

Nanoindentation and microindentation of weathered unplasticised poly-vinyl chloride (UPVC)

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The comparatively novel technique of nanoindentation has been used to provide unique information on the hardness and modulus of artificially weathered window-grade unplasticised polyvinyl chloride (UPVC) at the sub-micron level. Indentations, in plan, were made to depths ranging from about 140 nm to 5.5 μm while indentations in section were made at distances ranging from about 2.5 μm to 1.0 mm from the top surface. The technique was applied also to Darvic[®] UPVC which, by virtue of its more homogeneous microstructure, was used as a reference material for assessing the effect on properties of the detailed loading procedure. The sensitivity of the hardness to loading rate and to hold-time at maximum load was investigated. Hold-time was the key variable and an optimum period of 200 s was recommended. The hardness of the artificially weathered window-grade UPVC varied with exposure period and with depth. At long exposure times, the hardness of the top 147 nm was very much greater than the underlying material, which had softened with exposure. This very-near surface hardening, which is attributed to cross-linking, would not be detected by conventional techniques. After extended exposure, evidence of recovery of properties was observed, consistent with the mechanism of surface layer removal by erosion. The modulus was less affected by weathering than hardness with a modest decrease being observed only at very prolonged exposures. Measurements of hardness in section were not consistent with measurements in plan suggesting that the sectioning and polishing process was inducing changes in properties in the near-surface region. This problem may restrict the application of the technique for detailed depth profiling close to the weathered surface, at least for some materials. Use of the nanoindentation technique for detecting the early onset of degradation is feasible but more work is required to understand the depth dependence of degradation in relation to hardness and to isolate this effect from local material variability.

1. Introduction

Prediction of the "life" of polymeric materials exposed to natural weathering is intrinsically difficult because of the complex nature, time-dependence and geographical variation of the environment [1]. A mechanistic approach to prediction of the rate of degradation is unlikely to be successful because of the range of reactions and chemical products and because of lack of specific knowledge of rate constants and diffusion coefficients. Empirical models based on time-temperature-dose rate superposition, for example, depend on the assumption that the rate controlling factors are identical for the full range of exposure conditions, and are also limited.

Accordingly, prediction of the performance of materials in service is mostly dependent on accumulated experience supported by measurements of degradation under more severe natural conditions and/or laboratory test conditions. The increased severity of

these tests requires a sufficient understanding of the kinetics of degradation to ensure reliable interpretation of the test data.

In this context, measurement of the time-dependent development and penetration of the degraded layer into the material is of particular value in characterizing rate controlling factors. A range of techniques can be used to provide information on the variation in chemical and physical properties with depth including Fourier transform infra-red spectroscopy with photoacoustic cell, scanning electron microscopy in section, and microtoming followed by gel permeation chromatography and differential scanning calorimetry.

Measurement of the mechanical properties such as hardness and modulus can provide useful complementary information. However, conventional microhardness instruments are restricted in the range of information generated, being dependent on the

measurement of indent depth after removal of load and employing comparatively large loads.

The development of load–displacement instruments such as the nanoindentation technique in which displacement and load are monitored continuously has altered the perspective on mechanical property measurement and opens up the possibility of evaluating properties flexibly on the scale of nanometres to microns [2–6]. Nanoindentation has been applied to a range of metals and ceramics and is of particular interest in characterizing the properties of thin films [7]. The technique has not been applied significantly to polymers though sub-micron indentations have been made by Ion *et al.* [8] for measuring the hardness of polyethylene terephthalate films.

This paper describes the application of the nano-indentation technique to the characterization of hardness and modulus of weathered UPVC as part of a broader strategy aimed at characterizing mechanical, physical and chemical property changes induced by varied weathering parameters.

2. Experimental method

2.1. Materials

The material investigated was a PVC-U chlorinated polyethylene-modified window-sill section (Hostalit® Z, Hoechst AG) with the composition described in Appendix 1. For consistency with terminology used elsewhere [9] this material is given the code AHS8. The material is very heterogeneous from the perspective of indentation measurement. Hence, indentation measurements were also undertaken with Darvic® (Appendix 1) which because of the more limited incorporation of additives would provide a useful, if not ideal, reference material in evaluating the effect of loading variables.

2.2. Exposure conditions

The AHS8 material used in these experiments were exposed in an Atlas Weatherometer, Model Ci3SA, which utilizes a xenon arc radiation source. For these tests, the radiation was filtered using borosilicate glass to give a Miami “average” 45 °C daylight spectrum in the range 300–800 nm. The exposure conditions are listed in Table I. More extensive exposure tests were conducted and are reported elsewhere [9]. The total radiation per unit area is measured only in the wavelength band 340 ± 2 nm. The total radiation per unit area in the energy band 300–800 nm was estimated [10] by multiplying the measured value at 340 nm by a factor of 1160.

2.3. Microindentation

Conventional microhardness measurements were made using a Vickers microhardness facility with applied loads in the range 0.29–1.03 N and with a 15 s hold at maximum load. The Vickers microindenter is a square pyramidal indenter with an angle of 68° with respect to the normal to the base. Hardness is calculated from measurement of the diagonal of the

TABLE I Artificial weathering cycle

Black standard temp	65
Black panel temp ≈ 58 °C	
White panel Temp (°C)	44
Air temp (°C)	36
Wet bulb depression (°C)	6
Relative humidity 65%	
Light/dark cycle	Continuous light
Water spray cycle	102 min/18 min (light/light + water spray)
Irradiance @ 340 nm (Wm^{-2})	0.35
Inner filter	Borosilicate
Outer filter	Borosilicate
Maximum radiant energy (GJm^{-2})	6.6
Maximum duration (h)	4500

indent after unloading and reflects residual plastic deformation. The microindentation technique was used to measure properties in plan, i.e. by indenting directly on the weathered surface. Since the load is maintained constant in this test the depth of indent varies according to the hardness of the near surface material. A minimum of 10 indents were made for each exposure condition to ensure a good statistical representation.

