Oxidation of Polypropylene Homopolymer in Presence of an Aqueous Solution of Phenyltrimethyl Ammonium Permanganate

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ABSTRACT

The oxidation of polypropylene homopolymer film and powder (film grade) in presence of an aqueous solution of phenyltrimethyl ammonium permanganate (Ph.TMAP) at room temperature would be desirable if the original morphology of the polymer must be maintained. The oxidation process leads to the formation of polar groups (such as, alcoholic, hydroperoxide, etc.) mainly carboxylate ions and quaternary ammonium hydroxides liberating MnO2 as a by-product from the decomposition of the Ph.TMAP. The treated surfaces are studied by scanning electron microscopy (SEM), Fourier Transform IR and electron spectroscopy for chemical analysis (ESCA). The analyses show an increase in the number of oxygen atoms absorbed as compared to the molar concentration of the oxidizing agent and time. As a result of the decomposition of Ph.TMAP the polypropylene surface was covered with MnO2 and it was corroded. The MnO2 formed was analyzed by ESCA analysis as well as by chemical tests. The oxidation reaction of polypropylene homopolymer and Ph.TMAP as an effective oxidant system produce interesting products, which can be used as compatibilizer in some industries. A reaction mechanism of the polypropylene oxidation, at room temperature and in an aqueous solution of Ph.TMAP, is proposed.

Key Words: polypropylene, oxidation, aqueous solution, Ph.TMAP, polar groups

INTRODUCTION

Polypropylene (PP) and other polyolefins surfaces may be modified by various methods [1 and 2], which aim at improving adhesion, painting, dyeing, and other characteristics of these materials but preserving their bulk (thermal, electrical, mechanical) properties [3–5].

Oxidative surface modification procedures have been widely studied and used. These procedures have some advantages such as: low cost, adequacy to large surface treatments; and some
disadvantages like: environmental problem associated with the chemical reagents used, long required times [6—10].

The oxidation of PP in solid phase, has been reported which is carried out in the reactions with ozone, γ-initiated, corona method, UV ray [11—15] or in the presence of copper oxides and ferrous chloride [15—18].

In this paper we present the results of the oxidation of PP in the solid phase which is carried out using oxidative aqueous solution of phenyltrimethyl ammonium permanganate (Ph.TMAP). The effects of temperature, time and concentration on the oxidation reaction are also studied.

The Ph.TMAP was prepared in our laboratories by a novel method.

EXPERIMENTAL

Material
The PP of grade T30G was supplied by Arak Petrochemical Co. Iran. (MFI: 3.0, isotactic index: 93—97%). The potassium permanganate, phenyltrimethyl ammonium bromide (Ph.TMABr) and the solvents were all of analytical grade and supplied by Merck.

Apparatus
The samples were characterized by NMR (Bruker W.H. Spectrometer, 80 MHz), FTIR-4300 (Shimadzu), UV (Shimadzu UV-visible recording spectrophotometer-UV-265 FW), ESCA, electron spectroscopy for chemical analysis, (Escalab 3 MK II) and scanning electron microscopy, SEM, (Cambridge Instrument; Stereoscan 360).

Preparation of Phenyltrimethyl Ammonium Permanganate as an Oxidizing Agent
Initially 1.24g (0.057 mol) of Ph.TMABr was dissolved in 3.4 mL of deionized water (solution 1). A second solution (solution 2) was prepared by dissolving 0.92 g (0.057 mol) of KMnO₄ in 10 mL of water. Solution 2 was added to solution 1 under constant stirring at room temperature. A purple precipitate of Ph.TMAP was formed immediately. The agitation was stopped after 30 min, and the solution was let to settle for 1 h and it was cooled down to 6 °C. After rinsing the purple precipitate with 5 mL of cold water, it was dried under vacuum for 22 h at room temperature. The reaction yield of 83% was achieved.

Ph.TMAP is soluble in solvents such as acetone, water, chloroform, ethanol. The best film (for IR) was obtained in acetone. Ph.TMAP is an explosive product in its dry state, and it must be handled with care. It must not be broken down physically with a hard metallic instrument.

Method
At first PP as a transparent film with dimension of 3×7 cm² and 0.5 mm thickness and a powder of

<table>
<thead>
<tr>
<th>Trial number</th>
<th>PP (g)</th>
<th>Ph.TMAP (mg)</th>
<th>Water (mL)</th>
<th>Temperature (°C)</th>
<th>Reaction time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.3</td>
<td>300</td>
<td>20</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>1.3</td>
<td>300</td>
<td>20</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>1.3</td>
<td>300</td>
<td>20</td>
<td>25</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>1.3</td>
<td>200</td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>1.3</td>
<td>400</td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>1.3</td>
<td>600</td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>1.3</td>
<td>600</td>
<td>20</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>1.3</td>
<td>600</td>
<td>20</td>
<td>50</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>1.3</td>
<td>600</td>
<td>20</td>
<td>30</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>1.3</td>
<td>500</td>
<td>20</td>
<td>25</td>
<td>120</td>
</tr>
</tbody>
</table>
T30G grade, were oxidized in the presence of water (as a solvent) and Ph.TMAP as an oxidizing agent. The surface of PP was oxidized.

