SURFACE FREE ENERGY OF POLY(ETHYLENE TEREPTHALATE) AND NYLON 6 FILMS TREATED WITH LOW TEMPERATURE PLASMA

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Abstract

Poly(ethylene terephthalate) (PET) and nylon 6 films were treated with low temperature plasma in various gases, oxygen, nitrogen, hydrogen, helium, argon, methane, tetrafluoromethane, trifluoromethane, monochlorotrifluoromethane, and tetramethylsilane. The contact angles of various liquids of different surface tensions on the plasma-treated films were measured. The lowest surface tension $\gamma_c$ (Zisman) and the highest surface tension $\gamma_c$ (max) of the polymers were determined on the basis of the Zisman plots. Furthermore, the contributions of nonpolar dispersion, dipole, and hydrogen bonding forces to the surface tensions for the plasma-modified polymers were evaluated by the extended Fowkes equation. In addition, the plasma-treated samples were characterized by X-ray photoelectron spectroscopy (ESCA). The change in surface free energy of the plasma-treated films was correlated with their surface chemical compositions measured by ESCA.

1. INTRODUCTION

Low temperature plasma treatment has received considerable attention for the surface modification of polymer matrices, in particular those in film form, from an industrial point of view. It is known that the plasma treatment functionalizes the surface of polymers without change in bulk properties of the matrices. Thus the plasma surface treatment has been applied recently to the field of electronics and film industries. Also application of plasma treatment to dyeing and textile finishing is of great interest.1−3

There has been much work on the modification of polymer surfaces by low temperature plasma treatment. Surface properties of the resultant polymers have been examined in terms of wettability or contact angle of liquids. Water is most frequently employed as the wetting liquid for this purpose and liquids other than water are rarely used.3−7

In this study the effect of low temperature plasma on surface tension of polymer films was investigated for poly(ethylene terephthalate) (PET) and nylon 6 films using glow discharge in various gases. The contact angles of various liquids, which have different surface tensions and are classified into four groups, on the plasma-modified polymers were evaluated by the extended Fowkes equation. In addition, the plasma-treated samples were characterized by X-ray photoelectron spectroscopy (ESCA). The change in surface free energy of the plasma-treated films was correlated with their surface chemical compositions measured by ESCA.

2. EXPERIMENTAL

PET and nylon 6 films were washed with benzene and acetone for 10 hrs each, followed by distilled water.
Glow discharge was generated using Yamato Plasma Generator PR-501A (Yamato RF Generator Model RFG-500A and Yamato Plasma Chamber Model PC-101A). The current frequency was 13.56 MHz. Gases used in this experiment were oxygen, nitrogen, hydrogen, helium, argon, methane, tetrafluoromethane, trifluoromethane, monochlorotrifluoromethane, and tetramethylsilane. Discharge power was kept constant at 300 W. All plasma treatments were carried out at a pressure of 1 torr for 3 min. After exposure of the plasma the samples were allowed to stand in air for seven days and then subjected to the measurements of contact angle and ESCA.

The contact angle of a liquid on the film surface was measured using a Contangleometer (Elma Optics Co.). Four series of liquids, (A), (B), (C), and (D), were used as the wetting liquids. The surface tension \( \gamma_L \) of the liquid can be divided into three components, nonpolar dispersion force \( \gamma_{L}^{a} \), dipole force \( \gamma_{L}^{b} \), and hydrogen bonding force \( \gamma_{L}^{c} \), and their values are known. These values taken from ref. 11 are listed in Table 1. According to Kitazaki and Hata, the liquids of series (A), (B), (C), and (D) are characterized as follows. The liquids of series (A) consist of saturated hydrocarbons (a type of \( \gamma_{L} = \gamma_{L}^{a} \)). The liquids of series (C) and (D) are classified as a type of \( \gamma_{L} = \gamma_{L}^{a} + \gamma_{L}^{b} \). The liquids other than series (A), (C), and (D) are grouped into series (B) (a type of \( \gamma_{L} = \gamma_{L}^{a} + \gamma_{L}^{b} \)). The corresponding three components, nonpolar dispersion force \( \gamma_{L}^{a} \), dipole force \( \gamma_{L}^{b} \), and hydrogen bonding force \( \gamma_{L}^{c} \), of the PET and nylon 6 films were evaluated by the extended Fowkes equation (1) proposed by Kitazaki and Hata, where \( \theta \) and \( \gamma_L \) represent contact angle and surface tension of liquid, respectively.

\[
\gamma_L(1 + \cos \theta) = 2\left(\sqrt{\gamma_L^{a2} + \gamma_L^{b2}} + \sqrt{\gamma_L^{c2}}\right)
\]

The ESCA measurements (Shimazu ESCA 750) were made for characterization of chemical species of surface layers of the films. MgK\(\alpha\), X-ray was used as the source. Operating parameters were 8 kV and 30 mA. The ESCA curves obtained were separated into the components of C, O, N, F, Si, and Cl. The corrected and relative peak areas of each component, as measured by the integrated areas of the peaks, were determined.

