Applied Surface Science 285P (2013) 697–701

Contents lists available at ScienceDirect

Applied Surface Science

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

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

ARTICLE INFO

Article history:
Received 11 July 2013
Received in revised form 22 August 2013
Accepted 23 August 2013
Available online 30 August 2013

Keywords:
Abrasion resistance
Biaxially oriented polypropylene
Sol–gel
Surface modification
$KMnO_4$

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).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.08.112

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.

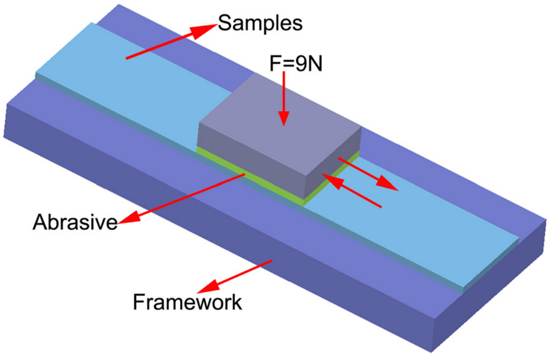

Fig. 1. Schematic of reciprocating wear tester.

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

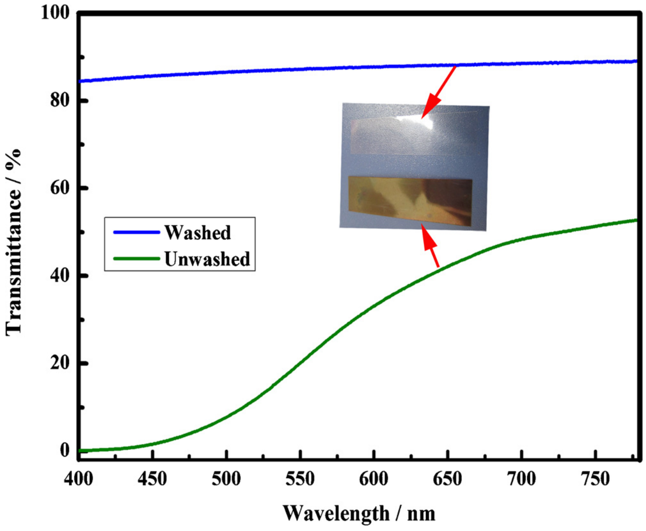

Fig. 2. Transmittance spectra in the visible range for samples untreated and treated with $KMnO_4$ solution.

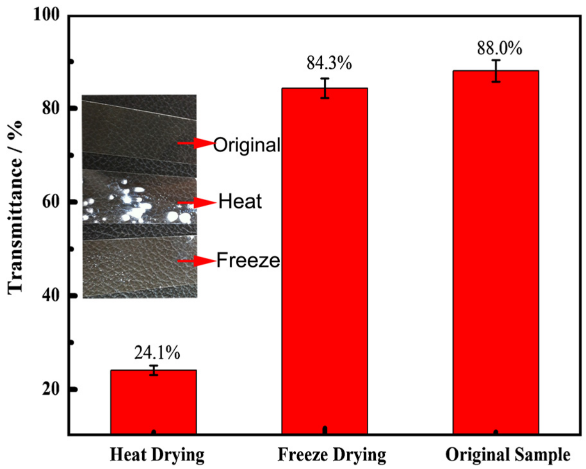

Fig. 3. Transmittance in the visible range for samples with varied drying conditions.

successfully introduced onto the surface of the BOPP films with prolonged time. The water contact angle of the films also decreased from 74.5° to 71.4° between treatments (0.05 M, 4 h) and (0.25 M, 4 h). This increase in solution concentration may have favored the hydrolysis reaction involving the breaking and movement of oxidized polymer chains away from the film surface, and may explain the aforementioned inversion. $KMnO_4$ concentration affected the water contact angle more than the time of modification.

