Selective surface functionalization using underwater plasma technique

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Abstract
Among new types of plasma processes the underwater plasma is attracting considerable attentions, for its efficacy towards selective functionalization of polymer surfaces. This class of non-equilibrium solution plasmas offers denser and selective polymer surface –OH functionalization in comparison to the well-known and frequently used low-pressure oxygen plasma treatment of polymer surfaces. Use of Fenton-like catalysts was found supportive to enhance the overall oxidation as well as selective functionalization at the same time.

Key words: Surface, functionalization, underwater plasma, capillary discharge, hydroxyl radical, selectivity

Introduction
Functionalization of polyolefin surface is a prerequisite for many subsequent industrial application processes such as adhesion, coating, printing, metallization etc. [1-4]. Most often oxygen functional groups such as OH groups must be formed at the polyolefin surface in order to introduce an adhesion promoting group between the inert polyolefin surface and the polar coating, thereby creating chemical and physical interactions between the polymer substrate and the coating for sufficient adhesion. For this purpose, the CHx groups of the polyolefin surface must be selectively oxidized to preferentially OH groups [5]. The exposure of the aliphatic polymer to an underwater plasma (UWP) that is enriched with OH features (•OH, HO) pertains greater possibilities to introduce OH groups onto the polymer surface in much higher concentration and with higher (OH) selectivity than the treatment in oxygen low-pressure gas plasma. Idea, motivation and realization of the theoretical assumption about the underwater plasma with the experimental result of the selectivity aspects of underwater plasma are discussed in detail earlier [1-3]. In a consequent study it was understood that the hydrogen peroxide plays a key role in altering as well as affecting the selectivity of hydroxyl functionalization [6]. It was seen that during the later stages of underwater plasma processes the selectivity slashes significantly and it was concluded experimentally that hydrogen peroxide accumulation perhaps the reason for the selectivity recession. The addition of a OH species [9]. The in-situ formed Fenton-type reagent was added to the UWP and its effect on the hydroxyl functionalization of PP-surface was studied. Simultaneously the presence of hydroperoxy functionality was also found to be important for the functionalization. It was assigned by the ESCA analysis and later the same was identified by the gas phase derivatization of UWP.
exposed films using sulfur dioxide.

Fenton’s Chemistry:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^• /I/ \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^• /II/
\end{align*}
\]

Another interesting feature of this technique is its flexibility to use a variety of additives in the water phase. Extending the similar idea of pacification of plasma evolved/moderated species using capillary discharge technique, study was focused to equip the polymer surface with carboxylic functionality was attempted and studied\(^{[10]}\).

Experimental Part:
The scheme used for generation of the underwater plasma is schematically depicted in Fig. 1. The underwater plasma generating device comprises an electrochemical cell, which is divided by a dielectric barrier into two compartments. However, the two compartments are connected by a capillary, the core of this UWP process. The water-filled chambers are complemented by graphite (or metallic) electrodes. The quartz capillary had an inner diameter of 2.5 mm ± 0.1 mm and a length 25.0 mm ± 0.5 mm. Details concerning the experimental setup and related topics are discussed in detail in earlier communications \(^{[1, 6]}\). Alternating current of 20 kHz was applied with a voltage ranging from 12 to 15 kV. The discharge was generated using laboratory grade sodium chloride as electrolyte imparting initial conductivities ranging from 400 to 650 µS/cm. Zeolite ZSM5 was cordially received from Süd Chemie, India Ltd., Baroda, India. Ferrous sulphate was used for the ion exchange process with the zeolite for preparation of the catalyst. The catalyst Fe-ZSM5 was prepared in the laboratory as follows: To the solution, comprising of 15 mg ferrous sulphate diluted in 100 ml bi-distilled water, 11.5 mg ZSM-5 powder was added. The mixture was heated to 80°C and kept at this temperature while stirring for 4-6 h. After 6 h of stirring the mixture was filtered and washed thoroughly with distilled water 3-4 times (with 150-200 ml water each time). The filtered cake was heated at 90-120°C for 2 h and then underwent calcination between 520-550°C for 6 h. The temperature for calcinations was attained slowly from 120 to 520 °C in a period of 2-3 h. The material recovered was analysed by Mössbauer spectroscopy to detect the active ferrous and ferric sites on and within the zeolite ZSM5. The spectroscopic analysis suggests that the synthesized catalyst contains at least 1.8 to 2.0 % ferric Fe\(^{3+}\) sites and less than 0.2% ferrous Fe\(^{2+}\).

