

Change in Surface Properties of Polymers with Immersion in Sulfuric Acid

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Synopsis

By using a similar apparatus to that described by Baer and McLaughlin but differing in detail, the surface characteristics of samples of polyethylene, polypropylene, and a woven glass fiber/polyester laminate have been studied after periods of immersion in sulfuric acid at 60°C. Results show considerable progressive variation over the range of immersion times employed (up to 170 hr.), suggesting that surface changes might be considered as a measure of the corrosion involved. (No measure of the corrosion was attempted.) The presence of a water layer on the surface of the test piece is suggested as being the reason for the plot of $\sin \alpha_s$ versus $V^{-2/3}$ giving an intercept on the $\sin \alpha_s$ axis whereas in the original work of Baer and McLaughlin the plot passes through the origin.

The variation of physical properties of polymeric materials with chemical corrosion is important in the proper selection of these materials.¹ Corrosion tests based on change in weight, size, and appearance of plastics have been formulated by The British Standards Institute² and The American Society for the Testing of Materials.³ Arbitrary rating systems¹ have been used to classify results into a range of divisions from "not attacked" to "badly attacked."⁴⁻¹⁰ This qualitative approach can be confusing, since different experimenters will have different interpretations of the terms used. The measurement of the change in a surface property due to the chemical attack could possibly be used to advantage.

A method for study of the surfaces of solid polymers by depositing drops of liquid, of various sizes, on a horizontal surface, then tilting the surface and measuring the angles of inclination at which the drops begin to slide has been evolved.¹¹⁻¹³

It can be shown that

$$\sin \alpha_s = KV^{-2/3}$$

where α_s is the angle of inclination of the plane to the horizontal, K is the surface characteristic constant, and V is the volume of the drop.

Baer and McLaughlin¹¹ showed that, when drop sliding just occurred, plots of $\sin \alpha_s$ versus $V^{-2/3}$ for drops on the surface of various plastic materials, a straight line was given, substantiating the validity of the equation. These workers also showed that the effect of machine roughness on the

plastic sheet is negligible, and the major variables which control the drop stability are the air-liquid, liquid-solid, and solid-air interfacial forces.

It is reasonable to assume that as a polymer material is attacked by a chemical reagent the contact angle is likely to change.

Apparatus and Experimental Method

Random samples (2 in.²) of the materials to be tested were cut and thoroughly cleaned in distilled water and a small quantity of cold isopropyl alcohol, which was allowed to dry off, followed by a final washing with distilled water. The samples were immersed in the environment to be studied, contained in a vessel in a constant temperature bath. Samples were so arranged that they were suspended on a rod in the solution and completely separate from each other. The bath temperature was maintained at $60 \pm 0.5^\circ\text{C}$. during the tests.

Initially the apparatus consisted of a stainless steel tank within the constant temperature bath but the early results suggested that there was probably some effect due to metallic ions in the solution. All the results reported here were obtained by immersing the samples in the environment contained in a Pyrex glass tank.

After the required immersion time, the samples were removed and washed thoroughly with distilled water and cold dilute isopropyl alcohol and allowed to dry off as before. Each sample was then fitted, in turn, to

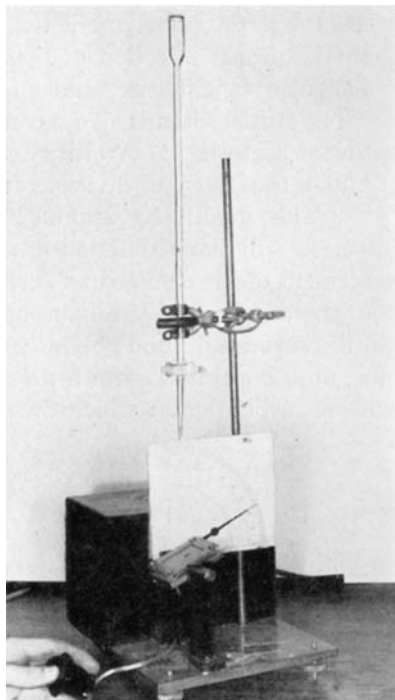


Fig. 1. Tilting plane apparatus.

a small platform which could be tilted. The apparatus was specially designed (Fig. 1) so that the plane of plastic material under test could be slowly ($2^\circ/\text{sec.}$) and smoothly inclined from the horizontal "rest" position, by a very low geared electric motor (generally as described by Baer and McLaughlin¹¹ but differing in detail). Alternate stopping and starting every 5° intervals was employed in order to reduce any dynamic effects which might be present if the movement was carried right through the cycle. The apparatus was carefully leveled before a test and set up away from draughts and vibration, although not in a constant temperature environment. A single drop of distilled water of known volume, from a buret, was placed on the sheet and the plane tilted as described until the drop moved. At the moment of commencement of slide the rotation was stopped and the angle at which the drop began to move was recorded. This procedure was repeated at different points on the surface under test and an average value for the angle of inclination obtained.