2.4. Nanoindentation

The nanoindentation measurements were made using the Nano-Indenter II® which is illustrated schematically in Fig. 1. The diamond tip is in the form of a Berkovich trigonal pyramid indenter whose facets form an angle of 65.3° with respect to the normal to the base. Atomic force microscopy measurement confirm that the gradient of the planes of the indenter are constant up to 150 nm from the tip. The tip itself is slightly rounded with a radius of curvature of about 10 nm or slightly higher. The indenter is mounted on an Invar (65% Fe 35% Ni) rod that is suspended on thin leaf springs. At the opposite end of the rod is a coil and magnet assembly that provides the controlling loading force. In essence, the gravitational force is balanced by the magnet thus holding the rod in a reference position above the specimen. Reducing the current to the coil then allows the indenter to move to the specimen under gravitational pull. A thin plate, which forms the moving element of a capacitive displacement transducer is attached at the centre of the tube. Indenter displacement is reflected in the movement of this plate and can be measured with a resolution better than 1 nm. The nanoindenter was calibrated [11] to an accuracy of 5 nm in displacement of 10^{-6} N in load.

The indentation process is computer controlled. The position of the surface is estimated for each indent using an approach procedure which identifies the surface through a sharp increase in stiffness (Fig. 2). The method proved effective for UPVC though careful choice of parameters would be necessary for less stiff materials. Indentation of the specimen can proceed under load or displacement control. Load,

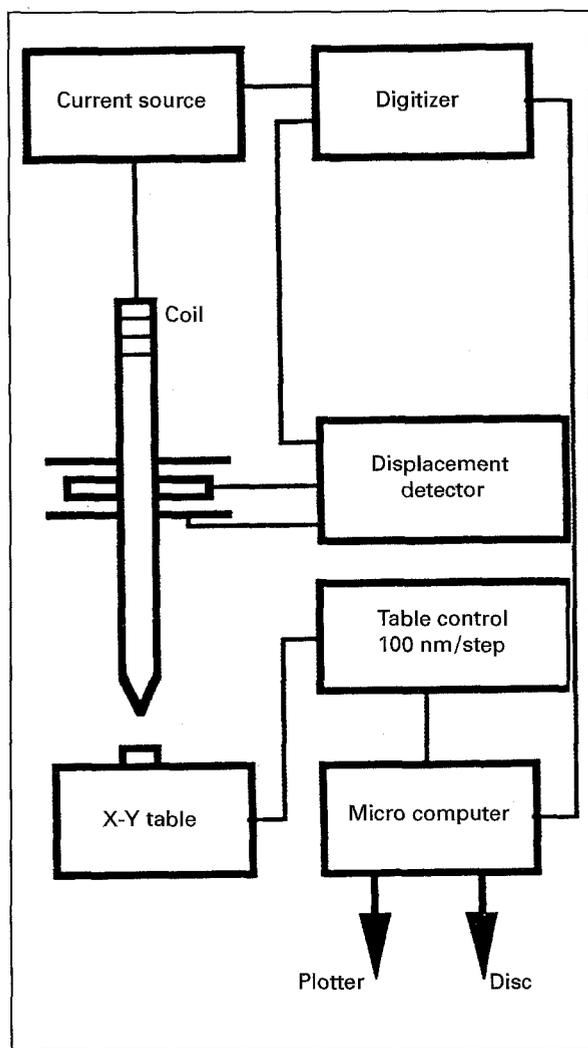


Figure 1 Operating schematic of the Nano-Indenter II®.

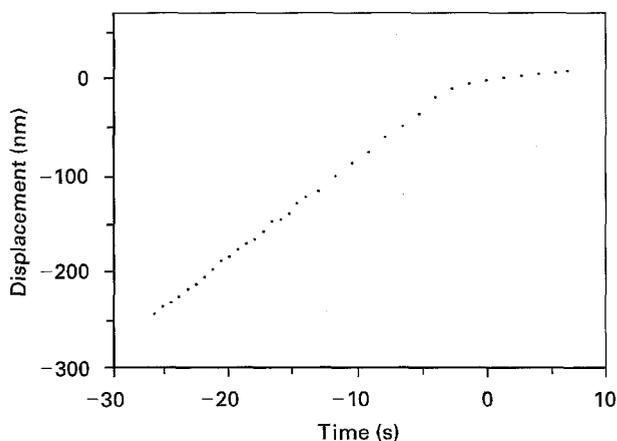


Figure 2 Typical plot of variation of displacement with time during the approach segment for Darvic.

displacement and time are measured and recorded continuously. In this particular study, the loading rate was controlled until a preset displacement was attained; the load was then held constant for a period to allow time-dependent displacement to develop; finally it was reduced to zero at the same loading rate.

The procedure prior to application of load is important because of the potential impact of thermal drift

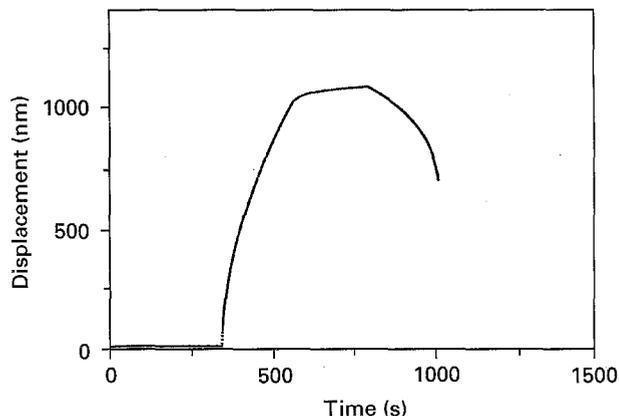


Figure 3 Typical plot of variation of displacement with time during the loading segment for Darvic.

on the measured displacement at small indent depths. Thermal drift arises because of differential expansion of components and can be generated by variation in room temperature and by joule heating associated with the varying current applied to the coil. For the Invar alloy rod used, expansion due to joule heating is insignificant.

