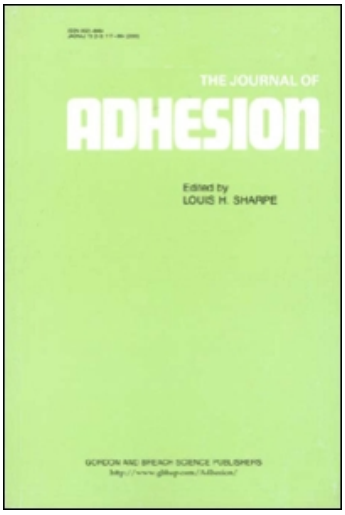

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Effect of surface roughness on the adhesion of electrolessly plated platinum to poly(ethylene terephthalate) films

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EFFECT OF SURFACE ROUGHNESS ON THE ADHESION OF ELECTROLESSLY PLATED PLATINUM TO POLY(ETHYLENE TEREPHTHALATE) FILMS

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Poly(ethylene terephthalate) films were treated with aqueous sodium hydroxide solutions of different concentrations for various times. The rate of weight loss increased with the addition of a swelling agent (methylene chloride) or a cationic surfactant. The surface roughness of the treated films was determined from atomic force microscopy (AFM) and pore diameter was obtained from scanning electron microscopy (SEM). In general, surface roughness was found to increase with increasing weight loss for the treated films. A maximum roughness was obtained for samples with a weight loss of approximately 15–20%, beyond which the roughness of the samples decreased. The addition of methylene chloride and surfactant resulted in an almost two-fold increase in the roughness for all treatment times investigated. The adhesion of electrolessly plated platinum film was dependent on the contact area produced by chemical treatment. Treatments producing smaller diameter pores of greater depth gave better adhesion.

Keywords: Polyethylene terephthalate; Roughness; Atomic force microscopy; Adhesion; Electroless plating; Surface modification

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INTRODUCTION

Aqueous alkaline hydrolysis is a common technique for altering the surface of poly(ethylene terephthalate) (PET) [1, 2]. In the textile industry sodium hydroxide treatment is used to create softer feel, improve handling, and increase hydrophilicity. Such treatments increase the surface roughness of PET, which accordingly offers a mechanism for improved adhesion through greater mechanical interlocking and increased surface area. One of the potential uses of sodium hydroxide-treated PET is as a substrate for electroless metallization. Electroless plating offers a number of advantages over other plating techniques; these include cost effectiveness and the ability to coat complex shapes uniformly. The metallisation of PET fibres or film results in a material suitable for many applications, for example as a biomaterial [3]. The advantages of such a material include the conductivity and electrode performance of a metal combined with the flexibility and fatigue resistance of a polymer.

The reaction mechanism of hydroxide with PET is considered to be the random scission of the polymer chain by hydroxyl ions at the ethylene glycol portion of the monomer [1] as shown in Figure 1. This results in hydroxyl and carboxylate end groups. Reaction is typically confined to the surface region of the PET with sections of polymer chain being removed, leading to etch pits. The tensile strength of the material remains relatively unaffected for fibres exhibiting weight losses up to 30%, suggesting that bulk material is not significantly affected [4]. However, for greater weight losses significant reduction in strength occurs.

The degree of weight loss of PET has been shown to be determined by the reaction time, temperature, and concentration of the sodium

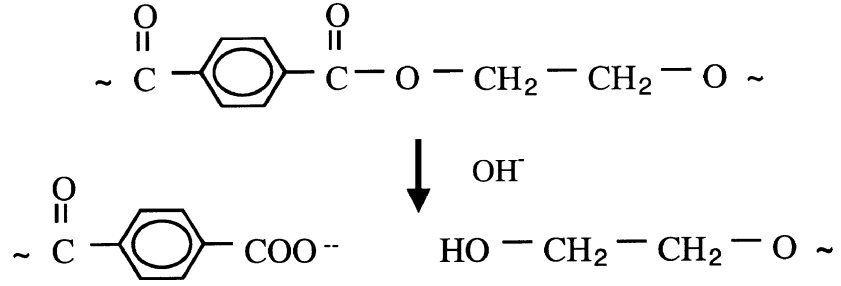


FIGURE 1 Mechanism for scission of a PET chain by hydroxyl ion at the ethylene glycol group [1].

hydroxide [5]. Researchers have found that, for a given concentration and temperature, weight loss varies linearly with time [2, 4, 6–8], whereas the relationship between weight loss and sodium hydroxide concentration has not been resolved. Some workers [9, 10] have found a linear relationship while others [2, 5] obtained nonlinear results.

