



Article Polyacrylate Decorating Poly(ethylene terephthalate) (PET) Film Surface for Boosting Oxygen Barrier Property

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Abstract: Polymeric barrier materials are critical in contemporary industries for food, medicine, and chemical packaging. However, these materials, such as PET films, are impeded by the optimization of barrier properties by virtue of molecular design. Herein, a new methyl methacrylate-methyl acrylate-diallyl maleate-maleic acid (MMA-MAc-DAM-MA) was synthesized to tailor the surface properties of PET films for maximizing oxygen barrier properties. During the MMA-MAc-DAM-MA coating and curing process, the chemical structure evolutions of MMA-MAc-DAM-MA coatings were characterized, indicating that the cross-linking conversion and proportion of -COOH groups are critical for the oxygen barrier properties of coatings. The inherent -COOH groups are transformed into designed structures, including intramolecular anhydride, inter-chain anhydride and retained carboxylic acid. Therein, the inter-chain anhydride restraining the activity of coated polymer chain mainly contributes to enhanced barrier properties. The thermal properties of novel coatings were analyzed, revealing that the curing behavior is strongly dependent on the curing temperatures. The impacts of viscosity of the coating solution, coating velocity, and coating thickness on the oxygen permeability (Po2) of the coatings were investigated using a gas permeability tester to explore the optimum operating parameters during practical applications, which can reduce the Po_2 of PET film by 47.8%. This work provides new insights on advanced coating materials for excellent barrier performance.

Keywords: film; barrier property; surface modification; cross-linking; gas transport

1. Introduction

High-barrier packaging materials are capable of inhibiting the penetration of osmotic molecules such as oxygen, water vapor, and carbon dioxide, and they have been extensively applied to prolong the shelf life of food [1,2], cigarettes, medicine, and chemicals [3–6]. The solution-diffusion model is a classic model used to describe the penetration of osmotic molecules through barrier materials. It divides the penetration into three steps: (1) the osmotic molecules dissolve into the membrane by the contact surface, (2) the osmotic molecules diffuse in the membrane under a concentration gradient, and (3) the osmotic molecules desorb at the other side of the membrane [7–9]. The second step is the principal process that affects the transfer process [10,11]. There are two models to explain diffusion [12–14]. One is the free volume model, which holds that the increased activity of chains brings about new conformation to arouse the expansion of free volume, which would provide more free space for the movements of permeating molecules [15–18], thus facilitating the diffusion process [19]. The second model is based on the percolation theory, which suggests that improving the activity of polymer chains is critical to creating channels for the osmotic molecules' transmission [20], which can greatly shorten the time of



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). diffusion [21–23]. So, it is convincing that reducing the activity of molecular chains is the decisive method to block diffusion [24–26].

PET film as a packaging material does not fully fulfill the requirement of the oxygen barrier property [27,28]. Polymeric coating, which is characterized by a simple operation, low cost [29,30], diverse functionality [31,32], and benign adhesion [33], is promising for the functionalization of PET film. Currently, two types of polymer coatings have been mainly studied to promote the barrier capability of PET films: crystalline polymers and amorphous polymers [34,35]. The former includes polyvinyl alcohol (PVA) [36] and polyvinylidene chloride (PVDC) [37]. The other one is an amorphous polymer coating with a cross-linking structure and entangled network [38]. However, the development of crystalline polymers is impeded by several shortcomings during practical applications. For example, PVA with rich hydroxyl groups brings out two problems: One is that high-density hydroxyl groups easily form hydrogen bonds [39], resulting in the low solid content but high viscosity of the solution [40] and huge difficulty in the coating operation. The other is that the coating is moisture absorption-sensitive, easily resulting in the serious deterioration of the oxygen barrier property [41] and peeling strength [42]. For PVDC, the surface tension of emulsion is larger than PET film, causing surface cratering in the coating process to reduce the barrier property [43–45]. Moreover, both the weak adhesion of PVDC coating with PET substrate [46–48] and the brittleness of the coating deteriorate the barrier property [49–51]. However, solvent-based amorphous polymers with a high oxygen barrier property [52–54] are promising solutions for avoiding these problems [55–57].