To minimize thermal drift due to room temperature variations, a period of 5 h was allowed after setting up of the specimen to enable re-establishment of normal thermal conditions. The background drift due to the inherent variation in temperature of the sealed room ($20.0 \pm 0.5^\circ\text{C}$) was evaluated by holding the indenter just off the specimen surface for about 300 s prior to each indent. The variation of the displacement with time was used to calculate the drift rate, which was subsequently used to correct the measured data. A typical displacement-time curve during loading is shown in Fig. 3.

For indent depths less than or about 800 nm, 12–16 individual indents were made but for deeper indents 9 separate indents provided adequate statistics. The measurements were made predominantly in plan, i.e. indenting from the top surface, but a number of measurements were made in profile, in which the indents were made perpendicular to the top surface. Since the latter involves sectioning and polishing the material a short study of the influence of polishing on measured hardness was undertaken. The mechanical polishing procedure involved 1200 grit, 30 μm , 6 μm , and 1 μm diamond paste, followed by 0.05 μm γ -alumina. The only solvent used was distilled water and the material was cleaned in distilled water in an ultrasonic bath for 5 min between each stage. Sections were cut using a sharp knife.

3. Results

An example of a load-displacement curve is shown in Fig. 4a and a schematic illustration of the features and processes involved is given in Figs. 4b and 5. It is important to establish a consistent procedure for analysing the results and a measurement methodology which accounts for the time dependent nature of the material properties.

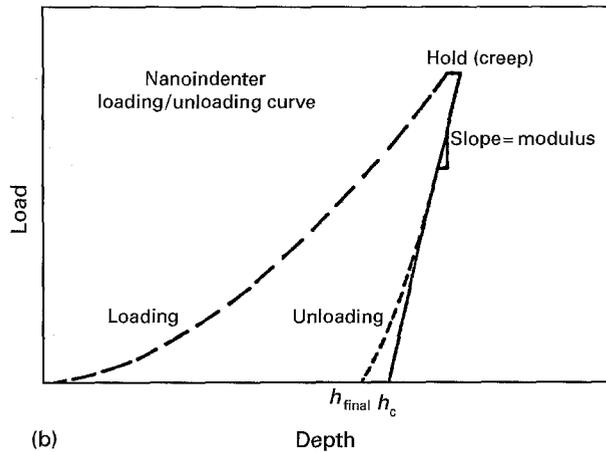
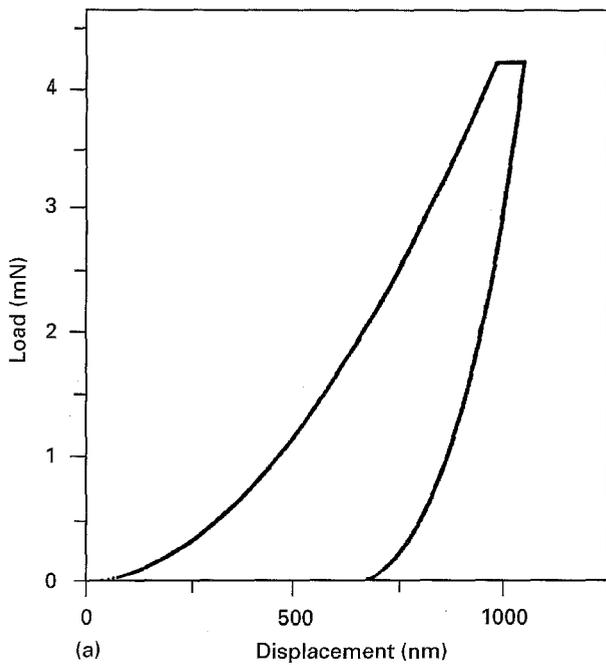


Figure 4 (a) Load displacement curve for Darvic; (b) Schematic illustration of features.

3.1. Procedure for calculating modulus and hardness from nanoindentation data

The elastic properties of the material are evaluated from the unloading curve since even in the early stages of loading the high stress associated with the sharp indenter tip results in inelastic behaviour. Oliver and Pharr [5] describe a procedure for fitting to the unloading curve using a power-law relationship between load and displacement and evaluating the stiffness from the derivative of this equation at commencement of unloading. The stiffness, dP/dh is related to the reduced modulus by

$$\frac{dP}{dh} = \frac{2}{\pi^{1/2}} E_r A^{1/2} \quad (1)$$

where A is the area of contact at maximum load and E_r is the reduced modulus given by

$$\frac{1}{E_r} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu_1^2)}{E_1} \quad (2)$$

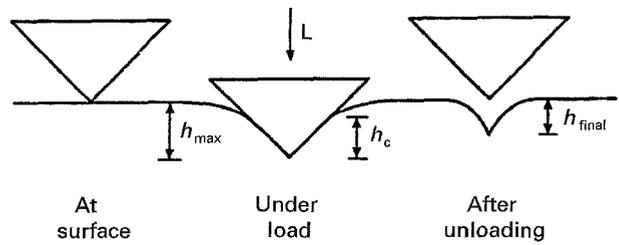


Figure 5 Schematic of the indentation experiment.

The parameters E and ν are Young's modulus and Poisson's ratio for the polymer respectively and E_1 and ν_1 are the same quantities for the indenter. For this diamond indenter $E = 1141$ GPa and $\nu_1 = 0.007$. Poisson's ratio for UPVC [12] was taken as 0.37.

Extrapolation of dP/dh at maximum load to zero load yields the magnitude of the depth of material in contact with the indenter at maximum load (h_c) (Figs 4 and 5). This value is used to calculate A . The value of A for an ideal Berkovich indenter shape is given by

$$A = 24.5 h_c^2 \quad (3)$$

This relationship becomes unsatisfactory at shallow depths for which the detailed shape of the indenter tip becomes important. For these cases the following relationships [13], based on studies on fused silica, were used:

$$A = -38840 + 2861.64 h_c + 15.139 h_c^2$$

$$24 \leq h_c < 197.419$$

$$A = 447170 - 2328.37 h_c + 30.137 h_c^2$$

$$197.419 \leq h_c \leq 580.817 \quad (4)$$

where the units of h_c are nm. At a depth of about 380 nm the error in using Equation 3 is about 10% but increases progressively with decreasing depth of indent.