The effect of increasing temperature on the rate of reaction has been shown to increase the hydrolysis of PET significantly [2, 8]. At temperatures above the glass transition temperature of the polymer, approximately 67°C, the reaction rate accelerated further [2]. This suggests that the hydroxide ion preferentially attacks the more amorphous regions of the PET.

A number of researchers have noted that the rate of the hydrolysis reaction of PET is greatly increased by the addition of surfactant [5, 11] and hydroxylic organic solutions [5]. Latta [5] determined that hydroxylic solvents were, in general, catalytic and proposed that the acceleration of the hydrolysis was due to improved solvation of the polymer, with resultant enhancement of the rate of chain cleavage. In addition, the less crystalline PET samples were more readily etched, and thus the more amorphous regions of the PET surface are expected to be preferentially attacked.

Previous studies of the change in surface roughness of PET with aqueous sodium hydroxide treatment are limited. Most researchers have examined the results of this treatment only qualitatively by methods such as scanning electron microscopy (SEM). Quantitative measurements made by recent workers [12, 13] utilised the adsorption of either nitrogen gas or the surfactant Tergitol (a nonylphenol ethoxylate) to determine the "true" surface area of treated fibres. It was found that the true surface area was significantly greater than the geometric surface area, suggesting the presence of a large amount of pitting arising from the hydrolysis reaction.

The aim of this study was to determine the surface roughness of PET film after various treatments with sodium hydroxide. The roughness is expected to influence the adhesion of electrolessly deposited platinum coatings. The temperature of reaction was kept constant, whereas the length of treatment times and concentration of sodium hydroxide were varied. Also the influence of a surfactant and a swelling agent on the weight loss/roughness was determined. Weight loss was calculated from mass measurements of samples before and after sodium hydroxide treatment. Surface roughness was observed by SEM and determined by AFM. Roughened samples were electrolessly coated with platinum and adhesion determined *via* tape testing.

EXPERIMENTAL

Biaxially oriented PET film (Goodfellows Ltd., UK) was cut into pieces (45 mm × 50 mm) from a large roll and grouped into sets of three. Samples were weighed on an analytical balance and cleaned by immersion in ethyl acetate (AR grade, Ajax Chemicals, Aust.) at a temperature of 60°C for 30 min using a shaker water bath (OLS200, Grant Instruments). After cleaning, the samples were dried in air at room temperature and then placed in an aqueous sodium hydroxide solution at a temperature of 80°C. Each sodium hydroxide concentration was used in quantities of 250 mL in a 400 mL Pyrex® glass container. A small amount (0.1% w/v) of cationic surfactant (Mercerine PE-S, Meisei Chemical Works Ltd., Japan) was included with the majority of the treatments. All processes were carried out at a shaking speed of 100 strokes per minute.

Swelling of PET was accomplished by soaking the samples in methylene chloride (AR grade, Ajax Chemicals, Aust.) for 5 min at room temperature prior to sodium hydroxide treatment. Methylene chloride was chosen as it has a solubility parameter similar to that of the semirigid aromatic segment of PET [14].

The range of concentrations of sodium hydroxide used was from 1 to 10% w/v, and the time of exposure of the PET to the hydroxide solutions was varied from 10 to 120 min.

After a particular treatment samples were rinsed thoroughly, three times in deionised water for 30 min, and then allowed to air dry at room temperature for a few hours. This was followed by oven drying overnight at a temperature of 50°C. Samples were cooled to room temperature and reweighed. The oven treatment, cooling, and weighing were continued until constant weight was obtained.

