

Scratch deformation of methanol plasticized poly(methylmethacrylate) surfaces

B. J. Briscoe*, E. Pelillo, F. Ragazzi and S. K. Sinha

Particle Technology, Department of Chemical Engineering and Chemical Technology,
Imperial College, London SW7 2BY, UK

(Received 16 December 1996; revised 16 May 1997)

The results of a series of scratch measurements are reported for a number of methyl alcohol (methanol) plasticized poly(methylmethacrylate) (PMMA) surfaces to investigate the deformation mechanism and solvent diffusion characteristics when a PMMA is exposed, to various extents, in a methanol environment. The study confirms that the solvent diffusion in this system occurs by the Case II diffusion process. The scratch deformation map described indicates that there is a major change in the deformation mechanism as the exposure time proceeds and this is related first to a sample plasticization and then to a restructuring process of the PMMA-methanol system due to the greater mobility and relaxation of the polymer molecules as they imbibe the solvent. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: plasticization; scratch hardness; scratching method)

INTRODUCTION

Common examples of the usage of polymers are in bearings, composites for furniture and structural applications, electrical and electronics applications, domestic appliances and so on. These applications often involve the contact of the polymeric component with different chemical environments, such as lubricating oils, solvents, detergents and cleaning liquids. A common practical problem with the usage of polymers in such active environmental conditions is that the surface becomes softened or plasticized if exposed for a long period of time'. Alternatively, the surface may become sensitive to brittle cracking or crazing. The plasticization of the surface produces a softening effect which changes the surface mechanical and optical properties of the polymer. This may cause a drastic loss of the working life of the polymeric component. Environment/polymer interactions are important also in the study of wetting, adhesion, corrosion, tribology and thin film technology².

Plasticization is a diffusion controlled phenomenon where a solute penetrates into the bulk of a polymer and thereby causes either the swelling or the dissolution of the polymer molecules. The diffusion may take place, in the extremes, by either Case I or Case II processes depending upon the characteristics of a particular polymer/solvent system'. The rate of the diffusion process determines the rate, or depth, at which plasticization will occur in the polymer surface.

An important phenomenon which occurs on a plasticized polymer surface is the inevitable change in the deformation mechanisms of the material when it interacts at the surface with another material in applications such as bearings and in other sliding components. The change in the

deformation mechanism may progress from a predominantly brittle response for a dry amorphous polymer surface, such as poly(methylmethacrylate) (PMMA), to a plastic/ductile or rubber-like behaviour after plasticization. The working life of a polymeric component greatly depends upon the type of deformation mechanism that takes place when the polymer surface interacts with a counterface. The deformation mechanism determines the amount of energy being dissipated at the interface and in the deformation of the material during a mechanical interaction. Hence, it is desirable that not only the rate of plasticization should be determined but also the changes in the mode of deformation should be identified for a given polymer/environment system.

A number of methods have been implemented in the past to measure the extent of plasticization of polymer surfaces in an active chemical or thermal environment. The methods which have been employed previously have used either the spectroscopically detectable structural changes in the polymer or the changes in the mechanical properties of the polymer surface such as the hardness or the coefficient of friction. For instance, vibrational spectroscopy⁴ and Fourier transform infrared spectroscopy⁵ have been used to examine the structural changes during the crystallization and melting behaviour of PEEK. Briscoe *et al.*⁶ used Fourier transform infrared spectroscopy and sliding friction methods to study the plasticization of a Nylon 6/6 by water. They also carried out friction coefficient measurements for the same system⁷. In the present study we have used the scratch hardness measurement to compute the scratch hardness of a PMMA when it is plasticized by methanol. The scratch hardness method is a very useful and convenient technique for studying some of the surface mechanical properties of materials, which can be used for both the measurement of the hardness, or the flow stress, and the identification of the prevailing deformation mechanism during scratching. This method has been used previously in order to obtain deformation mechanism maps (which define

* To whom correspondence should be addressed. Imperial College of Science, Technology and Medicine, Chemical Engineering and Chemical Technology Department, Prince Consort Road, London SW7 2BY UK

the major damage modes) as well as the time and temperature dependent yield properties of 'dry' polymers⁸. However, the response of polymeric surfaces, such as PMMA, to scratching is rather complex, since bulk, surface and near-to-surface deformation phenomena may occur. Therefore, the present paper does not attempt to describe in detail the entire range of contact mechanical deformation processes involved in scratching. These are described in more detail elsewhere (refer to⁸⁻¹²).

The present paper reports on the scratch hardness behaviour of a PMMA exposed for various periods in a liquid methanol environment. PMMA was chosen as the model material because the scratch and indentation deformation behaviour of this polymer has been widely examined^{8,9} and also because reliable data on the diffusion rate of methanol in PMMA are available in the literature (see for example ref. ¹³). In addition, it was anticipated that the plasticization behaviour of PMMA would be relatively straightforward in character; such processes as antiplasticization, apparent in semicrystalline systems, were not anticipated^{1,7}.

Scratches were produced on the PMMA surface using rigid cones of various included angles and under four different normal loads. The scratched surfaces were studied in order to identify the prevailing deformation mechanisms using laser profilometer and scanning electron microscopy (SEM). The scratch hardness of the polymer surface, a parameter which is defined later, shows a strong dependence upon the alcohol exposure time and the normal load. The deformation mechanism during scratching also depends upon the normal load, the imposed strain and the extent of the plasticization.

