Relaxation and Recovery Measurements by the Microhardness Indentation Technique for Transparent Polymeric Materials

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Synopsis

A simple microhardness testing technique is described that enables the indentation process to be continuously observed for transparent materials. Photographic recording gave measurements of the indentation area and its changes with time, both during the on-load period and during the subsequent period following the removal of the load. To illustrate the techniques, the time-dependent mechanical properties of poly(methyl methacrylate) (Perspex) and diallyl diglycol carbonate (CR39) have been studied. Two parameters are defined that could be useful in identifying time-dependent deformation properties of polymeric materials. The relaxation hardness, analogous to the relaxation modulus, describes the stress–relaxation that occurs for an indentation-loaded material. The surface resistance to damage, defined as the ratio of the applied indentation load to the remaining deformation area after load removal, is useful as an abrasion or wear indicator, particularly for assessing optical deterioration. The changes in this parameter with time describe the mechanical recovery that occurs at an indentation site in the material.

INTRODUCTION

Microhardness testing is a well-established technique for assessing the resistance to deformation of materials, in which a loaded indenter, typically a 136° diamond pyramid (Vickers), is applied to the surface of the material to be tested.[1-3] If the load is L and the projected area of contact is A, then the mean contact pressure or mean supported stress is the definition of hardness of the material first given by Meyer,[4] i.e., $L/A = H$. The Vickers hardness is defined as the ratio of the load to the true contact area so that $H_V = 0.927H$.[5] For metals (elastic/plastic materials) the hardness gives an indication of strength, i.e., $H \sim 3Y$, where Y is the yield stress of the metal.[5] For ceramics and glasses (elastic/fracture materials) recent developments in the understanding of indentation mechanisms and associated localized cracking for brittle materials has led to a renewed interest in microindentation techniques for measuring the fracture toughness of these materials.[6-8] For polymers (viscoelastic materials) hardness studies and attempts to relate hardness to yield stress have been made,[9-11] but the time-dependent viscoelastic properties were not considered. Müller[12] established that the indentation test for such materials gives different results, depending upon whether the indentation measurements were made after the load was removed (normal procedure) or while the load was still being applied. If the indentation process can be followed in time, then clearly useful information can be obtained relevant to the time-dependent relaxation and recovery properties of the materials tested.

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Although the detailed stress field developed in the indented material is much more complex than in the conventional tensile test, the indentation characteristics can be related to the mechanical properties of strength, brittleness, and viscoelasticity. The deformation involved in the indentation is related to both cutting and stretching process for these materials. The indentation test is also empirically relevant to resistance to damage associated with sharp contact events, dynamic impact, abrasive scratching, and wear. In comparison with other tests the indentation method is simple and economic in test procedure.

In discussing hardness, Tabor[5] very quickly distinguishes between resistance to deformation under load and resistance to permanent deformation. For metals the difference is usually small, the deformation being predominantly plastic, but for polymeric materials the difference can be large and each can be time-dependent. With a big difference it is useful to distinguish the significance of the two parameters; the ratio of the applied load to the deformation area produced, i.e., the mean supported stress, is properly the measurement of hardness, and in this case $L/A = H$. However, the ratio of the originally applied load to the deformed area after load removal is of significance as a measure of surface resistance to damage (SRD), rather than hardness, so that in this case L/A = SRD. This concept of force applied divided by resultant damaged area has been used before to describe surface resistance to damage[13] and is of practical importance, for example, in optical applications of materials.

The present work originated in an interest in the assessment of resistance to damage of optical components. It was realized that, for transparent materials, the indentation process could be continuously observed from the other side of a plate shaped specimen. Both H and SRD parameters could then be measured, distinguished, and their variations with time studied. It seemed likely that this could be of interest as a comparatively simple test giving information on the general viscoelastic properties of transparent materials.

