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Transparent and super-gas-barrier PET film with surface coated by a polyelectrolyte and Borax

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Abstract

Thin films of polyacrylic acid (PAA), 4,4'-diphenylmethane diisocyanate (MDI) and borax were separately grown on a poly (ethylene terephthalate) (PET) film to afford a transparent film material with super gas barrier performance. Unlike electrostatic interactions or clay-loaded barrier thin films, which were easily peeled when subjected to exoteric force, excellent peel strength was obtained due to the formation of high density urethane chemical bonds. The gas vapor barrier value is dramatically decreased to the detection limit of commercial instrumentation (<0.005 cc/m²/day). These outstanding performances are attributed to the reaction between sodium metaborate and PAA, which is confirmed using online infrared radiation (IR) and X-ray photoelectron spectroscopy (XPS). The XPS of the multilayer film revealed that borax can permeate the PAA thin layer to completely crosslink the carboxyl group of PAA. The gas barrier properties are obviously improved by the permeating borax solution. In particular, compared to commercial PET film, the oxygen transmission rate (OTR) is reduced from 75 to <0.005 cc/m²/day. Moreover, the OTR value is almost same as that of poly(ethylene-co-vinyl alcohol) (EVOH) film, which is currently the best gas barrier plastic. Therefore, the PET/MDI/PAA/borax composite films show great potential for various packaging materials due to their excellent oxygen and moisture barrier characteristics, as well as other performance.

Introduction

Barrier materials have attracted considerable attention in the fields of food preservation and pharmaceuticals packaging [1] to eliminate water vapor and oxygen in the environment that leads to deterioration of food and drugs. Barrier materials play an increasingly important role in the field of packing application. Approximately twenty years ago, layer-by-layer (LbL) self-assembly was first reported by Decher [2] and most often exploits ionic processes. This LbL method was widely used for thin film surface modification and provides a way to construct multifunctional thin films through alternating exposure to different attractive molecules or particles [3–5]. These species are usually

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☑ Yuezhong Meng mengyzh@mail.sysu.edu.cn positively and negatively charged polymers [6]. In this process, the film thicknesses can be effectively controlled by different experimental conditions. In this way, the desired surface properties can be obtained and applied to substrates of any shape [7–11]. Most of all, in some harsh conditions, like strong acid, strong basic, the hydrogen bonded LbL assemblies may be disassembled [12].

As a common barrier material, polyethylene terephthalate (PET) has been widely studied and used in the fields of pharmaceuticals packaging and food preservation. In order to obtain thin PET composite film with high barrier properties, several methods have been reported, such as the following: (1) Deposition of a thin inorganic film onto a surface by the vacuum vapor deposition process [13]. This

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barrier structure has reached an oxygen permeability of lower than $5 \times 10^{-8} \text{ cm}^3$ (STP) $\text{m}^{-2} \text{dav}^{-1} \text{Pa}^{-1}$ (at 37 °C and 30% RH). However, this method suffers from problems that include cracking and poor adhesion to plastic substrates [14–16]. (2) Layer-by-layer (LbL) self-assembly, though alternating exposure of a PET film to oppositely charged aqueous mixtures [17, 18]. This barrier structure reached an oxygen transmission rate (OTR) below the detection limit of commercial instrumentation ($<0.005 \text{ cc/m}^2/\text{day/atm}$ at 23 ° C and 0% RH) [19] Although ionic or hydrogen bonded self-assembly processes are experimentally simple and broadly useful, they have drawbacks. Specifically, ionic or hydrogen bonded LbL assemblies can disassemble under conditions (strongly acidic, strongly basic, or high ionic strength solutions) where the ionic or hydrogen bonds are unstable [20].

It is well known that covalent layer-by-layer assembly can modify the surface of film materials effectively [21]. First, covalent layer-by-layer assembly is usually a spontaneous favorable process, and covalent bonding affords high stability to the produced thin film, allowing it to withstand harsh conditions such as extreme pH or ionic strength [22–26]. Second, many different reactions can be adapted to create a multilayer graft to afford a wide variety of functional polymers [26–30]. Third, this process can be performed in aqueous or organic solutions depending on the type of reaction [27–34]. Finally, a covalent LbL assembly process leaves behind excess reactive groups inside the multilayer matrix, which can further react with other molecules to tailor the functional interfaces of the product for other functions [35–41].