3.3. *Effects of surface modification as analyzed by attenuated total reflectance (ATR)–FTIR*

Figs. 5 and 6 show the FTIR spectra of the BOPP films modified under different conditions. The absorption peaks at 2944, 2912, 1455, and 1373 cm^{-1} were attributed to CH_3 non-symmetric stretching vibrations, symmetric C–H stretching vibrations, CH_3 non-symmetric changing angle vibrations, and symmetric changing angle vibrations, respectively. The main spectral changes found in the region between 1740 and 1600 cm^{-1} in the modified and untreated polymers were attributed to the different carbonyl groups that formed on the modified film surfaces.

Fig. 5 shows no significant change in absorption peaks, indicating that the treatment time is not a major factor affecting film modification. Fig. 6 shows that the (0.05 M, 4 h) BOPP film exhibited small absorption bands at approximately 1740 and 1600 cm^{-1}, which may correspond respectively to COO— and C=O stretching vibrations. The (0.25 M, 4 h) BOPP film showed an intensification of the band at 1740 cm^{-1}, a broad band at around 3200 cm^{-1} attributed to O—H stretching vibrations, and a large shoulder at 1094 cm^{-1} corresponding to C—O stretching vibrations. The spectra of the BOPP films indicated that increasing the $KMnO_4$ solution concentration can significantly promote the oxidation of these films.

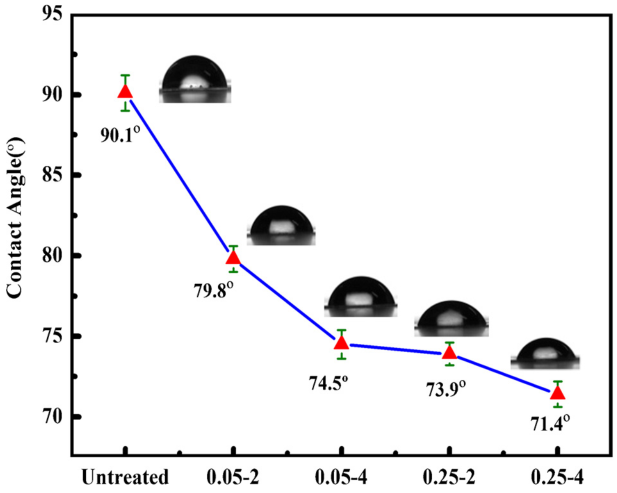

Fig. 4. Drop water contact angle of BOPP film surfaces placed under different oxidation conditions.

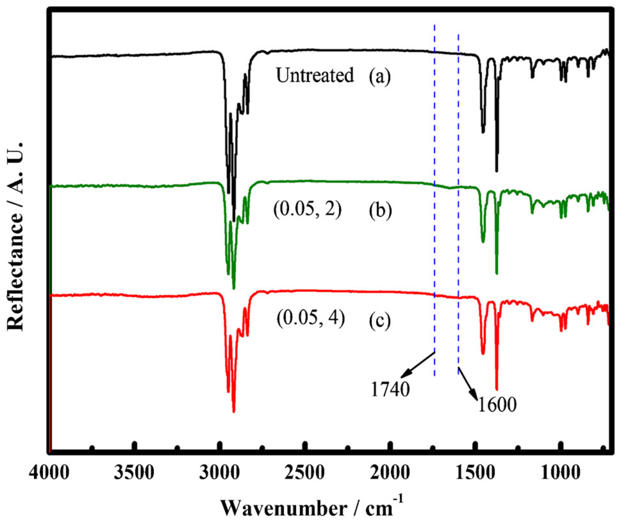

Fig. 5. FTIR–ATR spectra of BOPP films treated with 0.25 M $KMnO_4$ solution for different times: (a) 0 h; (b) 2 h; (c) 4 h.

3.4. *Morphology of nanoparticles and sols*

The morphology and dispersion of silica nanoparticles were investigated using TEM. Fig. 7 shows that the average size of the silica nanoparticles was 30 nm, and that the silica nanoparticles were generally spherical and relatively uniformly dispersed. Nanoparticles can strengthen the abrasion resistance of films [22]. As shown in Fig. 8, the SiO_2 sol can be more stable under isolation from air without adding deionized water. At the same time, the SiO_2 sol rapidly becomes muddy and opaque after the addition of deionized water. Fig. 9 shows that the SiO_2 sol remains transparent after aging for 30 days, indicating that the SiO_2 sol prepared in this work is convenient for storage and application in the industry.