EXPERIMENTAL

The microhardness tester used was of the balance type, designed to sit on top of the stage of an inverted type metallurgical microscope so that the indentation made on the top side of the specimen could be microscopically observed from beneath. The basic arrangement is shown in Figure 1, the

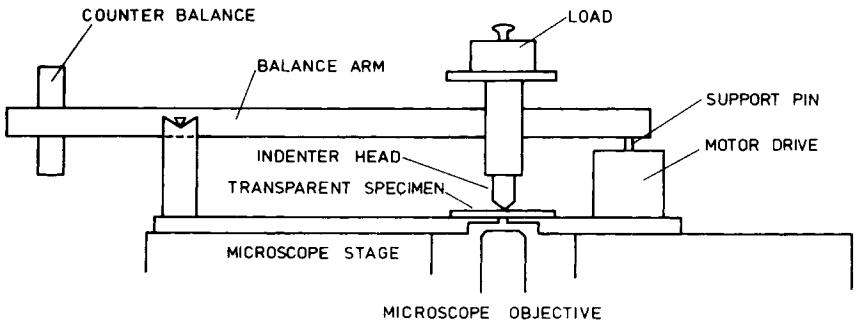

Fig. 1. Diagram of the basic arrangement of the balance-type microhardness tester used.

details have been described elsewhere.[14] The indentor used was a standard commercial Vickers diamond pyramid. The magnification for observation and measurement of the indentation area was limited by the thickness of the specimen because of the required working distance of the microscope objective. (The load used was generally selected to give a microindentation big enough to be accurately measured at the maximum magnification available.)

The materials used to illustrate the technique were polymethyl methacrylate or perspex (P) and diallyl diglycol carbonate or CR39 (C). Each was in the form of a cast sheet, 2 mm thick. Sequential photographic recording gave measurements of the indentation area and its change with time, which initially was very rapid, both during the on-load period and during the subsequent period following the removal of the loaded indenter. The loading was quasistatic, the time taken to apply the load was approximately 0.5 s. The photographic measurements made in the experiments were at constant load, commencing at approximately 5 s after loading. The tests were carried out at a temperature of 25°C, which is far below the glassy transition temperatures for the materials tested.

Although it was the indentation area that was directly measured, the parameter used in describing and discussing the results is the ratio L/A. This is because, as described in the Introduction, this parameter has the significance of hardness (H) for the on-load period and the significance of surface resistance to damage (SRD) for the subsequent off-load period.

RESULTS

For an indentation load of 150 g, Figure 2 shows how the parameter L/A changes with time during the load-on and the load-off periods for both Perspex (P) and CR39 (C). Each point represents measurements made from a separate photograph; the scatter indicates the experimental error in measur-

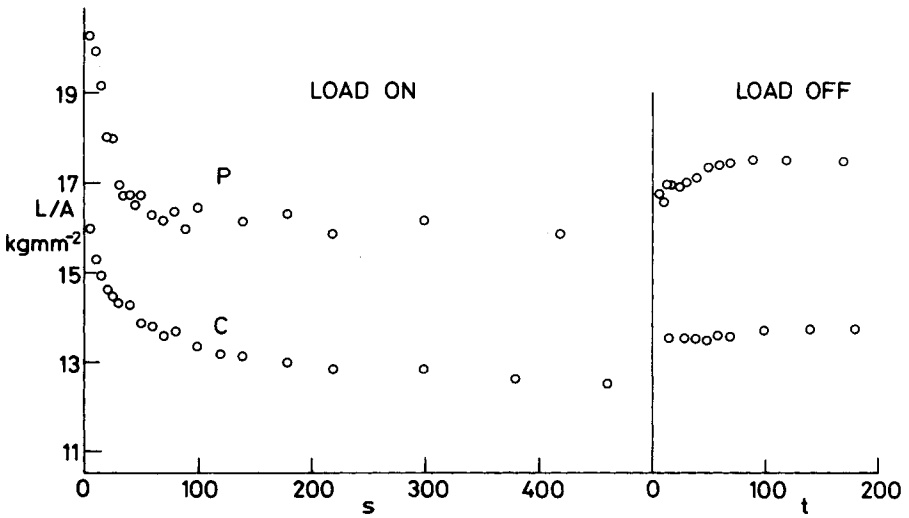

Fig. 2. Variations of L/A with time for indentations in Perspex (P) and CR39 (C), while the load of 150 g was applied and after it had been removed.