It is known that borax can dissociate completely into equal quantities of boric acid [B (OH₃)] and sodium metaborate [NaBO₂•4H₂O] [42]. It can also yield many useless byproducts such as B_5O_6 (OH)⁻. Borax is widely used as a cross-linking agent because it can be hydrolyzed to form sodium metaborate; however, sodium metaborate only forms in alkaline solution [43].

Given the above-mentioned considerations, in this study, a stable polymer multilayer film composed of a single polymer layer, which was cross-linked using borax for barrier applications, was designed and developed by covalent LBL assembly. Polyacrylic acid (PAA) is usually used in barrier material research, but the hygroscopicity of PAA limits its application range. In this article [Na₂B₄O₇] was used as a cross-linking agent to cross-linked PAA to obtain a dense barrier layer. The superior barrier properties of the LBL multilayer film were confirmed by OTR and water vapor transmission rate (WVTR) measurements. The mechanism investigation shows that the superior barrier property improvement is mainly attributed to the reaction of borax with PAA. The adhesive properties of PET and barrier layers in the presence or absence of MDI were measured by standard peel strength assays.

Experimental

Materials

PAA (Mw = 450,000 g/mol), 4, 4'-diphenylmethane diisocyanate (MDI), reagent grade toluene, borax (Mw = 201.22g/mol) and reagent grade methanol were purchased from the Aladdin Industrial Corporation (Guangzhou, China). Corona PET (PET thickness = $180 \,\mu m$), corona PET (PET thickness = $18 \,\mu$ m), and corona polypropylene (PP thick $ness = 25 \mu m$) were purchased from the Foshan Plastic Co. Ltd. (Foshan, China), and the thickness of PET (180 µm) was determined by using scanning electron microscopy (SEM). Double component poly-urethane adhesive (main agent: curing agent = 5:1), and reagent grade ethyl acetate were purchased from the Dongguan Lanbao Material Co. Ltd. (Dongguan, China). A twin-roller machine was purchased from Shenzhen Kejing Zhida Technology Co., Ltd. (Shenzhen, China). Ultrapure Milli-Q water was used for all experiments.

Preparation of composite films

Preparation of starting materials

(I) Aqueous solutions of PAA (1~8 wt.% deionized water) were prepared by stirring in water at 90 °C for 2 h, and the PAA DI water solution was left to sit at ambient temperature for 12 h to allow completing the dissolution. When using the PAA solution directly, it was found that it could not coat on corona PET if the PAA DI water solution was left to stand for less than 12 h. (II) MDI was dissolved in toluene and stirred for 10 min at room temperature to form a 0.05~0.8 wt.% solution. (III) Borax and sodium hydroxide (2:1) were dissolved in a mixture of methanol (95 vol.%) and deionized water (5 vol.%), and stirred for 4 h at 40 °C to yield a borax solution.

Fabrication of LBL composite films of PET/MDI/PAA/borax

As shown in Fig. 1, the 0.1~0.8 wt.% MDI toluene solution were bar-coated onto a corona PET substrate (SKC, SH-34, 18 µm) using a coating stick with a gap of 9 µm, which can accurately control the thickness of the liquid film. The MDI surface treated PET film was placed in a drying cabinet at 80 °C for 10~60 min. (The symbol PM_x represents substrates coated with MDI coatings, and "x" indicates the content of MDI in toluene). Then, the PM_x film was cooled to room temperature in desiccators. The 1~8 wt.% PAA



Fig. 1 Schematic preparation of PET/MDI/PAA/Borax thin film a and the chemical reactions of the components in circles (b-d)



Fig. 1 (continued)

deionized water solution was bar-coated onto the MDI surface treated PET film surface (PM_xA_y represents PM films coated with PAA coatings, and "y" indicates the content of PAA). It is distinctly important that the PMA surface is free of defect. The PMA composite films were then placed in a drying cabinet at 80 °C for 60 min. Finally, the PMA films were dipped into borax solution using dipcoating machine at a speed of 40 mm min⁻¹. The PMA films were immersed in the above-prepared borax solution for 5 s to prevent PAA from washing away into the solution (PM_xA_yB_z represents PMA films further coated with borax coatings, and "z" indicates the content of borax). The finally coated substrates were dried at 80 °C for 3 h and then keep the samples in anhydrous desiccators for 1 h prior to characterization.

