POLYESTER KNIT-FABRICS TREATED WITH CATIONIC DIRECT DYES USING PLASMA -INDUCED GRAFT-POLYMERIZATION

Cuong K. Nguyen[1*] and Seiichi Kataoka[2]

[1]School of Engineering & Technology, Vietnam National University, 144 Xuan Thuy, Hanoi, Vietnam.
[2] Advanced Industrial Science & Technology, Midorigaoka, Ikeda,Osaka, 563-8577, Japan.

Abstract

Polyester knit-fabrics were treated by argon-helium plasma at room temperature and ambient pressure, subsequently graft-polymerized with acrylic acid in vapor. Plasma interaction to the polyester fibres and graft-polymerization of carboxyl functional groups were investigated. Finally, the polyester knit-fabric grafted with carboxyl groups were treated with cationic direct dyes at around 80^{0}C and ambient pressure. Results obtained show that grafted surface of the knit fabrics was dyed with the red color, and then their color surface becomes dark pink while their untreated surface has pinkish white. The graft polymerization of the carboxyl groups and the absorption of cationic direct dyes will be discussed in details.

Keywords: plasma-induced graft-polymerization, polyester-fiber knit-fabrics, cationic direct dyes, polyester.

1. Introduction

PET (knit or woven) fabrics produced by poly (ethylene terephthalate, PET) fibers are usually unable to absorb moisture as well as to be dyed at ambient temperature and atmospheric pressure. These drawbacks of the PET-fabrics are owing to the high degree of crystalline of PET structure, and lack of functional polar groups on the fiber's surface that cause the PET fibers to have low surface free energy and poor wettability. Though the PET fibers show low moisture absorbance and unable dye at room temperature and ambient pressure, they possess some excellent properties such as high resistance to surface abrasion, to wrinkling clothes… that are useful for wearing clothes. Therefore, to achieve PET fibers -like cotton properties to enlarge their capable uses, it requires surface modification of PET fibers.

Surface modification is usually used to roughen PET-fiber surfaces to enhance mechanical interlocking, and form chemical groups on the surface that improve wetting and/or chemical bonding. Furthermore, the surface modified by the APP is, in general, confined to a thin layer less than 100 μm so that desirable properties of bulk materials are usually unchanged. The conventional surface modifications have been performed by various chemical treatments. These processes are usually accompanied with damaging bulk fibers and leaving behind residual chemical substances that can affect PET fiber's properties. Recently, drying treatment processes using various energies from e-beam, ion collision and UV-rays…have been widely employed not only in university laboratories but also in industry factories These processes have great advantages in comparison to chemical treatment processes (wet processing) as they do not leave any residual chemicals and dry-processing is easy to be controlled. One of dry-processes is atmospheric pressure (glow-discharge) plasma (APP) operated at radio-frequency of 13.56 MHz. Furthermore, the plasma process at ambient pressure has widely been developed in the textile industry as its machines are familiar with conventional textile machine lines.

Exposed to APP using inert gases like helium (He), argon (Ar) and nitrogen (N_2), PET fibers can enhance theirs moisture absorption, dyeing behavior, and especially surface adhesion etc... Effects of discharge power, time of exposure and gas-pressure on improvement in wettability, dyeing and bonding capability of various polymer fibers were also investigated [1-3]. However, almost plasma research has been carried out using small, batch plasma machines with rather ideal conditions designed for laboratory research-experiments while effects of plasma treatments on changes in surface properties of textile fabrics in a large scale-like industrial production (pilot-production scale) have not been reported yet.

In this paper, PET knit-fabrics were irradiated with helium (He) precursor gases at atmospheric pressure, subsequently grafted with hydrophilic acrylic acid (AA) monomer using a remote plasma machine of a large-scale industrial production-line operated at ambient. Grafted PET-fiber fabrics were then dyed with cationic dye substance one-atmospheric pressure. After that, chemical compositions of the control PET-fiber surface in comparison to those of the surface treated by plasma-induced graft polymerization were characterized by X-ray

[1]Corresponding author: Tel.: (+84) 98.211.4032
Email: cuongnk@vnu.edu.vn

photoelectron spectroscopy (XPS). And, changes in morphology of the grafted surface compared to the control one were observed by scanning electron microscopy (SEM). Results obtained from the analysis of the chemical composition and changes in morphology would account for why the grated PET fabrics could be dyed with cationic dyes at ambient pressure....

