Studies in Surface Properties of Carbon Fibres: Part II — Effect of Surface Oxidation on Surface Areas of Polyacrylonitrile-based Carbon Fibres

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Surface areas of polyacrylonitrile-based Beslon and Torray carbon fibres before and after oxidation with nitric acid, hydrogen peroxide and potassium persulphate as well as after evacuation at 1200°C have been determined. Each treatment results in a considerable increase in surface area, the magnitude of the increase varying with the nature of the oxidant and the carbon fibre. The surface areas record a further increase on evacuation of the oxidised fibres. Pore size distribution curves indicate an increase in the average pore diameter after oxidation and evacuation treatments. The nitrogen surface areas are generally less than the CO₂ surface areas indicating a molecular sieve effect. This is supported by much smaller surface area obtained from the adsorption isotherms of benzene and α-pinene.

The mechanical properties of carbon fibre-resin composites depend upon surface functionality and surface area of carbon fibres. Since, the relative importance of the two factors is not completely understood, it is, therefore, of interest to study the effect of oxidative treatments on the surface functionality of polyacrylonitrile (PAN)-based carbon fibres. The influence of surface oxidation on the formation of carbon-oxygen surface complexes has been reported in Part I of the present series. The present paper describes the influence of different oxidative treatments on surface areas of these materials.

Materials and Methods

Beslon and Torray PAN carbon fibres were oxidised in nitric acid, hydrogen peroxide, potassium persulphate before and after evacuation at 1200°C. The details of the procedures for oxidative treatments and evacuation were the same as described elsewhere. The surface areas of the fibre samples before and after various treatments were determined by adsorption of nitrogen at 77 K, adsorption of CO₂ at 273 K and from the adsorption isotherms of benzene and α-pinene vapours at 308.16 K using a quartz spring balance.

Results and Discussion

Surface area — Surface areas of PAN-based Beslon and Torray carbon fibres calculated from their adsorption isotherms of nitrogen at 77 K using BET equation and of CO₂ at 273 K using Dubinin-Polanyi equation before and after different oxidative treatments are recorded in Table 1. There is a considerable increase in surface area on each oxidative treatment in both Baslon and Torray fibres. The effect of oxidation on surface area varies not only with the nature of the oxidant but also with the nature of the carbon fibre.

The increase in surface area is, in general, larger in the case of Torray fibre than that for Beslon fibre. In the case of Beslon fibre the magnitude of increase in surface area is up to seven-fold on treatment with hydrogen peroxide which incidentally results in the maximum chemisorption of oxygen (cf. Table 1, column 2). The treatment with 60% nitric acid which is the next best effective method for the chemisorption of oxygen causes a four-fold increase of surface area while treatment with 70% nitric acid and potassium persulphate which are effective in the decreasing order for chemisorption enhance the surface area by 3-4 fold of the original surface area. In the case of Torray carbon fibre, however, the increase in surface area as a result of oxidation is much larger and varies between 12 and 21 fold of the original surface area. The increase is maximum when Torray fibre is treated with 60% nitric acid. Similar observations of the increase in surface areas of a variety of carbon fibres on oxidative treatments have been recorded by other workers also.

This increase in surface area on oxidation probably results due to the formation of etch-pits of molecular dimensions on the basal planes which expose additional prismatic surfaces. This is further supported by the fact that the surface area both in Beslon and Torray fibres increases with increase in burn-off of the fibre during oxidation (cf. Table 1, column 1). In the case of oxidation with 70% nitric acid the increase in surface area is very small as compared to the burn-off of the fibre. It is highly likely that treatment with strong oxidising agents causes a burn-off of the very fine crystallites in the carbon fibre.

Surface areas of original and oxidised carbon fibres have also been determined after evacuation at 1200°C and the results are recorded in Table 2. It is interesting to note that the surface area record a further increase after evacuation of both original and oxidised Beslon and Torray fibres. The magnitude of increase...
Table 1 — Amount of Burn-off, Oxygen Chemisorbed and Surface Area of Beslon and Torray Carbon Fibres Before and After Different Oxidative Treatments

<table>
<thead>
<tr>
<th>Fibre sample</th>
<th>Burn-off (%)</th>
<th>Oxygen chemisorbed* (g/100 g)</th>
<th>Surface area (m²/g) from N₂-adsorption at 77K</th>
<th>Surface area (m²/g) from CO₂-adsorption at 273K</th>
<th>Surface area (m²/g) from Benzene</th>
<th>Surface area (m²/g) from α-Pinene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>nil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fibre treated with:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>60% Nitric acid</td>
<td>9.1</td>
<td>9.8</td>
<td>38</td>
<td>45</td>
<td>40</td>
<td></td>
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<tr>
<td>70% Nitric acid</td>
<td>27.5</td>
<td>8.4</td>
<td>35</td>
<td>38</td>
<td>30</td>
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</tr>
<tr>
<td>Potassium persulphate</td>
<td>6.8</td>
<td>8.5</td>
<td>28</td>
<td>36</td>
<td>30</td>
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<td>Hydrogen peroxide</td>
<td>13.6</td>
<td>12.1</td>
<td>64</td>
<td>74</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Torray carbon fibre</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Original</td>
<td>nil</td>
<td>4.1</td>
<td>9</td>
<td>10</td>
<td>14</td>
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<td>Fibre treated with:</td>
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</tr>
<tr>
<td>60% Nitric acid</td>
<td>8.1</td>
<td>8.3</td>
<td>109</td>
<td>203</td>
<td>43</td>
<td>14</td>
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<tr>
<td>70% Nitric acid</td>
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<td>7.1</td>
<td>110</td>
<td>145</td>
<td>40</td>
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<tr>
<td>Potassium persulphate</td>
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<td>7.8</td>
<td>72</td>
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<td>42</td>
<td>15</td>
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<tr>
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<td>10.2</td>
<td>108</td>
<td>140</td>
<td>53</td>
<td></td>
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</tbody>
</table>