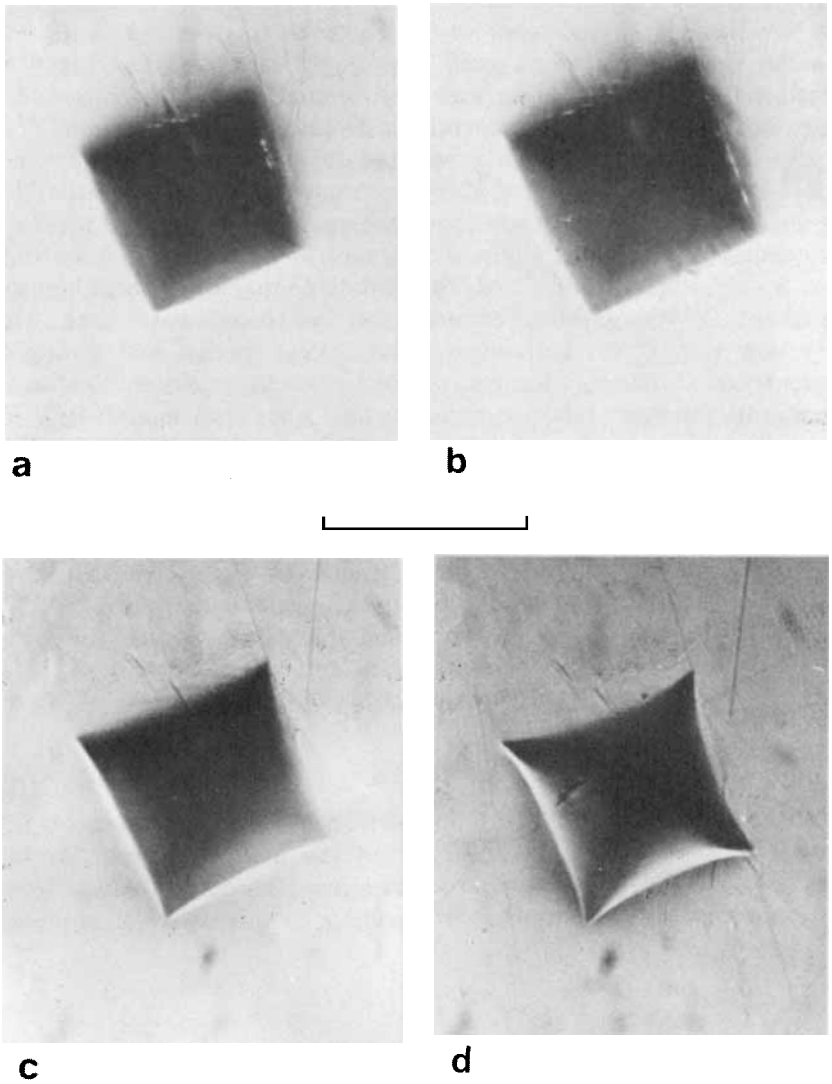

Fig. 3. Appearance of indentations in Perspex for load of 150 g: (a) after 5 s; (b) after 500 s; (c) 5 s after load was removed; (d) 500 s after load was removed. The marker represents 100 μm.

ing the indentation areas. The type of changes that occur are shown in Figure 3. An indentation in Perspex after the load was on for 500 s [Fig. 3(b)] is bigger than it was after only 5 s [Fig 3(a)]. Immediately after the indenter was removed, the indentation became curved and smaller [Fig. 3(c)], while 500 s after the indenter was removed the deformed area was smaller still [Fig. 3(d)].

Clearly from Figure 2 the Perspex was harder than the CR39. From the different shape of the curves, it can be seen that the relaxation characteristics of the two materials were quite different. The off-load region shows that the Perspex had greater surface resistance to damage (SRD) than the CR39 and that whereas the recovery was apparently elastic for CR39, the Perspex had both elastic and time-dependent viscoelastic recovery.