The potential sensitivity of the calculated modulus to time-dependent displacement and, more importantly, the possible uncertainty in calculating the contact depth from the unloading data suggests that calculation of hardness on the basis of the area of contact with the indenter at maximum load may not be the most reliable approach for these polymer materials. The implicit assumption by Oliver and Pharr [5] that the depth of indent associated with plasticity is represented by h_c , the final depth, and that the unloading curve is wholly elastic is also likely to be invalid for polymers.

The definition of hardness has been debated [14, 15], with the essential disagreement resting on whether it is the resistance of the material to plastic deformation or total deformation when indented with a much harder material. For materials which exhibit significant time-dependent plastic flow, and for which plastic deformation is very much greater than the elastic deflection, there are virtues in adopting a recent draft proposal for an ISO standard on hardness

testing [16] which specifies a universal, idealized, hardness, HU given by

$$HU_{(\text{idealized})} = \frac{\text{Test force}}{\text{Surface area of indentation under working test force}}$$

The term idealized arises because it is assumed that the indenter is in contact with the surface for the full depth defined by the maximum displacement in the load–displacement curve, in contrast to real behaviour illustrated in Fig. 5 in which elastic deflection of the surface occurs ($h_{\text{max}} - h_c$). The definition will be adopted in this study because of the uncertainty in measuring the true area of contact.

It should be emphasized that hardness of many ductile metals and polymers in particular is not an absolute characteristic of the material but is sensitive to the measurement method with the hold time at maximum load being of greatest importance [17].

3.2. Establishment of methodology for measurement of hardness and modulus using load–displacement instruments

Measurements of the mechanical properties of polymeric materials using indentation methods based on load–displacement instruments such as the nanoindenter are few and there is no standardization of test method. A necessary step in the application of indentation techniques applied to polymers is to establish a suitable methodology for testing which accounts for the time-dependent flow of the material.

The factors of importance are the loading rate and, more particularly, the hold time at maximum load. The effect of the latter on the load–displacement curves for Darvic® is shown in Fig. 6. The slow time-dependent increase in displacement at maximum load is most probably associated with visco–plastic flow.

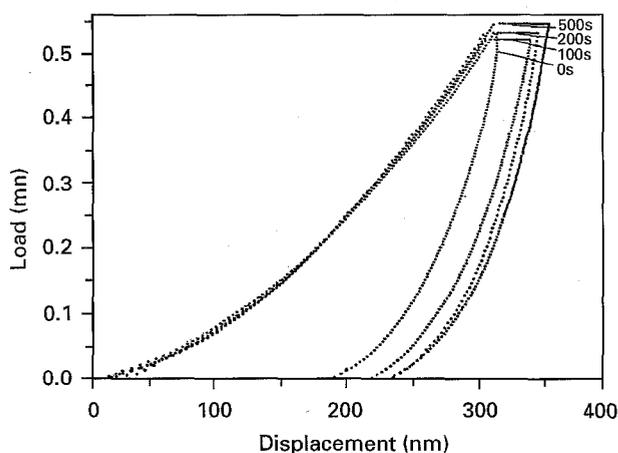


Figure 6 Effect of hold time at maximum load on a load–displacement curve for Darvic.

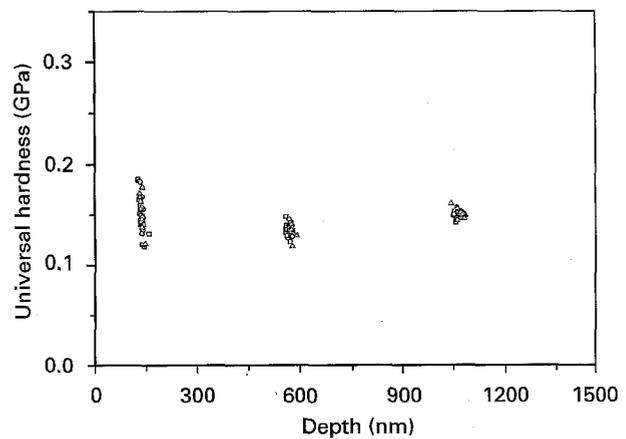


Figure 7 Effect of loading rates on values of universal hardness for Darvic. The loading rates investigated were; (□) $6 \mu\text{Ns}^{-1}$, (○) $13 \mu\text{Ns}^{-1}$ and (△) $20 \mu\text{Ns}^{-1}$.

With no hold period the initial part of the unloading curve indicates some increase in displacement despite the reduced load. Since evaluation of the elastic displacement and of the modulus depends on analysis of the initial part of the unloading curve this procedure is unsatisfactory. With increasing hold times the extent of time-dependent displacement decreases indicating a decrease in creep rate. Although it would be possible to hold for longer times until creep exhaustion it is necessary to optimize the use of the equipment in terms of the statistics of measurement and the range of test materials to be examined. Hence, a hold period of 200 s was adopted in subsequent tests. This hold time is arbitrary but is sufficiently long so that the unloading characteristics are equivalent to those determined for longer times, indicating that the creep process has no effects on the elastic unloading and modulus at the unloading rates used. The effect of the hold period on the hardness varied according to the depth of indent. Using Darvic® as the reference material the hardness decreased by 45% after a 200 s hold at an initial indent depth of 100 nm but by less than 16% for an initial indent depth of 5 μm .

The choice of loading rate is also somewhat arbitrary but again constrained by the statistics of measurement and the efficiency of testing. No more than three data points are recorded per second and to produce well-defined loading and unloading curves about 30 data points are usually required. Hence, the overall time should not be less than about 10 s.

The loading rate will depend then on the maximum load in the test. In practice, varying the loading rate in the range $6\text{--}20 \mu\text{Ns}^{-1}$ had little effect on the measured hardness values (Fig. 7), presumably because of the long hold times at maximum load. In the same range of loading, and correspondingly, unloading rates the modulus of the Darvic material was between 5.1–5.2 GPa. For shallow indents, less than 1 μm with loads less than 1 mN, a loading rate of $20 \mu\text{Ns}^{-1}$ was adopted. At indent depths greater than 1 μm a loading rate of 1mNs^{-1} was adopted. Similarity of results was obtained at 1 μm despite the large difference in loading rate.

