

A novel preparation of milk protein/polyethylene terephthalate fabric

J F Zhou^{1,4}, D D Zheng^{1,4}, L Zhong², F X Zhang³ and G X Zhang^{1,4,5}

¹College of Textile & Garments, Southwest University, Chongqing, China

²Chongqing Municipality Fibre Inspection Bureau, Chongqing, China

³School of Chemistry and Chemical Engineering, Southwest University, Chongqing, China

⁴Chongqing Engineering Research Center of Biomaterial Fiber and Modern Textile, Chongqing, China

E-mail: zgx656472@sina.com

Abstract. In this work, $-NH_2$ groups were introduced to polyethylene terephthalate (PET) fibers by nitration and reduction method, and then milk protein was grafted on the nitrated and reduced PET (NR PET) fibers by sucrose glycidyl ether crosslinking agent. FTIR suggested the milk protein was successfully grafted on PET fiber surface. SEM images showed a layer of substance covered on the PET fiber surface. DSC demonstrated an excellent thermal stability of milk protein/PET fiber. The moisture regain was improved by milk protein/PET fiber. Moreover, the crease recovery angle and stiffness were retained by the milk protein/PET fabric.

1. Introduction

PET fabrics are widely used in the textile industry due to its excellent mechanical property, dimensional stability and wash-and-wear property [1]. However, the poor skin-friendly property of PET fabric limits its application in other fields, such as underwear clothes, bedding and sports wearing. The milk protein is skin-friendly due to its wonderful biocompatibility [2]. Therefore, grafting milk protein on the PET fiber surface can improve the wearing comfort of PET fabric and retain the excellent mechanical properties.

Then, the first step is to endow PET fibers reactive species. Various modification technologies were developed, including chemical hydrolysis [3, 4], UV irradiation [5], plasma treatment [6, 7], surface oxidation [8] and aminolysis methods [9, 10]. Nevertheless, these modification methods would result in a decrease of mechanical property or produce waste in the effluent.

In this study, reactive $-NH_2$ groups were introduced to the PET fiber by nitration with gradually concentrating method and reduction process. And then the milk protein could be grafted on the NR PET fibers surface at the presence of sucrose glycidyl ether to produce a milk protein/PET fabric with high skin-friendly and excellent mechanical property.



2. Experimental

2.1. Materials

PET fabrics ($27.0 \text{ tex} \times 22.2 \text{ tex}/480 \times 320,210 \text{ g/m}^2$), sucrose and milk protein were purchased from Chaotianmen market of Chongqing, China. Nitric acid, sodium sulfide, epoxychloropropane, sodiumhydroxide and tetrabutylammonium bromide were purchased from Chengdu Kelong, China.

2.2. The nitration and reduction of PET fibers

The PET fabric ($20 \text{ cm} \times 20 \text{ cm}$) was immersed in 20 g/L HNO_3 solution for 10 min at room temperature with a bath ratio of 1:30. The PET fabric was then cured at 70°C for 20 min in a drying oven. After that, the nitrated PET fabric was washed with distilled water and reduced in a $25 \text{ g/L Na}_2\text{S}$ solution at 98°C for 30 min. Finally, the nitrated and reduced PET fabric with reactive $-\text{NH}_2$ groups was washed with distilled water and dried at 110°C (NR PET).

2.3. Synthesis of sucrose glycidyl ether crosslinking agent

Sucrose (20 g) was firstly dissolved in 200 ml distilled water, and then tetrabutylammonium bromide (0.1 g) and epoxychloropropane (27 mL) were added to the solution. After 30 min reaction at room temperature, NaOH (11 g) was gradually added into the solution, the temperature was kept at 40°C for 4h with a mild agitation.

2.4. Grafting milk protein onto the NR PET fibers

NR PET fabrics were immersed into a mixed solution of sucrose glycidyl ether and milk protein (sucrose glycidyl ether/milk protein: 1/5) ranging from 10 g/L to 50 g/L for 10 min at ambient temperature with a bath ratio of 1:30. Then the immersed PET fabrics were padded to reach a wet pickup of 100% followed by parching at 60°C for 30 min and curing at 110°C for 30 min. Finally, the milk protein/PET fabric was produced. The weight gain rate (WGR) of milk protein/PET fabric was determined by weighing.