Herein, an amorphous polyacrylate was synthesized by methyl methacrylate (MMA)methyl acrylate (MAc)-diallyl maleate (DAM)-maleic acid (MA) in the coating process, and the oxygen barrier properties of as-prepared composite PET films were investigated. We characterized and analyzed the cross-linking structure and density of MMA-Mac-DAM-MA at different curing temperatures and their influences on the oxygen barrier properties of PET films. The influence of the viscosity of the coating solution on the surface morphology of the coating, coating velocity, and coating thickness were also investigated to optimize their oxygen barrier performances.

2. Experimental

2.1. Material

Methyl methacrylate (MMA), methyl acrylate (MAc), diallyl maleate (DAM), maleic acid (MA), benzoyl peroxide (BPO), and N-methylpyrrolidone (NMP) are all analytical reagents and were purchased from Aladdin (Shanghai, China). These chemicals were used without further purification.

2.2. Polymer Synthesis

MMA (50 g), Mac (12 g), DAM (0.5 g), MA (15 g), and NMP (55 g) were mixed with BPO (0.21 g) in the four-necked flask. The temperature was raised to 88 °C. The mixture was stirred for 2 h. Then, the temperature was increased to 90 °C, and the mixture of NMP (130 g) and BPO (0.14 g) was dripped into the solution. The dripping time was controlled for 4 h. Finally, the temperature was raised to 94 °C and maintained for 4 h. After that, the solution was cooled to room temperature.

2.3. Preparation of Oxygen Barrier Coatings

Vacuum distillation was employed to remove solvent from the synthetic polymer. The solvent-free polymer was ground into powder. Then, the powder was extracted thrice with deionized water at 50 °C to remove the residual monomer of MA. Additionally, the purified powder was filtered by vacuum distillation again to eliminate water. Then, the anhydrous powder was dissolved in NMP to compose a polymer solution with specific viscosity. The polymer solution was coated with a specified thickness on PET film (210 mm \times 297 mm \times 15 µm) with a small coater (type PT-5000PL, Baoda, Dongguan, China) at designated coating speed. The coating rod was 16 inches long and available

in 4 diameters. Finally, the coated PET films were stored at the assigned temperature of 130–210 °C in an air circulation oven (DHG-9140 A, Yiheng, Shanghai, China).

2.4. Characterization

2.4.1. Morphology of Coatings

The substrate and coated PET films were all tested by F20 thin-film analyzer (Filmetrics, San Diego, CA, USA) to measure their average thickness. The surface morphology of the coating was investigated by BX51 polarization microscope (Olympus, Tokyo, Japan) using the light transmission method with the magnification of 100 times.

2.4.2. Oxygen Permeability of Coating

The oxygen permeability (Po_2) of the coated PET films was determined by OX-TRAN Model 702 Gas Permeability Tester (Mocon, Minneapolis, MN, USA) at 80% RH and 23 °C. The thickness of the PET substrate was about 12 μ m, 15 μ m, 25 μ m, and the thickness of the coating was related to specified requirements.

2.4.3. Structure of the Coating

The coatings were separated from the coated PET film. Additionally, the coating samples were analyzed by Nicolet IS5 Fourier Transform Infrared Spectroscopy (FT-IR) (ThermoFisher, Waltham, MA, USA). The spectral resolution was 4 cm⁻¹. The scans were 32 times. Additionally, the range was from 600 to 3600 cm⁻¹.

2.4.4. Curing Mechanism Analysis

The coatings were separated from the coated PET film. The thermal performances of the coatings were detected by DSC200F3 Differential Scanning Calorimetry (DSC) (NET-ZSCH, Selb, Germany) at a heating rate of 5 °C/min under nitrogen atmosphere. The test interval was from 10 to 220 °C.

