EFFECT OF CALCIUM ION ON TRANSFORMING REACTION OF CARBOXYL GROUPS INTO THEIR SODIUM SALTS IN POLY (ETHYLENE TEREPTHALATE) GRAFTED BY ACRYLIC ACID AND METHACRYLIC ACID*1

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ABSTRACT: The grafting of acrylic acid (AA) and methacrylic acid (MAA) made poly (ethylene terephthalate) (PET) hydrophilic. The alkali-treatment of the grafted PET enhanced the hydrophilicity, transforming carboxyl groups into their Na-salt form. However, the use of natural water, which contained multi-valent metal ions, in the alkali-treatment of the grafted PET did not bring as high a hydrophilicity as expected. From model reactions in which aqueous CaCl2 solutions was used as media of the alkali-treatment, it became clear that the presence of Ca ions in the alkali-treatment suppressed transforming reaction of carboxyl groups of the grafted PET into the Na-salt form. It was suggested that gel formation of the grafted poly (AA/MAA) shut up the reactive sites, thus preventing transformation of carboxyl groups. The addition of a sequestering agent to the alkali-treating solution was useful in preventing multi-valent metal ion's effect and in bringing about smooth transformation of carboxyl groups into the Na-salt form.

1. INTRODUCTION

It is known that some properties of PET fibers are modified by grafting of AA and MAA1-3). Na-salt form of carboxyl groups of AA- or MAA-grafted PET became more hydrophilic than the acid form1,3). The Na-salt form was obtained by means of the alkali-treatment of the grafted PET with aqueous Na2CO3 or NaOH solution.

However, it was observed that the use of natural water (ground water) in the alkali-treatment of the grafted PET did not bring about as high a hydrophilicity as expected from the alkali-treatment with deionized water. From a chemical analysis, it became clear that: (1) the natural water contained Ca and Mg ions and its hardness4) was 41 degrees as represented ppm of CaCO3. This hardness was near the value reported for standard river water in Japan5), and (2) Na content of the alkali-treated grafted PET was less than that expected3).

From these findings, it seems that the presence of multi-valent metal ions in the alkali-treating aqueous solution affects transformation of carboxyl groups of the grafted PET into their Na salts. In the present work, several experiments were carried out to investigate the effect of Ca ion on the alkali-treatment of the AA and MAA-grafted PET.

2. EXPERIMENTAL

2.1 PET and Grafting

PET filament interlock which was the same as that reported previously1) was used as the sample fabric. The graft polymerization of AA and MAA (AA/MAA = 2.5/7.5 molar ratio) onto PET interlock was carried out by 1-step grafting6). The grafting ratio was 10.8 %. Deionized water was used in the grafting process*2.

2.2 Water and Alkali-treatment

By dissolving a certain amount of CaCl2 into deionized water, aqueous solutions of different hardness were prepared. Assuming Ca content of deionized water as 0, aqueous Ca solutions of the hardness from 5 to 50 degrees (as ppm of CaCO3) were prepared. Into
each Ca solution, NaOH (2 g/l) was dissolved and the
grafted PET was treated with the solution at 80°C for
30 min. with a liquor ratio of 1 : 100.

2.3 Moisture Regain

After measuring dry weight (W₀), the grafted PET
was conditioned under the atmosphere of 20°C, 65 %
RH for 48 hours. Then, the weight (W) of the grafted
PET was measured. Moisture regain of the grafted
PET was calculated from the following equation.

\[ \text{Moisture regain (\%) = } 100 \times \frac{W - W₀}{W₀} \]

2.4 Na and Ca analysis

Metal content of the alkali-treated grafted PET was
determined by atomic absorption spectroscopy
according to JIS K021. The metallized state of the car-
boxyl groups in the grafted PET fiber was analyzed
by X-ray microanalysis (XMA) for the carbon de-
posited cross section of the sample fiber. The dis-
tribution of Na or Ca in the fiber cross section was
visualized as white dots in the XMA image.

As a qualitative elemental analysis, XMA spectrum
was taken for the center area (2 μm × 2 μm) of the
sample fiber's cross section.

3. RESULTS AND DISCUSSION

3.1 Moisture Regain

The results of moisture regain of the alkali-treated
grafted PET are shown in Fig. 1. With increasing
hardness of alkali-treating water, moisture regain of
the grafted PET decreased. Moisture regain of the
sample which was alkali-treated with water of the
hardness above 20 degrees was almost the same as
that of the acid–from grafted PET.

3.2 Metal Analysis

The results of metal analysis of the alkali-treated
grafted PET are summarized in Table 1. Four types
of grafted PET were also analyzed as references: (1)
acid form which was not alkali-treated, (2) Na-salt
form which was alkali-treated with NaOH (2 g/l) at
80°C for 30 min. with deionized water, (3) Ca-salt
form (I) which was obtained from Na-salt form by
treating with CaCl₂ (1 g/l) aqueous solution at 80°C
for 30 min. and (4) Ca-salt form (II) which was
obtained from direct treatment of the acid form
grafted PET with CaCl₂ (1 g/l) aqueous solution at
80°C for 30 min..