THEORY

Plasticization and diffusion in polymers

When a solid polymer interacts with a solvent, a slow, and often arrested, dissolution process can occur. The process is usually divided into two stages. First, solvent molecules slowly diffuse into the polymer structure to produce a swollen gel; this happens if the polymer-polymer intermolecular forces are large compared to the self-affinity of the solvent. If these forces are overcome by the introduction of a strong polymer-solvent interaction, the second stage of the solution process can then take place. Here, the gel gradually dissolves to form a solution. The penetration of a solvent plasticizer through the polymer matrix causes a partial relaxation of the polymer chains by reducing the intermolecular forces of attraction, hence producing a greater freedom of movement among the polymeric macromolecules. The result is a change in the material properties, i.e. a greater flexibility and plasticity, a decrease in the tensile strength and the lowering of the glass transition temperature.

Based upon equilibrium thermodynamic considerations^{14,15} it has been shown that for the system PMMA-methanol, the solution process stops at the first stage of plasticization, which means that only a swelling of the polymer structure occurs; later we confirm this but also deduce that a time dependent restructuring of the plasticized layer occurs. In a polymeric system, the penetration rate of a plasticizer depends upon the relaxation rates of the polymeric molecules and the structural constitution. Hence, the diffusion process in a polymer cannot be described only by a consideration of the concentration difference, as the Fick's law relationships do not take into

account the time dependent structural changes that might occur within the polymer-solvent front interface. Alfred *et al.*¹⁶ have proposed a classification of the diffusion behaviour based on the comparison between the polymer segment relaxation rates and the rate of the penetrant mobility:

- (1) Case I (Fickian): the penetrant mobility is much less than the polymeric segmental relaxation rate.
- (2) Case II: the penetrant mobility is much greater than segmental relaxation rate, which is a case peculiar to glassy polymers.
- (3) Anomalous: the two values are comparable.

The main feature characterising Case II diffusion is the presence of a relatively sharp boundary, separating the swollen layer from the unpenetrated region (glassy core), which advances at a constant velocity. The amount of the penetrant absorbed, M_t , after a certain time, t , is often generally expressed as:

$$M_t = Kt^n \quad (1)$$

where K and n are constants. For Fickian systems $n = 1/2$, for Case II, $n = 1$ and in the case of anomalous diffusion region the value of n lies in between. The system PMMA-methanol has been previously analysed for the diffusion behaviour by Windle and Thomas^{13,17,18} and by Sarti *et al.*¹⁹. Using optical or mass sorption measurements they have found that the diffusion in this system is largely that of the Case II kind.

Scratch hardness

The experiment is conveniently carried out by drawing a rigid indenter of a specified geometry on the surface of a softer material under a constant applied normal load and at a constant relative contact velocity. Generally for polymers, all facets of the scratching behaviour are influenced by the external variables such as the load, the indenter geometry and the sliding velocity⁸. The dimensions of the scratch (width and depth) thus produced is measured after the deformation and the scratch hardness, mainly a plastic deformation characteristic, of the softer material is taken as²⁰:

$$H_s = \frac{8W}{\pi(d_s)^2} \quad (2)$$

where H_s is the computed scratch hardness of the material, W is the applied normal load and d_s is the scratch width. Since d_s is the width of the scratch measured after the deformation, the scratch hardness given by equation (2) provides only the yield and post-yield properties of the material. The logic behind using equation (2) is that since the hardness is a measure of a flow stress then the normal load has to be normalized by a chosen area; the area chosen is half the projected area of a static indent of diameter d_s . The assumption is that the load is only supported upon one half of this area in the scratching process. The argument is sufficient in view of subsequent assumptions which must be introduced.

It is also worth noting that the scratching process will sense the material properties in a volume which is between two and three times the maximum depth of penetration of the indenter. The influence of the interface friction is also significant¹⁰; a lower interface friction, produced by lubrication or plasticization, will generally produce an increase in the scratch hardness (d_s is reduced). The level of imposed strain in scratching is not readily defined; far away

from the scratch it is zero. The 'effective' strain is conventionally taken as about $0.2 \tan \theta$, where θ is the angle that the cone makes with the polymer surface (the attack angle); a further advantage of conical indenters is that the strain imposed is nominally not a function of the penetration depth¹⁰. The effective strain rate may be taken as V/d , where V is the sliding velocity (see for example ref. 8).

EXPERIMENTAL PROCEDURE

The plasticization of a commercial grade of cast PMMA (ICI, UK) was achieved by using a commercial methanol (99.9 + %, A.C.S. h.p.l.c. grade, Aldrich, UK). The PMMA was in the form of smooth plaques (20 mm × 20 mm) of ca. 6 mm thickness. The scratch machine consisted of a free lever arm with an indenter attached onto one side. The indenter rested on the PMMA specimen and fixed dead weights were used for applying the normal load. After applying the normal load to the indenter, the specimen, which was mounted on a stage was moved at a constant

speed using a stepper motor. In this way scratches were produced on the specimen. Conical steel indenters, of included angles 30, 60, 90 and 120°, were used for the scratching. These types of indenters have many advantages over other geometries such as spheres; see for example ref. 8. However, they do have some shortcomings, including the fact that they are not perfectly sharp. These conical indenters had spherical tips whose radii were of the order of 5 μm. The practical requirement is that the depth of the scratches should be significantly greater than this value.

