Oxygen plasma induced ultralong lifetime of heat sealing effect of PET films

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Introduction

Biaxially oriented PET (polyethylene terephthalate) films are versatile for industrial uses [1,2]. A structural formula of PET is shown in Fig.1. It ought to be merit to use it for food packages, but unfortunately it has no heat sealing nature. Molecules are crystallized and oriented in biaxially oriented PET films, then they cannot be bonded with each other and with other films such as metal foils at temperatures lower than melting point (258ºC). For this reason PET films are coated with layers having the heat sealing nature using organic solvents when they are applied for the food packaging [3]. We have succeeded to bond PET films at low temperatures as 100ºC without using such coatings and adhesive glues, by oxygen-implicated plasma exposure [4].
It is usually observed that unique chemical reactions occur on polymer surfaces when they are exposed by plasma. Excited plasma particles cause such complicated reactions which cannot take place in usual chemical processes. Thus we can obtain higher hydrophilic and adhesive properties, called surface modifications by the plasma [5,6]. However, the effects are usually kept only in short periods, say one week at most [7]. It is known that hydrophilic functional groups are induced on the plasma-exposed PET surface, but normally a water contact angle is recovered to the original value soon in atmosphere. Then the surface becomes back to hydrophobic immediately at higher temperatures [8,9]. In this paper we report that a water contact angle is gradually recovered certainly to the original value after the exposure, though the heat sealing nature is maintained marvelously for long as six years.

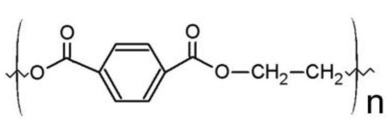

Fig.1 Structural formula of PET (glass transition temperature T_g=70°C, melting point T_m=258°C).

Experimental

PET films (Lumirror, Toray) were used as samples, those have 100 mm width, 200 mm length, 100 μm thickness and surface roughness of around 0.46 nm. The sample was attached on the drum electrode in the plasma equipment, and oxygen plasma was generated by discharge of oxygen gas at 120 W (2000 V, 60 mA). The drum electrode was rotated at a rate of 0.5 m/min, then the plasma energy E was 200 W·min/m^2. After the plasma exposure, the sample was taken out in the atmosphere.
We measured a pure water contact angle θ (deg) on the film surface using Drop Master (Kyowa). The value of θ was taken as an average of 6-10 times measurements. The sample surface was chemically analyzed by X-ray photoelectron microscopy (XPS) (VG Scientific). Surface morphologies were observed on the films using atomic force microscopy (AFM) (Veeco Digital). Surface roughness Ra (mean value) was evaluated by AFM images.
The two sheets of plasma-exposed PET films were lapped over with both exposed surfaces faced, then it was pressed at 100 kg/cm^2 at 150ºC for 10 min using a press machine (Kitagawa Seiki). Bonding strength was measured on the laminated sample using a peel test machine (Touyouseiki Seisakusho) at a pulling rate of 100 mm/min based on the JIS-C2151 standard. It gives 180º-peel strength S_p.

Results and Discussion

The results of 180º-peel strength S_p are shown in Fig.2 for non-exposed and plasma-exposed films. The value of S_p is 10 N/cm for the exposed films just after the exposure. Then the films are bonded very strongly because it shows adherent failure when peeled with over 10 N/cm. We tried to press and bond the films kept in the atmosphere for six years after the exposure. All the exposed films show strong bonding after 1-6

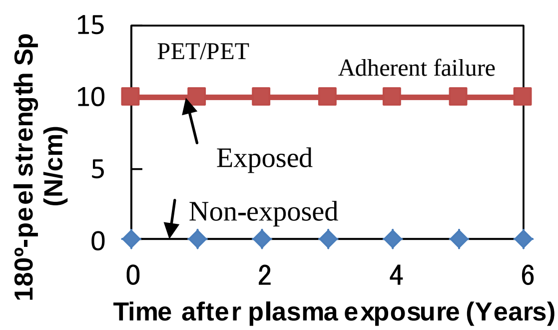

Fig. 2 180°-peel strength S_p vs time of keeping the exposed-films in atmosphere, for non-exposed and plasma-exposed laminated PET.