2. Experimental

Rib fabric, supplied by Nissin Fiber Co., Ltd., Osaka, Japan, was fabricated using 75 denier PET fibers. Their stitch densities, corresponding to weight of 135 g/m^2, measured in the wale and course directions were 44 loops and 59 loops per inch, respectively. The PET fiber fabric demonstrates the high resistance to water penetration. Wicking time is over 15 mins when placing a distilled water droplet of 10 µl onto the fabric's surface until the droplet completely loses its image on the fabric surface. This means that the PET fiber surface is not wettable (hydrophobic).

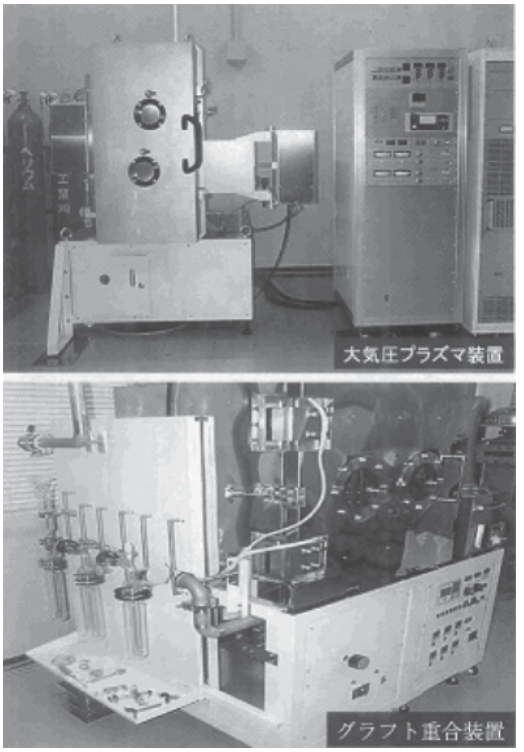


Fig.1. *Atmospheric pressure plasma machine (left) and graft-polymerization machine (right) used in large-scale-like industrial production-lines.*

Washed in 60^{0}C neutral-detergent water to remove starch, grease and colloids attached to fiber surfaces, a 0.8 meter-wide roll of the PET fabric was dried in a vacuum chamber before the plasma-induced graft polymerization onto PET fabrics. Theses fabrics from a roll came into the space between the upper and lower electrodes and were wide electrodes at one-atmosphere pressure with argon/helium-inert gases. Both large-scale plasma machine operating in the radio-frequency of 13.56 MHz and grating machines were manufactured by Pearl Kogyo Co.Ltd. in Osaka, Japan. (Fig. 1). Plasma treated fabrics in a roll was then grafted with Acrylic acid (AA), 99.5% conc. in the grafting machine evacuated to 133 Pa at a constant temperature of 70^{0}C for 1 hour. And then, taken from the grafting chamber, the grafted fabric was extracted by hot methanol for over 2 hours to remove unreacted and residual AA monomer. Wettability of the grafted fabrics was calculated by the grafting degree, which was used to estimate the degree of the glow discharge subsequent to graft polymerization. Moreover, the grafted fabrics (samples) were washed several times in the neutral-detergent water at 60^{0}C; the durable wettability of the grafted fabric was estimated by the wicking technique.

Deeply understanding changes in surface compositions of the PET fabric before and after plasma-grafted polymerization with the AA monomer, samples of 5x5mm cut from the untreated and grafted fabric were measured by the X-ray photoelectron spectroscopy (XPS) measurement. The XPS measurement was performed on a Shimadzu 3300 spectrometer, employing MgKα X-ray source running at an anode voltage of 8 kV and current of 30 mA. Moreover, PET-fiber surface-morphology was observed on a scanning electron microscope (SEM), model JEOL JSM-5200. The observation would determine the quality of the grafted PET surface, and especially it can be used to reveal whether micro-pores were created on the PET-fiber surface. Finally, the grafted PET fabrics were dyed with cationic dyes at ambient pressure at around 80^{0}C for 15 min.

3. Results and disscution

3.1. Chemical composition of the grafted PET-fiber surface

Glow-discharge-plasma irradiation degraded the PET surface. This process led to breakdown of C-H or C-C bonds (PET molecular structure) into carbon (•C) and hydrogen (•H) radicals on the PET-fiber surface. Subsequently exposed to air, these radicals were reacted with oxygen in air to form peroxides and hydro-peroxides. These peroxides are initiators for the graft-polymerized AA monomer. Therefore, the chemical compositions of the grafted PET-fiber surface were analyzed by XPS.