Immediately after the scratching, the PMMA samples were placed under a laser profilometer (Rhodenstock, Germany) for the recording of the topographical profiles of the scratches. The scratching of the plasticized samples was carried out while the sample was submerged under methanol. The duration of the time between scratching and profilometric characterization was kept to a minimum, ca 15 min, in order to minimize the desorption of the methanol and the resulting distortion of the scratch profile.

For the SEM studies, the samples were allowed to dry and then gold coated. Thus, the images obtained from the SEM

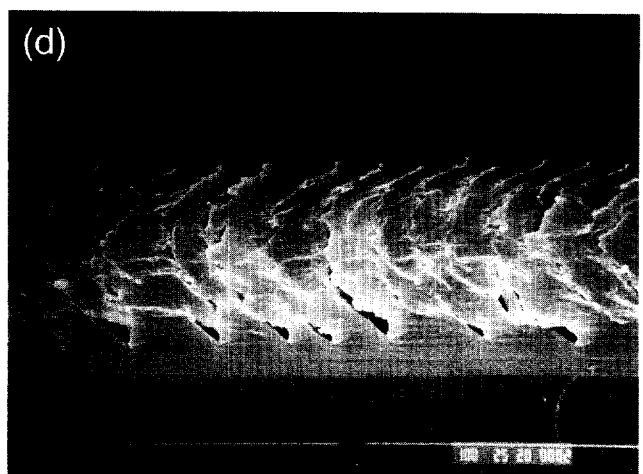
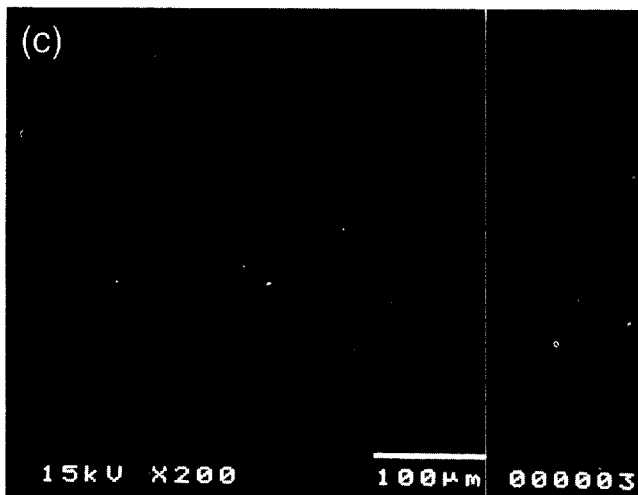
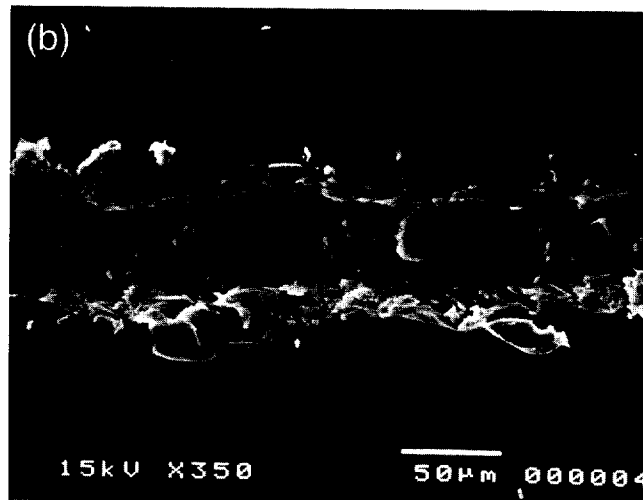
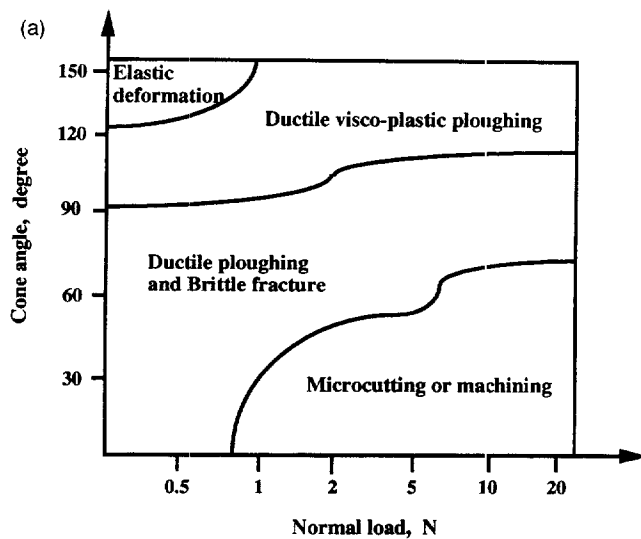