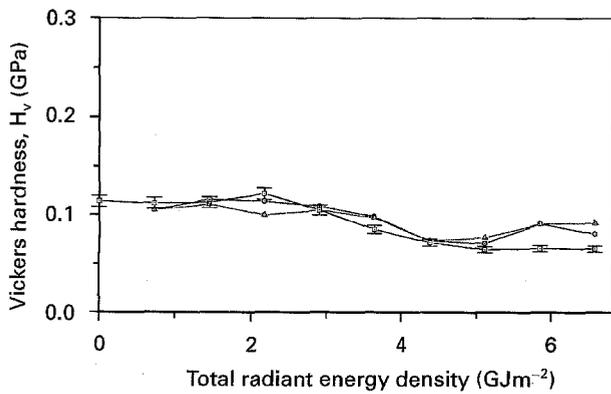


Figure 8 Effect of load on value of Vickers hardness for artificially weathered AHS8 material. The loads investigated were; \square 0.29 N; \circ 0.54 N and \triangle 1.03 N.

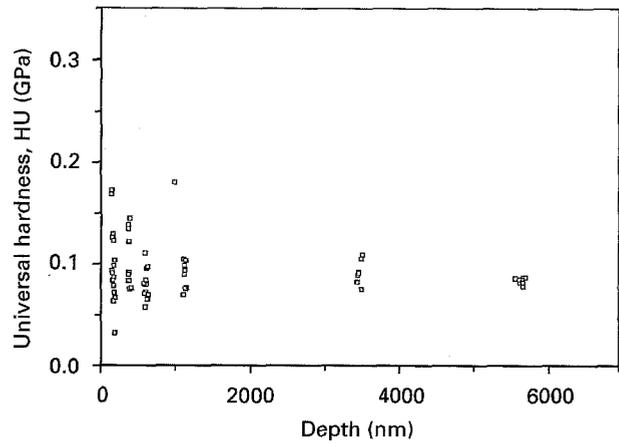


Figure 9 Variation of universal hardness with indent depth for AHS8 (unweathered) material.

3.3. Measurement of mechanical properties of window-grade UPVC

3.3.1. Microindentation

The variation of the Vickers microhardness with total radiant energy per unit area for AHS8 is shown in Fig. 8. The individual values represent the mean of a minimum of 10 measurements. The repeatability of the mean value was within 10%. The number of indents required was determined by measuring the mean value as a function of the number of indents until satisfactory convergence.

Three different loads were applied, namely 0.29, 0.54 and 1.03 N, in order to vary the degree of sensitivity to the degraded layer. At a total radiant energy density of 6.6 GJm^{-2} the nominal indent depths were 19, 23 and $30 \mu\text{m}$ respectively, and for the unexposed samples 14, 19 and $26 \mu\text{m}$ respectively.

It is evident from Fig. 8 that there is a progressive softening of the material to a minimum at 5.0 GJm^{-2} followed by some degree of recovery. Nevertheless, there are specific variations depending on the load. For example, at 2.0 GJm^{-2} there is perhaps an indication of near-surface hardening reflected in the data for the smallest load. The lack of recovery between 5.0 – 6.5 GJm^{-2} for the smallest load requires explanation.

The general observations for this material [9, 18] on prolonged exposure to weathering indicate a loss of surface layer due to erosion resulting in some degree of recovery of near-surface properties. For this pyramidal indenter, the layer constituting the first 10% of overall indent depth contributes 49% of the volume of the indent. A change in hardness of the top surface could then have a significant effect on the hardness measurements. The lack of apparent recovery for the smallest load may reflect greater sensitivity to the very near surface conditions and thus subsequent exposure damage to the newly exposed surface. Alternatively, the sustainment of softening of the shallower indents may be due to the gradual loss of the thin hard outer crust (see later). The recovery in relation to the deeper indents is due to a greater fraction of the indent being associated with the underlying unchanged bulk of the material.

3.3.2. Nanoindentation

3.3.2.1. Measurements in plan. The variation of the universal hardness (HU) with depth of indent for the unweathered AHS8 material is shown in Fig. 9. In conducting these tests the procedure adopted of indenting to a specific depth at maximum load then allowing creep means that the indent depths vary slightly for each indent for the same initial set values. The most noticeable feature of Fig. 9 is the increasing range of distribution of the hardness values with decreasing depth of indent. The spread is greatest at the smallest indent depth because of the considerable heterogeneity of this material, with calcium carbonate (CaCO_3) and titanium dioxide (TiO_2) particles present in addition to a chlorinated polyethylene impact modifier (Appendix I). The crystalline regions in polyvinyl chloride itself are typically less than 10% of the material and the size of these regions is small, less than 5 nm with an intercrystalline spacing of 10 – 20 nm .

The size of the CaCO_3 and TiO_2 particles were evaluated using the scanning electron microscope with energy dispersive X-ray analysis (SEM-EDX) [9]. The CaCO_3 particles had dimensions up to a few microns whereas the TiO_2 particles were much smaller, typically 0.2 – $1.0 \mu\text{m}$, and more finely dispersed. The chlorinated polyethylene impact modifier exists in the PVC as a melt dispersion, sometimes referred to as a network structure, and as such does not exist as individual particles. The scale of the associated microstructure will depend on the detailed processing history and could vary through the material. Nevertheless, 300 nm would be typical of the size scale.

It is evident that the depth of indents associated with Fig. 9 can be smaller than the scale of the added particles. Hence, a distribution of hardness values will be detected with the largest reflecting indentation on a chalk particle or a TiO_2 particle (albeit embedded in a more ductile medium) and the smallest values being reflective of indentation of the impact modifier.

Indents of the order of 200 nm or less in depth could be influenced by surface roughness also. Ideally, the surface of the specimen should be flat relative to the scale of the indent depth. The procedure of measuring

the surface position every time an indent is made might be expected to eliminate effects of surface roughness but if the indent is made on an incline in the surface profile then non-uniform loading round the indenter could give rise to some variability in calculated hardness depending on the slope of the incline. However, the latter is likely to be shallow compared to the slope of the indenter and the impact on hardness would be expected to be low.