Fabrication of PMAB/PU/BOPP laminated films for peel tests

PMAB/PU/BOPP laminated film were prepared by coating PMAB films with a layer of two-component polyurethane adhesive, followed by the laminating BOPP films with a twin-roller machine just before the polyurethane adhesive solvent was evaporated. The thickness of the twin-roller machine was controlled at 47 μ m. The laminated films were placed at ambient temperature for 2 h, transferred to vacuum oven at 50 °C for 12 h. The drying temperature was set to 50 °C to avoid different thermal shrinkages of PET and BOPP, which may affect the peel strength between the coated PET and BOPP. The prepared laminated films were thereafter subjected to peel strength measurements.

Characterization

X-ray photoelectron spectroscopy (XPS)

The chemical composition of the film surfaces before and after each stage was investigated using an INCA ENERGY 300 XPS with monochromatic Al radiation. Data analysis was performed using Casa XPS software. The PET, PET/ MDI, PET/MDI/PAA and PET/MDI/PAA/borax sample films were cut into pieces (2×2 cm; testing area: 4 cm^2). The measurements were performed in duplicating for each sample.

Scanning electron microscopy

PET (thickness: $180 \mu m$)/MDI/PAA/borax films were frozen in liquid nitrogen for 30 min and fragmented to produce a cross-section. The films were attached onto the side edge of copper, and were dried under an infrared lamp for 10 min. Fractured surface measurements were observed via SEM (SEM, JEOL JSM-6330F). For fractured surface measurements, all specimens were coated with a thin layer of gold prior to examination.

Atomic force microscopy (AFM)

AFM images of the surface structure of the film specimens were imaged in tapping mode under stable air conditions (25 °C and 0% RH) using a Solver Pro-M atomic force microscope (NT-MDT, Russia). Before analysis, all samples were cut into pieces (1×1 cm; testing area: 1 cm^2) and mounted on glass stubs using carbon adhesive tape. The measurements were performed in triplicate for each sample and all the samples were conditioned at 25 °C and 0% RH for 6 h before testing.

T-peel test

The peel strength between the PET polymer film and BOPP polymer film was determined by a 180° peel test performed by a HIWA200 Universal Testing Machine with a cross-head speed of 50 mm/min at 20 ± 5 °C according to the GB/T2791-1995 standard. Five specimens of per sample were measured, and the average results were recorded.

On line infrared test

In this work, in situ infrared experiments can indicate weather PAA reacts with $B_5O_6(OH)^-$ and the reaction rate. This test was performed using iCIRTM 4.3 reaction analysis software with an in situ React IR 45 m (Mettles Toledo) spectrometer equipped with a silicon probe. The silicon probe was inserted into the PAA solution to collect an infrared background for about 10 min. The borax solutions were poured into the PAA solution to detect the reaction. This work showed consistent results was repeated for four times.

Optical properties

The optical properties of the films were measured using a light transmittance/haze tester (WGT-2s, Yidian Physical Optical Instrument Co., Ltd., China) according to GB 2410-2008. Samples were cut into circles (diameter: 50 mm; testing area: 50 cm^2). Three specimens of each sample were measured and the average results were recorded. To eliminate the influence of temperature and humidity the tests were conducted at 25 °C and 50% RH.