Figure 1 (a) Deformation map for dry PMMA. The diagram shows the dependence of the observed scratching deformation modes upon the cone angle and the applied normal load; i.e. nominal strain *versus* depth. The scratches were produced at room temperature at a constant scratching velocity of 0.004 mm s^{-1} and under unlubricated contact conditions. (b) SEM of a scratch produced on dry PMMA using a 60° cone indenter (normal load = 1.2 N; scratching velocity = 0.004 mm s^{-1} ; $T = 20^\circ\text{C}$). The picture shows the presence of a brittle fracture together with plastic deformation. (c) SEM of a scratch produced on dry PMMA using a 120° cone indenter (normal load = 1.2 N; scratching velocity = 0.004 mm s^{-1} ; $T = 20^\circ\text{C}$). The picture shows the highly ductile nature of the deformation. (d) SEM of a scratch produced on dry PMMA using a 90° cone indenter (normal load = 1.2 N; scratching velocity = 0.004 mm s^{-1} ; $T = 20^\circ\text{C}$). The picture shows an example of a transitional scratch deformation; the brittle fracture starts occurring within the plastically deformed scratch groove.

images will be somewhat different to the features than it would have been apparent just after the scratching in the plasticizing environment. However, the interpretation of the images, in terms of ductile/brittle responses, is unlikely to be influenced by this effect.

The diffusion rates of methanol in the PMMA were studied using the procedures described by Windle and Thomas^{1,3}.

RESULTS AND DISCUSSION

Deformation mechanism

Polymers are peculiar materials, in that they show a wide range of surface deformation characteristics for relatively small variations in the applied strain (cone angle in the present cases), normal load, rate of deformation (the sliding velocity), or bulk temperature of the polymer. Hence, the response of the material, measured in a hardness (normal or scratch) experiment, greatly depends upon the actual mechanism which occurs during the deformation. A number of studies have been carried out by the present authors in order to construct surface deformation maps for polymers during single point scratching deformations. *Figure 1a* shows a typical deformation map drawn for a dry (unlubricated) PMMA surface when it is scratched by cones of different included angles and under various applied normal loads at a fixed sliding velocity (for results on scratching for polymers, see also ref. ⁸). As was mentioned previously, the nominal contact strain, based upon a comparison of scratching with normal indentation, is about $0.2 \cot \theta$, where θ is the cone angle. As may be seen in the map, the prevailing deformation mechanism changes from brittle failure (*Figure 1b*) to that of a ductile ploughing (*Figure 1c*) through transitional deformation regimes (*Figure 1d*) and then to an elastic deformation as the cone angle is varied from 30 to 150°; this is as the nominal or effective contact strain is reduced. Also, at higher applied normal loads the material responds in a more brittle manner than for the lower loads. The prevailing deformation mechanism greatly influences the measured value of the scratch hardness; see ref. ⁸. The actual mechanism, which

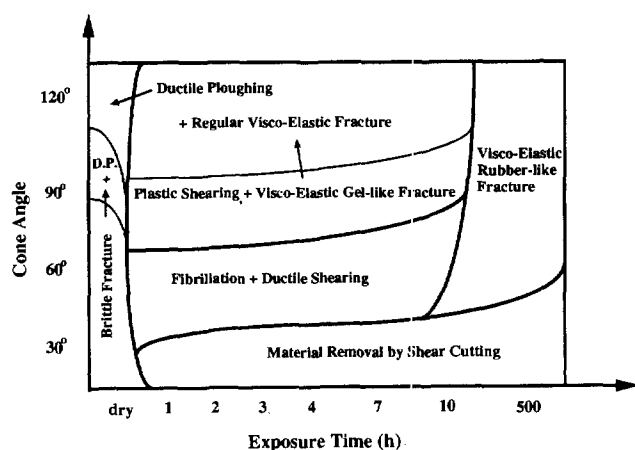


Figure 2 Deformation map for methanol plasticized PMMA surface. The diagram shows the dependence of the observed scratching deformation modes upon the cone angle and the exposure time in a methanol environment ($T = 25^\circ\text{C}$). The scratches were produced under a constant load of 2.6 N at a constant scratching velocity of 0.004 mm s^{-1} . The figure, compared with *Figure 1*, illustrates the dramatic change in the deformation mechanisms of the PMMA from brittle (dry case) to plastic and viscoelastic with the increasing exposure time, e.g. thickness of the plasticized layer

acts during any material deformation process, is the most energy efficient process for any particular set of conditions of load, strain and temperature.

