the performance of the fluorocarbon monomer on cotton fiber was investigated employing Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM), water contact angle (WCA) and bending length (BL). FTIR results indicated that the ozone-gas pre-treatment oxidized the surface of the fibers increasing reactivity of the substrate toward the fluoromonomer. The contact angle and microscopic tests showed that the combination of ozone and fluorocarbon treatments on cotton can increase the contact angle due to higher efficiency of the water repellent polymer on the surface of the ozone-gas treated fibers. The results obtained from the weight of the samples verified the successful grafting of the fluoromonomer on the cotton fabrics.

1. Introduction

Cotton is the "king" of textile fibers with a unique combination of properties including high strength, durability, softness, good dyeability and biodegradability, and for many centuries it has found use in numerous textile products [1]. Besides many beneficial properties, there are various disadvantages of using cotton clothing such as shrinking in the wash, high wrinkling, low resistance to acids, color loss through bleeding, being damaged by sunlight and mildew, retaining water after wetting and high flammability [2].

Over the last decades, there has been an increasing application of different chemical finishes to the cotton such as oil- and water repellency, softening, antimicrobial, antistatic, flame retardancy and easy-care [3–6]. Fluorocarbon polymers have always attracted significant attention for cotton protective clothes due to excellent chemical and thermal stability, superior water and oil repellency, low surface energy and low flammability [7–9].

Several physical and chemical methods have been utilized in order to introduce reactive groups into textiles including corona discharge treatment [10], plasma functionalization [11–13], laser induced surface modification [1], gamma irradiation [14], UV irradiation [15], ultrasound vibration [16,17], electron beam irradiation [2], microwave curing [18], neutron irradiation [1], supercritical carbon dioxide technique [2], vapor deposition [2] and ozone-gas treatment [19,20]. These methods can make the monomers firmly grafted on the substrate through covalent bond [1]. In this regard, the ozone-gas treatment alone or in combination with UV light has long been known as a surface modifier of different polymers and degrading agents for textile-dye effluents [21–25]. It has been shown by several researchers that ozone-gas is not only able to enhance polarity and adhesion to surfaces but also improves efficiency of grafting reactions on synthetic polymers [26–29]. However, to the best of our knowledge, there is no study on the effect of ozone-gas treatment on grafting of different monomers on cotton. In this study, we used fluorocarbon monomer for grafting due to the fact that it is among the most common functional finishing agents for cotton. To achieve the necessary results, different analytical methods were used to analyze physical and chemical properties of the samples prepared for the study.

2. Experimental

2.1. Materials and methods

A desized, scoured and bleached plain weave 100% cotton fabric with 36 warp/cm and 26 weft/cm was supplied by Yazdbaf Fabrics Company (Yazd, Iran). Fluorocarbon monomer was Waterless 6064 provided by Chemipakhsh Iran Co. Ltd (C.P.I.C) as a water repelling

---

[*] Corresponding author. Department of Textile, Islamic Azad University, Second Floor, No. 134, Second Golestan, Pasdaran Street, Tehran 1666933611, Iran. Tel.: +98 9123137115; fax: +98 2122593135.
E-mail address: mparvinzadeh@gmail.com (M.P. Gashti).

0042-207X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2012.10.015

agent. The chemical structure of monomer was based on hexafluorobutyl methacrylate resin. It appears to be a slightly beige liquid and weakly cationic. Magnesium chloride was supplied by Merck Chemical Co., Germany.

The ozone treatment was carried out in a manner similar to those reported in earlier studies [25,30,31]. Ozone was generated from high purity oxygen (99.6%) in a vacuum cylinder. A concentration of 60 g/m^3 of ozone with a flow rate of 0.5 l/min was used. The samples were ozonated for 30, 60 and 90 min at room temperature. Fluoromoner was applied immediately on the untreated and ozone-gas treated fabrics by the padding method with concentrations of 20, 40 and 60 g/L in water at 30 °C and 70% wet pick-up. The cross-linking reaction of fluoromonomer was catalyzed by 7, 14 and 20 g/L of the magnesium chloride separately for each bath and the pH was maintained at 5 using 0.5% acetic acid. The treated fabrics were then dried/cured in an oven at 150 °C for 1 min. All the treated fabrics were washed separately at 50 °C for 10 min using 1% nonionic detergent. It was found useful for removing the loosely bonded monomers.

2.2. Characterization

The normalized FTIR spectra of the fabrics were measured using a ThermoNicolet NEXUS 870 FTIR spectrophotometer (Nicolet Instrument Corp., USA).

The morphology of the fibers was characterized with a wide angle X-ray diffractometry using a computerized SEIFERT/PTS 3003 X-ray diffractometer. Ni-filtered Cu Ka radiation generated at 40 kV ($k = 0.1542$ nm) and 30 mA was used.

The percentage of grafting was determined as follows:

$$\text{Grafting yield }(\%) = (W_g - W_0)/W_0 \times 100 \tag{1}$$

where W_0 and W_g are the weights of the fabric samples before and after grafting, respectively.