### 3. RESULTS AND DISCUSSION

#### 3.1 Critical surface tension of PET film

The Zisman plots, \( \cos \theta \) vs. \( \gamma_L \), of PET films irradiated with low temperature plasma in oxygen, tetramethylsilane, and tetrafluoromethane are

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Surface tensions of liquids of four series at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series</td>
<td>Liquid</td>
</tr>
<tr>
<td>A</td>
<td>Hexadecane</td>
</tr>
<tr>
<td></td>
<td>Dodecane</td>
</tr>
<tr>
<td></td>
<td>Decane</td>
</tr>
<tr>
<td></td>
<td>Hexane</td>
</tr>
<tr>
<td>B</td>
<td>Tetrabromoethane</td>
</tr>
<tr>
<td></td>
<td>1-Bromonaphthalene</td>
</tr>
<tr>
<td></td>
<td>Tetrachloroethane</td>
</tr>
<tr>
<td></td>
<td>Hexachlorobutadiene</td>
</tr>
<tr>
<td>C</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td>Glycerol</td>
</tr>
<tr>
<td></td>
<td>Formamide</td>
</tr>
<tr>
<td></td>
<td>2,2-Thiobisethanol</td>
</tr>
<tr>
<td>D</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td></td>
<td>Diethylene glycol</td>
</tr>
<tr>
<td></td>
<td>Polyethylene glycol 200</td>
</tr>
</tbody>
</table>

\( \gamma_L^{a} \): Nonpolar dispersion force  
\( \gamma_L^{b} \): Dipole force  
\( \gamma_L^{c} \): Hydrogen bonding force
shown in Figure 1 as typical examples. The corresponding data of the untreated sample are also included in Figure 1 for comparison. It is evident from Figure 1 that the relationship between \( \cos \theta \) and \( r_L \) is approximately linear. The oxygen plasma-treated film was wetted thoroughly by the liquids of series (A), (B), and (D) except (C). The former three liquids were spread over the film. Therefore the Zisman plots can be obtained only for the liquids of (C). In contrast, the tetrafluoromethane plasma-treated film was not wetted by the liquids of all the series employed as shown in Figure 1. Subsequently, the Zisman plots are available for these liquids, (A), (B), (C), and (D). Wettability of all the liquids used for the PET film was decreased by the tetrafluoromethane plasma treatment. The extrapolation of the linear \( \cos \theta \) vs. \( r_L \) plot to \( \cos \theta = 1 \) gives the critical surface tension \( r_c \). The values of \( r_c \) estimated by using various series of liquids scatter considerably. Therefore the lowest value obtained refers to \( r_c \) (Zisman) and the highest one \( r_c \) (max). The lowest surface tension \( r_c \) (Zisman) and the highest surface tension \( r_c \) (max) of the films treated with plasma of various gases are listed in Table 2. It is obvious that the surface tension of the PET film depends on the gas type employed. As is apparent from the data in Table 2, the surface tension \( r_c \) (max) of the oxygen plasma-treated film is the order of 56 dyne/cm, which is higher than that of the control film. The PET film is changed to higher energy surface after irradiation in plasma of oxygen. Also nitrogen, helium, and argon plasma treatments give high energy surfaces similar to the case of oxygen plasma treatment, forming hydrophobic PET surfaces. In marked contrast, with tetrafluoromethane and trifluoromethane plasmas the value of \( r_c \) (max) is as low as 20 dyne/cm, indicating considerably lower energy surface than that of the untreated sample (46 dyne/cm). A

![Figure 1. Zisman plots of plasma-treated PET film.](image)

Table 2 Surface tensions of poly(ethylene terephthalate) films treated with low temperature plasma