Figure 2 shows the comparable deformation map for a plasticized PMMA surface, constructed for different exposure times in methanol, and with cones of various included angles. This map shows, as for the case of the 'dry' surface, that the plasticized PMMA surface undergoes a broad, and indeed more complicated, range of deformation mechanisms. Plasticization of the PMMA initially induces a localized surface swelling and a gel formation. The initially plasticized gel is a soft and ductile material which has a predominant plastic response upon deformation. However, with an extended exposure, the structure of the polymer appears to change to that of a more elastic and rubber-like material; some macromolecular reorganization seems to occur. These general response features, observed on the deformed surfaces, may be seen in the SEM photographs presented in *Figure 3a–d*, which show PMMA surfaces when scratched by a 90° conical indenter. A dry PMMA system, when scratched by a 90° cone shows a combination of brittle failure and ductile ploughing. These features change to a more ductile flow character when the PMMA surface is first exposed to the methanol environment. After 1 h of exposure there are no signs of cracks in the scratch groove; the surface still shows a predominantly ductile behaviour. The surface of the material effectively behaves like a soft plastic gel and continues to deform rather plastically after about 2 h of methanol exposure. Upon further plasticization, the material shows some signs of structural reorganization, which causes it to behave more like a crosslinked rubber or a viscoelastic material⁸. This effect can be seen in *Figure 3d*. The figure also shows formation of some cracks which occur periodically along the scratch groove. However, the surface is still soft and gel-like in character. When the PMMA surface is exposed for a longer period of time (3 weeks), the surface of PMMA effectively shows an exclusive rubber-like behaviour during the scratching process. This indicates that as the indenter passes on the polymer surface, there is a large accumulation of elastic strain energy and, subsequently, the formation of cracks. This behaviour is typical of crosslinked elastomers. Hence, the study of the deformation mechanism clearly shows that plasticization of PMMA by methanol takes place in at least two stages. In the first stage, which takes place in the first 4 h or so of the methanol exposure at 25°C, the swelling and mass sorption produces a gel-like material which is soft and rather plastic. PMMA is a glassy material and hence the polymer chains tend to relax due to the diffusion of methanol into the bulk of the material. Upon a further lapse of time in the methanol environment, the polymeric chains tend to form some kind of interconnected structure, which causes the PMMA to behave like a viscoelastic solid. This viscoelastic nature of the material causes the computed hardness of the material to increase for exposure times more than 4 h; it was noted previously that the hardness value monitored is sensitive to the mode of deformation. The hardness results are presented in the next section. Upon further diffusion of the methanol, the PMMA continues to change, showing a complex response of both gel-like and viscoelastic behaviours.

Scratch hardness of methanol plasticized PMMA

Figure 4 shows plots of the computed scratch hardness of the PMMA surface, using equation (2), as a function of the exposure time in the methanol environment. The scratches

were produced by 90° angle cones and the data are plotted for four different normal applied loads. There is some uncertainty in the computed values as the scratch width, d_s , cannot be clearly and uniquely identified for all cases; the values provided are a first order evaluation. As was expected, there is a sharp decrease in the computed scratch hardness values of the PMMA surface with the increase of the exposure time. This is obviously due to the gradual

softening of the outer layer of the PMMA. As the methanol penetrates into the material, the depth and hence the width of the scratch increases for the same applied normal load. Hence, the computed hardness value decreases with the increase of the time of exposure. In this figure, it is observed that after *ca* 4 hours of methanol exposure to PMMA, the scratch hardness shows a slight increase before it finally stabilizes at a constant value. A preliminary explanation of

