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Abrasion resistance of biaxially oriented polypropylene films coated with nanocomposite hard coatings

Jing Wang, Yaofeng Zhu, Yaqin Fu*

The Key Laboratory of Advanced Textile Materials and Manufacturing Technology Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, China

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ABSTRACT

$KMnO_4$-treated, functionalized, biaxially oriented polypropylene (BOPP) films coated with nano-silica hybrid material were synthesized. The abrasion resistance of the films was examined using a reciprocating fabric abrasion tester. Functional groups were confirmed by Fourier-transform infrared spectroscopy. Contact angle measurements were performed on the BOPP film surface to quantify the effectiveness of the functionalization. Results indicate that the abrasion resistance and roughness of the composite film were significantly affected by the modification of the BOPP film. Water surface contact angle of the modified BOPP films decreased from 90.1° to 71.4°,when $KMnO_4$ concentration increased from 0 M to 0.25 M. Wettability of the BOPP films clearly improved after $KMnO_4$ treatment. Abrasion resistance of the functionalized films coated with hybrid materials improved by 27.4% compared with that of the original film.

1. Introduction

Biaxially oriented polypropylene (BOPP) films are some of the most important commercial polyolefin films because of their excellent properties, such as chemical resistance, toughness, and high thermal stability [1–3]. These films are widely used in food packaging, as protective coating for other films, in printing, and other applications. However, BOPP films have low scratch resistance and lack adhesiveness [4,5].

Sol–gel coatings are frequently used to improve the scratch resistance of polymeric materials. However, the interfacial interaction between highly crosslinked coatings and polypropylene films is low, thereby requiring further modification of the polymer surface. A number of surface modification techniques can be used to improve interfacial interactions, including plasma treatment [6], ion beam treatment [7], corona discharge [8,9], surface grafting [10], and chemical oxidation [11]. Blees et al. [12] reported the use of chromosulfuric acid to modify polypropylene surfaces. This method increases friction by enhancing the interactions of the films using a sapphire indenter. Bellel et al. [13] showed that the surface wettability of polypropylene films can be significantly improved by depositing thin SiO_x layers on the surface. Jeon et al. [14] prepared hard coating films using organosilane-modified boehmite nanoparticles under UV/thermal dual curing. Yin and Wang [15] and Dinelli et al. [16] synthesized hybrid materials using a sol–gel technique by adding water to improve the abrasion resistance of the substrate. However, research on the preparation of a sol–gel solution in the absence of water is limited [17].

In the current study, $KMnO_4$ solution was used to modify the surface of BOPP films to improve adhesion. Using $KMnO_4$ solution for chemical oxidation is more eco-friendly than using other solutions. A sol–gel method in which the sol was synthesized without adding deionized water was used to prepare uniformly dispersed nanosilica. The nanosilica hybrid materials were then coated on the BOPP films using a dip-coating technique.

Abrasion resistance is used to characterize shear deformation imposed by a hard material on another softer material [18–20]. In the present study, $KMnO_4$ solution was used to modify the surface of polypropylene film to enhance the abrasion resistance of films coated with nanosilica hybrid materials.

2. Experimental

2.1. Materials

BOPP films (thickness = 47 μm) were supplied by the Zhejiang Kelly Packaging Materials Company (China). $KMnO_4$, 98% (w/v) H_2SO_4 solution, 37% (w/v) HCl solution, tetraethoxysilane (TEOS), *p*-toluene sulfonic acid (PTSA), 99.7 wt% absolute ethanol, and 3-triethoxysilylpropylamine (KH550) were provided by Hangzhou Mike Chemical Instrument (China). All chemicals were used without further purification.

* Corresponding author. Tel.: +86 13958199325; fax: +86 571 86843151.
E-mail address: fyq01@zstu.edu.cn (Y. Fu).

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Table 1
Factors and levels used in 2^2 factorial design for the chemical surface oxidation of BOPP films.

Factor	Name	Units	Level (−1)	Level (+1)
A	Time	h	2	4
B	$KMnO_4/H_2SO_4$ concentration	$mol\,L^{-1}$	0.05/0.10	0.25/0.10

2.2. Surface modification of BOPP films

The BOPP films were washed with deionized water and dried in a baking oven prior to modification. The films were then cut into 210 mm × 70 mm pieces and then oxidized in $KMnO_4/H_2SO_4$ solution at 50 °C. Time and $KMnO_4/H_2SO_4$ concentration were the two parameters varied for the surface modification treatment (Table 1). Afterwards, the films were washed with HCl solution to remove any oxidation residue from the surface of BOPP films. The films were then dried for 30 min at 100 °C.

2.3. Nanosilica sol synthesis

A total of 25.000 g TEOS, 0.250 g PTSA, and 50 mL ethanol were added to a small reaction vessel at room temperature under stirring for 2 h. The homogeneous mixture obtained was marked as Solution A. Meanwhile, 5.000 g 3-triethoxysilylpropylamine and 50 mL ethanol were added to another small reaction vessel at room temperature under stirring for 2 h. The resulting mixture was marked as Solution B. Solution B was then added to Solution A using the titrimetric method under stirring for 2 h. The obtained sol was stored in a fresh vessel and isolated from air.