<table>
<thead>
<tr>
<th>Plasma treatment</th>
<th>Zisman plot</th>
<th>Surface tension (dyne/cm)</th>
<th>Extended Fowkes equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( r_c ) (Zisman)</td>
<td>( r_c ) (max)</td>
<td>( r_a^b )</td>
</tr>
<tr>
<td>Untreated</td>
<td>43</td>
<td>46</td>
<td>37.6</td>
</tr>
<tr>
<td>O(_2)</td>
<td>56</td>
<td>56</td>
<td>16.6</td>
</tr>
<tr>
<td>N(_2)</td>
<td>57</td>
<td>57</td>
<td>17.6</td>
</tr>
<tr>
<td>H(_2)</td>
<td>39</td>
<td>50</td>
<td>33.6</td>
</tr>
<tr>
<td>He</td>
<td>56</td>
<td>56</td>
<td>16.8</td>
</tr>
<tr>
<td>Ar</td>
<td>56</td>
<td>56</td>
<td>17.6</td>
</tr>
<tr>
<td>CF(_4)</td>
<td>20</td>
<td>20</td>
<td>19.7</td>
</tr>
<tr>
<td>CHF(_3)</td>
<td>19</td>
<td>20</td>
<td>22.6</td>
</tr>
<tr>
<td>CClF(_3)</td>
<td>36</td>
<td>44</td>
<td>41.8</td>
</tr>
<tr>
<td>(CH(_3))(_4)Si</td>
<td>34</td>
<td>35</td>
<td>42.5</td>
</tr>
<tr>
<td>O(_2)→CF(_4)</td>
<td>20</td>
<td>20</td>
<td>21.2</td>
</tr>
<tr>
<td>CF(_4)→O(_2)</td>
<td>58</td>
<td>58</td>
<td>17.0</td>
</tr>
</tbody>
</table>
remarkably high surface tension is obtained by
the treatment with monochlorotrifluoromethane
plasma as compared with tetrafluoromethane and
trifluoromethane plasmas. The surface tension
\( r_c \) (max) of the film subjected to the plasma
treatment with CClF\(_3\) is of the order of 44 dyne/cm,
which is similar to that of the control and much
higher than that of the CF\(_4\) or CHF\(_3\) plasma
treatment. The tetramethylsilane plasma treatment
also shows a low \( r_c \) (max) value as compared to
the control.

The surface tension of the plasma-modified
films was divided into three components, nonpolar
dispersion force \( r^* \), dipole force \( r^b \), and hydrogen
bonding force \( r^\alpha \), which can be calculated by the
extended Fowkes equation.\(^8\) The results ob-
tained are summarized in Table 2 also. The
hydrogen bonding force \( r^\alpha \) is increased markedly
but the nonpolar dispersion force \( r^* \) is decreased
by the plasma treatments with oxygen, nitrogen,
helium, and argon. Therefore it is apparent that
an increase in surface tension by these plasmas is
due to the substantial increase in the hydrogen
bonding force. The lower values of surface tension
observed for exposure of tetrafluoromethane and
trifluoromethane plasmas are attributed to the
lower dispersion force \( r^* \). The value of \( r^\alpha \) for
CClF\(_3\) is very close to that of the control but
significantly higher than that for CF\(_4\) or CHF\(_3\).

Comparison was also made with two-step
processes of plasma treatment: oxygen and then
tetrafluoromethane plasma treatment (O\(_2\)→CF\(_4\))
or vice versa (CF\(_4\)→O\(_2\) ). The two procedures
give \( r_c \) (max) of 20 and 58 dyne/cm, respectively
(Table 2). These values are very close to the surface
tensions of the films achieved by CF\(_4\) and O\(_2\)
plasmas alone, respectively. This result indicates
that the characteristics of the film is governed by
the final plasma gas irrespective to the first plasma
gas employed.

### 3.2 Chemical compositions of PET surface

The wettability of a polymer matrix is related
to the presence of a particular functional group
that resides in the outermost surface layer. Thus
the plasma-treated PET films were characterized
by ESCA to identify the species present in their
surface layer. The oxygen, nitrogen, helium, and
argon plasma treatments lead to an increase in O\(_{1s}\)
intensity and a decrease in C\(_{1s}\) intensity (Table 3).
Yasuda et al.\(^{13}\) have already demonstrated that
argon and nitrogen plasma treatments introduce
oxygen functionalities into the PET surface. To
facilitate comparison of these gases, the ratio of
the number of oxygen to carbon atoms, O\(_{1s}/C\(_{1s}\),
was evaluated. The values of O\(_{1s}/C\(_{1s}\) for the
oxygen, nitrogen, helium, and argon plasma-treated
films are 0.53, 0.44, 0.44, and 0.47, respectively.
The corresponding value for the control sample is
0.38. From these data it is evident that the films
treated with these gases, in particular oxygen,
show higher O\(_{1s}/C\(_{1s}\) value in comparison with
the untreated film. The information available from
the ESCA experiment indicates that the plasma
reatments with these gases lead to an increase in