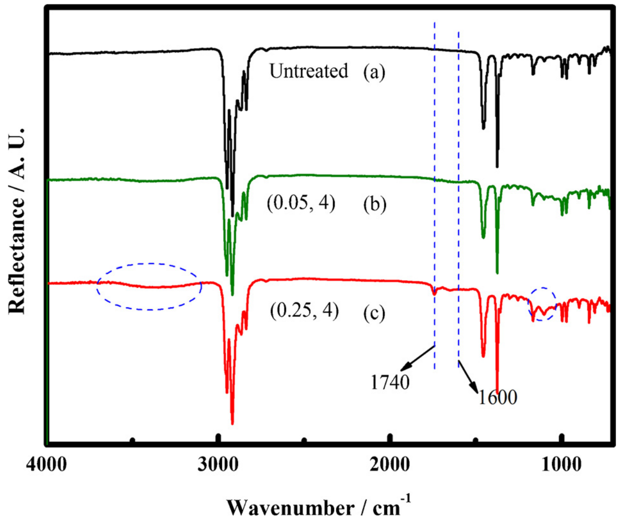

Fig. 6. FTIR–ATR spectra of BOPP film treated with $KMnO_4$ solution at different concentrations for 4 h: (a) 0 M; (b) 0.05 M; (c) 0.25 M.

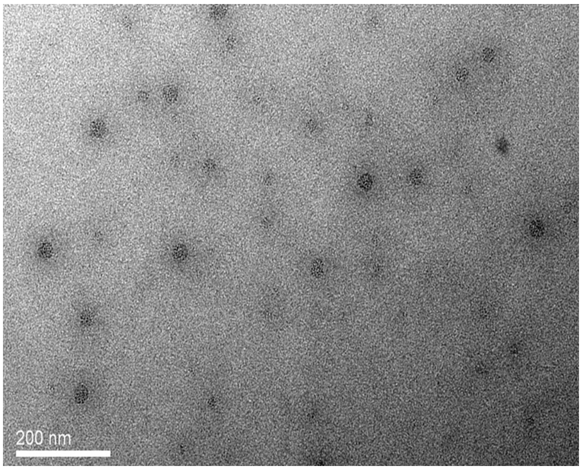

Fig. 7. TEM image of the sol.

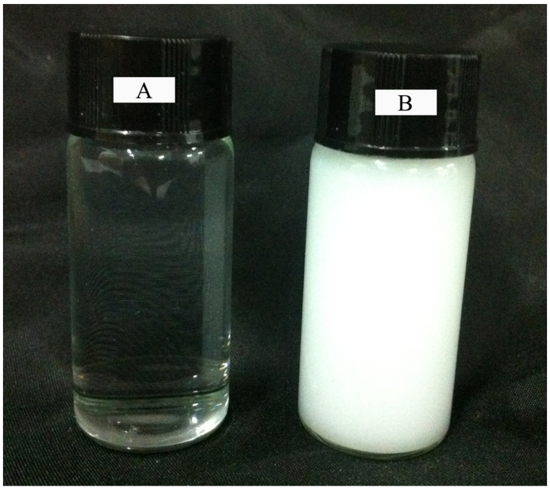

Fig. 8. Photograph of two sols: (A) without deionized water, and (B) with deionized water.

