Mechanical and Abrasion Properties of Polyethylene Terephthalate Films Coated with SiO_2 /Epoxy Hybrid Material

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Abstract: Hybrid materials were prepared using a silane coupling agent, tetraethoxysilane (TEOS) as the precursor, dilute hydrochloric acid as the catalyst, and epoxy as the matrices. The films coated with hybrid materials were expected to improve abrasion resistance and mechanical properties. The morphology, mechanical properties, adhesion, and abrasion resistance of the polyethylene terephthalate (PET) films were characterized using an atomic force microscope, a tensile testing machine, a bagger knife, and a reciprocating fabric abrasion tester. The result of research indicated that the modification significantly affected the abrasion resistance and roughness. The -tensile strength and abrasion resistance of the modified PET films increased by 40% and 50% respectively at 3% TEOS mass fraction.

Key words: *polyethylene terephthalate (PET) films; surface modification; sol-gel; abrasion resistance*

CLC number: TB383 **Document code**: A

Article ID: 1672-5220(2013)06-0521-04

Introduction

Polyethylene terephthalate (PET) films are widely-used materials for soft packaging, electrical insulation, photography, and decoration because of their low cost, excellent gas barrier ability, high transparency, and high dimensional stability[1-3]. However, PET films have very poor scratch resistance[4] and unsatisfactory mechanical properties[5], which limit their development. Epoxy resins are widely used as adhesives[6-8], coatings[9], casting materials[10], and matrix resin for composites[11-12], because of their excellent mechanical properties, low cost, good adhesion, and chemical stability. Thus, a composite of epoxy resin and polyester film seems promising. However, modification only by epoxy resin cannot satisfy the application of higher requirement in mechanical properties and abrasion resistance[13-14]. SiO_2 is usually used as an abrasion material because of its extreme hardness and high thermostability. However, SiO_2 alone is difficult to be used as coating. The introduction of an organic group to coating has good prospects[15-16]. To improve mechanical properties, epoxy resins are used in coating to prepare epoxy resin/silica hybrids[17]. However, little research has been reported in early articles about preparing a sol-gel solution without adding water.

Epoxy resin is most commonly used for top coats in aerospace coating systems because of its high abrasion resistance. In this paper, the sol-gel was prepared using a silane coupling agent, tetraethoxysilane (TEOS) as the precursor, and dilute hydrochloric acid as the catalyst. The sol-gel is used as a modifier to prepare epoxy resin/silica hybrids. The properties of the hybrid materials and the relationship of the contents of silica and silane coupling agents with the tribological properties of the epoxy resin/silica hybrid thin film are concluded in the article.

1 Experimental

1.1 Materials

The reagents used were TEOS, coupling agent (KH550), ethyl alcohol, sodium hydroxide, epoxy resin E-51, and 10% by weight diluted hydrochloric acid, provided by Hangzhou Mike Chemical Instrument Co., Ltd., China. The substrate was PET films (thickness = 271 μm) from Hangzhou Zheng Bang Plastic Company, China. All these chemicals were used without further purification.

1.2 Surface modification of PET films

The films were rinsed with deionized water and dried in a baking oven prior to modification. The sample films were then cut into 10 mm × 100 mm sizes and oxidized in 2% by weight NaOH solution at 90 ℃. After 40 min, the films were pulled out, rinsed with deionized water, and dried in a baking oven for further use.

1.3 Preparation of surface modifier

Epoxy resin and a curing agent were added to a small reaction vessel at room temperature. TEOS, silane coupling agent, ethyl alcohol, and diluted hydrochloric acid were then added to the same reaction vessel. The reaction vessel was placed in a water bath at 60 ℃ under stirring for 15 min. Six parameters of surface modifier were shown in Table 1.