C_{1s} spectra of the control PET-surface were de-convoluted into three distinct peaks which can be assigned to the C*-H, C*-O (e.g., ether, ester) and O-C*=O (e.g., carboxylic acid, ester) groups, corresponding to binding

energy (BE) at 285.0 eV, 286.6 eV and 288. 9 eV, respectively. These data analyses suggest that plasma-induced AA graft polymerization mainly involves in the modification of -C_6H_4-, -CO- and O-C*=O groups of the PET-molecular structure while post-plasma reaction in air of free radicals generated by broken chains and dehydrogenation mechanisms led to the formation of the C*=O carbonyl group, a new linkage created by oxidation processes.

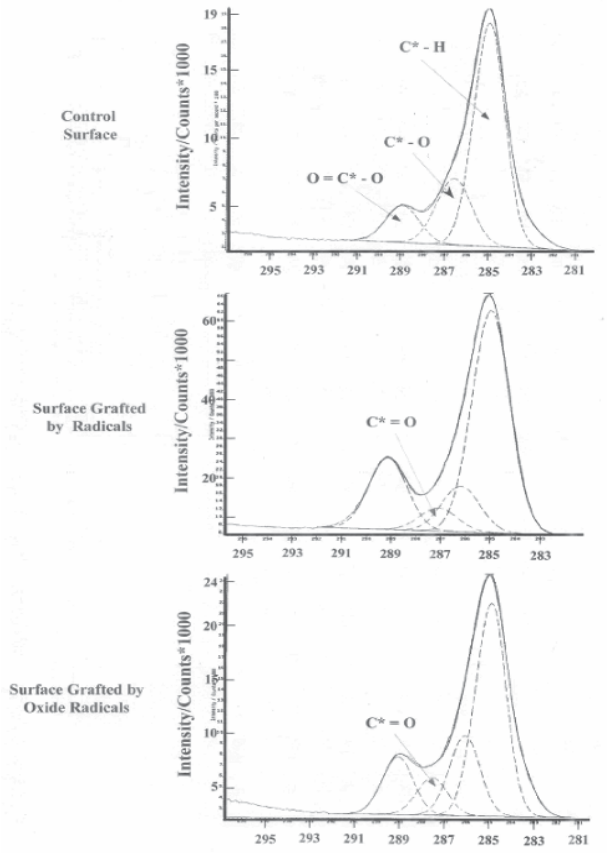
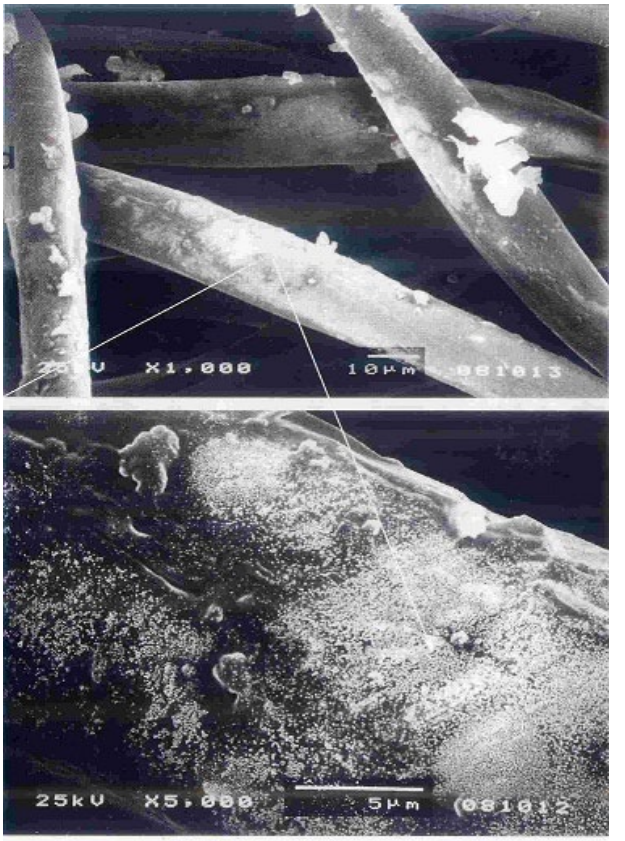