2.4.5. Thermogravimetric Analysis

The coatings were separated from the coated PET film. The coating samples were measured by TG209F3 Thermogravimetric analysis (NETZSCH, Selb, Germany). The test interval was from 10 to 450 $^{\circ}$ C under nitrogen atmosphere with a heating rate of 10 $^{\circ}$ C/min.

3. Results and Discussion

3.1. Synthesis and Characterization of MMA-MAc-DAM-MA Copolymer

The MMA-MAc-DAM-MA copolymer was synthesized from MMA, MAc, DAM, and MA. The schematic diagram of synthesizing process is shown in Figure 1, and the structure was studied by FT-IR, as shown in Figure 2.

As for the results of FT-IR spectra, the stretching bands at 1149 and 1193 cm⁻¹ correspond to the stretch vibration of -C-O-C-groups. The peak at 1448 cm⁻¹ refers to $-CH_3$ groups, and the 1730 cm⁻¹ peak is attributed to C=O groups. The characteristic peak of the -OH bond rose at 3338 cm⁻¹ in the MMA-MAc-DAM-MA coating, owing to the -COOH groups. In the spectrum of the copolymer, the bands of the vinylic bond at 1640 (from MMA and MA) and 1647 cm⁻¹ (from DAM) all disappeared, which reveals that MMA, MAc, DAM and MA reacted.



Figure 1. Schematic diagram of MMA-MAc-DAM-MA copolymer synthesized process.



Figure 2. FTIR spectra of monomers (MA, MMA, Mac, and DAM), compared with the copolymer (MMA-MAc-DAM-MA).

3.2. Effect of Curing Temperature on the Barrier Performance of Coated PET Film

The polymer coating of MMA-MAc-DAM-MA contains a considerable number of carboxyl groups (–COOH), which can form inter-chain crosslinking during the curing process. This is critical for improving the oxygen barrier performance of coating because the enhanced cross-linking degree could restrict the movement of the copolymer chains. As for coating, the formation of the cross-linking structure requires heating. So, curing temperature was the most significant parameter influencing the oxygen barrier property of the coated PET films in the coating process. First, we prepared the coated PET films with a consistent thickness of 19 μ m (15 μ m substrate and 4 μ m coating) and dried them at specific temperatures for exactly 40 s each. Afterward, the *P*o₂ of the coated PET films was investigated (Figure 3).



Figure 3. Po₂ of coated PET film cured at different temperatures.

The Po₂ of the coated PET film at different curing temperatures was divided into four regions. The first is 130–140 °C (region 1). The coating cured at these two temperatures did not improve the oxygen barrier property of the PET films. The second region is 150–170 °C (region 2). When the curing temperature was 150 °C, the Po_2 of the coated PET film decreased dramatically by 14.3%. This is evidence that the barrier performance improved. However, when the curing temperature was set at 160 and 170 °C, the Po2 of the coated films just slightly decreased by 1.7% and 3.8%, respectively, similarly to the coating cured at 150 °C. So, the coatings cured at the region 2 temperatures were all able to block oxygen, but their barrier capacities were similar to each other. The third region is the curing temperature at 180–190 °C (region 3). When the curing temperature was 180 °C, the barrier performance of the coating improved significantly again. The Po_2 of the coated film decreased by 14.4% compared to that cured at 170 °C. When the curing temperature was 190 $^{\circ}$ C, the Po₂ of the coated film decreased by 22.6%, further contrasting with the coated film cured at 180 °C. Additionally, it was the minimum record of coated PET films at any curing temperature. So, the coatings cured at region 3 can better improve the oxygen barrier of the PET film. The fourth region is the treatment temperature of 200–210 °C (region 4). The Po₂ of the coated PET films cured at region 4 were 0.864 and $0.971 \times 10^{-15} \text{ cm}^3 \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$, respectively, both greater than the Po₂ of the coated PET films cured at 190 °C ($0.795 \times 10^{-15} \text{ cm}^3 \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$), indicating their barrier performances degraded.