Table 1 Formula of the modifier

Formula	Epoxy /g	Amilan /g	TEOS /g	EtOH /g	HCl /mL	KH550 /g
1	6	4	—	—	—	—
2	6	4	0.3	0.066	0.2	—
3	6	4	0.3	0.066	0.2	0.3
4	6	4	0.5	0.066	0.2	—
5	6	4	0.5	0.066	0.2	0.5

1.4 Coating deposition

A viscous flow modifier was uniformly coated on the modified PET films. The samples were then dried in a baking oven at 70 ℃ for 3 h and kept sealed until further use. The samples were named EP, TEP3, TKEP3, TEP5, and TKEP5 based on the content of their TEOS and silane coupling agent: "3" and "5" stand for the mass fraction of TEOS at 3% and 5%, respectively, and "K" denotes the surface modifier containing the silane coupling agent.

1.5 Characterization

The surface roughness of the coating films was analyzed using an atomic force microscopy (AFM) system (XE-100E, Park Systems, Korea). Transmittance measurements were

Received date: 2013-03-22

Foundation item: Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education of China (No. 2005-383)

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performed using an ultraviolet and visible spectrophotometer (TU-1901, Persee, China) The intensity of the films was measured with GB/T 1040. 3-2006 by a universal testing machine (INSTRON 3367, America). The improvement of strength T_I is defined as

$$T_I/\% = \frac{T_f - T_0}{T_0} \times 100,$$

where T_0 is the strength of PET sample, and T_f is the strength of samples.

The adhesion of the films was determined using a cross-cut tester (QFH, Shanghai High Precision Instrument, China). The hardness of the films was analyzed with abrasives (CS-17, 3M, America) at 9 N loading 1 000 times. The improvement of abrasion resistance M_I is defined as

$$M_I/\% = \frac{M_0 - M_f}{M_0} \times 100,$$

where M_0 is the abrasion loss of PET sample, and M_f is the abrasion loss of samples.

2 Results and Discussion

In the presence of sodium hydroxide, hydrolysis can produce hydroxyl and carboxyl groups that can improve the adhesion of PET films[18-20]. The structure of the product created by the reaction between the silane coupling agent and TEOS is shown in Fig. 1. When the modifier is coated on the films, the amino group of the curing and silane coupling agents easily reacts with the hydroxyl group of the surface of PET films and epoxy resin. The connection between the modifier and PET films can be firm, which affects the mechanical properties.

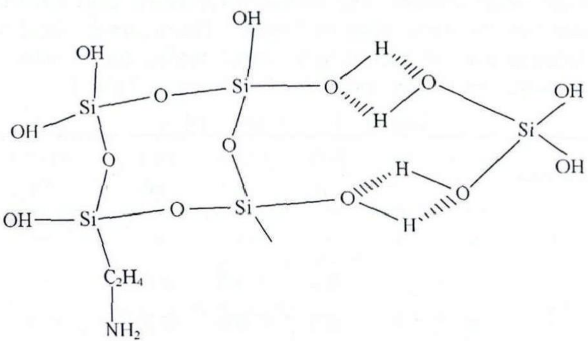


Fig. 1 Schematic diagram of TEOS and silane coupling agent product structure

2.1 Effect of modifier on the surface morphology, abrasion properties, and transmittance

The surface of materials considerably affects scratch resistance and application[21]. Thus, the surface roughness of the samples was observed by XE-100E before and after modification. The results are shown in Figs. 2-4 and Table 2.

The surface roughness R_a of untreated films is 4. 04 nm (Fig. 2), whereas that of PET films treated with epoxy resin is 1. 13 nm (Fig. 3). The surface becomes smoother because uncured epoxy resins have good liquidity at 60 ℃ and can thus fill the holes on the surface. Figures 4(a) - (d) show the AFM images of PET film samples modified under different conditions. The surface of these films is glossier than those shown in Figs. 2 and 3. TEOS and the silane coupling agent make the film surface smoother. In fact, the addition of silane coupling agent increases the fluidity of epoxy resin and improves the surface smoothness of PET films.