Light transmittance is relative to both T_1 (incident light flux) and T_2 (penetrating luminous flux), and results were normalized using the following Equation 1:

$$T_t = \frac{T_2}{T_1} \times 100 \tag{1}$$

Haze is relative to T_1 (incident light flux), T_2 (scattering light flux of the instrument), T_3 (penetrating luminous flux) and T_4 (scattering light flux of the instrument and sample), and results were normalized using the following Equation 2:

$$\mathbf{H} = \left(\frac{\mathbf{T}_4}{\mathbf{T}_2} - \frac{\mathbf{T}_3}{\mathbf{T}_1}\right) \times 100\tag{2}$$

Oxygen transmission rate

According to ASTM D3985-05, OTR measurements were operated at 23 °C under dry conditions. The OTR of film specimens were measured with a Y202D oxygen permeation analyzer (GBPI Packing Test Instruments Co. Ltd, Guangzhou, China), which operates using a coulometer theory and an equal-pressure method. It has two chambers that are separated by the test sample, the upper and lower chambers are filled with oxygen (test gas) and nitrogen (carrier gas), respectively. The oxygen permeating the test sample is captured by nitrogen, and then carried to the sensor. The amount of oxygen detected by the sensor and the transmission rate (OTR) were determined. Moreover, all film specimens were cut into 100-mmcircles (testing area:

Table 1 Elemental composition of the PET surface

Sample surface	C1s (%)	O1s (%)	N1s (%)	Na (%)	B (%)
Pure PET	66.61	28.86	0	0	0
PET/MDI	66.42	29.24	0.50	0	0
PET/MDI/PAA/ Borax	28.06	40.98	0.95	11.97	18.04

201 cm²) and dried in vacuum for 24 h before analysis. Two specimens of each sample were tested and the results were averaged.

Water vapor transmission rate

The WVTR measurements was measured at 23 °C under 85% RH conditions. The WVTRs of abovementioned composite films were measured with "infrared detection sensor methods" (ISO 15106-2) using a WVTR analyzer (PERMATRAN-W Model 3/61, Mocon. Inc., USA). During measurement, the test gas (water vapor) is present in the upper half of the test cell, and the carrier gas (nitrogen) fills the lower half of the test cell. The cell halves are separated by the film sample to be tested. Water vapor that permeates the film is picked up by the carrier gas nitrogen, which exits the cell and reaches the sensor. Mocon WVTR software was used to calculate the WVTR. Moreover, all film specimens were cut into 40-mm circles (testing area: 29 cm^2) and dried in vacuum at room temperature for 24 h before analysis. All samples were usually placed on an uncoated surface at the feed side during the WVTR measurement according to the actual conditions. The measurements were performed six times for per sample and the results were averaged.

Results and discussion

Surface treatment of PET film

XPS can only detect the composition of the surface of a sample to ~1.5 nm. Thus, the PET and PMA multilayer film were cleaned with Milli-Q water and the PM multilayer film was cleaned with anhydrous toluene. To remove any physically adsorbed materials. Chemical modification of the PET film surface was determined by XPS analysis, and the elemental composition is summarized in Table 1. It was found that the pristine PET film did not contain N element on the surface. However, N elements appeared on the PET surface after MDI treatment. This demonstrates that MDI successfully reacted with the hydroxyl groups on the PET surface (Fig. 1b). This was also proved by the T-peel test of PET/MDI/PAA/Borax/BOPU/BOPP composite films which have a higher peel strength than without MDI treatment.



Fig. 2 O 1s binding energy distribution for a pure PET film, b PET/MDI_{0.1} film, and c PET/MDI_{0.1}/PAA₂, and d B 1 s binding energy distribution for PET/MDI_{0.1}/PAA₂/Borax₃ film

As shown in Fig. 2a, XPS results reveal that the O 1 s binding energy at 533.31 eV relative to 531.74 eV corresponds to C=O and C-O bonds. The PET film modified with MDI has a C-O/C=O ratio of 1.02 (Fig. 2b); after coated with PAA, the C-O/C=O ratio increases to 1.41 (Fig. 2c). The increase in the C-O/C=O ratio suggests that new ester functional groups are formed on the surface of the PET/MDI/PAA film. This implies that the ester functional groups are successfully grafted onto the surface (Fig. 1c).