3.3. Analysis of Cross-Linking Structure of Curing Coating

The oxygen barrier property of the coating is dominated by the structure and activity of the coated polymer chains. So, we applied FT-IR to analyze the structure of the coating dried at specific temperatures. The results are shown in Figure 4a.

When the coating was cured at 130 and 140 °C, 1630 cm⁻¹ was the C=O stretching of –COOH, as shown in Figure 4b. The stretching peak was absent at 1776 cm⁻¹ and 1832 cm⁻¹, as shown in Figure 4c,d, respectively. This indicates that the structures of anhydride (–CO–O–O–C–) do not exist in these coatings. So, the –COOH groups remained without cross-linking. The schematic of the presumed coating polymer chain structures at 130 and 140 °C is shown in Figure 5a. Similarly, the structure analyses of the as-prepared coating at other curing temperatures are also proposed in Figure 5.



Figure 4. FTIR spectra of the coatings cured at different temperatures in the range of (**a**) 3600–600 cm⁻¹, (**b**) 1670–1610 cm⁻¹, (**c**) 1780–1768 cm⁻¹, and (**d**) 1840–1827 cm⁻¹.



-COOH goups with narrow space -COOH goups with narrow space

Figure 5. The structure of coating cured at different temperatures: (**a**) coating cured at 130 and 140 °C; (**b**) coating cured at 150 °C; (**c**) coating cured at 160 °C, (**d**) coating cured at 170 °C; (**e**) coating cured at 180 °C; (**f**) coating cured at 190 °C; (**g**) coating cured at 200 °C; (**h**) coating cured at 210 °C.

For the coating cured at 150 °C, a stretching peak is displayed at 1776 cm⁻¹ which is related to the symmetric –C=O of –CO–O–C–, as shown in Figure 4c. This indicates a few –COOH groups were converted to anhydride structures. Combining with the result as shown in Figure 3, the barrier performance of the coating improved dramatically when the treatment temperature of 150 °C replaced 140 °C. This illustrated that these anhydride structures can effectively limit the movement of the chain. So, it is possibly the cross-chain anhydride created by dehydration. Additionally, we assume this cross-linking is formed

by the –COOH groups, whose chain spaces are narrower than intramolecular carboxylic acid spacing (Figure 5b).

For the coating cured at 160 °C, the intensity of the 1630 cm⁻¹ peak, as shown in Figure 4b, is weaker than that of the coating cured at 150 °C. The intensity of the 1776 cm⁻¹ stretching peak is greater than that of the coating cured at 150 °C, as shown in Figure 4c. This illustrates that more –COOH groups are turning to –CO–O–O–C– groups. However, the diminution of –COOH groups fails to bring evident improvement of barrier performance, as shown in Figure 3. So, this indicates that the vanished –COOH groups tend to convert to the structure that has a very weak restriction on the movement of the chain. This is most likely intramolecular anhydride, which is useless for improving the oxygen barrier ability of coating.

For the coating cured at 170 °C, the intensity of 1630 cm⁻¹ peak weakened again compared with that of the coating cured at 160 °C, as shown in Figure 4b, while the intensity of the 1776 cm⁻¹ stretching peak strengthened, as shown in Figure 4c. However, the improvement of the barrier performance is still poor. Similar to the coating cured at 160 °C, the –COOH groups also convert to intramolecular anhydrides. The schematic of the presumed coating polymer chain structures at 170 °C is shown in Figure 5d. We found that at the higher temperatures of 160 and 170 °C, the –COOH groups tend to transform into intramolecular anhydrides instead of inter-chain cross-linking anhydrides. So, we speculate that the –COOH groups that transformed into inter-chain cross-linking anhydride at the lower temperature of 150 °C possess a narrower chain space than intramolecular ones.