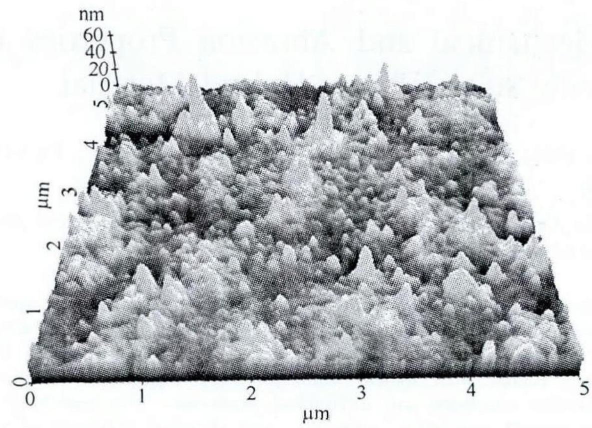


Fig. 2 Surface morphology of unmodified PET film

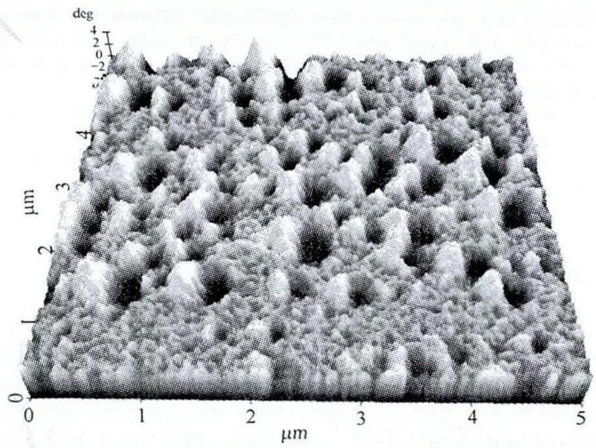
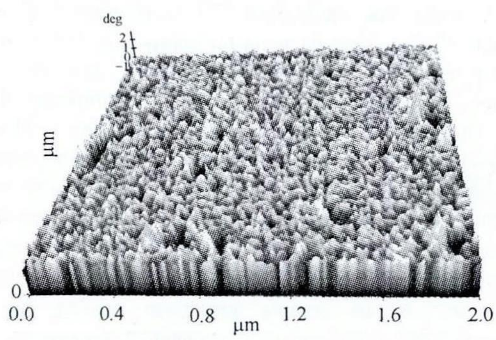
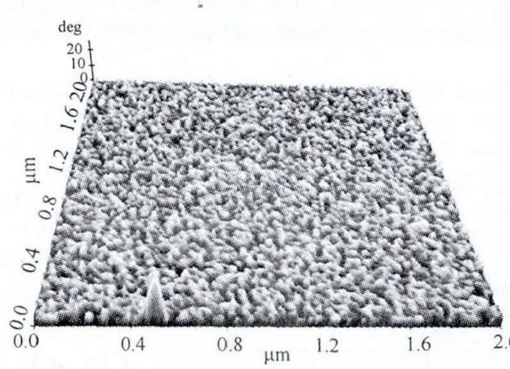


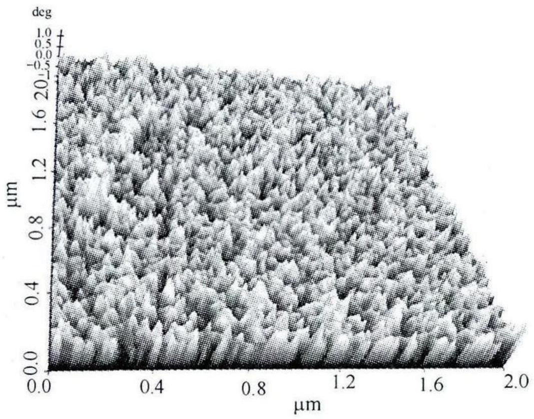
Fig. 3 Surface morphology of PET film modified with epoxy