Figure 2d shows the XPS results for the surface of PET/ MDI/PAA coated with borax. The results indicate that the B 1 s binding energies at 191.22 eV, 191.87 eV, 192.12 eV, and 192.44 eV (Fig. 2d) correspond to B–N bonds, Na₂B₄O₇, B–O–C bonds and B–N–C bonds [44–46]. This means that the borax not only reacts with PAA but also permeates the PAA coating layer to react with MDI (Fig. 2d). It should be noted that the intensities of B–N bonds, Na₂B₄O₇, B–O–C bonds and B–N–C bonds are much low than those of C=O and C–O bonds, indicating their extremely low concentrations. The detectable B-N bonds arise from the presence of trace MDI that migrates onto the surface of PET/PAA, as evidenced in Table 1.

SEM examination for PET/MDI/PAA/Borax composite films

To examine the thickness of the barrier layer coated on the PET (Thickness: $180 \mu m$) surface, the cross sections of multilayer-coated PET films were carefully examined using SEM. PET with a thickness of $180 \mu m$ was chosen instead of PET with a thickness of $180 \mu m$ to avoid substrate deformation. In Fig. 3a, the SEM micrographs clearly show that MDI/PAA/Borax layers were well deposited on the surface of the PET film. Particularly, in Fig. 3b, the coated layer on the PET surface is visible as dark lines in a laminar structure, similar to previously observed structures. The thickness of the multilayer was estimated as $2 \sim 3 \mu m$ on average. The smooth surface of the



15=413 SEI 15.0kV ×1,500 10µm WD22mm b

Fig. 3 SEM images of PET/MDI_{0.1}/PAA₂/borax₃ composite film crosssection **a** magnification $95 \times$ image, **b** magnification $1500 \times$ image

coating layer was considered to explain the excellent barrier properties.

AFM examination of the surface of PET/MDI/PAA/ borax composite films

AFM surface images of PET virgin substrate and MDI modified PET substrates are shown in Fig. 4. The surface roughness of MDI-modified PET film (~3.0 nm) is much clearer than that of pristine PET film (~0.1 nm) (Fig. 4a, b), which were all calculated using a $1 \times 1 \mu m$ area methodology. The surface of PET virgin film shows an even topography (Fig. 4a). However, the surface of MDI-modified PET film is covered by a small quantity spherical particles (Fig. 4b), which indicates that there are small agglomerations on MDI coated PET surface.

The surface of the PET/MDI/PAA film, shown in Fig. 4c, in AFM images, clearly demonstrates a smooth, continuous surface morphology after coated with the PAA layer. The surface of PET/MDI/PAA (~2.5 nm) is less rough than that of PET/MDI (~3.0 nm) (Fig. 4b, c). A desert-like surface morphology of the PET/MDI/PAA/borax film is shown in Fig. 4d. The roughness of the surface of the PET/MDI/PAA/borax film is almost negligible, with a value of ~0.46 nm. This demonstrates that there is no aggregation when borax cross-links with PAA and dramatically increases the density of PAA, which is believed to account for the superior barrier performance.

Barrier properties of PMAB composite films

The polar functional groups of a polyelectrolyte generally offer a superior barrier property to non-polar gases. Reducing the free volume of a polymer can improve gas barrier performance by cross-linking the polymers. For example, borax as a cross linking agent can yield sodium metaborate under alkaline conditions.

It should be noted that, for the PET/MDI/PAA multilayer film, the content of MDI can greatly affect the oxygen barrier properties. Figure 5 shows the relationship of OTR measured at 23 °C and 0% RH vs. MDI content. We changed the loading level of MDI from 0.1wt % to 0.8wt % to investigate the optimal value. The OTR increases from 11.2 to 36.5 cc/m^2 /day with increasing MDI content. This could be due to the aggregation of MDI; some drawbacks emerge at the interface between the PAA coating layer and PET matrix.

Therefore, the OTR value is the lowest when 0.1wt% MDI is used. We adopted this MDI content to serve as the adhesive to bind PAA and PET layers together.