*Reference 5

of surface area is larger on evacuation of the original sample (8–12 fold) than for the oxidised samples. This increase in surface area may be attributed to the elimination of chemisorbed oxygen on evacuation resulting in the availability of additional surface which is previously occupied by the oxygen complexes, and to the release of trapped carbonisation products as well as to the opening up of the micropore structure. Mimeault and McKee have adduced evidence for the development of microporosity on evacuating graphitized PAN-based fibres at temperatures upto 1200°C. The surface area of the fibre at 1200°C evacuation corresponded to a four-fold increase.

The pore-size distribution curves, obtained from the adsorption isotherms of nitrogen for Torray fibre before and after oxidation and evacuation treatments are shown in Fig. 1. It is seen that evacuation of the carbon fibre increases both the pore diameter and micropore volume. The oxidation of the fibre is also

Fig. 1 — Pore size distribution curves of Torray carbon fibre before and after different treatments.
found to increase the pore volume of the fibre. It appears, that the oxidation and evacuation treatments result in opening up of the microporous structure in carbon fibres.

It has been shown\(^4\) that the amount of burn-off and the chemisorption of oxygen during each oxidative treatment depends upon the amount and the nature of the oxygen already present on the carbon fibre surface. A sample of Torray fibre has, therefore, been evacuated at 1200°C to eliminate the associated oxygen completely. The surface areas of oxygen-free fibre samples treated with different oxidising agents are given in Table 3. It is seen that the surface area once again increases on oxidation. The surface areas of the oxidised samples in this case are larger than the surface areas of the corresponding samples obtained by the oxidation of original Torray fibre. The magnitude of increase in surface area appears to be independent of the nature of the oxidative treatment. This may be due to the fact that the amount of burn-off during oxidation in these samples which is a measure of etch-pitting is about of the same order of magnitude (varying between 6.1 and 6.7\(^\%\)), except in the case of 70\% nitric acid in which case there is excessive burn-off. When these oxidised samples are evacuated at 1200°C, a decrease in surface area (cf. Table 3) is observed, probably due to excessive degradation of the carbon fibre.

**Molecular sieve effect** — A comparison of the surface areas obtained from \(\text{N}_2\) adsorption at 77 K and \(\text{CO}_2\) adsorption at 273K (cf. Tables 1–3) shows that, in general, the \(\text{N}_2\) surface areas are smaller than the \(\text{CO}_2\) surface areas. These differences are of a lower magnitude in the case of the evacuated samples. This indicates that original and oxidised fibre samples have extremely fine micropores which are sufficiently narrow to impede the ingress of nitrogen at 77 K. When the carbon fibre is evacuated at 1200°C, a widening of these micropores occurs, resulting in greater accessibility of \(\text{N}_2\) at 77 K so that the two surface areas agree more closely. These observations are in agreement with the works of Walker and Kin held, Anderson et al.\(^{13}\), Kin held, Marsh and Wynne-Jones\(^{15}\) and Nandi and Walker\(^{16}\) who studied the adsorption of nitrogen and carbon dioxide in the temperature range 77 to 400 K on coals and activated carbons.

Surface areas of a few carbon fibre samples before and after oxidation and evacuation have also been determined from the adsorption isotherms of benzene and \(\alpha\)-pinene vapour-adsorbates with larger molecular diameters using BET equation. The results included in Tables 1–3, show that, in general, the surface area of a carbon fibre decreases with increase in the molecular diameter of the adsorbate. \(\alpha\)-Pinene (molecular diameter 8A) could cover less than 10\% of the nitrogen surface in most cases. In other words only a small fraction of the BET (\(\text{N}_2\)) surface could be covered by these larger molecules. This is attributed to the screening effect of the smaller pores towards the bigger adsorbate molecules. Similar screening effect in the case of polymer charcoals has been observed by several workers.\(^{17–20}\)

The results presented in this paper clearly show that surface oxidation of carbon fibres followed by elimination of combined oxygen on evacuation at 1200°C places at our disposal a convenient method for enhancing surface area by 10–20-fold. It may be mentioned that the elimination of chemisorbed oxygen may lower wettability and lyophilic character.
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but the considerable rise in surface area may itself have a highly beneficial effect in improving composite quality of the carbon fibres.

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References