<table>
<thead>
<tr>
<th>Plasma treatment</th>
<th>O(_{1s})</th>
<th>N(_{1s})</th>
<th>F(_{1s})</th>
<th>Si(_{2p})</th>
<th>Cl(_{2p})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>73.1</td>
<td>26.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O(_2)</td>
<td>64.3</td>
<td>34.3</td>
<td>1.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N(_2)</td>
<td>67.9</td>
<td>29.7</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H(_2)</td>
<td>77.7</td>
<td>22.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>He</td>
<td>68.3</td>
<td>29.7</td>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>Ar</td>
<td>67.5</td>
<td>31.6</td>
<td>0</td>
<td>0</td>
<td>0.9</td>
</tr>
<tr>
<td>CF(_4)</td>
<td>41.8</td>
<td>6.5</td>
<td>0</td>
<td>51.6</td>
<td>0</td>
</tr>
<tr>
<td>CHF(_3)</td>
<td>45.4</td>
<td>1.2</td>
<td>0</td>
<td>53.3</td>
<td>0</td>
</tr>
<tr>
<td>CClF(_3)</td>
<td>53.4</td>
<td>13.5</td>
<td>0</td>
<td>8.4</td>
<td>0</td>
</tr>
<tr>
<td>(CH(_3))(_4)Si</td>
<td>68.6</td>
<td>10.2</td>
<td>0</td>
<td>21.2</td>
<td>0</td>
</tr>
<tr>
<td>O(_2)→CF(_4)</td>
<td>39.6</td>
<td>6.6</td>
<td>0</td>
<td>53.8</td>
<td>0</td>
</tr>
</tbody>
</table>
oxidative functionality. It has been pointed out already that some oxidation of carbon and the possible addition of oxygen at the surface occur during exposure of plasma or due to a postreaction of trapped free radicals with oxygen from the atmosphere.\textsuperscript{12,13} In the case of nitrogen, helium, and argon plasma treatments, it is suggested that living radicals formed by the plasma treatments incorporate oxygen atoms into the polymer surface immediately after the sample is taken out from the plasma chamber. Surface oxidation also occurs. As a result of plasma-induced oxygen incorporation into the PET surface, the contribution of the hydrogen bonding force $r_s$ of oxygen, nitrogen, helium, and argon plasma-treated samples becomes significant and thereby the surface tension increases as mentioned above. The relationships between $r_s$ (Zisman) or $r_s$ and the $O_{1s}/C_{1s}$ value are represented in Figure 2. As is readily evident in Figure 2, a good correlation exists between them: an increase in surface tension is attributable to an increase in the $O_{1s}/C_{1s}$ ratio.

The plasma treatments with CF$_4$ and CHF$_3$ incorporate over 50% of F$_{s}$, whereas the values of C$_{1s}$ and O$_{1s}$ decrease considerably. It is suggested that the plasma treatments with these gases lead to their polymerization or chemical modification on the polymer surface. The introduction of fluorine atom is effective to decrease the dispersion force $r_s$ and thereby diminishes the surface free energy of the film. The CCIF$_3$ gas shows ESCA spectra very different from the CF$_4$ and CHF$_3$ gases. The extent of fluorine incorporation is much less than that produced by CF$_4$ or CHF$_3$ plasma. However chlorine atoms tend to be incorporated into the polymer surface and 24% of Cl element is introduced when exposed to CCIF$_3$ plasma. The surface tension $r_s$ of the CCIF$_3$ plasma-treated film is the order of ca. 48 dyne/cm, which is almost the same as that of the control film. Table 2 indicates that Cl atoms enriched increase the nonpolar dispersion force $r_s$.

Exposure to tetramethylsilane plasma produces a substantial amount of Si incorporation (ca. 21%) in the PET surface and hence reduces its surface tensions, $r_s$ (Zisman) and $r_s$ (max). It is described that tetramethylsilane and its related compounds are polymerized by plasma discharge to form film.\textsuperscript{14,15} The treatment leads to the formation of hydrophobic polymer surface. It is likely that water repellency of the PET film is more enhanced by CF$_4$ or CHF$_3$ plasma than (CH$_3$)$_4$Si plasma. The plasma modification with these gases is useful for the water repellency of the film in dry system.