2.5. Test methods

2.5.1 Characterization. FTIR measurement of PET fabric samples was carried out by a Spectrum GX spectrometer (Perkin-Elmer Co., USA). SEM images of PET fabric samples were obtained using an S-4800 cold field-emission scanning electron microscope (Hitachi Limited, Japan). DSC of PET fabric samples was measured using a PerkinElmer DSC 200 F3 Maia instrument (Waltham, MA, USA).

2.5.2. Moisture regain. The moisture regains of PET fabric samples were evaluated according to the GB/T 6503-2008 standard test method.

2.5.3. Mechanical properties. The crease recovery angles of PET fabric samples were measured by a YG(B)541D-II automatic digital fabric crease elasticity measuring instrument (Wenzhou DaRong-Textile Instruments Co., Ltd.) following the AATCC method 66-2008 method. An LLY-01 computer-controlled stiffness measurement apparatus (Universal Textile Instruments Co., Ltd., Changzhou, China) was used to determine the stiffness of the PET samples following the ASTM D 1388-96(2002) standard test method.

3. Results and discussion

3.1. The FTIR of PET fabric samples

Figure 1 shows the FTIR spectra of PET fibers. After the grafting of milk protein, the spectrum of milk protein/PET fiber has the same main peaks as that of original PET fibers. However, the spectrum of milk protein/PET fiber exhibits characteristic absorptions of amide group at 1558 cm^{-1} (amide II)

and 1650 cm^{-1} (amide I). Moreover, the absorption peak at 3540 cm^{-1} was assigned to the -NH stretching vibration. These indicated that the successful grafting of milk protein onto the PET fiber.

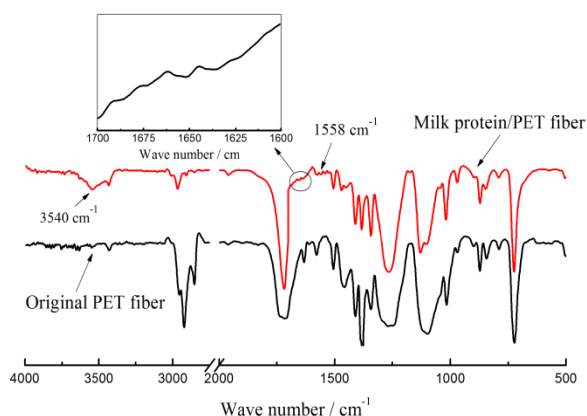


Figure 1. FTIR of PET fabric samples.

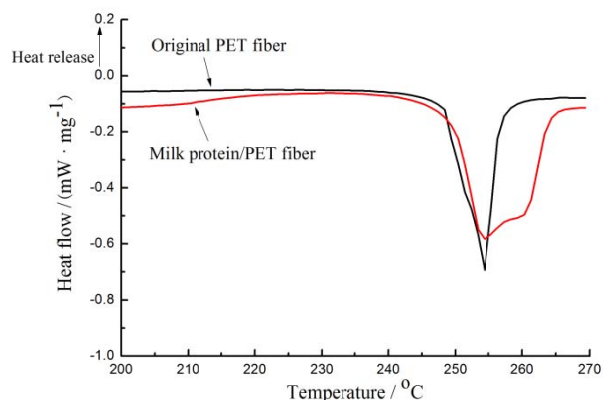


Figure 2. The DSC of PET fabric samples.

3.2. The DSC of PET fabric samples

The DSC thermograms of original PET fibers and milk protein/PET fibers are exhibited in figure 2. The endothermic peak of the original PET fibers is sharp while that of the milk protein/PET fibers is blunt, indicating that the melt of original PET fibers is faster than that of the milk protein/PET fibers. This was because the strong interactions between the -NH_3^+ , -COO^- , and -OH groups in the milk protein and the crosslinking actions prevented the melt of PET fibers.

3.3. The SEM of PET fabric samples

The surface morphology of original PET fibers and milk protein/PET fibers are showed in figure 3. From figure 3, it can be seen that the initial PET fibers are smooth while the milk protein/PET fibers are covered with a layer of substance. These SEM images manifest the milk protein has been successfully grafted on the PET fibers surface.