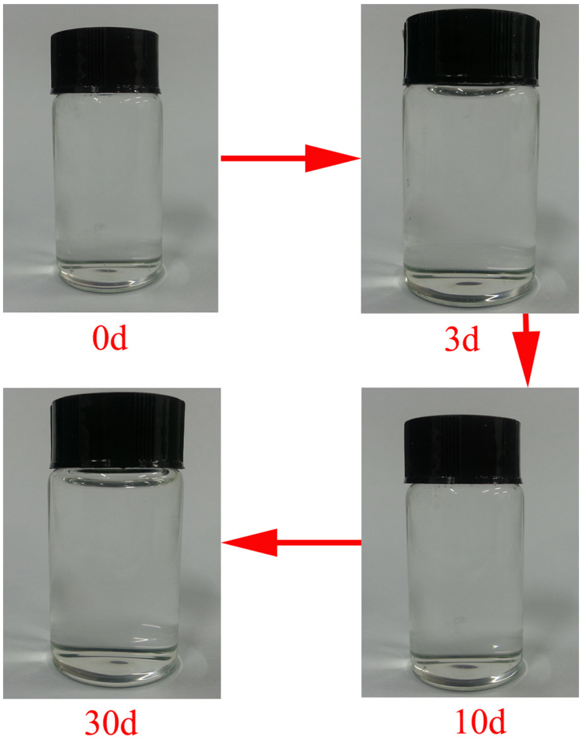

Fig. 9. Sol aging with different times.

3.5. *Abrasion resistance*

The surface morphologies of BOPP films before and after the abrasion test are shown in Fig. 10. Sample F exhibited deep grooves, as seen in Fig. 10(d). Meanwhile, the scratch on the surface of Sample FC was clear, as shown in Fig. 10(e), but not as deep as that on Sample F, indicating that abrasion resistance was improved by the coating. In Fig. 10(f), the grooves on the surface of FCM are shallow, indicating significant improvement compared with Samples F and FC. This result shows that the surface modification of the films

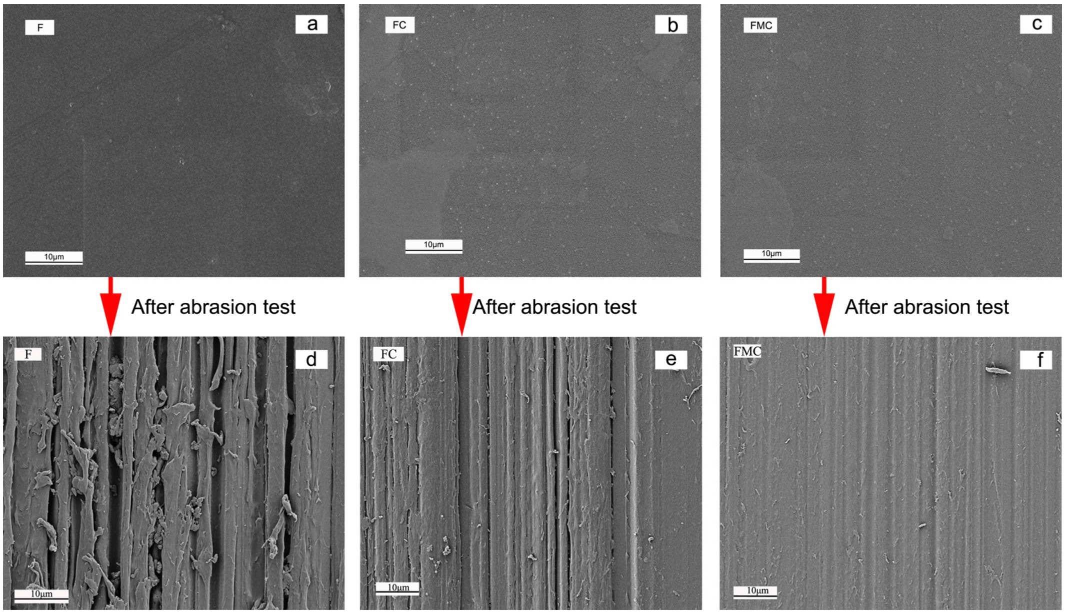

Fig. 10. SEM image of the sample surfaces: (a–c) before abrasion test; (d–f) after abrasion test.