A fully homogeneous material would provide a useful reference though with the constraint that the surface roughness should be comparable with the window grade UPVC. The Darvic material is probably the best that can be achieved and shows a reduced spread in values of hardness compared to the AHS8, though there is still a significant spread at the smallest indent depth (Fig. 7).

The variation in hardness values of AHS8 with depth after 4500 h of artificial weathering at a radiant energy density of 6.6 GJm^{-2} , is shown in Fig. 10. There is very evident softening compared to Fig. 9 and a somewhat reduced spread in results at a given depth. The latter is almost certainly a consequence of the loss of CaCO_3 particles, which SEM-EDX reveals to be significant [9]. Indeed, some of the softening may be reflective of the loss of these particles.

The variation of the mean values of the hardness with indent depth and exposure period (expressed as increased radiant energy density) is illustrated in Fig. 11. Since the indent depth for each experiment varied slightly the mean values of a set of measurements of depth together with the range of variation are quoted. There was no distinct variation in hardness with depth of the unexposed material suggesting that there was no significant process-induced segregation of filler materials to the surface.

A philosophical concern with regard to the local surface hardness is that the mean hardness measured in deep indents is a consequence of the physical interaction of the various additives and bulk polymer which is effectively *volume* averaged in the indentation process because the indents are larger than the scale of the microstructure. In calculating the mean hardness of the shallow indents, which are on the same scale of the microstructure, the data are *mathematically* averaged to produce a value of the mean hardness of that layer. This distinction is probably not significant in view of the similarity of results for shallow and deep indents of the unexposed UPVC.

The material appears softer than indicated by the microindenter but this is a consequence of the different definition of hardness which for the microindenter is based on the residual indent depth which is smaller than the value at maximum load.

The response to exposure period is depth-dependent with the very near surface layer ($\leq 147 \text{ nm}$) showing apparent softening followed by hardening and then softening again at the longest exposure period. Interpreting these data is not easy because of the varying factors which can induce softening or hardening of the material. It is clearly established that there is a significant loss [9] of CaCO_3 , which would certainly lead to softening, although molecular scis-

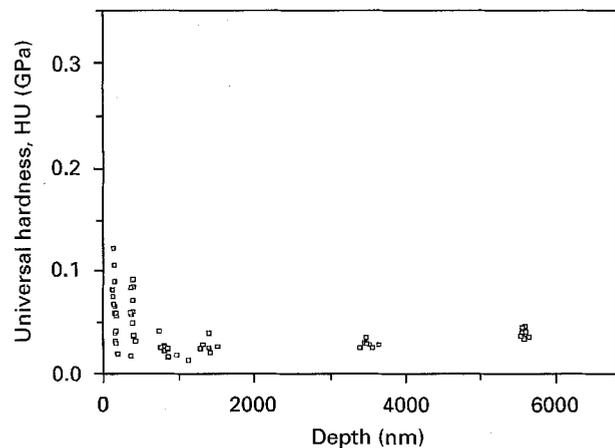


Figure 10 Variation of universal hardness with indent depth for artificially weathered AHS8 (6.6 GJm^{-2} material).

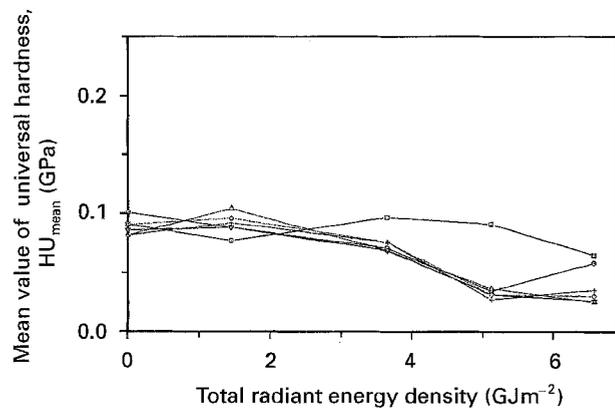


Figure 11 Variation of mean value of universal hardness with indent depth and exposure period for AHS8 material. The indent depths investigated were; \square $147 \pm 25 \text{ nm}$; \odot $381 \pm 15 \text{ nm}$; \triangle $791 \pm 70 \text{ nm}$; ∇ $1320 \pm 60 \text{ nm}$; \diamond $3454 \pm 45 \text{ nm}$; $+$ $5524 \pm 120 \text{ nm}$.

sion would also contribute in a similar manner. The subsequent hardening could simply represent a recovery of properties because of surface erosion. However, the commensurate softening at greater depths would appear to rule out this simple idea since it is not reasonable to expect a recovery of calcium carbonate particles at the surface but not at greater depth. The implications are that marked cross-linking has occurred. Cross-linking would retard the ability of the long chain molecules to move past each other and hence would reduce the ability to flow plastically under stress. The softening at the longest exposure times may indicate some surface removal.

It would appear that the surface loss suggested by Magnus [18] is less than 147 nm since there would be expected to be a much greater impact of surface loss on the hardness value measured at this depth. From the nanoindentation results the perspective on surface erosion is one of a gradual process rather than a catastrophic loss associated with a layer breaking up.

At greater depths of indent, softening reflecting chain scission and loss of carbonate filler, becomes clearly apparent beyond 4.0 GJm^{-2} with the onset of recovery of properties becoming evident at about

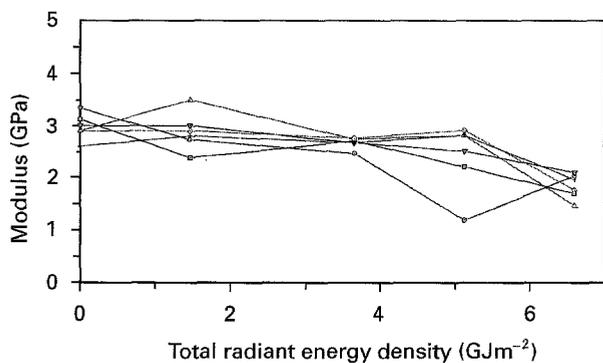


Figure 12 Variation of mean value of modulus with indent depth and exposure period for AHS8 material. The symbols have the same meaning as in Fig. 11.