Figure 6 shows the OTR and water vapor transmission rate (WVTR) of PET/MDI_{0.1}/PAA films vs. PAA content. A clear decrease in OTR is observed when coating 1 wt% PAA solution onto the surface of the PET/MDI_{0.1} composite film. However, with further increasing the PAA concentration, no obvious decrease in OTR was observed when PAA concentration exceeded 2 wt%. This could be due to the barrier properties of PAA itself, which limited improvements to the composite film. Consequently, 2wt % PAA concentration was selected to coat PET/MDI bilayer films.

Figure 7 presents the OTR of PET/MDI_{0.1}/PAA₂/borax_z films coated with varying borax concentrations; the OTR decreases dramatically with increasing borax concentration. As discussed in the Experimental section, the borax was dissolved in a mixture of methanol and water using the borax solution preparation method. This means that the borax solution contains a higher concentration of water for 6 wt% borax. Consequently, the PAA on the surface of the



Fig. 4 AFM topography images of specimen surfaces: a virgin PET film, b $PM_{0.1}$ multilayer film, c $PM_{0.1}A_2$ multilayer film and d $PM_{0.1}A_2B_3$ multilayer film

PET/MDI_{0.1}/PAA₂ film can be dissolved in borax solution, leading to increased OTR. This can well explain why the OTR of the PET/MDI_{0.1}/PAA₂/borax₆ film is higher than that of the PET/MDI_{0.1}/PAA₂/borax₃ film. The optimum value of the borax concentration is 3 wt%. The excellent results are due to the reaction PAA with Na₂B₄O₇ to yield a dense layer, which can be identified via in situ infrared experiments.

Figure 8 is a three-dimensional stack plot of IR spectra collected every 30 s during the reaction of PAA and borax.

The online IR spectra for the first ten minutes represent pure PAA. After that, the sodium metaborate reacts with PAA rapidly upon addition of an alkaline solution of borax to the PAA deionized water solution. As shown in Fig. 8, carboxylated PAA reacts with sodium metaborate to form BCO bonds, which can be seen at the peak centered at 1028 cm⁻¹ assigned to BCO bond stretching in the online IR spectrum (Fig. 1d) [47]. After 3 min of reaction, the intensity of the peak at 1028 cm⁻¹ decreases with further increasing reaction time due to the precipitation of PAA



Fig. 5 Oxygen gas transmission rate (OTR) of PET/MDI_x/PAA₂ films coated with varying MDI concentrations



Fig. 6 Oxygen gas transmission rate (OTR) and water vapor transmission rate (WVTR) of PET/MDI $_{0.1}$ /PAA_y films coated with varying PAA concentrations

upon reacting with sodium metaborate for long period. This is due to the formation of the highly cross-linked products between PAA and borax.

Borax reacts with NaOH to yield sodium metaborate. As shown in Fig. 8; sodium metaborate cross-linked with the carboxylic groups in PAA. The cross-linking reaction can not only decrease the free volume of PAA but also enhance the barrier property of the PAA layer on the PET film. The increase in density can also account for the decrease in hydrophilic functional groups with decreasing OTR for the PMAB films. The OTR decreased from $9.8 \text{ cc/cm}^2/\text{day}$ to <0.005 cc/cm²/day after coating borax with different concentration from 0 wt% to 3 wt% on PM_{0.1}A₂ films. This phenomenon can also be attributed to the lower free volume of PAA after PAA is cross-linked with borax. Meanwhile,



Fig. 7 OTR of $\text{PET/MDI}_{0,1}/\text{PAA}_2/\text{borax}_z$ films coated with varying borax concentrations

the water vapor barrier property of the PET/MDI/PAA/ borax film is obviously enhanced compared to virgin PET and PET/MDI/PAA films.

Table 2 lists the gas barrier performance of different polymer films used for flexible packaging applications [48, 49]. The oxygen and water vapor permeability of the PET/MDI/PAA/borax composite film is lower than those of PE, PP, PA6 and PET, and is even slightly lower than that of ethylene-co-vinyl alcohol (EVOH). It can also be as good as those of PET films carrying deposited inorganic and polymeric layers, which usually have excellent barrier properties and are efficient to produce. Thus, the PET/MDI/PAA/borax composite films exhibit the best gas barrier performance and have strongly competitive potential as packaging materials. Moreover, the preparation process of the PET/MDI/PAA/borax composite film is relatively easier preparation methods for other commercially available barrier film materials.