For each set of conditions two polymer films were plated with platinum using a procedure described previously [15], and one additional film was kept for further analysis. Briefly, films were initially treated with a catalytic palladium solution (0.2% palladium chloride in dimethylsulfoxide (AR grade, Sigma Aldrich, USA)), reduced with hydrazine hydrate, followed by immersion in a commercially available aqueous platinum bath (2g/L Platinum, Lectroless PT 100, Enthone, Australia) to which further reducing agent was added. The average coating thickness was determined by weighing the samples before and after coating. Throughout this work the thickness of the metal films was ($0.32 \pm 0.02\,\mu m$).

Surface roughness was assessed on uncoated samples using an AFM (Model LS, Park Scientific Instruments, California, USA) in contact mode using Ultralever™ all-silicon tips. The tips were conical

TABLE 1 Tape Test Rating System

Rating	Description
0	No coating removed
1	Less than 10% of coating removed
2	Less than half of the coating removed (<50%)
3	More than half of the coating removed (>50%)
4	All of the coating removed (100%)

in shape with an end radius of approximately 10 nm. The system was calibrated using a standardised silicon grating, and the surface roughness determined at each data point along a scan line from the following relationship:

$$R_{rms} = \sqrt{\frac{\sum_{n=1}^{N} (Z_n - Z_{av})^2}{N-1}},$$

where Z_n is the height at point n, Z_{av} is the mean height, and N is the number of data points within the selected area.

Three different areas of 25 μm × 25 μm were scanned and the calculated R_{rms} surface roughness values were averaged. Scanning electron microscopy (SEM, Model Jeol 6300, Japan) backscattered images were also used to monitor changes in surface morphology and were compared with the AFM results.

The test used to determine the relative adhesion strength of the thin metal film to the polymer was adapted from ASTM D3359. Pressure-sensitive tape (Permacel, New Jersey, USA), specified in the standard used in this work, was applied to the test specimen using a cylindrical 2 kg weight. The tape was then peeled at an angle of approximately 90° from the sample. Both the tape and the sample were then examined for any removed material. An indication of the level of adhesion between the coating and the substrate was taken as the amount of coating removed (Table 1). The test was repeated five times and an average rating was recorded.

RESULTS AND DISCUSSION

The change in weight loss with reaction time for the four different concentrations of aqueous sodium hydroxide containing surfactant is given in Figure 2. The weight loss values are averages of three films, with a probable error of less than 0.5% in all instances. A linear fit to

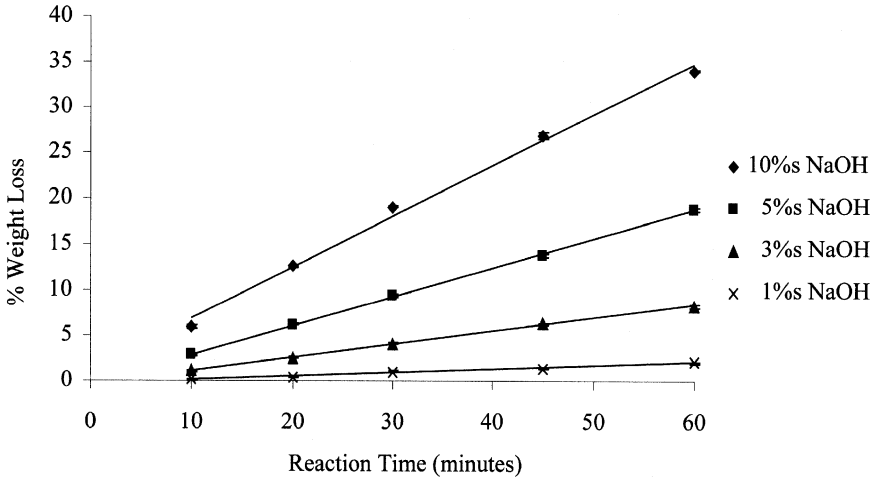


FIGURE 2 Plot of weight loss (% w/v) of PET film *versus* reaction time for various concentrations of aqueous sodium hydroxide treatments containing surfactant, s.

the data of time *versus* weight loss, for each of the sodium hydroxide concentrations, resulted in a correlation coefficient (R^2) in excess of 0.994. The slope of the lines increases with an increase in the sodium hydroxide concentration, indicating an accelerated rate of reaction. Other workers [2, 4–8] found a similar relationship for sodium hydroxide treatment of PET fibres.