Hydrogen peroxide with 30% concentration in water was supplied by Fluka Chemicals. Polypropylene films of 100 µm thickness and 25 mm×75 mm size were used, supplied by Goodfellow, Cambridge Ltd., UK. The modified polymer surface was inspected using X-Ray Photoelectron Spectroscopy (XPS). The introduction of oxygen (O\(_{\text{total}}\)), and among all oxygen-containing groups that of the OH-groups, was controlled by measuring the C1s and O1s peaks. The F1s and S2p peaks were used for quantifying the presence of –OH and –O–OH groups among all oxygen-containing carbon bonded (C-O) species (C-OH-alcohols, C-O-C-ethers and hydroperoxides-C-O-OH), by derivatizing them with trifluoroacetic anhydride (TFAA) and sulphur dioxide (SO\(_2\)) gas respectively, according to:

\[
\begin{align*}
\text{–OH} + \text{O-(CO-CF}_3)_2 & \rightarrow \text{–O-CO-CF}_3^+ + \text{HOOC-CF}_3 \quad /\text{III}/ \\
\text{–O–OH} + \text{SO}_2 & \rightarrow \text{–O-SO}_2\text{-OH} \quad /\text{IV}/
\end{align*}
\]
Results and Discussion:
Qualitative comparison: Addition of hydrogen peroxide and Fe-ZSM5 catalysts to the underwater plasma system

It was reported earlier, the hydroxyl radical presence and its concentration inside the solution remains the key for the effective hydroxyl functionalization of the polymer surface. It was expected that the OH radical concentration in the UWP is proportional to the XPS-detected concentration of OH groups at the polypropylene surface. The highest OH-selectivity (OH/100 O total) was found to be at 20 mm distance from the tip of the capillary. However, at this distance the effective oxidation of the polymer surface is lower than in the case of smaller distances from the capillary tip. This problem was effectively resolved by addition of hydrogen peroxide at sufficiently higher concentrations, about 125-150 mol/Liter. Incurred Fe-ZSM5 heterogeneous material and forming in-situ the Fenton’s catalytic system, this effective oxidation was even further enhanced (see Fig. 1).

Figure 1: Comparative direct surface oxidation using UW-plasma system with additives H2O2 and Fenton like catalyst system

The figure also comprises C1s and O1s curve comparison of PP-surface exposed to UW-plasma with the subsequent addition of hydrogen H2O2 & Fe-ZSM5 catalyst. It was expected to get a higher surface oxidation after addition of hydrogen peroxide though its interesting as well as noteworthy to point out the increased extent of oxidation in the late stages of UWP process by addition of Fe-ZSM5 catalyst. The effectiveness of the Fenton’s catalytic system consists of the enhanced production of hydroxyl radicals by decomposition of the UWP-generated H2O2. Figure 2 explains the differential role of Fenton’s system (Fig. 2, curve D) and Fe-ZSM5 catalytic system (Fig. 2, curve B). Similar comparison in context with Figure 1 of C1s and O1s comparison indicates towards the need and necessity of OH radical presence for effective surface oxidation and selective OH functionalization of the polymer surface. It was seen that in the plasma process, this typical situation only occurs during the initial 1-5 min of the process.

Figure 2: Comparative selectivity’s:
A) UW at neutral pH; B) UW + Fe-ZSM5 at neutral pH; C) UW at pH 2; D) UW + catalyst Fe-ZSM5 at pH 2

Later, the simultaneous dimerization (quenching) of these radicals produces hydrogen peroxide which enters the radical chain mechanism causing a drop in the yield of OH functionalization. Fenton’s chemistry is well suited to cleave the thus generated hydrogen peroxide.

Embedded Fe3+ cations impregnated over the ZSM-5 molecular sieve network together with hydrogen peroxide re-generates the hydroxyl radical thereby
increasing the efficiency as well as the selectivity of functionalization.

It is important to note that using Fenton’s type of catalyst systems, the total oxygen concentration growth was almost linear in time (Fig. 1 similar to that of selectively bonded hydroxyl groups (Fig. 2, D). The surface oxidation of PP by underwater plasma with and without hydrogen peroxide also increases exponentially (Figure 2). Nevertheless, the significant differences to the OH functionalization as shown in Fig. 2 should be noted. Most importantly it must be mentioned that using the Fe-ZSM5 catalyst, the overall-oxygen introduction could be even enhanced as compared to the pure UWP, and also with hydrogen peroxide as an additive (cf. Table 1).

<table>
<thead>
<tr>
<th></th>
<th>maximum total oxygen/100 carbon atoms</th>
<th>C1s peak[bonds/100 carbon atom]</th>
<th>C-O %</th>
<th>C=O %</th>
<th>O=C-O %</th>
<th>C-O bond selectivity [C-O/100 oxygen bonds]</th>
<th>OH groups per 100 OH groups within O_{total} [TFAA-derivatisation]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure UWP-plasma</td>
<td>4-6</td>
<td></td>
<td>12,5</td>
<td>3,5</td>
<td>2</td>
<td>69,4</td>
<td>25-40</td>
</tr>
<tr>
<td>UWP with hydrogen peroxide</td>
<td>7-9</td>
<td></td>
<td>21,5</td>
<td>3,6</td>
<td>2,4</td>
<td>75,4</td>
<td>12-24.7</td>
</tr>
<tr>
<td>UWP with Fenton’s catalyst</td>
<td>8-9,5</td>
<td></td>
<td>18,1</td>
<td>3,9</td>
<td>1,1</td>
<td>78,7</td>
<td>15-27</td>
</tr>
</tbody>
</table>