For the coating cured at 180 °C, the intensity of the 1630 cm⁻¹ stretching peak decreased, as shown in Figure 4b, while the intensity of the 1776 cm⁻¹ peak strengthened, as shown in Figure 4c. It can be observed that the stretching peak of reverse symmetric –C=O of –CO–O–C– emerged at 1832 cm⁻¹. More anhydride structures were formed. With the *P*o₂ of the coated PET film cured at 180 °C decreasing again, a part of –COOH groups may have converted to inter-chain anhydrides. Additionally, this may be distinctive of the interchain cross-linking anhydrides formed at 150 °C. The chain spaces of cross-linking –COOH groups at this temperature are probably more than intramolecular spaces. The schematic of the presumed coating polymer chain structures at 180 °C is shown in Figure 5e.

For the coating cured at 190 °C, the 1630 cm⁻¹ peak was eliminated, as shown in Figure 4b. It was demonstrated that the –COOH groups of the coating were consumed completely (Figure 5f). The intensity of the stretching peak at 1776 cm⁻¹ kept growing, as shown in Figure 4c. Additionally, the intensity of the stretching peaks at 1832 cm⁻¹ was the strongest of all the coatings, as shown in Figure 4d. Since the Po_2 of the coated PET film was the lowest, as shown in Figure 3, the coating may be characterized by the maximum proportion of inter-chain anhydrides.

For the coating cured at 200 °C, the peak at 1630 cm⁻¹ was eliminated, as shown in Figure 4b. However, the intensity of the stretching peak at 1834 cm⁻¹ was weaker than that of the coating cured at 190 °C, as shown in Figure 4d. At this curing temperature, the curing speed is excessive, so the molecular chain movement is restricted prematurely to form large network cross-linking structure, which results in the decrease in the proportion of cross-linking carboxylic acid. The –COOH groups that were too late to participate in the inter-chain cross-linking reaction transformed into intramolecular anhydrides or remained as they were. That is why the Po_2 of the coated PET film treated at 200 °C rebounds, as shown in Figure 3. The schematic of the presumed coating of the polymer chain structures at 200 °C is shown in Figure 5g.

For the coating cured at 210 °C, the 1630 cm⁻¹ peak appeared again, as shown in Figure 4b. The intensity of the stretching peaks at 1776 and 1832 cm⁻¹ were all weaker than that of coatings cured at 190 or 200 °C. This curing temperature exceeds the boiling point of NMP (203 °C). Therefore, the solvent volatilizes quickly, arousing the rapid curing of the coating. This leads to the incomplete rearrangement of molecular segments and finally results in –COOH residue. Thus, the *P*₀₂ of the coated PET film treated at 210 °C

exceeded those at 190 and 200 $^{\circ}$ C, as shown in Figure 3. The schematic of the presumed coating polymer chain structures at 210 $^{\circ}$ C is shown in Figure 5h.

3.4. DSC Analysis of Coatings Cured at Different Temperatures

The DSC of the curing coatings is shown in Figure 6. All coatings cured at different temperatures showed two endothermic intervals. The first is the glass transition of the coating (from 30 to 95 °C). The second is the temperature interval of the residual –COOH that corresponds to the transformation of anhydride by dehydration in the heating process.



Figure 6. DSC spectra of coatings cured at different temperatures.