The endpoint at which the drop moved was important. This was defined as a definite and sustained movement of the whole of the trailing edge of the drop over the plane. This was not equitable with the first movement of part of the trailing edge. It was noted that the humidity of the air around the apparatus was important, since at high humidities there appeared to be a definite "wetting effect" on the surface. In consequence of these observations, a clean cloth moistened with distilled water was rubbed across the surface prior to testing, to ensure a "wet" surface, (Extreme care was taken to have a layer which was not thick or visible, but consistent with wetting.)

Results and Discussion

The variation of the surface characteristic constant K with immersion time for polyethylene in 98% sulfuric acid is given in Figure 2. There is some variation from sample to sample, although the trend for each sample is similar. During the first 5 hr. the surface characteristic decreases to a minimum, indicating an increase in wettability, until a maximum surface

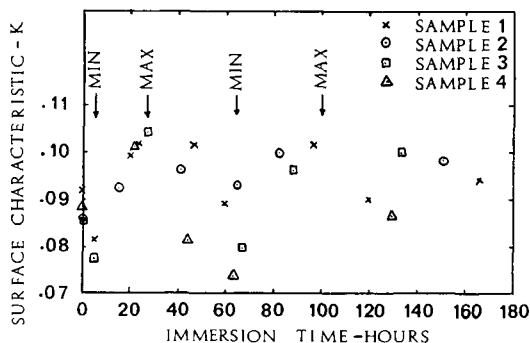


Fig. 2. Surface characteristic K vs. immersion time of polyethylene in 98% sulfuric acid at 60°C. : (\times) sample 1; (\circ) sample 2; (\square) sample 3; (\triangle) sample 4.

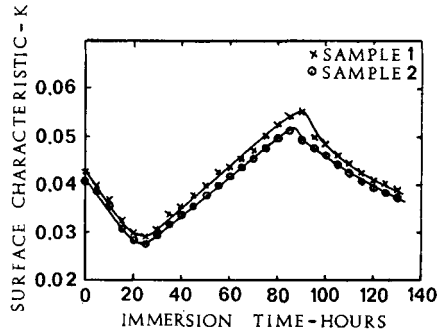


Fig. 3. Surface characteristic K vs. immersion time for polypropylene in 98% sulfuric acid at 60°C.: (X) sample 1; (O) sample 2.

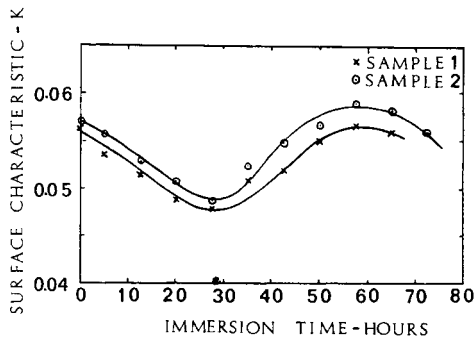


Fig. 4. Surface characteristic K vs. immersion time for polyester laminate (woven fabric) in 20% sulfuric acid at 60°C.: (X) sample 1; (O) sample 2.

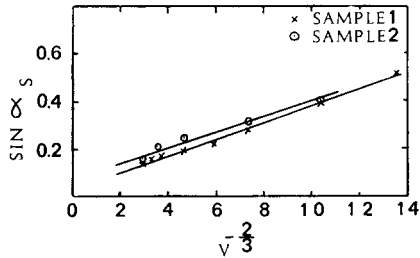


Fig. 5. Plots of $\sin \alpha_s$ vs. $V^{-2/3}$ for polyethylene: (X) sample 1; (O) sample 2.

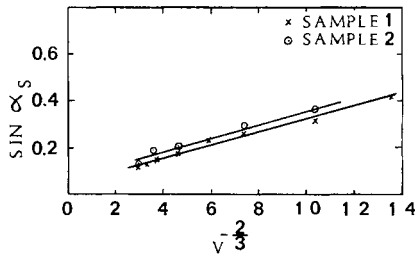


Fig. 6. Plots of $\sin \alpha_s$ vs. $V^{-2/3}$ for polypropylene: (X) sample 1; (O) sample 2.