The effect of additives on the weight loss as a function of time is shown in Figure 3. The relationship between reaction time and weight loss is linear regardless of prior swelling treatment by methylene chloride or the presence of surfactant in the sodium hydroxide solution. It is clear from the relative slopes of the lines that the surfactant greatly increases the rate of the reaction. The increase in the rate is approximately sevenfold. The effect of preswelling does not significantly affect the rate of weight loss in the absence of surfactant; however, an increase in the reaction rate by an additional factor of two is obtained if surfactant is present.

The influence of the concentration of aqueous solutions of sodium hydroxide containing surfactant on the weight loss of PET film is given in Figure 4. For all time intervals the results are nonlinear, and the degree of nonlinearity increases with time. The sigmoidal shape of the curves shows that at the inflexion point a maximum weight loss per unit concentration occurs, and this point occurs at the same concentration for all curves, *i.e.*, $(4.0 \pm 0.3)\%$ w/v NaOH.

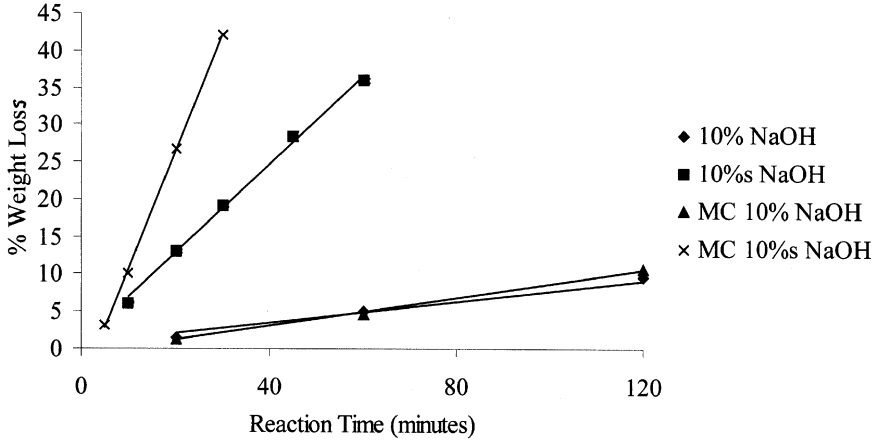


FIGURE 3 Plot of weight loss (% w/v) of PET film *versus* reaction time for 10% w/v aqueous sodium hydroxide treatments and treatments containing surfactant, s, and prior swelling with methylene chloride, MC.

Consideration of the rate of weight loss with concentration of sodium hydroxide resulted in a rate loss expression of order 1.3. This result is consistent with that of Latta [5], who found results that suggested a rate expression which lies between first and second order. It was concluded that the mechanism of the hydrolysis reaction involved at least two competing reactions occurring simultaneously.

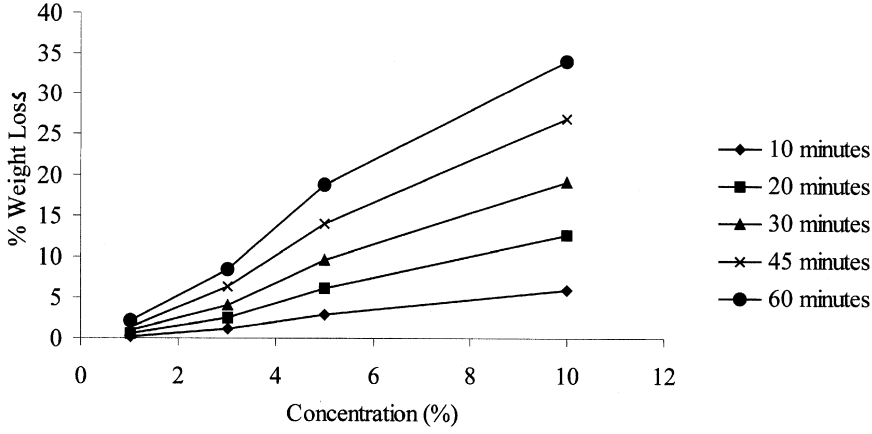


FIGURE 4 Plot of weight loss (% w/v) *versus* concentration (w/v) of aqueous sodium hydroxide containing surfactant for various times.