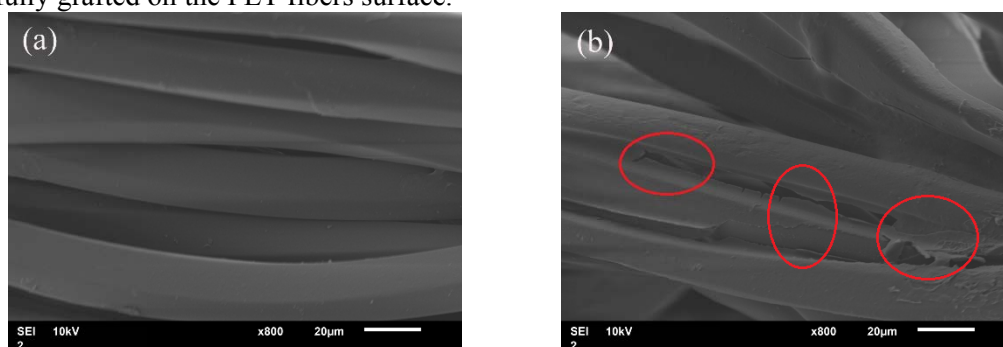


Figure 3. The SEM images of (a) original PET fibers and (b) milk protein/PET fibers.

3.4. The moisture regains of PET fabric samples

Figure 4 shows the relationship between the moisture regain and the weight gain rate. From figure 4, the moisture regain increases with the growth of WGR. The moisture regain of the original PET fabric is 0.45%, whereas that of the milk protein/PET fabric with 3.34% WGR is 1.14%, 153% higher. This was because the -OH , -NH_2 , -COOH and -CONH- groups of milk protein on the surface of milk protein/PET fabric have high ability to absorb water vapor.

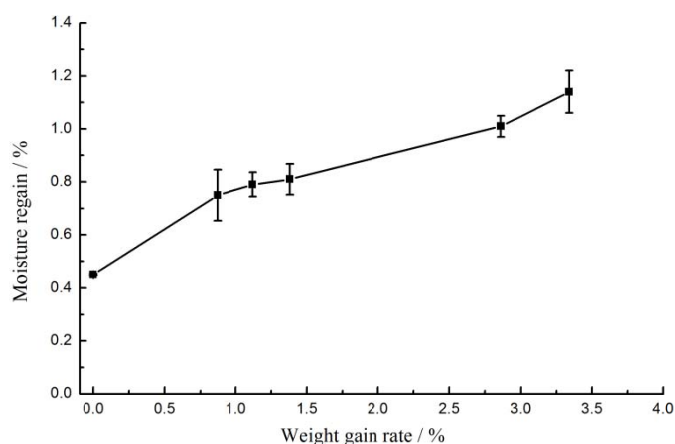


Figure 4. The relationship between the moisture regain and WGR.

3.5. The crease elasticity of PET fabric samples

The relationship between the crease recovery angle and weight gain rate is shown in figure 5. The crease immediate and delay-recovery angles all decreased slightly with the increase of WGR. This is because the grafting of milk protein has introduced some polar groups ($-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$) on the PET fabric surface. The polar groups would interact with each other when folding the milk protein/PET fabric, and the interactions would not disappear thoroughly after the vanished of external force. The crease recovery angle only decreased a little and retained well by the milk protein/PET fabric.

3.6. The stiffness of PET fabric samples

Figure 6 exhibits an increment of the stiffness after grafting milk protein on the PET fabric. The more milk protein was grafted, the higher the flexural rigidity of PET fabric would be. The flexural rigidity of original PET fabric is $0.013 \text{ cN}\cdot\text{cm}$, whereas the flexural rigidity of milk protein/PET fabric with 2.34% WGR is $0.048 \text{ cN}\cdot\text{cm}$. In general, the stiffness of fabric grafted macromolecule will increase. This is because many polar groups of milk protein/PET fabric interact with each other, resulting an increase of stiffness. However, the increment is not so much, and the hand feeling of milk protein/PET is still very excellent.