However, the two intervals' characteristics vary for coatings cured at different temperatures as follows: (1) the glass transition temperatures (Tg) of the coating cured at 130 and 140 °C were 46.2 and 46.1 °C, respectively. Additionally, the area of the second endothermic peak was larger than that of coatings cured at other temperatures. This indicates that the coating cured at these two temperatures contains abundant -COOH groups without reacting. (2) the second endothermic peak of the coating cured at 150 $^{\circ}$ C decreases, which indicates that the content of -COOH in coating reduced, while the Tg rose to 50.1 °C, which demonstrates the diminished –COOH groups converting to the structure that could restrict the motion of chain. (3) The Tg of the coating cured at 160 and 170 °C were 38.3 and 41.5 °C, respectively, which are below that of the coating curried at 150 °C. However, the area of the second endothermic peak decreased significantly. This indicates, again, that the diminished -COOH groups were converted to intramolecular anhydride, because, with the consumption of -COOH, the proportion of acid anhydride in the molecule increased gradually, but the proportion of hydrogen bonds decreased. Restricting the motion of the polymer chain had a negative effect. So, the Tg values of coatings descended. (4) The Tg of the coating cured at 180 °C was 57.6 °C, and the area of the second endothermic peak decreased further. From the analysis of FT-IR, it is known that the new cross-chain anhydrides that strengthen the restricting of chain motion are formed at this treatment temperature. So, the Tg and oxygen barrier properties all rose again. (5) The Tg of the coating cured at 190 °C was 65.9 °C, which was the highest of all the coatings. The chains with the lowest mobility can be attributed to the maximum proportion of inter-chain cross-linking. (6) The Tg of the coating cured at 200 °C was 63.0 °C, which was less than that of the coating cured at 190 $^{\circ}$ C. However, the area of the second endothermic peak was similar to that of the coating cured at 190 °C. It corresponds exactly with the precondition that when most of the–COOH groups are depleted, the coating cured at 200 °C becomes less proportionate in the cross-linking structures between chains, and the oxygen barrier performance is also inferior to that of the coating cured at 190 °C. (7) The Tg of the coating at 210 °C descended to 58.4 °C. The area of the second endothermic peak was enlarged compared with that of the coating cured at 190 °C. This is attributed to the remaining –COOH groups from the rapid curing. The remained -COOH groups resulted in the decreasing numbers of

cross-linking structures and releasing the mobility of partial molecular chains. So, the Tg and oxygen barrier performance of the coating both descended. The DSC results are consistent with the Po_2 test data in Figure 3 and the structure analysis conclusions about Figure 4. So, the oxygen barrier performance relates to the cross-linking structure and density, which are determined by the curing temperature in the coating process.

3.5. The Effect of Coating Thicknesson Oxygen Barrier Property of Coated Film

It is well known that the permeability of dense polymeric films decreases with their increasing thickness. For coated PET films, the effect of thickness on coated film permeability can be expressed as follows in parallel-type Equations (1) and (2):

$$\frac{d}{p} = \frac{d_c}{p_c} + \frac{d_s}{p_s} \tag{1}$$

$$d = d_c + d_s \tag{2}$$

where *d* is the thickness of the coated film, *p* is the permeability of the coated film, d_c is the thickness of the coating, p_c is the permeability of the coating, d_s is the thickness of substrate, and p_s is the permeability of the substrate. Combine Equations (1) and (2) to Equation (3) to achieve:

$$\frac{d_c + d_s}{p} = \frac{d_c}{p_c} + \frac{d_s}{p_s} \tag{3}$$

where d_s , p_s and p_c are fixed, as set $\frac{d_s}{p_s}$ as constant c_0 , d_s as constant c_1 , set p_c as constant c_2 . The Equation (3) is converted to Equations (4)–(8):

$$\frac{d_c + c_1}{p} = \frac{d_c}{c_2} + c_0 \tag{4}$$

$$\frac{d_c c_2 + c_1 c_2}{p} = d_c + c_0 c_2 \tag{5}$$

$$p = \frac{d_c c_2 + c_1 c_2}{d_c + c_0 c_2} \tag{6}$$

$$p = \frac{d_c c_2 + c_0 c_2 c_2 - c_0 c_2 c_2 + c_1 c_2}{d_c + c_0 c_2} \tag{7}$$

$$p = c_2 + \frac{c_1 c_2 - c_0 c_2 c_2}{d_c + c_0 c_2} \tag{8}$$

Set $c_1c_2 - c_0c_2c_2$ as constant c_3 , c_0c_2 as constant c_4 . The Equation (8) is converted to Equation (9):

$$p = c_2 + \frac{c_3}{d_c + c_4} \tag{9}$$

The increasing d_c makes the p decrease. So, increasing the thickness of the coating is one of the easiest ways to improve the barrier properties of the coating film. But we found that the results are inconsistent with expectations in practical applications. The relationship between coating thickness and coating film is shown in Figure 7a.