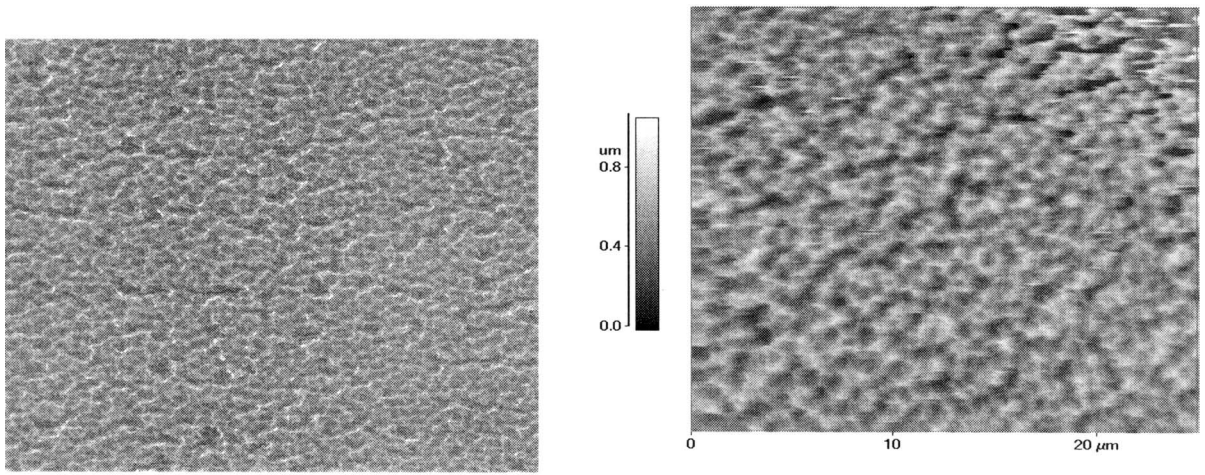
Figures 5a, 5b, and 5c show SEM and AFM images obtained on PET film, treated with 10% w/v aqueous sodium hydroxide solution, containing surfactant, at three different times, namely 10, 30, and 60 mins, respectively. The initially smooth ($R_{rms} \approx 6$ nm) untreated PET film is roughened through the formation of pits, similar to those observed with PET fibres [4]. AFM images show that the depth of these pits increases from 132 to 200 nm over the 50 min period. The pore distribution, obtained from the SEM images, is uniform over the polymer surface and the pits increase in size, as a function of time, from approximately 1 μm in diameter to approximately 5 μm over the 50 min period. This contributes to the increased weight loss observed. The smaller diameter pits result in higher normalised surface areas which provide more sites for attachment of platinum films of improved adhesion.

Preswelling of the samples before sodium hydroxide treatment resulted in micrograph images similar to those obtained in Figure 5. However, the inclusion of surfactant with the sodium hydroxide treatment of the preswelled samples produced changes in the surface morphology. After 5 min a series of connected pores were observed on the surface. With increasing weight loss these connected pores became larger and remained well-defined.

Unlike previous studies concerning the surface roughness of hydrolysed PET, AFM was utilised in this work to obtain semiquantitative measurements of pore depth. The calculated R_{rms} surface roughness with increasing weight loss for various sodium hydroxide concentrations was investigated. It was found that, in general, there was an increase in surface roughness with weight loss. The degree of roughness was dependent upon sodium hydroxide concentration and time; that is, low concentrations of sodium hydroxide for long etching times produce the same degree of roughness as high sodium hydroxide concentrations for short etching times. This behaviour suggests that the reaction mechanism is constant for the range of conditions utilised (1% to 10% w/v NaOH for etching times up to 120 mins duration).

