Surface Studies on Amine-treated Polyethylene Terephthalate Filaments

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The surface structure (up to top 50 Å) and morphology of oriented polyethylene terephthalate (PET) fibres etched with ethylamine have been studied by ESCA and SEM. The peak intensities of the carbon Is levels and oxygen Is levels of the treated fibres are significantly different compared to those for the undrawn PET fibres. The effect of amine degradation at different draw ratios has been examined.

Amine degradation of oriented polyethylene terephthalate (PET) fibres is of considerable interest while studying the morphology of films and fibres. Very little information is available in literature on this subject. Kurita suggested that aminolysis reaction is selective, starting with the amorphous region and extending to the crystalline region. This report concerns etching phenomenon for the bulk which occurs on amine treatment of PET. It has been observed that although the use of ESCA has been extensively made in the field of polymers, the structural attributes of synthetic fibres have not been studied extensively using this versatile technique. Recently, Clark et al. used ESCA for studying oxidative degradation. The effect of acid treatment on the top surface of PET fibres has been reported elsewhere.

In the present investigation, an attempt has been made to use ESCA and SEM to study the top 50 Å morphology of the amine treated PET fibres vis-à-vis untreated PET fibres of different draw ratios.

Materials and Methods
Commercial undrawn polyethylene terephthalate fibre and ethylamine (Analar grade) were used. The intrinsic viscosity of PET used was 0.62. The undrawn PET fibres were drawn in a pilot plant nearly at the glass transition temperature (69°C) and at draw ratios 3.5 and 4.2.

The amine treatments were given at 25 ± 1°C in a beaker for 6 hr. For treatments with ethylamine, nearly 10 cm long fibre samples were put in the beaker containing some ethylamine and the beaker was shaken. The amine treated samples were thoroughly washed nearly 10 times, dried and kept in a vacuum desiccator for 20 hr. Surface structural studies were conducted on the treated fibres using ESCA and SEM.

The X-ray photoelectron spectra of C Is and O Is levels in the fibres were recorded on the X-ray photoelectron spectrometer using Mg Kα anode (1253.6 eV). ESCA model II was used for this study. Arbitrary units of intensity (I) were plotted on Y-axis and the binding energy (eV) was plotted on the X-axis. All typical experimental conditions were kept the same and due care was taken in handling the fibres. ESCA and SEM studies were made on the treated and three untreated fibres. The fibres were coated in vacuum coating unit before taking their SEM photographs.

Results and Discussion
Figs. 1 and 2 show the variation of IC/IO ratio with the draw ratio of treated and untreated PET fibres respectively. C Is and O Is peaks of the treated and untreated fibres are shown in the figures.

Fig. 1—IC/IO variation with draw ratio of treated fibres

Fig. 2—IC/IO variation with draw ratio of untreated fibres
untreated filaments appeared at 285.2 and 532.3 eV respectively; the count was always kept constant. $IO_{1s}$ and $IC_{1s}$ have been determined from the heights of the peaks. For amine treated fibre with draw ratio 1, binding on the sample cell could not be possible. The variation of the $IO_{1s}/IC_{1s}$ ratio clearly shows that as the draw ratio increases the effect of amine degradation decreases. Decrease in $IO_{1s}/IC_{1s}$ ratio with the draw ratio was also observed in the acid treated PET fibres. Padhya and Nadaf have shown, on the basis of IR and X-ray data, that the degradation is more pronounced at higher concentrations and at higher temperatures.

The aminolysis of ester is reported to take place according to the following reaction:

$$R'COOR + H_2NR'' \rightarrow R'CO \text{NHR''} + ROH$$

where $R' = C_6H_{14}$, $R = CH_2-CH_2-O-$ and $R'' = -C_2H_5$.

The peak position of the $C_{1s}$ peak was observed at 285.2 eV. The shift in the binding energy of the $C_{1s}$ peak by 0.2 eV to the higher side is probably due to the nitrogen, as has also been observed by Clark and Thomas. $O_{1s}/C_{1s}$ ratio at all the draw ratios of the treated fibres up to top 50 Å surface is always higher than that in the case of untreated fibres. The SEM photographs of the degraded fibres of draw ratios 1, 3.5 and 4.2 (Figs. 3a, b, c) show that the surface microstructure changes due to the severe degradation at the surface by the amine treatment. The action of amines has been attributed to the removal of the amorphous portions. It affects first the amorphous parts and then proceeds towards the crystalline parts. This view is confirmed on examining the outer regions of the fibres of different draw ratios which show that the fibrous morphology of the highly oriented crystalline parts had not been destroyed. Degradation of the surface of the fibres having draw ratio 3.5 was more than that of fibres with draw ratio 4.2. This supports the results of X-ray photoelectron spectrometric study of the different draw ratio fibres.

References