Figure 7. The effect of coating thickness on the oxygen barrier property: (**a**) theoretical and test Po_2 of PET films coated by with different thicknesses; (**b**) Po_2 of substrate, coatings with different MMA-MAc-DAM-MA coating thicknesses.

According to theoretical calculations, the Po_2 variation of the coated film with increasing thickness should be present as the dash in Figure 8a. However, the test values deviated from the theory. To verify the universality of this result, we selected three PET substrates with different thicknesses for testing. The conclusion is unanimous. Whatever the thickness of the PET substrate is, whether it is 12, 15 or 25 µm, the Po_2 of coated PET films is decreased in accordance with the theoretical calculation up to a coating thickness over 4 µm. However, when the coating thickness reaches 5 µm, the test Po_2 of the coating film deviates from the theoretical value. Additionally, with increasing thickness, the deviation becomes larger and larger. However, the Po_2 of the substrate is constant, and the discrepancy is bound to coating. By using Equation (1), we calculated the Po_2 of the coating at various thicknesses, as shown Figure 7b.



Figure 8. (a) FTIR analysis of the MMA-MAc-DAM-MA coating thicker than 4 μ m, (b) thermogravimetric analysis of the MMA-MAc-DAM-MA coating with different thicknesses.

We found that when the thickness of the coating exceeded 4 μ m, the Po_2 of the coating begins to increase. This reveals that the coating thickness should not be as thick as possible. The effect of the coating with a thickness above 4 μ m on improving the barrier property was gradually weakened due to the efficiency decline in its own oxygen barrier. In addition, we found that regardless of the substrate thickness, the Po_2 of the coating at the same thickness is almost the same in comparison. This is not an accident. The same problem exists in these coatings thicker than 4 μ m. We found that the new stretching bands of 2882, 1666, 1507, and 1401 cm⁻¹ emerged, as shown in Figure 8a. They do not belong to the structure of MMA-MAc-DAM-MA copolymer but perfectly fit the characteristics of NMP. The NMP remained in the coating with greater thickness. Thermogravimetric analysis was applied to test the coating with different thicknesses. The results are shown in Figure 8b.

The thermo stability of a coating with a thickness between 2 and 4 μ m is nearly the same in the temperature range of 200–300 °C. However, the thermo stability of the coating decreases with raising thickness between 5 and 8 μ m in the temperature range of 200–300 °C. The principal reason for this is that the increased thickness of a coating makes volatilization of the solvent in the coating greatly difficult. So, it can be considered that 4 μ m is the critical thickness of MMA-MAc-DAM-MA coating. This difficulty is easily eliminated by multiple thin layers of coating. Moreover, excessive curing temperature or curing time easily causes film wrinkling, which results in breaking the oxygen barrier property of PET-coated film. Additionally, the residual solvent supplies activity for molecular chains, resulting in the *P*o₂ increase in the coating speed, solution viscosity, and the self-leveling property of the coating. In summary, a 4 μ m thickness for coating can provide the most efficient barrier property and is suitable for industrial applications.