### 3.3 Critical surface tension of nylon 6 film

Nylon 6 film was subjected to plasma in various gases. The Zisman plots of nylon 6 films treated with oxygen, methane, and tetrafluoromethane plasmas are shown in Figure 3 as typical examples.

![Fig. 2. Relationship between surface tension and $O_{1s}/C_{1s}$ ratio for plasma-treated PET.](image1)

- (O) untreated;
- (●) oxygen plasma;
- (●) nitrogen plasma;
- (●) helium plasma;
- (○) argon plasma;
- (⊙) hydrogen plasma.

![Fig. 3. Zisman plots of plasma-treated nylon 6 film.](image2)

- (O) (A) series of liquids;
- (△) (B) series of liquids;
- (□) (C) series of liquids;
- (●) (D) series of liquids.
- (1) untreated;
- (2) oxygen plasma;
- (3) tetrafluoromethane plasma;
- (4) methane plasma.
Table 4  Surface tensions of nylon 6 films treated with low temperature plasma

<table>
<thead>
<tr>
<th>Plasma treatment</th>
<th>Surface tension (dyne/cm)</th>
<th>Zisman plot</th>
<th>Extended Fowkes equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_c$ (Zisman)</td>
<td>$\gamma_c$ (max)</td>
<td>$\gamma_s^0$</td>
</tr>
<tr>
<td>Untreated</td>
<td>41</td>
<td>45</td>
<td>25.7</td>
</tr>
<tr>
<td>O₂</td>
<td>59</td>
<td>59</td>
<td>13.0</td>
</tr>
<tr>
<td>N₂</td>
<td>59</td>
<td>59</td>
<td>10.9</td>
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<tr>
<td>H₂</td>
<td>41</td>
<td>56</td>
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<tr>
<td>He</td>
<td>43</td>
<td>55</td>
<td>24.0</td>
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<tr>
<td>CH₄</td>
<td>36</td>
<td>41</td>
<td>40.9</td>
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<tr>
<td>CF₄</td>
<td>19</td>
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<td>20.9</td>
</tr>
<tr>
<td>CHF₃</td>
<td>19</td>
<td>26</td>
<td>21.2</td>
</tr>
<tr>
<td>CClF₃</td>
<td>38</td>
<td>40</td>
<td>25.0</td>
</tr>
</tbody>
</table>

The values of $\gamma_c$ (Zisman) and $\gamma_c$ (max) and the components of surface tension are listed in Table 4. The general trends found in the surface tensions of the plasma-treated nylon 6 films are very similar to those observed with PET: nylon 6 is affected similarly by the plasma treatments with the various gases. However, the contribution of $\gamma_s^0$ to $\gamma_s$ for untreated nylon 6 is substantially larger than that for untreated PET because the amide groups of nylon 6 can form hydrogen bonding with polar liquids.

It has been suggested that wettability of a polymer matrix is also related to its surface morphology, in particular surface roughness even though the chemical constitution of the polymer surface is unchanged. Thus, the relation between the surface tension and the change in the surface roughness by plasma treatment will be described in subsequent papers.

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低温プラズマ処理ポリエチレンテレフタレートおよび
ナイロン6フィルムの表面自由エネルギー

京都工芸繊維大学工芸学部   円田登美司, 河村晴夫, 安 鎌哲
ユニチカ株式会社加工基礎研究室  後藤 慎樹
大阪府立大学工学部   高岸 健

ポリエチレンテレフタレートおよびナイロン6フィルムを、空素、窒素、水素、ヘリウム、アルゴン、メタン、
テトラフルオロメタン、トルフルオロメタン、モノクロロ
トリフルオロメタンおよびジフッ化チタンで処理した。そして、表面張力の異なる4つのシリーズの液体群による接触角を測定した。Zismanプロットを行った。これより表面張力$\gamma(zisman)$, $\gamma(max)$をもとめ、さらに拡張Fowkes式を用いて、低温プラズ
マ処理フィルムの表面張力を非極性分散力、双極子力、
水素結合力の各成分に分けた。さらに、プラズマ処理
フィルムの表面特性をESCAによって調べ、プラズマ処
理によるフィルムの表面自由エネルギーの変化とフィル
ム表面組成との関係について検討した。