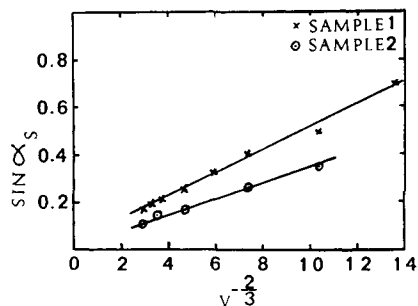


Fig. 7. Plots of $\sin \alpha_s$ vs. $V^{-2/3}$ for polyester laminate (chopped strand): (X) sample 1; (O) sample 2.

characteristic constant is obtained after approximately 25–30 hr. immersion. Further immersion reverses the trend again until a second minimum is reached after 60–70 hr. contact with 98% sulfuric acid. Continued immersion produces a further maximum surface characteristic constant in the region of 100 hr. contact time. After this maximum has occurred, it would appear that there is a gradual falling off in the value of K with immersion time.

Figure 3 shows a similar plot for polypropylene with 98% sulfuric acid. The variation between the two samples does not show the scatter obtained with the polyethylene specimens. The first minimum value of K seems to occur at 25 hr. immersion, whereas the reduced wetting of the sample occurred in the region of 85 hr. contact. Further contact with the acid shows an increase in wettability.

The results of immersing woven glass fiber polyester laminate in 20% sulfuric acid are given in Figure 4. It shows a similar minimum value of K at 25–30 hr. to the curves for polypropylene with a maximum in the region of 55–60 hr.

In contact with sulfuric acid all three materials displayed a considerable variation in the surface characteristic with time, suggesting that changes at the surface were taking place. Progressive darkening, which penetrated into the layers below the surface of the samples with time of immersion was observed on all samples.

It has been shown that $\sin \alpha_s$ varies as $V^{-2/3}$. Plots for $\sin \alpha_s$ versus $V^{-2/3}$ are given for all materials in Figures 5–7. Although there is scatter, the results indicate an intercept on the $\sin \alpha_s$ axis. It is suggested that the theoretical equation could be empirically modified for these tests, i.e.,

$$\sin \alpha_s = V^{-2/3} + b$$

where b is the intercept on the vertical axis.

It is not clear why there is an intercept on the $\sin \alpha_s$ axis when the results of Baer and McLaughlin show, for polyethylene and Teflon with different liquids, no such intercept. It is possible however, that the presence of the water layer, even though it is thin, on the surface of the test piece could modify the theory.

The experiments indicate that if maximum wetting of a surface is a desired property in any application of these materials then careful control of the etching process, particularly as regards time of immersion, is required.

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Résumé

En utilisant un appareil similaire à celui décrit par Baer et McLaughlin mais différent en détail, les caractéristiques de surface d'échantillons de polyéthylène et de polypropylène et de laminés de fibres polyesters et de verres ont été étudiés après des périodes d'immersion dans l'acide sulfurique à 60°C. Les résultats montrent une variation progressive considérable suivant la durée d'immersion utilisée (jusque 170 heures), ce qui suggère que les modifications de surface peuvent être considérées comme une mesure de la corrosion (aucune mesure de corrosion n'a été effectuée). La présence d'une couche d'eau sur la surface de la pièce témoin est suggérée comme étant la raison pour laquelle un diagramme de sinus- α_s en fonction de $V^{-2/3}$ donne une interception à l'axe de sinus α_s , alors que dans le travail original de Baer et McLaughlin le diagramme passe par l'origine.

Zusammenfassung

Mit einem Apparat, der dem von Baer und McLaughlin ähnlich war, sich aber in Details davon unterschied, wurde die Oberflächencharakteristik von Proben von Polyäthylen, Polypropylen und Glasfasergewebe-Polyesterlaminaten nach Eintauchperioden in Schwefelsäure bei 60°C untersucht. Die Ergebnisse zeigen im Bereich der verwendeten Eintauchdauern (bis zu 170 Stunden) eine beträchtliche fortschreitende Variation und lassen die Oberflächenänderungen als ein Mass für die auftretende Korrosion erscheinen. (Es wurde keine Messung der Korrosion versucht.) Die Auftragung von $\sin \alpha_s$ gegen $V^{-2/3}$ liefert einen Abschnitt auf der $\sin \alpha_s$ -Achse, während in der ursprünglichen Arbeit von Baer und McLaughlin die Kurve durch den Ursprung geht. Es wird angenommen, dass die Anwesenheit einer Wasserschicht auf der Oberfläche der Testprobe der Grund für diesen Unterschied ist.

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