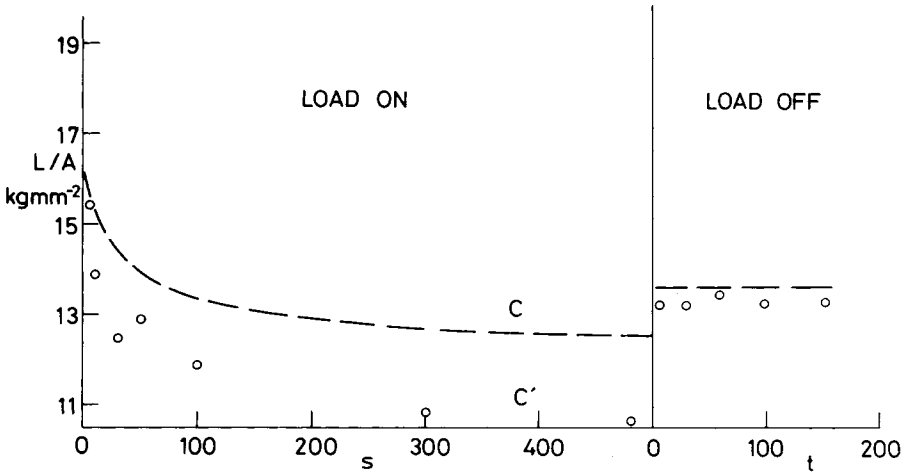

Fig. 4. Variations of L/A with time for indentations in CR39 with load applied and after it had been removed for loads of 20 g (C′) and 150 g (C—as in Fig. 2).

The hardness measured with a diamond pyramid indenter should be independent of load. Figure 4 shows results for L/A obtained for CR39 indented at a load of 20 g (C′), in comparison with the previous results for an indentation load of 150 g (dotted line C). Although the rapidly varying initial hardness appeared to be load independent, the stress–relaxation process varied with the load, increasing for the smaller load. The recovery upon load removal also increased so that the final value of L/A with load off, or SRD, was almost the same as for the larger load. The independence of initial hardness and final SRD with respect to load, and thus indentation depth, indicates that anisotropic surface properties were not significantly affecting these tests.

However, this recovery parameter (SRD) was found to be extremely sensitive to previous loading history. This is illustrated for Perspex in Figure 5, where the recovery curve after a 5-s indentation loading (P′) is compared with the previous results involving a 500-s loading (dotted line P). The load was 150 g in each case, and it is seen that the initial hardness measurement was approximately the same. For the short loading time test, with the absence of relaxation, the recovery was very much increased.

The recovery upon removal of the indenter, was always qualitatively observed by the resultant "pin-cushion" shape of the indent outline afterwards. However, observing the indentation under load showed up another difference between the two materials tested. The indentations in perspex always had a square outline under load [see Figs. 3(a) and (b)], indicating that the surface around the indent had remained flat, but for the CR39 the indent outline under load was "pin-cushion"-shaped, indicating that the material around the flat faces of the pyramid had been pulled down during indentation. For metals this "sinking-in" is associated with a capacity to work harden.[5]

It is to be noted that, for the materials tested, from the observations of the indentations, the indentation diagonals increased with time under load and

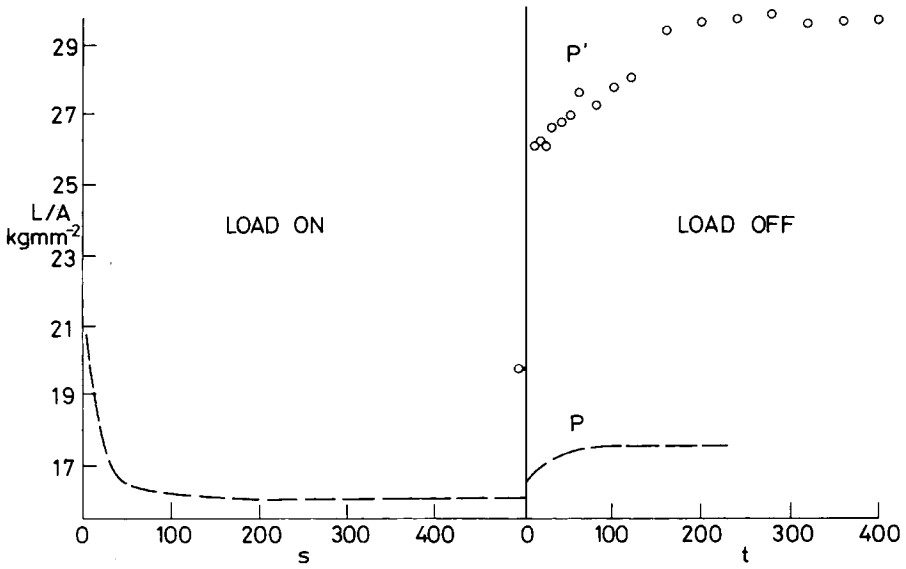

Fig. 5. Variations of L/A with time for 150 g indentations in Perspex with load applied and after it had been removed for load application times of 5 s (P′) and 500 s (P—as in Fig. 2).

decreased when the load was removed. Thus the conventional commercial Vickers hardness test must be considered inappropriate for such materials.