Optical properties of prepared composite films

For most packaging applications, especially applications in food packaging, film transparency is very important. Thus, we examined the transparency using the method of photographic images. PMAB films have a high level of transparency, similar to virgin PET films upon visual inspection (Fig. 9). As shown in Table 3, the transparency of PET/MDI/PAA/borax film is 90% of the transparency of virgin PET film. The high optical clarity of the PET/ MDI/PAA/borax film can be attributed to the chemical structure, i.e., the amorphous polymer structure and molecular scale distribution of borax within the crosslinked polymers. **Fig. 8** Three-dimensional stack plot of the IR spectra collected every 30 s during the crosslinking reaction of PAA and sodium metaborate



Table	2	Gas	barrier	performance	of	some	polymer	films	used	in
flexibl	e r	backa	ging app	olications						

Sample	OP (cc mm/($m^2 24 h$))	WVP (g mm/(m ² 24 h))
Pure PET	1.35	0.54
PET/MDI _{0.1} /PAA ₂ / borax ₃	< 0.005	0.02
PP	28.8	0.01
PE	50-200	0.5-2
PA6	1.41	0.5-10
EVOH-E	0.001-0.01	20~25

Table 3 Optical properties of PET and PET/MDI/PAA/borax film

Sample	Transmittance (%)	Haze (%)
PET	89.5	1.95
PET/MDI/PAA/borax	88.7	2.28

 Table 4
 Peel strength properties for neat PET and various coating layers

Sample	Average peel strength (kN/m)
(PET/PAA)/borax/PU/PP	0.06
(PET/MDI/PAA)/borax/PU/PP	0.27
(PET/MDI/PVA)/borax/PU/PP	0.10

T-peel test of PET/MDI/PAA/borax/PU/BOPP composite films

To investigate the bonding strength between PET film and PAA and assess the effect of isocyanide groups on the bonding of PET to PAA, T-peel tests were performed and the experimental results are summarized in Table 4. The Tpeel test was performed on PET/MDI/PAA/borax/PU/ BOPP composite films using a temperature-controlled HIWA200 Universal Testing Machine. To compare the



Fig. 9 Photographic images of virgin PET film and PET/MDI/PAA/ borax film

peel strength between BOPP and surface modified PET films, three different samples were prepared and measured. Table 4 reveals that the T-peel strength of PET/MDI/PAA/borax/PU/BOPP films was greatly enhanced compared to the corresponding films without MDI treatment. The tensile strength increases from 0.06 kN/m to 0.27 kN/m. Finally, for comparison with commercially available film, the T-peel strength of (PET/MDI/PVA)/borax/PU/PP was also determined as shown in Table 4. It is apparent that the bonding strength between BOPP and the surface modified PET is the highest one, demonstrating that the PET film subjected to surface modification can meet the needs of commercial lamination technology and industrial processes. The high strength is attributed to the hydroxyl and carboxyl groups on PET that react with the isocyanides groups on MDI.

Conclusions

Transparent thin films with superior gas barrier performance were successfully fabricated using layer-by-layer coating of polyacrylic acid (PAA) and borax solutions on surface modified PET films. The experimental results demonstrate that the covalent assembly of esterification between PET and MDI, as well as between MDI and PAA, can be used to readily fabricate multilayer coatings on the surfaces of PET substrates. The barrier material layer of PAA can be bonded tightly to PET substrates as confirmed by T-peel examination. The oxygen transmission rate (OTR) and WVTR decrease dramatically with increasing PAA concentration. An OTR value of $<0.005 \text{ cc/m}^2/\text{day}$ can be achieved after cross-linking of PAA using borax solution, which is the best value yet reported for a monolayer polymer composite film reported up to now. The polycarboxylic acid-containing multilayer-coated PET/MDI/PAA/Borax composite films are highly promising as packaging materials for food, medicine and other applications.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing financial interests.

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