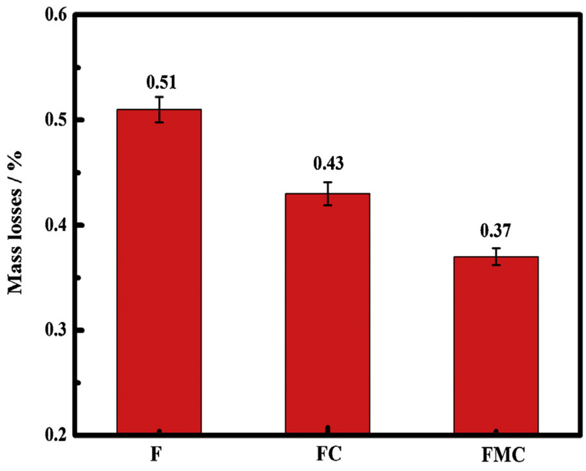

Fig. 11. Mass losses of samples after the abrasion test.

improved the interfacial interaction between the BOPP film and the coating, resulting in higher abrasion resistance.

The losses in mass of the samples are shown in Fig. 11. The mass losses of Samples F, FC, and FMC were 0.51%, 0.43%, and 0.37%, respectively. These results suggest that the surface modification of BOPP films by means of $KMnO_4/H_2SO_4$ and coating treatments can improve the abrasion resistance of these films. These findings, confirmed by SEM observations, were attributed to the strengthening effect of nanoparticles on the film surface [23] and to the presence of polar groups. Consequently, the interfacial property was high [24]. In the current study, a comparison of Sample F with FMC showed that the abrasion resistance of the modified BOPP films increased by 27.4%.

4. Conclusion

A series of surface modification conditions was applied to BOPP films. The results show that increased $KMnO_4$ concentration and prolonged treatment time can significantly increase the interaction between BOPP films and the coating. The $KMnO_4$-treated BOPP films have no effect on transmittance when washed with HCl solution. Uniformly dispersed spherical silica nanoparticles were obtained using the sol–gel method, and the sol can remain stable without the addition of deionized water. The BOPP films exhibited high abrasion resistance after modification, with a maximum improvement of 27.4%.

Acknowledgments

The authors gratefully acknowledge the Instrumental Analysis Center of Zhejiang Sci-Tech University for the use of their characterization facilities. We also thank the technicians for their assistance in the analyses and for the technical discussions.