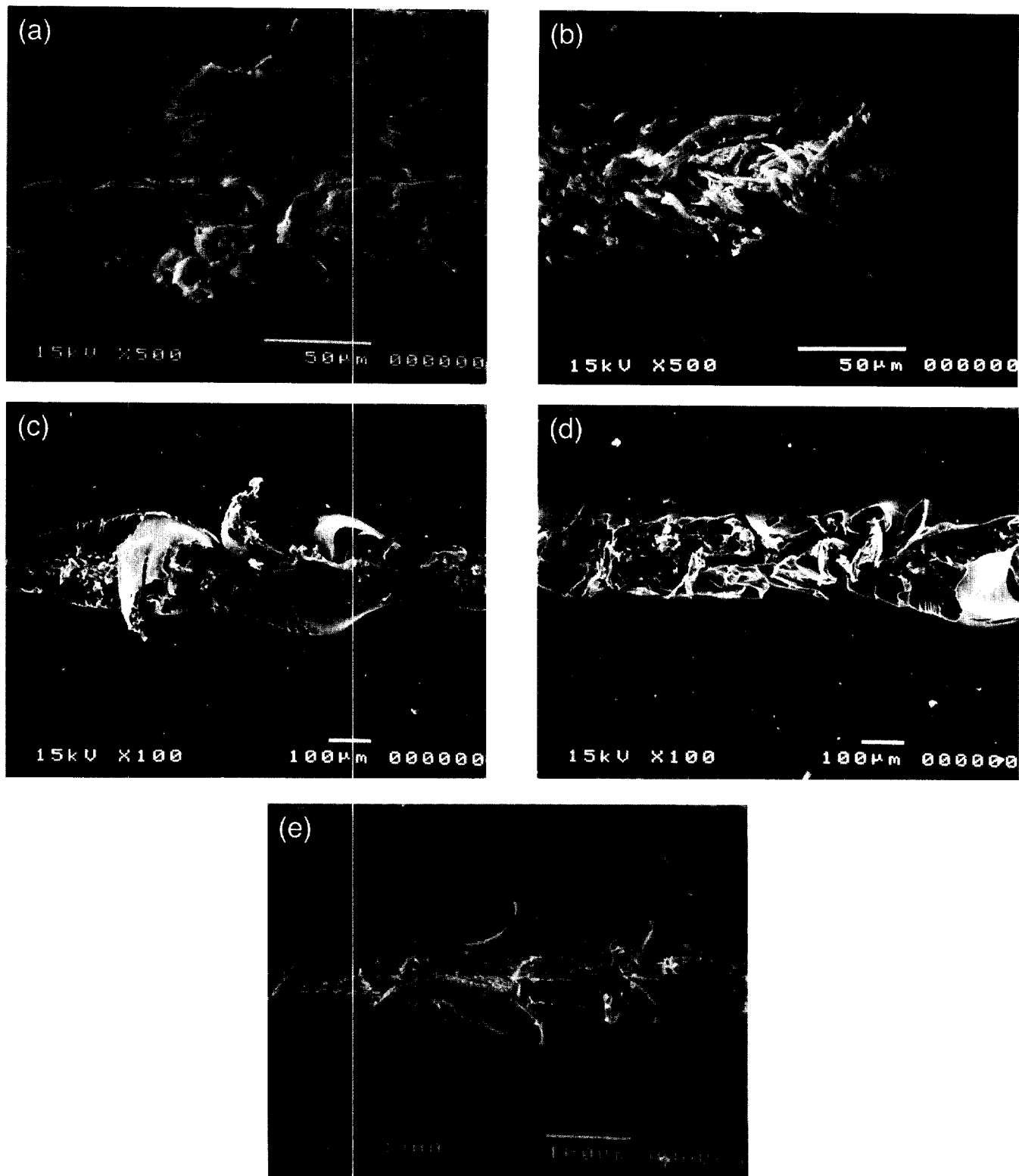


Figure 3 SEMs of scratched PMMA surfaces after different exposure times: (a) dry; (b) 1 h; (c) 2 h; (d) 4 h; (e) 3 weeks. The scratches were produced under a constant load of 2.6 N and at a constant velocity of 0.004 mm s^{-1} and at room temperature. The samples were allowed to dry and then gold coated prior to the SEM study

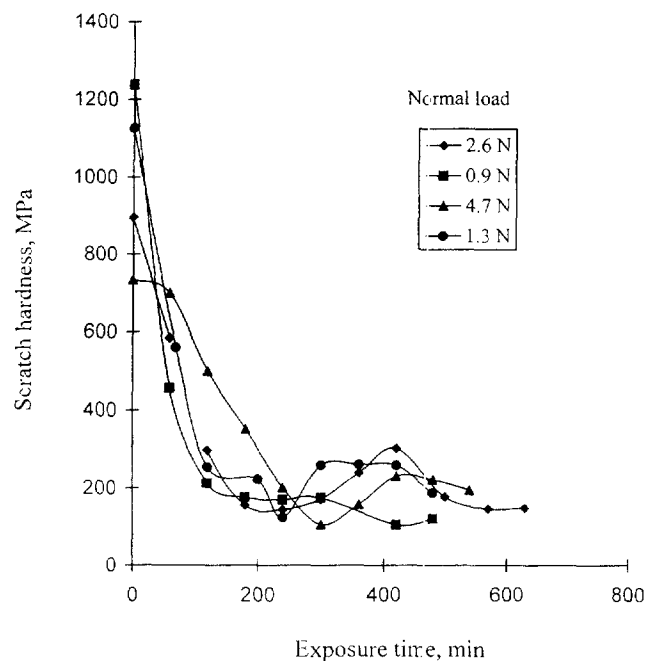


Figure 4 Scratch hardness of PMMA surface as a function of exposure time in a methanol environment for different applied normal loads (■, 0.9 N; ●, 1.3 N; ◆, 2.6 N; ▲, 4.7 N). The scratches were produced using a 90° cone angle at room temperature and at a constant scratching velocity of 0.004 mm s⁻¹

this behaviour of the material may be given as follows. The increase of the hardness value is attributed to a change in the structure of the PMMA. Due to the diffusion of the methanol into the PMMA the polymer molecule chains relax and tend to form more long range and regular structures. This causes the material, to some extent, to behave like a viscoelastic solid. Hence, the computed scratch hardness value is lower. The change in the material behaviour is also reflected in the deformation mechanism. This was observed in the deformation map presented in the previous section. Upon further plasticization the material tends to revert back to the lower hardness value. This can be either due to the breakage of the early structural changes or due to excessive plasticization and softening of the bulk of the polymer. However, the deformation mechanism continues to show complex gel and viscoelastic characteristics.

The magnitude of the scratch hardness for unlubricated PMMA may be as high as twice that obtained from normal indentation hardness¹¹, which is generally proportional to the yield stress properties of the material. This apparent discrepancy arises because of the assumptions on which equation (2) is based to compute the scratch hardness, H_s . As was mentioned earlier, equation (2) assumes that, during scratching, only the front half of the moving indenter is in contact with the polymer; this is largely true for highly plastic surfaces where the elastic recovery of the material after scratching is negligible. In this case, the area assumed to support the load of the contact is half of the cross-sectional area of the cone at the surface level. On the other hand, when the material properties are such that the assumption of a significant elastic recovery occurring at the rear of the scratching indenter is acceptable, the load bearing area is the full cross-section (i.e. $H_s \cong 4W/\pi d_s^2$)^{8,12}. The present authors observed in a previous study⁹ that the agreement between the scratch hardness and the normal hardness results is fairly good for PMMA when such assumptions are made. Typically, the indentation hardness

value for a glassy polymer is between 1.5 and 2 times the plastic flow stress²¹.

The variation of the scratch hardness data presented in Figure 4 for the dry PMMA as a function of load, i.e. for an exposure time equal to zero, is commonly found for organic polymers⁹; the hardness decreases with the imposed load or the extent of the penetration. It is not entirely clear at present why this occurs but it should be recalled that the scratch deformation process is very complex in nature and the observed effects are controlled by the interaction of several subtle contact deformation processes.