The thermal degradation properties of the samples were performed on a TGA-PL thermoanalyzer from UK. In each case a 5 mg sample was examined under an N_2 at a heating rate of 5 °C/min from room temperature to 600 °C.

The surface of the fibers was investigated using a Scanning Electron Microscopy (SEM) XL30, Philips. The surface of samples was first coated with a thin layer of gold (10 nm) by physical vapor deposition using a sputter coater (SCDOOS, BAL-TEC).

The contact angle measurements of the samples were carried out at room temperature on a Kruss G10 instrument of German origin. Water was used as the probe liquid at 23 ± 2 °C and 65% relative humidity. The average contact angle from six different locations on each sample was determined and the experimental uncertainty was within ±2°.

The bending length of the fabrics in the warp direction was determined using a Drapometer M003B (SDL) according to ASTM D1388-96.

The contact angle and bending length of the samples after repeated launderings were evaluated by washing cotton fabrics according to AATCC test method 61(2A)-1996. All the treated fabrics were subjected to 1, 10 and 20 consecutive launderings in the presence of non-ionic detergent. Home laundering is according to AATCC test method 124 (AATCC, 2000).

3. Results and discussion

3.1. Structural information by FTIR spectra

The infrared spectra of the untreated cotton and the sample grafted with fluoromonomer after the ozone-gas treatment are shown in Fig. 1. The intense C–H stretching, CH_2 asymmetric and symmetric stretchings, C=C asymmetric stretching, C–H wagging (in-plane bending), intermolecular O–H stretching and bending vibrations related to O–H in the cellulose chains appear at 2957, 2910, 1958, 1346, 3433 and 1245 cm^{-1}, respectively. The band appearing at 1708 cm^{-1} represents C=O stretching motions in the cotton chains. The C–O–C symmetric vibration of ether bonds and in-plane ring stretching for cotton are characterized at 1009 and 1094 cm^{-1} [32,33].

FTIR spectra of ozone-gas treated cotton (Fig. 1b) showed some new bands appeared at 1578, 1505, 1455, 1262 and 895 cm^{-1} which are assigned to carboxylate anions, OH in plane bending, CH wagging, CH deformation stretch and asymmetric stretch of glucose ring in cellulose chains, respectively.

After the ozone-gas treatment of the cotton followed by grafting with fluorocarbon (Fig. 1c), the bands at 2958, 1578, 1505 and 1262 cm^{-1} were disappeared and the band at 1641 cm^{-1} was appeared. These changes associated with C–F stretching of monomer indicated that fluorocarbon based groups were successfully grafted onto the cellulose. This is in agreement with the previous results obtained by researchers confirming the changes in inter- and intra-chain hydrogen bonds of cotton after fluorinated finishing [34–37]. It was found that the CH_2 stretching band at 2910 cm^{-1} was shifted to 2923 cm^{-1}. Some researchers have presented the same results for ozone-gas treated wool confirming the reaction between C–H component and O_3 [38–42]. Moreover, a new band observed at 1641 cm^{-1} indicated that cellulose chains were oxidized to generate C–O and carbonyl groups [31].

3.2. Evaluation of morphology by XRD

The XRD patterns for the untreated cotton, the ozone treated cotton for 90 min, the 40 g/L fluoromonomer grafted cotton as well as the samples grafted with 20, 40 and 60 g/L fluoromonomer after the ozone treatment for 90 min are shown in Fig. 2. Diffraction peaks in Fig. 2a are characteristic of cellulose I, with four reflections at $2\theta = 13.5°$, $19.5°$, $25.6°$ and $29.4°$ representing d(101), d(101), d(021) and d(002) Bragg's reflections [43]. The crystallite form was not changed by ozone-gas and the fluoromoner treatments. On this basis, it can be concluded that neither ozonation nor fluoromonomer grafting changes the crystalline structure of cellulose. The effects of these treatments must, therefore, be confined to the cotton surface. Other authors have confirmed this phenomenon after the crystallinity measurement of different polyesters and wool in cases where ozone was used for the surface modification [44–48].

3.3. Influence of ozone-gas on grafting yield of monomer

The effect of ozone-gas treatment on the degree of grafting of fluoromonomer was investigated and the results are shown in Fig. 3. The maximum exposure time was 90 min. It can be observed that grafting yield for different concentrations of monomer reached its maximal value as the irradiation time increased to 60 min and it became relatively constant for 90 min. This may suggest that grafting reaches the optimum value by the ozone treatment for 60 min. However, some researchers have confirmed that homopolymer chains attached on the surface of fibers are able to limit the grafting yield [49,50]. The degree of grafting for the cotton treated with 60 g/L can reach up to 14% when the ozone exposure time is 90 min. It is suggested that ozone treatment controls the grafting of monomer; the higher the exposure time up to 90 min, the more polymerization chains can be formed. This may be due to the consumption of catalyst and monomer, and the increasing surface