The grafted PET alkali-treated with deionized wa-
ter (ref. 1, Na-salt form) showed the highest Na con-
tent, and Na content of the grafted PET decreased
with an increase in the hardness of water used in the
alkali-treatment. Conversely, Ca content increased
with an increase in the hardness of water. However,
Ca content of the grafted PET obtained from the alka-
litreatment with aqueous Ca solution was not as high
as shown with Ca-salt form (I) which was trans-
formed from the Na-salt form (ref. 1). In addition,
total metal content decreased. The direct treatment of
the grafted PET with aqueous Ca solution, that was
Ca-salt form (II), resulted in the lowest metal con-
tent.

The results shown in Table 1 explain the low hyd-
rophilicity of the grafted PET which was alkali-tre-
ated with natural water.

For investigating the state of metal substitution of
the carboxyl groups, XMA analysis was applied to
the grafted PET which had been alkali-treated. Fig 2
shows the cross section (a) and XMA image corres-
dponding to Na in the cross section (b) of Na-salt
form grafted PET fiber prepared through alkali-treat-
ment with deionized water. White dots in the XMA
image of the cross section were distributed uniformly,
indicating that Na substitution of the carboxyl groups
took place uniformly from the surface to the center of
the fiber.

The qualitative XMA spectrum proved the presence
of Na in the center of the fiber.
Fig. 2. Cross section (a) and XMA image corresponding to Na in cross section (b) of Na-salt form grafted PET fiber prepared from alkali-treatment with deionized water. Density of white dots in the cross section area is higher than that of surroundings and white dots distributed uniformly in the same area.

Fig. 3. Cross section (a) and XMA image corresponding to Ca in cross section (b) of grafted PET fiber which was alkali-treated with aqueous CaCl$_2$ solution of 50 degree hardness. High density of white dots is shown in the surface area of the grafted fiber.
Fig. 4. Cross section (a) and XMA image corresponding to Na in cross section (b) of grafted PET fiber same as shown in Fig. 3. High density of white dots is absent from the cross section area.

Table 1 Metal Analysis of Alkali-treated AA/MAA (10.8%) Grafted PET

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Hardness of alkali-treating water (ppm as CaCO₃)</th>
<th>Metal content (ppm)</th>
<th>Na</th>
<th>Ca</th>
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<tbody>
<tr>
<td>1</td>
<td>0 (the same as Ref. 1)</td>
<td>9400</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>7680</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>3390</td>
<td>1770</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>990</td>
<td>2010</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>1070</td>
<td>1970</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>1100</td>
<td>2180</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>1100</td>
<td>2100</td>
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</tbody>
</table>

Ref. 1 Grafted PET; Acid form
2 Na-salt form
3 Ca-salt form (I) (ref. 3)
4 Ca-salt form (II)

Figs. 3 and 4 show the cross sections and XMA images of Ca or Na of the grafted PET fibers which were alkali-treated with the aqueous CaCl₂ solution of 50 degrees hardness. The results shown in Figs. 3 and 4 and XMA spectrum indicate that Ca was present mainly in the surface area of the grafted PET fiber and Na scarcely existed in the fiber. The results obtained from XMA analysis coincided with the results of metal content shown in Table 1.

3.3 Reaction Scheme

As described above, the metal content and moisture regain of AA and MAA grafted PET decreased with the increase in hardness of water used in the alkali-treatment. The scheme of transforming reaction of carboxyl groups of the grafted PET into their Na salts is considered as follows:

1) In the first stage of the reaction between carboxyl groups and metal ions, the reaction of Na ions with carboxyl groups takes place faster than that associated with Ca ions. The phenomenon is experimentally elucidated in Table 1 (ref. 2 and 4).
2) Generated COONa is immediately transformed into Ca salts under the presence of Ca ion.
3) Ca-salt form of poly (AA/MAA) forms gel like structure and reactive COOH or COONa groups are shut up in the gel structure. Consequently, further transforming reaction is restrained.

According to this scheme, the addition of a sequestering agent to the alkali-treating solution is expected to be effective in suppressing the Ca ion's
effect on the transforming reaction of carboxyl groups. The addition of a typical sequestering agent, tetra Na salt of ethylene diamine tetra acetic acid (EDTA) to the alkali-treating solution was found to be effective in transformation of carboxyl groups into their Na salts. (Table 2)

Table 2 Effect of a Sequestering Agent on Alkali-treatment of Grafted PET

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>EDTA*4 (g/l)</th>
<th>Metal content of alkali-treated grafted PET (ppm)</th>
<th>Na</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0</td>
<td>1100</td>
<td>2100</td>
<td></td>
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<tr>
<td>8</td>
<td>0.1</td>
<td>7800</td>
<td>860</td>
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<tr>
<td>9</td>
<td>0.2</td>
<td>9350</td>
<td>9</td>
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</table>

*3 Alkali-treatment was carried out in 2 g/l NaOH for 30 min at 80°C, with EDTA*4 Water of alkali-treatment contained Ca ions of 50 ppm as CaCO3.

*4 Tetra Na salt of ethylene diamine tetra acetic acid (sequestering agent)

4. CONCLUSION

The transforming reaction of carboxyl groups of AA and MAA-grafted PET into their Na salts was suppressed by multi-valent metal ions. As a result of model reactions, it was suggested that gel formation of grafted poly (AA/MAA) shut up the reactive sites, preventing further transformation of carboxyl groups into their metal salts. The addition of a sequestering agent to the alkali-treating solution was effective in suppressing multi-valent metal ions’s effect and in bringing about a smooth transforming reaction of carboxyl groups.

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