DISCUSSION

The microhardness testing technique used was similar to, but optically simpler than, that devised by Müller,[12] who investigated the load-on and load-off indentation properties of a range of polymeric materials. Although the present test is applicable to transparent materials only, the apparatus is simple and a standard Vickers diamond pyramid indenter-head can be used. In fact, most commercial micro-hardness testers could be adapted to sit on the stage of an inverted type metallurgical microscope.

The results of the present work have clearly shown that for the polymeric materials tested, hardness measured under load is a time-dependent parameter. Time-dependent deformation properties of viscoelastic materials are usually characterized by either a relaxation modulus (E_{R_t}) measured as the ratio of the time-varying stress to the controlled constant strain, or a viscoelastic modulus (M_{VE}) measured as the ratio of the controlled constant stress to the time varying strain. Both these moduli vary significantly with time, as well as temperature, and experimental evaluations are usually given as graphs or tables rather than as a single particular value. In the hardness test, the conditions are not quite as simple as in the above measurements since, although the load is held constant, the mean stress and the amount of deformation are uncontrolled and vary with time, the change in stress being directly related to the deformation. However, the simplicity, quickness, and cheapness of the hardness test make it attractive, and it might well be considered useful to have a parameter, analogous to those above, referred to as the relaxation hardness (H_{R_t}) and defined as the ratio of the applied

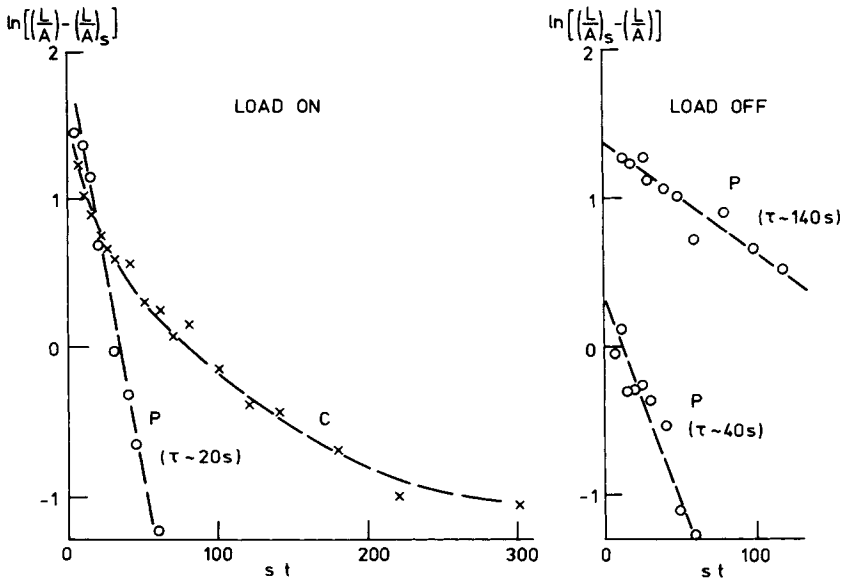

Fig. 6. Variations of $\ln[\Delta(L/A)]$ with time for indentations in Perspex (P) and CR39 (C), for loading period and period after load was removed. Estimations of relaxation times (τ) calculated from the straight line slopes are given.

constant load to the time-varying area of indentation. The on-load parts of Figures 2 and 4 would then illustrate how the relaxation hardness was different for different materials and was affected by different loadings. For example, the difference in variation of H_{R_t} with time for CR39 indented with loads of 150 and 20 g, seen in Figure 4, could be related to the smaller compressive displacements occurring in the latter indentation so that freedom for subsequent relaxation was greater (this would also explain the increased recovery that occurred when the smaller load was removed). The deformation properties of these materials are not linear, and it may be that the proportion of elastic to viscoelastic deformation around an indentation changes with load.