5.0 GJm^{-2} , broadly consistent with the microindentation. The data for depths of 381 nm or more are broadly similar with the exception of the longest exposure period for which recovery at 381 nm is more marked. It is important when interpreting data from greater depths in plan to be aware that the hardness reflects a complex interaction of all the material down to that depth weighted according to the shape of the indenter. Thus, the relative surface hardening observed at a depth of 147 nm will affect the hardness values measured at 1320 nm implying that the surface at depths between 147–1320 nm is softer than indicated by the values at 1320 nm. The measurements at different depths all represent individual sets of measurements and are not based on extracting values at different depths as the indenter traverses through the material.

The curious feature at the longest exposure time is that the relative recovery in hardness at a depth of 381 nm is occurring simultaneously with a softening at 147 nm. The apparent contradiction may be simply a reflection of exposure interval and some competition between surface loss and cross-linking extending to greater depths, although this is a rather tenuous explanation.

Use of the nanoindenter to indicate early development of degradation was of particular interest during this study. However, the nature of the variation of the hardness with depth in the early stages of exposure, e.g. at about 1.4 GJm^{-2} , was not simple to interpret and did not yield to a consistent physical explanation.

The variation in modulus with exposure period and indent depth is shown in Fig. 12. There is a degree of spread in results with no apparent pattern, in relation to depth, at any exposure period. With the exception of one particular point, at a depth of 381 nm the overall trend is of little average variation up to 4 GJm^{-2} but a gradual decline in modulus with increasing exposure period. The modulus reflects the elastic properties of the material which depends on intramolecular motions and would not be expected to be so sensitive to weathering unless the density of cross-links was very high or the reduction in chain size very marked. It is possible that at very long exposures the chain scission process has been sufficient to begin to lower the modulus to a discernible extent.

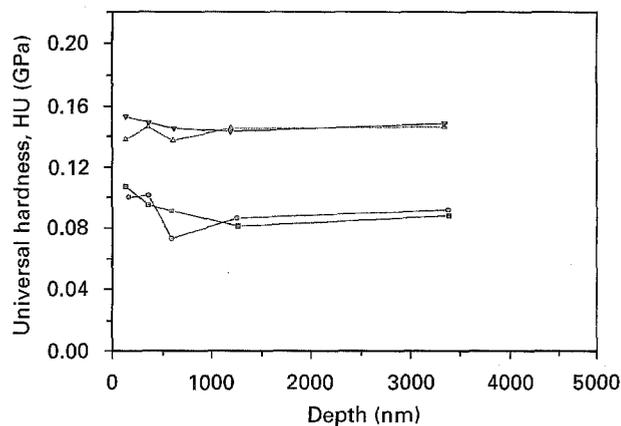


Figure 13 Effect of polishing on value of universal hardness with indent depth for Darvic and AHS8 (unweathered) material. The symbols represent data taken on: \square AHS8 polished; \circ AHS8 unpolished; \triangle Darvic polished; ∇ Darvic unpolished.

The unusually low modulus at 381 nm is not a calculation error although it is possibly due to an anomalous variation in local properties associated with loss of calcium carbonate or a locally high level of the impact modifier. However, since the single point represents the average of about 12 measurements, albeit very finely clustered, with the maximum value about 1.8 GJm^{-2} , it is not reasonable to readily dismiss the result. Unfortunately, it has not been possible to repeat these particular measurements. In view of the difficulty in providing an explanation for the trend in hardness as well as modulus for this indent depth, based essentially on this single set of data, it would not be prudent to draw explicit conclusions.

3.3.2.2. Measurements in section. Sectioning of the material induces mechanical damage to the surface of the section. Mechanical polishing to a fine finish as described in the experimental section is a necessary requirement to minimize the depth of damage. Therefore, a short study was undertaken of the effect of polishing on the measured hardness. Darvic and unweathered AHS8 were tested in plan prior to sectioning with and without polishing of the surface. The results are indicated in Fig. 13 in the form of the variation of the mean value of the universal hardness with indent depth. There is very little difference between the hardness values of the original material and the polished samples. Polishing of a comparatively soft material with alumina particles might have been expected to lead to particles becoming embedded in the surface and to cause the surface to appear harder. However, there was no specific evidence to support this supposition. The results suggest that the effect of polishing can be neglected.

Indentations in section were made to indent depths of about 372 nm at varying distances from the weathered surface. Since the opening at the "mouth" of the indent is about seven times the indent depth for the Berkovich indenter, it is essential to use as small a depth as possible to maximize depth resolution

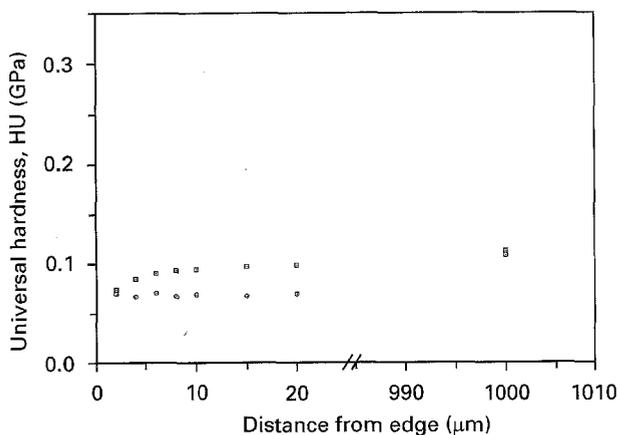


Figure 14 Variation of universal hardness with cross-sectional depth (polished) for AHS8 material for (□) unweathered material and (○) after cycle 1 (6.6 GJm^{-2}).

near the weathered surface. The choice of 372 nm represented a balance between maximizing depth resolution and minimizing any uncertainty due to polishing, although the latter now appears not to be too significant. The sections were prepared from the particular samples used to generate the data of Fig. 11 and were obtained by cutting with a sharp knife, followed by polishing for varying periods. In the first nanoindentation test on the unweathered window-grade UPVC, about $315 \mu\text{m}$ of the section surface was removed by polishing. The hardness of the section was about 25% higher than the values measured in plan at equivalent depths, suggesting some residual influence of the cutting process. Accordingly, further polishing was carried out until about 1 mm of material was removed. The same process was performed for the sample exposed to a total of 6.6 GJm^{-2} radiant energy density.