During the indentation test of this particular plasticized polymer the indenter measures the hardness of a composite system consisting of an outer soft layer on a hard inner core; the basic Case II phenomenon. The perceived hardness of the system may be separated into two parts; the hardness of the soft external and plasticized layer, and that of the inner hard and unmodified core. Thus, the scratch hardness of the system, H_s , may be expressed, to a first order, by the following empirical equation;

$$H_s = H_g(1 - X_p(h)) + H_p X_p(h) \quad (3)$$

where H_g and H_p are the scratch hardnesses of the dry PMMA and fully plasticized PMMA surfaces respectively. $X_p(h)$, which is a strong function of h , is a coefficient which is termed as the 'plasticization index' and the value of $X_p(h)$ varies between 0 and 1 from dry to fully plasticized polymer surfaces respectively. The coefficient indicates the extent of the plasticization which the indenter can sense for a particular indenter geometry and applied load; the main factor will be the depth of penetration, h . For $X_p(h) = 0$, the hardness is equal to the hardness of the dry PMMA which means there is no apparent plasticization effect; for the case of a plasticized layer, the penetration of the indenter is perhaps very deep into the surface and the plasticized layer makes little contribution to H_s . On the other hand, for $X_p(h) = 1$, the hardness of the system is equal to that of the plasticized gel which indicates that the indenter senses only the plasticized surface; the penetration of the indenter is small compared with the extent of the plasticized layer. This condition may be assumed when the whole polymer sample is practically fully plasticized. In an indentation test, the indenter does not sense the property of a material in contact with the indented material if the thickness of the sample (indented material) is much larger than the depth of the indentation; typically, a conical indenter will sense a volume of material which is two to three times greater than the volume of the indent¹⁰. Figure 5 shows the calculated coefficient, X_p , as a function of exposure time for different applied normal loads. The figure indicates that the magnitude of the coefficient, X_p , increases almost linearly with the exposure time as anticipated from the Case II process; the values of H_g and H_p were computed from the limiting case values. The rate of increase is also strongly dependent upon the normal load; this reflects the different levels of penetration produced by the various loads. This is because the initial depths of indentation are different for the different loads. Hence, the time when the indenter senses full plasticization is dependent upon the initial depth of indentation. Thus, the parameter, X_p , can be used for assessing the depth dependence properties of a polymer under chemically or thermally active environments. This depth dependence is examined in the next section using a rather more direct approach. However, from Figure 5 it is readily computed that the full apparent

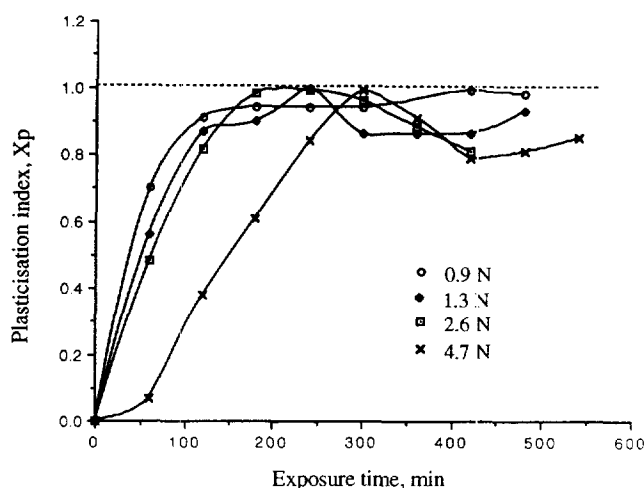


Figure 5 The plasticization index, X_p , as a function of exposure time for different applied normal loads (\circ , 0.9 N; \blacklozenge , 1.3 N; \square , 2.6 N; \times , 4.7 N). X_p is calculated according to equation (2). The plot shows that X_p varies almost linearly from zero (dry case) to 1. For $X_p = 1$ the indenter does not indent the glassy core of the polymer sample and only the fully plasticized layer is sensed. The scratches were produced using a 90° cone angle at room temperature and at a constant scratching velocity of 0.004 mm s^{-1} .

(depth dependent) plasticization limit is calculated for a particular time; for example for a 4.7 N load the value is *ca* 300 min.

Comparison between mass sorption and the depth of indentation

The diffusion process of methanol in PMMA may be easily monitored by a visualization experiment in which a small proportion of iodine is mixed with methanol before placing the PMMA sample in the methanol (see ref. ¹³). The diffusion 'front' of the methanol in the PMMA can be readily identified because of the distinct brownish red colour of the iodine tracer which can be seen inside the polymer after the diffusion. It has been shown, in previous studies, that the presence of the iodine tracer does not significantly affect the diffusion rate of the methanol in PMMA¹⁸. For the PMMA/methanol system, the diffusion process shows Case II behaviour and hence a rather sharp boundary for the diffusion front is observed. The measurement of the movement of the diffusion front, with respect to time, provides the rate of diffusion for the present system measured as *ca* 4.7 nm s^{-1} at 25°C . The experimental procedures adopted were similar to those reported in ref. ¹⁸.