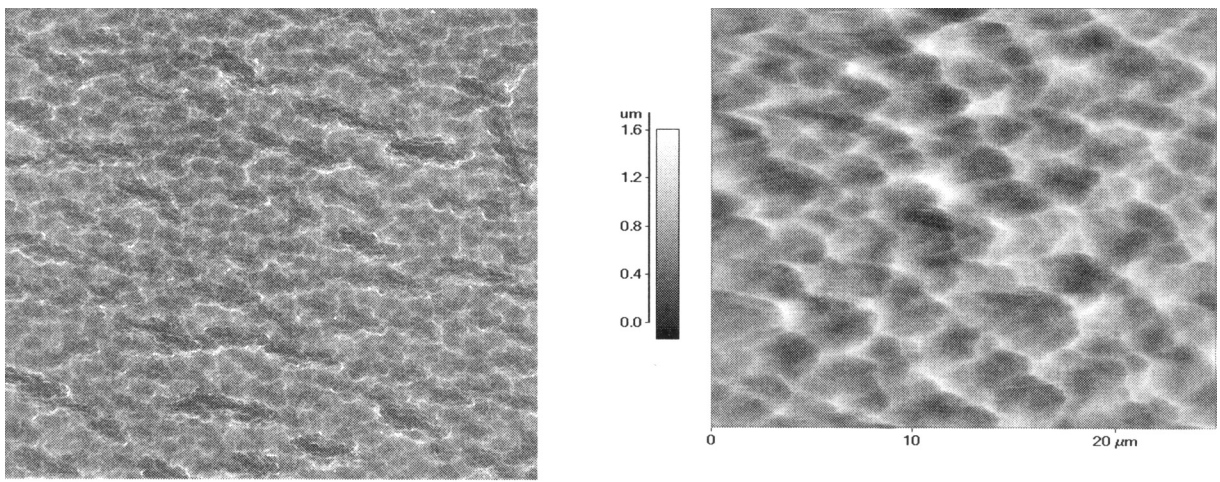
Samples preswelled and etched in sodium hydroxide solutions containing surfactant resulted in the highest levels of surface roughness, as shown in Figure 6. It can be seen that the level of roughness for these samples exceeds the roughness obtained by reaction without preswelling, as well as the treatments without surfactant, over the range of reaction times investigated.

The amorphous regions of the PET film are expected to be attacked by the sodium hydroxide before the crystalline zones. Pretreatment with a methylene chloride swelling agent would result in further penetration of the film, exposing the amorphous zones present at these



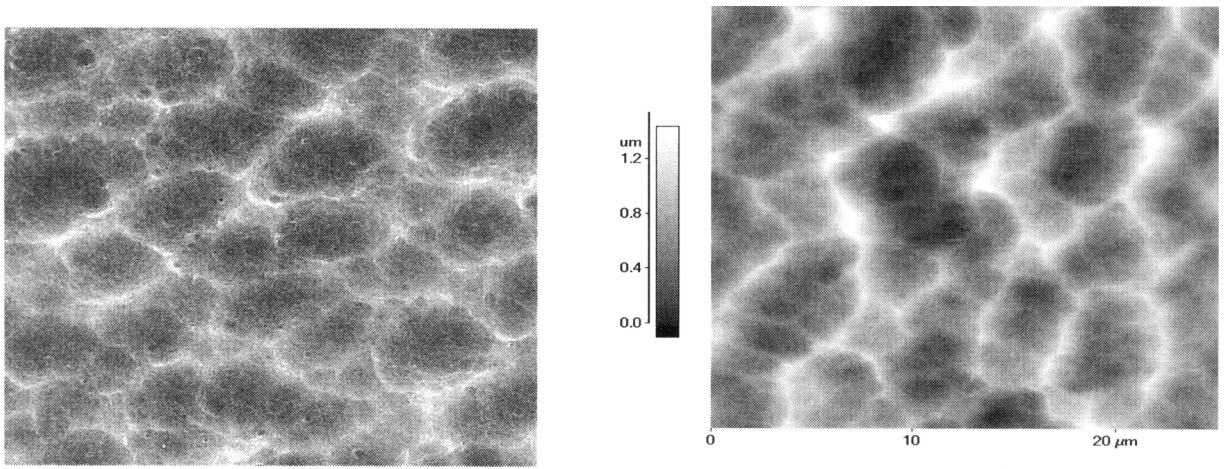
a)

FIGURE 5 Sodium hydroxide etched PET film after (a) 10 min, (b) 30 min, and (c) 60 min. SEM (left) and AFM (right) fields of view 25 × 25 μm (etchant: 10% w/v aqueous NaOH solution containing surfactant). (Continued.)



b)

FIGURE 5 (Continued.)



c)

FIGURE 5 (Continued.)