References

[1] N. Kalapat, T. Amornsakchai, Surface modification of biaxially oriented polypropylene (BOPP) film using acrylic acid-corona treatment: Part I. Properties and characterization of treated films, Surf. Coat. Technol. 207 (2012) 594–601.
[2] J. Ho, T.R. Jow, High field conduction in biaxially oriented polypropylene at elevated temperature, IEEE. Trans. Dielectr. Electr. Insul. 19 (2012) 990–995.
[3] N. Dilsiz, H. Yavuz1, S. Cörekçi, M. Cakmak, Plasma surface functionalization of biaxially oriented polypropylene films with trimethyl borate, Adv. Mater. Chem. Phys. 1 (2011) 50–55.
[4] J. Chu, L. Rumao, B. Coleman, Scratch and mar resistance of filled polypropylene materials, Polym. Eng. Sci. 38 (1998) 1906–1914.
[5] M.L. Maspoch, J. Gamez-Perez, E. Gimenez, O.O. Santana, A. Gordillo, Influence of processing on ethylene–propylene block copolymers: structure and mechanical behavior, J. Appl. Polym. Sci. 93 (2004) 2866–2878.
[6] A. Sarani, N.D. Geyter, A.Y. Nikiforov, R. Morent, C. Leys, J. Hubert, F. Reniers, Surface modification of PTFE using an atmospheric pressure plasma jet in argon and argon + CO_2, Surf. Coat. Technol. 206 (2012) 2226–2232.
[7] S. Venkatachalam, H. Nanjo, K. Kawasaki, Y. Wakui, H. Hayashi, T. Ebina, Preparation and characterization of nanocrystalline ITO thin films on glass and clay substrates by ion-beam sputter deposition method, Appl. Surf. Sci. 257 (2011) 8923–8928.
[8] L.H. Xua, Z.P. Fang, P.A. Song, M. Peng, Effects of corona discharge on the surface structure, morphology and properties of multi-walled carbon nanotubes, Appl. Surf. Sci. 256 (2010) 6447–6453.
[9] S. Tripatanasuwan, D.H. Reneker, Corona discharge from electrospinning jet of poly(ethylene oxide) solution, Polymer 50 (2009) 1835–1837.
[10] M. Kyomoto, T. Moro, Y. Takatori, H. Kawaguchi, K. Nakamura, K. Ishihara, Self-initiated surface grafting with poly(2-methacryloyloxyethyl phosphorylcholine) on poly(ether-ether-ketone), Biomaterials 31 (2010) 1017–1024.
[11] R. Mazeikiene, G. Niaura, A. Malinauskas, Chemical oxidation of aniline and *N*-methylaniline: a kinetic study by Raman spectroscopy, Spectrochim. Acta B 106 (2013) 34–40.
[12] M.H. Blees, G.B. Winkelman, A.R. Balkenende, J.M.J.D. Toonder, The effect of friction on scratch adhesion testing: application to a sol–gel coating on polypropylene, Thin Solid Films 359 (2000) 1–13.
[13] A. Bellel, S. Sahli, Z. Ziari, P. Raynaud, Y. Segui, D. Escaich, Wettability of polypropylene films coated with SiO_x plasma deposited layers, Surf. Coat. Technol. 201 (2006) 129–135.
[14] S.J. Jeon, J.J. Lee, W. Kim, T.S. Chang, S.M. Koo, Hard coating films based on organosilane-modified boehmite nanoparticles under UV/thermal dual curing, Thin Solid Films 516 (2008) 3904–3909.
[15] Y. Yin, C. Wang, Organic–inorganic hybrid silica film coated for improving resistance to capsicum oil on natural substances through sol–gel route, J. Sol–Gel. Sci. Technol. 64 (2012) 743–749.
[16] M. Dinelli, E. Fabbri, F. Bondioli, TiO_2–SiO_2 hard coating on polycarbonate substrate by microwave assisted sol–gel technique, J. Sol–Gel. Sci. Technol. 58 (2011) 463–469.
[17] L. Xu, Y. Fu, M. Du, Investigation on structures and properties of shape memory polyurethane/silica nanocomposites, Chin. J. Chem. 29 (2011) 703–710.
[18] V. Jardret, P. Morel, Viscoelastic effects on the scratch resistance of polymers: relationship between mechanical properties and scratch properties at various temperatures, Prog. Org. Coat. 48 (2003) 322–331.
[19] B.J. Briscoe, S.K. Sinha, Scratch Resistance, Localised damage characteristics of polymer surfaces—a review, Materialwiss. Werkst. 34 (2003) 989–1002.
[20] H. Jiang, R.L. Browning, M.M. Hossain, H.J. Sue, M. Fujiwara, Quantitative evaluation of scratch visibility resistance of polymers, Appl. Surf. Sci. 256 (2010) 6324–6329.
[21] N.Y. Cui, N.M.D. Brown, Modification of the surface properties of a polypropylene (PP) film using an air dielectric barrier discharge plasma, Appl. Surf. Sci. 189 (2002) 31–38.
[22] H. Zhang, L. Tang, Z. Zhang, L. Gu, Y. Xu, C. Eger, Wear-resistant and transparent acrylate-based coating with highly filled nanosilica particles, Tribol. Int. 43 (2010) 83–91.
[23] X. Tao, Z.J. Zheng, X. Kang, X.Q. Ji, Study on the tribological properties of ultradispersed diamond containing soot as an oil additive, Tribol. T. 40 (1997) 178–182.
[24] R.V. Lakshmi, T. Bharathidasan, B.J. Basu, Superhydrophobic sol–gel nanocomposite coatings with enhanced hardness, Appl. Surf. Sci. 257 (2011) 10421–10426.