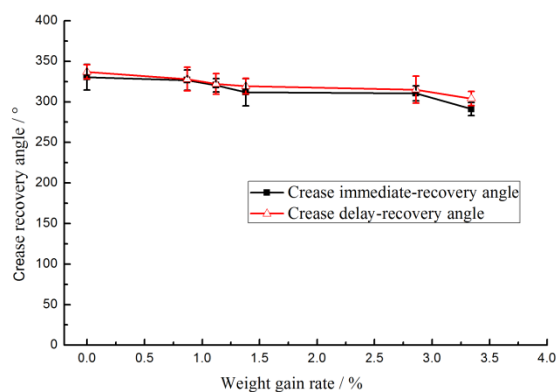


Figure 5. The creasability of PET fabric samples.

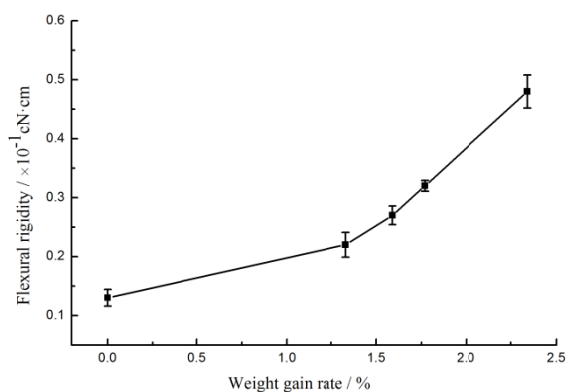


Figure 6. The stiffness of PET fabric samples.

4. Conclusions

Nitration and reduction method endowed the PET fibers reactive $-NH_2$ groups and then the milk protein could be grafted on the PET fiber surface with sucrose glycidyl ether to produce a high functional milk protein/PET fabric. The moisture regain of milk protein/PET fabric increased significantly. The crease elasticity and hand feeling were retained well by the milk protein/PET fabrics.

Acknowledgment

This study was supported by the Key Application and Development Project of the Chongqing Science & Technology Commission (Grant number CSTC2014yykfB50002) and the Fundamental Research Funds for the Central Universities (Project numbers XDJK2013A021 and XDJK2013D002).

References

- [1] Zhang F X, Liang H and Zhang G X 2015 Colorant-free coloration and superhydrophilic modification of poly(ethylene terephthalate) fabric surface by H_2O_2 and nano- TiO_2 ultraviolet photocatalysis *TextRes J* DOI: 10.1177/0040517515603800.
- [2] Yang L F 2007 Estimation of its biological function of milk protein fiber and its product development Shanghai *Text. Sci. Technol.* **35** 46-48.
- [3] Liu Y X, He T and Gao C Y 2005 Surface modification of poly(ethylene terephthalate) via hydrolysis and layer-by-layer assembly of chitosan and chondroitin sulfate to construct cytocompatible layer for human endothelial cells *Colloid Surface B* **46** 117-126.
- [4] Eberl A, Heumann S and Brückner T, et al. 2009 Enzymatic surface hydrolysis of poly(ethylene terephthalate) and bis(benzoyloxyethyl) terephthalate by lipase and cutinase in the presence of surface active molecules *J. Biotechnol.* **143** 207-212.
- [5] Zhu Z M and Kelley M J 2004 Poly (ethylene terephthalate) surface modification by deep UV (172 nm) irradiation *Appl. Surf. Sci.* **236** 46-425.
- [6] Gupta B, Hilborn J G and Bisson I et al. 2001 Plasma-induced graft polymerization of acrylic acid onto poly(ethylene terephthalate) films *J. Appl. Polym. Sci.* **81** 2993-3001.
- [7] Tompkins B D, Dennison J M and Fisher E R 2013 H_2O plasma modification of track-etched polymer membranes for increased wettability and improve performance *J. Membrane. Sci.* **428** 576-588.
- [8] Fávaro S L, Rubira A F and Muniz E C et al. 2007 Surface modification of HDPE, PP, and PET films with $KmnO_4/HCl$ solutions *Polym. Degrad. Stabil.* **92** 1219-1226.
- [9] Croll T I, O'Connor A J and Stevens G W, et al. 2004 Controllable surface modification of poly(lactic-co-glycolic acid) (PLGA) by hydrolysis or aminolysis I: physical, chemical, and theoretical aspects *Biomacromolecules* **5** 463-473.
- [10] Bech L, Meylheuc T, Lepoittevin B and Roger P, et al. 2007 Chemical surface modification of poly(ethylene terephthalate) fibers by aminolysis and grafting of carbohydrates *J. Polym. Sci. Pol. Chem.* **45** 2138-72.