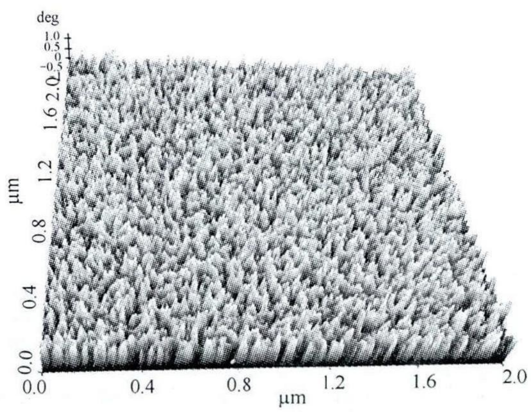
(a)



(b)



(c)



(d)

Fig. 4 Surface morphologies of PET films modified with hybrid materials: (a) TEP3; (b) TEP5; (c) TKEP3; and (d) TKEP5

Table 2 Surface roughness of samples

Samples	PET	EP	TEP3	TKEP3	TEP5	TKEP5
R_a/nm	4.040	1.130	0.328	0.294	0.330	0.286

The levels of bonding fastness of the coatings are generally divided from 0 to 5, with 0 as the best bonding fastness. And with levels up, the bonding fastness become worse. After a scratch test, the surface of the sample was observed with a magnifying glass. The adhesive properties of the modifier with the PET surface are shown in Table 3.

Table 3 Assessment of adhesive power level

Sample	EP	TEP3	TKEP3	TEP5	TKEP5
Appearance	Smooth	Peeling a little	Smooth	Peeling a little	Smooth
Level	0	1	0	1	0

Epoxy resin and the modifying agent containing a coupling agent have good adhesion to PET, whereas hybrid materials without a coupling agent have relatively poor adhesive fastness (Table 3). Given that the coupling agent has dual functional groups that can produce a coupling effect with sodium hydroxide-treated PET, bond performance can be improved.

The samples of PET, EP, and TKEP3 had visible range transmittances of 89.2%, 88.1%, and 87.8%, respectively (Fig. 5). EP and TKEP3 samples had a little lower transmittance than untreated PET film. But the samples all were transparent, which suggested that PET films coated with hybrid materials did not much affect the transmittance.

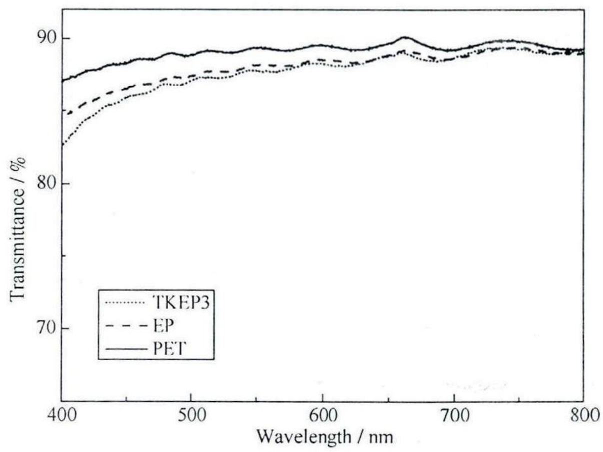


Fig. 5 Transmittance spectra in the visible range for samples of PET, EP, and TKEP3

2.2 Effect of surface modification on the mechanical properties of PET films

The mechanical properties of the samples were tested to study the impact of modification on them. The tensile curves of the samples are shown in Fig. 6.