Table 1: comparative bond selectivity obtained by XPS measurement

Curve fitting analysis of the C1s signal shows that the C-O bonds composed in the C1s spectra was 21.5% (UWP+H₂O₂) \(^1,\,6\) 18.1% (UWP + Fenton), Figure 3. Table 1 depicts the percentage of C-O bond selectivity \(^1\) (all singly bonded C-O features). Using the Fenton’s catalyst system, the C-O selectivity (C-OH, C-O-O, C-O-C) was slightly improved. Also an exponential pattern in selective functionalization was observed.

Hydroperoxide (-O-OH) functionality generated by the underwater plasma process

During the primary and secondary underwater plasma processes, the formation of a new component, the hydroperoxyl radical, was also expected as shown in eqn. VII. Theoretically, the O1s-curve fitting comprises components: 532.8 to 532.2eV (\(\text{C}=\text{O}\)) and 533.5eV (C-OH) results support this assumption\(^{11}\). The hydroperoxyl functionality allocation was given at 535.5eV \(^{12}\). These detected –O-OH moieties may be another key product in the hydroxyl surface functionalization process besides H₂O₂ and OH radicals.

Its presence was confirmed by the XPS analysis and discussed elsewhere \(^{12}\). They are unstable or metastable and are vicious for overall selectivity of the processes. The auto-oxidation chain-reaction may be one source of this type of functional groups, starting with the peroxy radical formation with O₂.

The abstraction of H from a neighbored polymer chain and the following slow auto-decay of the thereby formed
hydroperoxide to the mentioned broad variety of O-functional groups [13]:
\[ -C \cdot + \cdot O-O \rightarrow -C-O-O \cdot + +C \cdot \]

and finally,
\[ -C-O-O \rightarrow \rightarrow \rightarrow \text{decay, rearrangement, degenerate products} \ [14]. \]

Another mechanism may be plausible, the direct attachment of hydroperoxy radicals onto radical sites at the polyolefin surface according to:
\[ -C+ + \cdot O-O \rightarrow -C-O-O \] /VIII/

These metastable hydroperoxides can be traced by using the chemical derivatization of hydroperoxy moieties as shown in the equation IV. The gas phase derivatization technique was carried out at room temperature under atmospheric pressure conditions for 15-20 min.

Figure 4: XPS-peaks of SO₂-derivatized PP-surface exposed to UW-plasma for 10 min.

The procedure for the derivatization was followed as mentioned in the literature [13, 15]. The presence of atomic sulfur was considered the indicator for the hydroperoxide concentration on the polymer surface (cf Fig 4). It is quite clear from the equation IV that one hydroperoxy moiety corresponds to one sulfur atom detected by XPS. Presence of S2p signal indicates the UWP process gives rise to such species during the surface functionalization.
\[ -C-O-O + H₂O₂ \rightarrow -C-O-O \cdot + H₂O + \cdot OH \] /IX/

As per the equation IX-XI, experimental results and the literature suggest that the presence of hydroperoxy moieties could be erratic due to its unreasonable decay behavior to form decomposition products. It obviously causes deleterious effects for the desired hydroxyl functionalization process. To overcome formation of such species Fenton-like processes were employed into the underwater plasma process.

Figure 5: Comparison of –O-C=O-bond formation by varying the additives

It was seen that using UWP tool polymer surface could be also equipped with carboxylic bond on the surface [10]. A variety of additives such as oxalic, maleic, itaconic, acetic and acrylic acid enriches the PP surface with carboxylic bonds (cf. Figure 5). In addition the same data is also compared with using Fenton-like system into the UWP process. From the list of organic acids, oxalic acid was seen the least whereas acrylic acid was best in giving carboxylic bonds to the substrate surface. An exclusive study using these organic acids was studied earlier. The data is compared with the established gas phase low pressure plasma oxidation of PP and with the oxidation using UWP system. Interestingly it was seen that the ester bond linkages generated by the addition of Fe-ZSM5 catalysts together with the Fenton’s conditions the system
behaved more selectively for generating the least amount of ester bonds.

**Conclusion:**
The role of hydrogen peroxide generated during the underwater plasma process with and without combination with an externally added heterogeneous (Fenton’s) catalyst system was studied for selective polymer surface functionalization for predominant OH-groups formation. Role of the Fenton’s catalyst addition was studied in context to earlier results with hydrogen peroxide incursion. To increase the selective formation of hydroxyl groups Fentons-like processes were found very supportive. As expected this redox system accelerates surface oxidation and –OH functionalization simultaneously. The same system was also found reducing the portion of carboxylic bond linkages in comparison to the genuine underwater plasma surface functionalization process.

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