2.4. Coating and curing

The BOPP films modified by the $KMnO_4/H_2SO_4$ solution were immersed in the sol solution for 10 min, and then collected at a rate of 2 mm/min. The coated films were aged for 24 h and then freeze-dried at −55 °C and 0.01 MPa in a vacuum for 24 h. The aged films were cured for 1 h at 100 °C. In this study, three samples, labeled F, FC, and FMC, were prepared to determine the effect of the nanocomposite hard coating on BOPP film. F refers to pristine film without $KMnO_4/H_2SO_4$ solution and coating treatment. FC refers to film untreated with $KMnO_4/H_2SO_4$ solution but treated with coating. FMC refers to film treated with 0.25 M $KMnO_4/H_2SO_4$ solution for 4 h and with coating.

2.5. Characterization

The wettability of the specimens treated and untreated with $KMnO_4$ was measured with a water contact angle (OCA 20, Dataphysics, Germany). Changes in the surface functional groups were recorded on a Fourier-transform infrared (FTIR) spectrometer (Nicolet 5700, Thermo Electron Scientific Instruments Corp, USA). Surface topography of the BOPP films before and after the abrasion test was analyzed using a field-emission scanning electron microscope (Ultra 55, Zeiss, Germany) at an operating voltage of 3 kV. Sol dispersion was examined using a transmission electron microscope (TEM) (JEM-2100F, JEOL, Japan) operated at 200 kV. Abrasion resistance of the films was analyzed using a reciprocating wear tester (shown in Fig. 1) with abrasives (1000 Cw, 3M, USA) at a loading of 9 N 1000 times and lasting for about 30 min. The area of contact was 150 mm × 70 mm. Mass loss (M_L) was defined as

$$M_L = \frac{M_0 - M_f}{M_0} \times 100\%$$

where M_0 is the weight of the samples before the abrasion test, and M_f is the weight of the samples after the abrasion test.

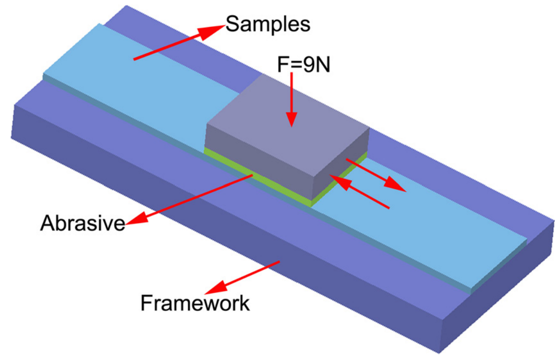

Fig. 1. Schematic of reciprocating wear tester.

3. Results and discussion

3.1. Factors of transmittance

The transmittance spectra show significant differences between the modified BOPP films washed with HCl solution and those that were unwashed (Fig. 2). The results show that the HCl solution can remove any oxidation residue, which makes the treatment ineffective on transmittance. Furthermore, the transmittance of the BOPP films were significantly affected by the drying condition (Fig. 3), indicating that the BOPP films have higher transmittance after freeze drying compared with thermal drying. This result may be because the nano-silica hybrid material treated with freeze drying had uniform, well-dispersed particles with no agglomeration.

3.2. Contact angle

Fig. 4 shows the water surface contact angles of the unmodified BOPP films and those modified by different treatments. Comparing the untreated films with those modified under extreme conditions (0.25 M, 4 h) shows that the BOPP films exhibited increased wettability, when the contact angle was decreased from 90.1° to 71.4°. This decrease was similar to that seen in a previous study using a different oxidation technique [21]. Comparing the condition (0.05 M, 2 h) with the condition (0.05 M, 4 h), the films presented a larger decrease in water contact angle, from 79.8° to 74.5°. This result was due to the increased number of functional groups

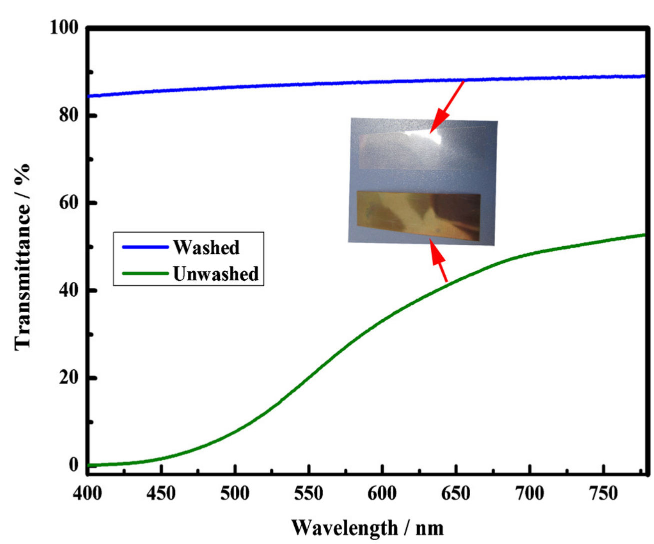

Fig. 2. Transmittance spectra in the visible range for samples untreated and treated with $KMnO_4$ solution.