Water dissolved the oxidizing agent without any effect on the PP film or the powder. The conditions for the oxidation reaction is shown in Table 1.

From samples No.1 to No. 9, PP was as a

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Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>v (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2000.0</td>
</tr>
<tr>
<td>2</td>
<td>1500.0</td>
</tr>
<tr>
<td>3</td>
<td>1000.0</td>
</tr>
</tbody>
</table>

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Figure 1. (a) IR; (b) NMR; (c) UV Spectra of Ph.TMAP.
Table 2. ESCA analysis of oxidized PP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O₁s (%)</th>
<th>C₁s (%)</th>
<th>N₁s (%)</th>
<th>Mn₂p (%)</th>
<th>Ratio or number of atoms O/C</th>
<th>MnO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>31.058</td>
<td>56.773</td>
<td>1.454</td>
<td>10.715</td>
<td>0.547</td>
<td>19.133</td>
</tr>
</tbody>
</table>

transparent film and sample No.10 was powder in the reaction with Ph.TMAP.

The PP transparent films and the powder were placed in glass tubes of 1.5×10 cm² and the oxidation was carried out under nitrogen atmosphere. The transfer of heat, controlled in glass tubes, was achieved by thermostatic baths. The glass tubes were placed at 80 °C at the oxidation system kept under vacuum, and then finally they were sealed in frozen salt water.

![Graph](image)

Figure 2. (a) IR; (b) NMR; (c) UV Spectra of Ph.TMAH.
Purification of Oxidized PP
After termination of the reaction, the oxidized films were laid in acidic solution for 48 h, and in addition they were washed with 20% $H_2SO_4$. Finally, the films were washed with water until pH: 7.0.

The oxidized PP was dried under vacuum and under nitrogen atmosphere at room temperature for 24 h. The polymer obtained was characterized by IR, SEM and ESCA.

RESULTS AND DISCUSSION

The Ph.TMAP was characterized by NMR, FTIR and UV. The NMR spectra show the presence of methyl groups attached to nitrogen in the region $\delta$: 3.66 ppm and phenylic ring at the $\delta$: 7.69 ppm.

The presence of $MnO_4$ ion was confirmed by the IR absorption band at 920–890 cm$^{-1}$, as well as by the UV spectra at $\lambda$: 565.6, 545.2, 525.0 and 507.2 nm (Figure 1).

During oxidation, the solution which was initially purple turned gradually into brown. Finally the solution changed into a colourless aqueous solution which was free of Ph.TMAP but containing a suspension of $MnO_2$. The brown precipitate ($MnO_2$) disappeared when either HCl or $H_2SO_4$ was added to the solution. In the reaction with PP and Ph.TMAP at room temperature and in different concentrations and times, the pH of the solution was 7.0. After filtering $MnO_2$ and evaporating the solution, no residue was remained.

The aqueous solution of reaction in different temperatures had a pH of 8.7–9 which suggest the existence of a basic product soluble in water. This reaction was carried out at 80, 50 and 30 °C. At 80 °C, after 96 h the whole solution was colourless. The survey on IR spectra of PP sample showed no polar groups.

According to the basicity of the solution and formation of a white precipitate, the existence of phenyltrimethyl ammonium hydroxide (Ph.TMAH) was expected. The IR, UV and NMR spectroscopy confirmed the existence of that compound. The NMR spectra showed the hydrogens of methyl

Figure 3. FTIR Spectra of PP film after treatment with Ph.TMAP for (a) 40; (b) 80; (c) 120 days.
groups in the region of $\delta$: 3.59 ppm and the hydrogens of phenylic ring in the region of $\delta$: 7.74 ppm (Figure 2).

On the other hand, the hydroxide ion was confirmed by IR absorption band at 3456 cm$^{-1}$ and UV spectra at 202 and 242.6 nm (Figure 2).

ESCA Analysis
ESCA analysis shows the presence of nitrogen in polymeric matrix (Table 2). The relative high percentage of oxygen and the presence of nitrogen atoms, as determined by ESCA and FTIR, confirm the existence of alcoholic, hydroperoxide groups and carboxylate ions such as quaternary ammonium salts. Also high absorbance of oxygen and manganese determined by ESCA was attributed to the polar groups and MnO$_2$ as well (Table 2).

Spectroscopy Study
IR spectra of PP oxidized by Ph.TMAP showed an absorption band at 1628 cm$^{-1}$ attributed to the carboxylate ions. The oxidized PP with mineral acids did not cause the absorption band in the region 1628 cm$^{-1}$ to shift. This matter confirmed the formation of quaternary ammonium groups which were stable [19] (Figures 3–5). These results were confirmed by ESCA analysis (Table 2).

The absorption bands between 3400–3420 cm$^{-1}$ was attributed to alcohol and hydroperoxide. Hydroperoxide group was measured by iodometry [20].