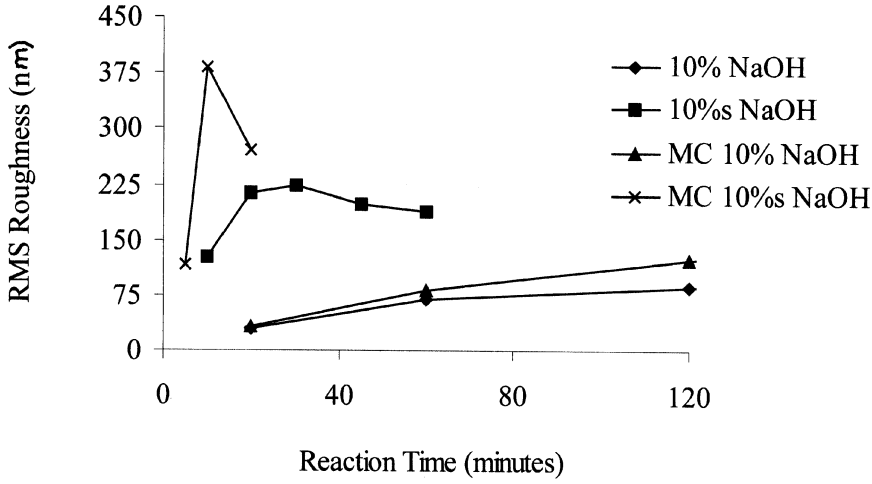


FIGURE 6 Dependence of RMS surface roughness on reaction time for PET films treated with 10% w/v aqueous sodium hydroxide containing surfactant, s, and prior swelling with methylene chloride, MC.

levels. The increased weight loss and roughness values obtained for these films are explained by the hydrolytic attack at these depths by sodium hydroxide and surfactant. It was noted that the treatment also increased the diameter of the pores.

Figure 7 plots the adhesion results of platinum thin films to PET film as a function of weight loss. These results were obtained from PET samples etched with sodium hydroxide solutions containing surfactant. The tape test rating (4.0) obtained for an untreated film is also included for reference. The absence of surfactant resulted in relatively low weight loss and surface roughness producing poor adhesion (exceeding 2.5). Figure 7 shows that for the relatively high concentration of 10% w/v sodium hydroxide maximum adhesion occurs at 10% weight loss, whereas at the lower concentration of 5% sodium hydroxide maximum adhesion appears between 10% to 15% weight loss. The influence of preswelling PET before etching with 10% sodium hydroxide containing surfactant is that maximum adhesion occurs at a 5% weight loss, with superior adhesion maintained over the other treatments for the range of weight loss given. These latter samples contained deeper pores with smaller diameters than those samples treated with the same concentration of sodium hydroxide, but without swelling or surfactant. At weight losses greater than approximately 20% the samples exhibit poor adhesion, as indicated by