If the decays in relaxation hardness seen in Figure 2 are exponential, then graphs of $\ln[(L/A) - (L/A)_s]$ against time (where $(L/A)_s$ is the final approximately steady value) should be straight lines and a relaxation time (τ) would be obtainable. Figure 6 shows that this appears to be so for the Perspex, at least in the early stages of the indentation process, with $\tau \sim 20$ s; but for CR39 the decay is not a simple exponential, and there is no single relaxation time. It is generally accepted that this is the case for many polymeric materials, which often require a spectrum of relaxation times to account for all phases of their behavior.[15]

Once the indenter has been removed, the important consequence is the damage remaining. The SRD parameter is a useful means for monitoring this effect, which is relevant to wear properties of materials such as abrasion—particularly optical deterioration. As with the relaxation hardness, SRD also varies with time and the off-load parts of Figures 2 and 5 illustrate how it varies for different materials and is affected by different previous loading histories. These graphs also distinguish between effective elastic recovery and

viscoelastic recovery and show up differences in the proportion of these recovery processes occurring for different materials. Effective elastic recovery refers here to a recovery process at least an order of magnitude faster than the subsequently observable time-dependent recovery. For example, it can be seen from Figures 2 and 5 that all the recovery is effectively elastic for CR39 (C) even after extensive indentation relaxation, approximately two thirds of the recovery is elastic for Perspex without relaxation (P′), but for Perspex where extensive indentation relaxation has been allowed (P) the recovery is mainly viscoelastic. Also the logarithmic graphs in Figure 6 (load-off) indicate that for Perspex the recovery process appears to have a characteristic time constant which is shorter for the material that has undergone extensive relaxation before the recovery takes place (P) than for the material where there had been virtually no relaxation beforehand (P′). Thus for indented Perspex with no relaxation beforehand, recovery is mostly elastic and the following viscoelastic recovery is slow, while after extensive relaxation the recovery is mostly viscoelastic and it is faster than that above.

The plotting of logarithmic graphs, as in Figure 6, is a means of looking for a simple exponential time dependency. It would be a great advantage to have a theoretical model for the indentation of viscoelastic materials. An interesting analysis has been given by Johnson[16] based on an approach by Lee and Radok,[17] in which the elastic constant in the solution for elastic contact is replaced by a viscoelastic time-dependent function, which depends upon the viscoelastic model appropriate to the material. However, the analysis is only carried out for a blunt (spherical) indentation into a simple Voigt or Maxwell model material. Unfortunately, the significant extension of this approach, to a sharp indentation with instant yield into a material described more realistically by a distribution of model elements with associated relaxation times,[15] has not yet been achieved.

The next step in the present experimental work is to attempt to automate the monitoring of the variation of indentation with time. An investigation of the possibilities of measuring indentation contact by an electrical resistance measuring technique has proved very encouraging.[18] Preliminary tests have shown that this method could be used to continuously record changes in indentation area for an insulating material such as an organic polymer, provided that a thin electrically conducting film is first put on the surface. Once the area is recorded, direct read-out of the ratio L/A and its variation with time is easily achieved. With electrical contact measurement, the technique could be extended to nontransparent materials, and the initial rapidly varying changes could be more readily studied. However, the optical technique will remain useful for studying the recovery at indentations after indenter removal, and details of the indent shape changes with time.

CONCLUSIONS

Microindentation testing with continuous observation is a simple and quick method of obtaining information on the time-dependent properties of transparent materials. These properties can be identified in terms of relaxation hardness, defined as the ratio of controlled constant load to time-dependent area of indentation under load, and surface resistance to damage, defined as

the ratio of the indentation load to the remaining deformation area after load removal. The latter is useful for assessing abrasion and wear properties, and its variation with time relates to the mechanical recovery properties of the material.

Although the rapidly changing initial hardness is load-independent, the relaxation hardness was found to be dependent on load. The recovery process after indentation has been shown to be very dependent on the previous indentation history.

The relaxation hardness and surface resistance to damage of Perspex and CR39 have been compared. Perspex is more resistant to indentation and relaxes to a stable indentation state more quickly than CR39. Perspex appears to have a simple exponential relaxation whereas CR39 does not. The recovery of CR39 was almost entirely effectively elastic, but for Perspex the recovery had a significant time-dependent component.

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