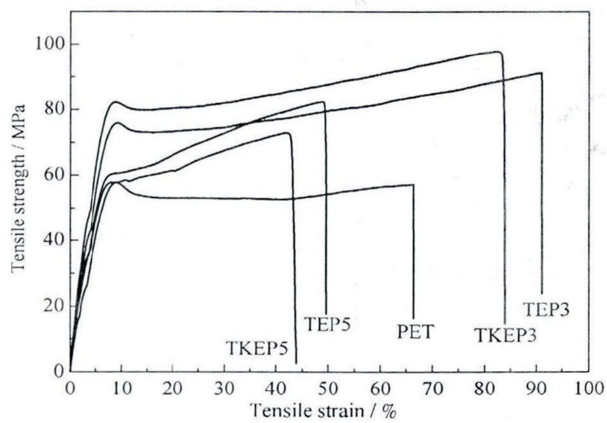


Fig. 6 Tensile curves of samples

The modifier remarkably affects the mechanical properties of PET (Fig. 6 and Table 4). Compared with raw PET, TEP3 and TKEP3 have significantly increased tensile strength and elongation at break. In the preparation of TEP3 and TKEP3, the addition of TEOS, ethanol, and KH550 decreases the viscosity of the system and increases mobility. Consequently, epoxy resin easily infiltrates the holes on the surface of the PET carrier, enabling the PET films to combine with the epoxy hybrid materials and ultimately improve the mechanical properties. On the other hand, no water was added to the sol-gel systems other than a small amount of water in the catalyst. Air moisture hydrolyzes TEOS and the coupling agent in the sol-gel process of the system, which effectively controls the rate of hydrolysis. Thus, the SiO_2 particles in the sample are smaller and more uniform, thereby enabling the self-healing of the PET surface as well as increasing the strength and elongation of the material.

Table 4 Mechanical properties of samples

Sample	PET	EP	TEP3	TKEP3	TEP5	TKEP5
Tensile strength/MPa	57.2	63.3	85.7	97.7	75.4	69.7
Tensile strain/%	66.2	64.6	88.9	83.5	51.2	48.6

Modified TEP5 and TKEP5 have significantly improved strength but decreased elongation. The increments in inorganic particles and stress concentration make the materials more brittle. The shape of each curve is also substantially the same, and the curves show the typical tensile shape of a single material (Fig. 6). The bonding between the modifier and PET is excellent, and the interface presents typical cohesive damage. Overall, when the mass fraction of TEOS is 3%, the tensile strength and elongation of modified PET films significantly increase. From the data of Table 4, at 3% mass fraction of TEOS and coupling agent KH550, the strength of the modified PET films increases by 70%, comparing with samples of PET.

2.3 Effect of surface modification on the abrasion resistance of the PET films

The samples were subjected to abrasion treatment to study the impact of modification on the abrasion resistance of PET. The results are shown in Table 5. The surface treatment of PET films improves their abrasion resistance (Table 5). A significant difference is observed among different modifiers. The wear resistance of PET films treated with the modifier and added with a coupling agent significantly improves, and the amount of wear decreases by more than 40%. What's more, the sample TKEP5 has the best abrasion resistance, with the maximum abrasion of the films improved by 57.7%. These improvements are due to the excellent bonding among the epoxy resin, PET films, and inorganic silica particles, which improves the abrasion resistance of epoxy resin. The coupling agent also improves the interfacial bonding among silica, epoxy resin, and PET.

Table 5 Abrasion loss of samples

Sample	PET	EP	TEP3	TKEP3	TEP5	TKEP5
Abrasion loss/mg	52	45	27	25	30	22

3 Conclusions

(1) PET films coated with hybrid materials are smooth and free of cracks based on visual observation. AFM images show that epoxy resin modified with TEOS has better appearance than unmodified epoxy resin and thus fulfills appearance requirements.

(2) The strength of PET films coated with hybrid materials is significantly better than those coated with unmodified epoxy. At 3% TEOS mass fraction, the strength and elongation at break significantly improve.

(3) The adhesion of PET films coated with the hybrid materials added with a coupling agent is excellent and prevents coating shedding. Epoxy can be improved with a coupling agent in the sol-gel system.

(4) The PET films have good abrasion resistance after modification, with the maximum abrasion of the films being 57.7%.

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