3.6. The Effect of Coating Solution Viscosity and Coating Speed on Barrier Property of Coated PET Film

According to our theoretical calculations, the Po2 value of the 19 µm coated film (15 µm substrate and 4 µm coating) should be 0.782×10^{-15} cm³·cm/(cm²·s·Pa). So, we collected many data at different coating speeds and copolymer solution viscosities in practical applications to find this key point in realizing the theoretical value. The results are shown in Figure 9. It can be observed that a high viscosity copolymer solution (1400-1600 cps) with a low coating speed (5 m/min) easily forms conspicuous protrusions on the coating surface, as seen in Figure 9a. If the coating speed is slow, the insufficient shear force causes the accumulation of shifted coating on the basement membrane, and the coating with high viscosity needs a long time to spread the accumulation to form a flat surface. The protrusions, which are harmful to barrier properties, are generated easily at low speed with a high viscosity copolymer solution. So, the Po2 of these coated films are over 1.45×10^{-15} cm³·cm/(cm²·s·Pa). On the contrary, low viscosity copolymer solutions (100–200 cps) with a fast coating speed (50 m/min) cause defects in the coating, as shown in Figure 9b. If the coating speed is fast while the solution viscosity is low, the air at the interface will likely remain. The residual air converts into bubbles, which break to form defects during the heating process. These defects are fatally destructive to the oxygen barrier property of the coating. In fact, the worst Po_2 of these coated films are 1.83×10^{-15} cm³·cm/(cm²·s·Pa). The P_c is 106 times the theoretical value. Eventually, a reasonable region of 400–600 cps copolymer solution viscosity and the ideal 15–25 m/min coating speed was found. In this range, the coating surface was smooth and flawless, as shown in Figure 9c. We tested the Po₂ of the coated film with these parameters. The results are all below $0.830 \times 10^{-15} \text{ cm}^3 \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$. At last, by trial and error, we confirmed the 600 cps copolymer solution viscosity and the 20 m/min coating speed as the optimum parameters. The Po₂ of the coated film at these two parameters was 0.786×10^{-15} cm³·cm/(cm²·s·Pa), infinitely close to the theoretical value of $0.782 \times 10^{-15} \text{ cm}^3 \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{Pa}).$



Figure 9. Effect of coating speed and copolymer solution viscosity on barrier properties of coated PET films. (**a**) Protrusions; (**b**) defect formed and bubble broken; (**c**) smooth surface.

3.7. The Optimal Coating Process Parameters

At the end of the experiment, we integrated the best obtained parameters to achieve an integral coating process. To verify the feasibility of this process, we prepared a 600 cps copolymer solution and coated it at the speed of 20 m/min with anRDS#10 Mayerrod to ensure a coating 4 μ m thick after curing. At last, we dried the coated film in an oven at the temperature of 190 °C. Then, we repeated this process ten times and tested the *P*o₂ of each coated PET film. The results are reproducible at 0.786 × 10⁻¹⁵ cm³·cm/(cm²·s·Pa), as shown in Figure 10a. Consequently, as shown in Figure 10b, in practical application, it was confirmed that a 600 cps copolymer solution viscosity, 20 m/min coating speed, 4 μ m coating thickness, and 190 °C curing temperature achieve the best oxygen barrier effect for the coated film.



Figure 10. (**a**) *P*o₂ of the coated film prepared at the optimal parameters, (**b**) key coating process parameters to obtain best barrier performance of coated film in practical application.

4. Conclusions

The synthesized copolymer of MMA-MAc-DAM-MA for coating can effectively improve the oxygen barrier property of the PET film. The curing temperature for coating is optimized at 190 °C. The coating cured at this temperature robustly enhanced the oxygen barrier performance for the coated PET film, maximizing inter-chain cross-linking and minimizing chain movement. The optimal coating thickness is 4 μ m. This can provide the most efficient barrier property and is promising for practical industrial applications in food preservation and medicine storage. The results illustrate that the optimum solution

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the best leveling property and oxygen barrier coefficient. The appropriate coating process reaches are 15–25 m/min, with an ideal speed of 20 m/min. At this speed, the coating surface is smooth and unblemished. Lastly and most importantly, a 600 cps copolymer solution viscosity, 20 m/min coating speed, 4 μ m coating thickness, and 190 °C curing temperature are the optimal coating process parameters. They were combined to reduce the *P*o₂ of the PET film (decrease by 47.8%) in practical application. The MMA-MAc-DAM-MA coating provides new insights into the high oxygen barrier performance development of PET.

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