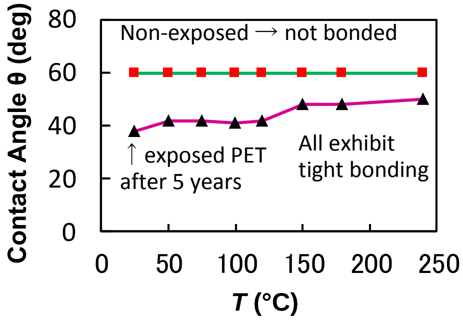

Fig.3 Water contact angle θ vs heating temperature T, for non-exposed film and the film exposed by plasma five years before.

years. Non-exposed films kept in the same atmosphere for 0-6 years never show such bonding naturally (Fig.2). This anomalous long life of plasma exposure effect on the bonding cannot be recognized by normal chemical mechanism at the surface. There must be enigmatic mechanism of the bonding at the exposed surface.

To clarify the mechanism we investigated the water contact angles θ on the exposed films. The results are shown in Fig.3 as a function of heating temperature T (ºC) during the measurement for the exposed and non-exposed films. The non-exposed film show the same contact angle θ=60 deg at any T. While just after the exposure, θ of the exposed film dropped from 60 to 18 deg at T=25ºC. This film was kept in the atmosphere for five years, then the contact angle was measured at various T. The magnitude of θ was recovered from 18 up to 38 deg at T=25ºC. It means, the plasma-induced excited surface was recovered considerably but not fully recovered even after five years. The θ increases up to 50 deg with raising T to 240ºC. It also means that the plasma-excited surface becomes less excited at higher T due to some accelerated relaxation reactions. But it implies that a part of the plasma-generated OH and COOH groups [4] still exists at the surface. We tried to press and bond these films once heated at 25-240ºC. Unexpectedly all the films were bonded tightly as the films just after the exposure.

The results indicate that (1) the water contact angle is not an exact measure of bonding, (2) the excitation of the surface having the contact angle (50 deg) only less by 10 deg than the original value (60 deg) is enough for the tight bonding. We are preparing the experiment for the bonding of films with the contact angle of 50 deg just after the weak plasma exposure.

In order to analyze the plasma-exposed surface, we measured XPS on the film surfaces. The results of C1s-related spectra are shown in Fig.4 for the non-exposed film ①, plasma-exposed film ② and heated film at 160ºC for 10 min just after the exposure ③. After the exposure ②, a peak at 284.6 eV arising from C-C bond in phenyl-like part in the original PET (Fig.1) is decreased much from the non-exposed value ①. The same trends are observed on a peak at 286.3 eV arising from ether C-O bond and a peak at 288.7 eV arising from carboxyl O=C-O in the original PET. These indicate that the C-C

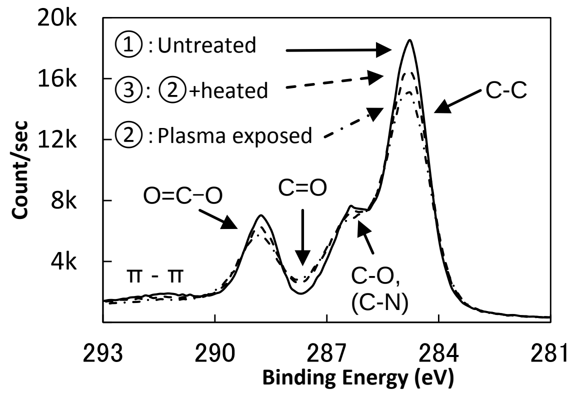

Fig.4 C1s-related XPS spectra of PET films; ① before exposure, ② after exposure, and ③ heated (160ºC, 10 min) after exposure of plasma.

bond in phenyl-like part, ether C-O bond and carboxyl O=C-O bond are broken by the plasma. It is consistent with a fact that higher molecular weight becomes smaller by the exposure [4]. On the other hand, a C=O bond-related signal at 287.7 eV appears. This must arise from carboxyl group COOH created on the surface of exposed PET.

The peaks located at 284.6, 286.3, and 288.7 eV, all related to the original PET bondings, are recovered in part by the heating ③. This indicates that the broken bonds by the plasma can be restored by the low temperature heating. However, the signal at 287.7 eV is recovered little, indicating the plasma-created COOH at the surface does not vanish at such a low temperature of 160ºC.

Summary

The PET films can be easily bonded by the plasma exposure. This bonding effect is kept for six years in the atmosphere. Even after the heating of exposed-films, the effect can be maintained although the water contact angle is recovered considerably. COOH may be created on the surface by the plasma.

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