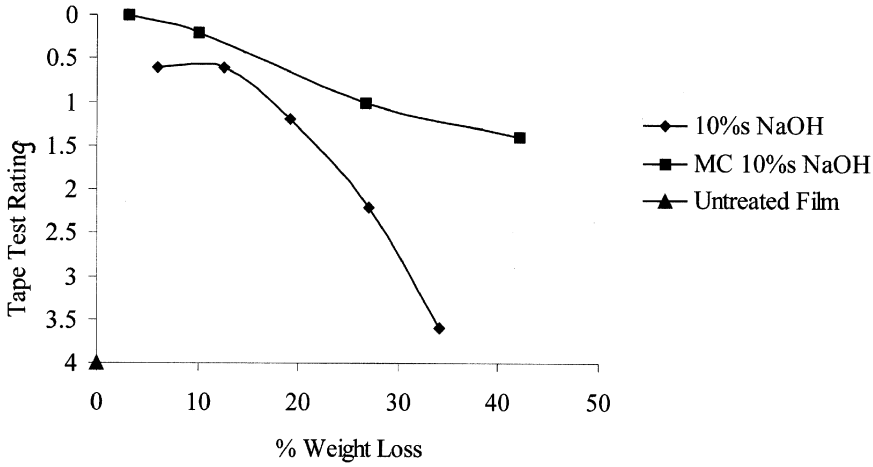


FIGURE 7 Dependence of adhesion rating (tape test) on weight loss of PET due to reaction with aqueous sodium hydroxide solutions containing surfactant, s, and prior swelling with methylene chloride, MC.

tape test readings exceeding 2.5. This corresponds to a decrease in roughness (Figure 6) and an increase in pore diameter (Figure 7).

A simple model of the pores was generated. The model considers the etched surface to be an array of cylinders stacked side-by-side. The diameter of the cylinders was taken as the mean diameter of the exposed pore rims (approximately circular) on the electron micrographs (Figure 5), and the number of cylinders per unit area was also determined from the micrographs. The smaller the measured pore diameters, the greater the number of cylinders. The corresponding roughness value was assigned as the height of the cylinders, which then enabled the total inside area of the cylinder array to be determined. Figure 8 shows the effect of the normalised contact area on the adhesion for swelled and nonswelled samples. It can be seen that a fivefold increase in the available surface area improves the retention of the platinum film from 50 to 100%. Further interpretation of the modelled curve shown in Figure 8 was not attempted due to the nonlinear nature of the tape test and the limitations of the model. It should be noted, however, that the best result for platinum adhesion was obtained for films preswelled with methylene chloride before treatment with sodium hydroxide solutions containing surfactant. This suggests that the surface structure of PET film may be optimised for improved attachment of platinum films by use of a swelling agent before chemical treatment.

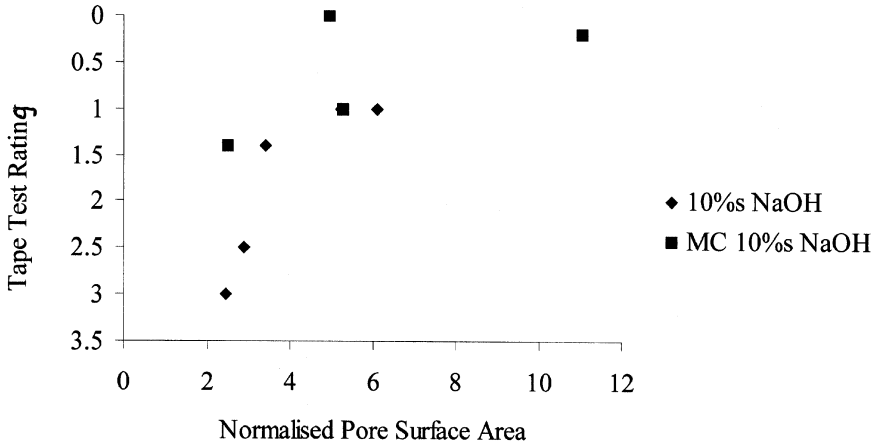


FIGURE 8 Dependence of adhesion rating (tape test) on normalised pore surface area due to reaction with 10% w/v aqueous sodium hydroxide solution containing surfactant, s, and prior swelling with methylene chloride, MC.

CONCLUSION

Aqueous sodium hydroxide treatment has successfully been used to improve the adhesion of platinum coatings to PET film. While use of alkaline hydrolysis is common with textile fibres, it is very seldom performed on films. The relationship between reaction time and weight loss was found to be linear for the conditions used. The surface roughness of the etched PET was determined *via* SEM and AFM analyses and reached a maximum with increasing weight loss. It was found that the adhesion of platinum films was dependent on the intrinsic surface area, which relates to both the pore diameter and depth (roughness). By controlling the level of roughness it was possible to control the level of adhesion of platinum.

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