The nanoindentation results are shown in Fig. 14. As usual the individual points represent the mean of about 10–12 indents. There is consistency for the weathered and unweathered sections remote from the surface which suggests that the measurements on different samples of material are repeatable.

The hardness of the *unweathered* material near the surface (at about $2.5 \mu\text{m}$) is somewhat less than the value measured in plan for a range of depths (Fig. 11) but is comparable at slightly greater distances from the surfaces. The hardness value at 1 mm from the surface is somewhat higher than the near surface value.

The measurements in section on the *weathered* sample show markedly higher hardness value relative to those made in plan (Fig. 11). A possible explanation for the hardening is simply that polishing has a greater impact on the weathered material because it is that much softer to start with. In principle, measurements can be made at greater indent depths but the associated loss of resolution will limit significantly the value of the data.

Clearly, indenting in section introduces the possibility of artefacts associated with the sectioning and polishing process.

4. Conclusions

The nanoindenter is an effective tool for measuring modulus and hardness of polymers over a range of indent depths.

The finer scale of indents compared to conventional microhardness measurements yields more detailed information about the distribution of material properties but adds to the complexity of interpretation for very heterogeneous materials. In addition, the statistics of measurement become important in deriving values of mean hardness or modulus.

The time-dependence of the mechanical properties of polymer necessitates standardization of measurement of hardness and modulus of polymers for instruments which monitor load and displacement continuously, such as the nanoindenter, with the emphasis being on defining the hardness in relation to the hold time at maximum load. This becomes of greater importance the smaller the indent depth because the relative change in depth due to creep is greater. It is particularly useful to include a reference material in each set of measurements as a check on repeatability and consistency of instrument calibration.

The variation of hardness with exposure period and depth of indent showed a complex dependence on the competing influences of hardening due to cross-linking, which might be expected to be near surface where the intensity of radiation is greatest, softening due to loss of CaCO_3 particles and molecular scission, and surface erosion.

The modulus of the material was less affected by weathering than hardness with a modest decrease in value occurring only at very prolonged exposures.

Mechanical polishing of Darvic and *unweathered* window-grade UPVC had no discernible effect on hardness at depths greater than or equal to about 147 nm, the shallowest depth measured.

The hardness of *weathered* samples subjected to prolonged exposure was more than a factor of two higher when measured in section rather than plan in the same near-surface region. A greater impact of polishing on initially very soft material may have been responsible.

Appendix 1 Materials

DARVIC®

SPECIFICATION

Calendered, transparent PVC-U sheeting

Manufactured by Weston Vinyls

General purpose-applications include cladding, food trays, ducting etc.

Optical transparency is generally unsatisfactory for domestic glazing applications; UV stabilization gives rise to tinting, the colour of which may vary depending on the type of stabilizer used (currently green, previously blue).

COMPOSITION:

Although the exact nature of the constituents in the commercial

DARVIC are not known, the formulations for the material used contains, in addition to PVC, tin stabilizer (3.2 phr), wax lubricant (0.74 phr), process aid (0.95 phr), UV stabilizer (0.74 phr), pigment (0.02 phr).

AHS8

SPECIFICATION:

Hostalit®Z (Hoechst AG) CPE modified window sill section; supplied by EVC UK Ltd, Runcorn, Cheshire.

COMPOSITION:

SPVC/70	100 (phr)
CPE Impact modifier	10
Ba/Cd stabilizer	2
Lubricants	1,7
CaCO ₃	6
TiO ₂	4

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References

1. J. WHITE and A. TURNBULL, *J. Mater. Sci.* **29** (1994) 584.
2. W. C. OLIVER, *MRS Bulletin*, September/October (1986) 15.

3. W. C. OLIVER, R. HUTCHINGS and J. B. PETHICA, "Microindentation techniques in materials science and engineering". ASTM STP 889, edited by P. J. Blau and B. R. Lawn (American Society for Testing and Materials, Philadelphia, PA 1986) pp. 90-108.
4. J. B. PETHICA and W. C. OLIVER, in *Mat. Res. Soc. Symp. Proc.* vol. 130 (*Materials Research Society*, 1989) 13-23.
5. W. C. OLIVER and G. M. PHARR, *J. Mater. Res.* **7** (1992) 1564.
6. S. P. BAKER, Ph.D. Dissertation, Stanford University (1993).
7. M. E. O'HERN, R. H. PARRISH and W. C. OLIVER, *Thin Solid Films.* **181** (1989) 357.
8. R. H. ION, H. M. POLLOCK and C. ROQUES-CARMES, *J. Mater. Sci.* **25** (1990) 1444.
9. A. TURNBULL, D. WHITE, N. FALLA and A. SMITH, *J. Mater. Sci.* (submitted).
10. A. WOOTON, Alpas Technology (UK), Private communication, 1994.
11. N. McCORMICK, M. G. GEE and D. J. HALL, In *Mat. Res. Soc. Symp. Proc.*, vol. 308 (Materials Research Society (1993) pp.195-200.
12. J. BRANDRUP and E. H. IMMERGUT, (Eds). "The Polymer Handbook", 3rd Edn (Wiley Interscience Publication, New York, 1989).
13. N. M. JENNET, SHAFIRSTEIN and S. R. J. SAUNDERS, (submitted).
14. W. W. WEILER, *J. Test. Eval.* (1990) 229.
15. M. E. O'HERN, *Ibid.* (1991) 413.
16. Metallic materials-Hardness test-Universal test. Draft proposal, ISO/TC 164/SC3 N556, 1992.
17. R. J. CRAWFORD, *Polymer Testing* **3** (1982) 37.
18. R. MAGNUS, *Kunststoffe* **81**, **12** (1991) 1113.

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