Fig. 2. *Analysis of deconvoluted C_{1s}-peak spectra for the control surface (upper) and for the surface irradiated for 30 s and grafted at 70^{0}C for 1 hour. (lower).*

It is noteworthy that the relative surface oxygen and carbon atomic concentrations of AA-grafted surface have been modified significantly. The $O_{1s/C1s}$ ratio increased from 34.4% to 42.6 and the oxygen content was enhanced up to 29.9% from 25.6%. These are due to a relative increase in the percentage of the functional groups like: O-C*=O carboxyl groups from 11.4% to 12.5%, C*-O group from 17.1% to 18.6%, and also C*=O carbonyl groups of 3.0% [1]. The significant increase in the functional group on the surface made the AA-grafted PET-fiber fabrics possessing certain properties similar to those of cotton and other natural fibers.

3.2. Morphology modification of the grafted PET-fiber surface



(a)

(b)

Fig. 3. *SEM micrographs at different magnification showing corn-structure surface-morphologies of PET-fiber fabrics treated with plasma-induced graft-polymerization of AA monomer.*

Figure 3 shows PET-filament morphologies showing non-treated (control) spots and plasma-induced AA-graft-polymerized spots with distinct magnifications (3a). Control spots looks like dark and smoother while the

ISSN 0866 - 7056
TẠP CHÍ CƠ KHÍ VIỆT NAM, Số đặc biệt năm 2016
www.cokhivietnam.vn

AA-grafted one seems to be rough and shining with regular corn-structure that can be seen clearly in SEM micrographs with higher magnification (3b). The distinction is attributed to the fragmentation of polymer chains (hydrogen cleave) caused by the surface etching, and subsequently grafting the monomer onto the radicals decomposed from hydro-peroxide.

3.3. Washing durability and cationic dyes of the grafted fabric

The figure 4 shows a T-shirt was made of PET fabrics treated by plasma-induced AA graft polymerization, and subsequently dyed with the cationic dyes at ambient pressure, 80^0C for 15 min. As we can see the T-shirt's front-side has dark-pink color while the inside appears pinkish-white. The color difference of the grafted PET-fiber fabrics after dying at the ambient pressure could account for cationic dyes absorbed to the AA-grafted PET-fiber fabric (the T-shirt's front side) while these dyes were washed out of the T-shirt's inside. This can be ascribed to functional groups: -COOH and C= O ended copolymers on plasma-grated surface. This copolymer can chemically react with the cationic dyes at the ambient pressure, and then the dark-pink color appeared on the T-shirt's front side.

Fig. 4. *The T-shirt dyed with the cationic dyes at ambient pressure showing color absorbance of the front side (treated surface) and the inside (non-treated surface).*

Washing durability of dyed T-shirt in hot water of 70^0C was examined. The dark pink color of the T-shirt seems to be unchanged when the number of laundry times was over 20 times.

4. Conclusion

Polyester (PET) fabrics can be dyed with cationic dyes at ambient pressure when their surface was treated by plasma-induced graft polymerization with acrylic acid. The production was continuously performed for rolled PET-fabrics in the large-scale plasma and grafting machines. XPS analysis and SEM observation shows significant increases in the oxygen content such as the functional group deposition that made PET-fiber possessing cotton-like properties and then able absorbing the cationic dyes at ambient pressure.

Based on the results obtained, further research applications would be focused on anti-bacteria, bad smell deodorization…when appropriate monomers would be deposited on plasma-induced graft-polymerization PET fabrics. This would be able produce various types of smart textile fabrics launched into the textile markets.

Acknowledgments

One of the authors would like to thank New Energy & Industrial Technology Development Organization (NEDO), Japan for the financial support for plasma-textile applications.

References

[1] Nguyen Kien Cuong, Noboru Saeki, Seiichi Kataoka and Susumu Yoshikawa. Hydrophilic Improvement of PET Fabrics Using Plasma-Induced, Journal of the Surface Science Society of Japan, 23, (2002), 202 – 208.

[2] Fevzihan Basarir, Nguyen Cuong, Woo-Keun Song, and Tae-Ho Yoon, Surface Modification via Plasma Polymerization of Allylamine for Antibody Immobilization, Macromol. Symp, 249–250, (2007), 61–66.

[3] Kien Cuong Nguyen, Quantitative analysis of COOH-terminated alkanethiol SAMs on gold nanoparticle surfaces, Adv. Nat. Sci.: Nanosci. Nanotechnol., 3, (2012), 045008 (5pp).