Normally, hydroperoxides produced by oxidation of hydrocarbons at high temperatures are unstable, but in reactions conditions of 25 °C temperature, these groups are relatively stable. In spite of low sensitivity, this measurement was confirmed with FTIR absorption spectrum.
Table 3. Absorption bands surface ratios between the carboxylate/methyl and hydroperoxide concentration.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Surface ratio between the absorption bands 1772-1532/1377 (cm⁻¹)</th>
<th>Ph.TMAP (mg)</th>
<th>Temperature (°C)</th>
<th>Hydroperoxide concentration (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Film 1</td>
<td>0.099</td>
<td>300</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.116</td>
<td>300</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.132</td>
<td>300</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>0.126</td>
<td>200</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.144</td>
<td>400</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.167</td>
<td>600</td>
<td>25</td>
<td>1.7x10⁻¹³</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>300</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>300</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>300</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>PP powder 10</td>
<td>2.777</td>
<td>500</td>
<td>25</td>
<td>2.3x10⁻⁴</td>
</tr>
</tbody>
</table>

No(s) 1—9: as film, and No 10 as powder. The oxidation for No(s) 7—9 do not take place.

At 1160—1174 cm⁻¹ one notices the ν(C—N aliphatic), the ν(N—CH₃) at 2880 cm⁻¹ and ν(N—Ph) at 1395-1385 cm⁻¹ groups. Table 3 shows the surface ratio between the absorption bands in the region 1772—1532/1377 cm⁻¹, as well as the concentration of the measured peroxide.

FTIR spectra of oxidized PP of constant concentration and different times are shown in Figures 3—5. Also the curve for the absorption band surface ratios of carboxylate polar groups to methyl versus time is shown. According to this curve the percent of polar groups is gradually increased (Figure 6).

**Scanning Electron Microscopy**

For studying the morphology and the external form of a material, SEM can be used. Figure 7 shows the morphology of different PP samples observed by optical microscopy (magnification ×200 and 500). The SEM picture shows that the surface of the unoxidized PP was apparently smooth, as the oxidized samples and MnO₂ were adsorbed on the PP surface, a granulated structure was observed.

If the surface of the oxidized PP is washed with a solution of 20% H₂SO₄, an image of bumps and craters can be observed. This roughness seems more uniformly distributed on the surface when

\[
2\text{Ph-N}^+\text{-MeMnO}_4^- + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 3[\text{O}] + \text{H}_2\text{O} + 2\text{Ph-N}^+\text{-MeOH}^- \quad (a)
\]

\[
\text{PP-H} + 2[\text{O}] \rightarrow \text{PP'-COOH} \quad (b)
\]

\[
\text{PP'-COOH} + \text{Ph-N}^+\text{-MeOH}^- \rightarrow \text{H}_2\text{O} + \text{PP'-COO}^-\text{Ph-N}^+\text{-Me} \quad (c)
\]
Figure 6. (a) Curve of the absorption bands surfaces ratio of polar groups to methyl (1772–1532/1377 cm⁻¹) measured by FTIR vs concentration of Ph.TMAP (mg/20 mL water); (b) Curve of the absorption bands surfaces ratio of polar groups to methyl (1772–1532/1377 cm⁻¹) measured by FTIR vs time (days).
Figure 7. Scanning electron microscope pictures on the morphologies; (a) unoxidized PP film; (b) oxidized PP film (after treatment with 20% H₂SO₄ solution) at 25 °C, concentration 0.117 (mol/L), 30 days; (c), (d) oxidized PP film with adsorbed MnO₂ from solution (magnification 200 and 500 X); (e) unoxidized PP powder; (f); (g) oxidized PP powder with adsorbed MnO₂ from solution (magnification 200 and 500 X); (h); (i) oxidized PP powder (after treatment with 20% H₂SO₄ solution at 25 °C, concentration 0.097 (mol/L), 120 days.
Oxidation of Polypropylene Homopolymer

Annealing treatment is applied after oxidation. Also in the oxidized PP powder bumps and craters were observed. The oxidized PP films and powder showed the maximum density of generated carboxylate and hydroperoxide groups which were in the polymer surface.

Proposed Reaction Scheme
From these results one can propose the following reaction mechanism:
Ph.TMAP being an unstable salt is decomposed in normal temperature and in presence of water as follows (equation a).

According to the mechanisms presented, the produced atomic oxygen oxidizes PP to its carboxylic acid (equation b) [21].

The presence of quaternary ammonium carboxylate groups (FTIR and ESCA analysis) can be related to the following reaction (equation c).

CONCLUSION

—Oxidation of PP in presence of Ph.TMAP forms polar groups such as carboxylate, hydroperoxide and alcoholic. Hydroperoxide and alchoholic groups are identified by FTIR and they are determined by chemical reagents.
—The MnO₂ is observed on the surface of polymer. The reaction of oxidized PP with mineral acids causes the MnO₂ to disappear(SEM).
—The formed carboxylate groups on polymers, are very stable and they are not affected by mineral acids.
—The Ph.TMAP used for oxidation reaction described here is proposed by a novel method, which gives a conversion yield of 83.0%.
—Finally, a reaction mechanism involved is proposed.

REFERENCES

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