Figure 6 compares the increase in the depth of the indentation during scratching as a function of the computed thickness of the swollen layer using the front velocity of 4.7 nm s^{-1} . For the calculation of the depth of indentation solely due to the plasticization, the depth of the indentation, for the corresponding dry PMMA case was subtracted from the value for the composite layer for the same contact conditions. As a result, the depth of indentation shown in the figure passes through the origin for zero methanol exposure time. The figure shows that the depth of indentation varies linearly with the thickness of the swollen layer up to the point when the indenter senses a full plasticization condition. Beyond this point, the depth of indentation remains same for all thicknesses of the swollen layer. This indicates that once the indenter senses a fully plasticized situation, the depth of indentation does not increase further. However, the diffusion front of the methanol in the bulk of the polymer continues to advance with time. The variation

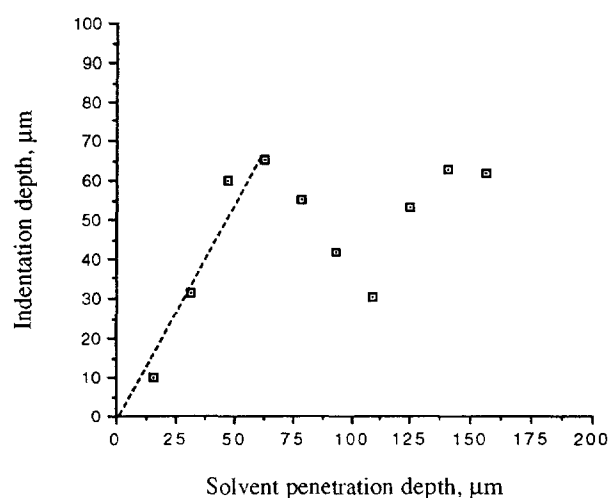


Figure 6 Comparison of depth of scratching indentation PMMA surface versus the solvent (methanol) penetration depth in PMMA after the same solvent exposure times. The scratches were produced using a 90° cone angle at room temperature and at a constant scratching velocity of 0.004 mm s^{-1} . The applied normal load was 2.6 N. The values of the indentation depth are calculated from the measured residual depth of the scratches subtracting the relative value of scratch indentation in the dry case. The broken line has a unitary slope. The figure shows that the indentation depth values are comparable with the values of the solvent penetration up to a value of *ca* $70 \mu\text{m}$. Beyond this value, e.g. for higher values of solvent penetration, the indenter is not sensing the glassy core of the material and the change in the trend is due to a reorganization of the material structure

in the depth of the indentation for the higher exposure times reflects the changes occurring in the structure of the polymer. The relationship between the depth of the indentation and the thickness of the plasticized layer, for any particular polymer/solvent system, will depend upon the diffusion process occurring for that system. It may also be mentioned again that the scratch hardness value is generally a function of the magnitude of the interface (indenter/polymer) friction or interface shear stress. Previously for PMMA systems the introduction of a lubricant increases the hardness⁹. Thus, if the marginal plasticization had provided an effective lubrication, that is a reduction in the boundary friction, then an initial increase in the scratch hardness would have been anticipated. No such effect is observed so we may conclude that plasticization of PMMA by methanol does not provide a lubrication action.

In this study, it is shown that scratch test can be used as a means for studying the surface plasticization characteristics of PMMA. There are two solvent-polymer interactions which occur during the plasticization of a polymer; swelling and dissolution of polymer. The hardness and other surface mechanical properties of the polymer change due to the material softening effect of the plasticization. A decrease in the scratch hardness of the material is also accompanied by a change in the deformation mechanism. The deformation mechanism during surface scratching depends, amongst several variables, upon the extent of the plasticization, the included angle of the indenter and the applied normal load. The SEM study of the scratched surfaces of the plasticized PMMA surfaces shows that the material deformation characteristics change as the plasticization process proceeds. PMMA is a glassy material and hence it often shows mainly a brittle behaviour in the dry state at room temperature. This type of deformation behaviour is characterized by the presence of deep cracks on the scratched groove. When in contact with methanol, PMMA is plasticized, which causes the surface behave like a plastic

gel. Further plasticization induces a partial structural reorganization and a more evident elastic/brittle response. Under this condition, the polymer behaves as a soft viscoelastic material.

This study has clearly shown that the scratch hardness method can detect even small variations in the surface mechanical properties of the polymer. A similar study was carried out previously using the normal hardness test for the system nylon/water. The scratch hardness has many advantages over normal hardness method. Firstly, the measurement of the scratch hardness is very simple in comparison to that for the normal hardness method in a form which is suitable for organic polymers. Problems associated with the measurement of the normal hardness have been outlined in ref. ²¹. Secondly, the scratch hardness method also provides information regarding the surface deformation characteristics. Especially for the surface plasticization problem, the scratch hardness method is most suited as the data from this method may also be directly correlated to the diffusion phenomenon in polymers. For most polymers, it is difficult to monitor the diffusion rate or the associated structural changes in the bulk when they are exposed to chemically active environment without resorting to expensive and time consuming methods. In the scratch hardness method, various types of information about the material can be obtained by simple experimentation.

CONCLUSIONS

The scratch hardness characterization method is applied to PMMA samples in dry state and after plasticization by methanol. The characterization is performed using conical steel indenters of varying included angles and under different normal loads. The surface deformation mechanisms were examined using laser profilometric and SEM studies. The scratch hardness, a predominantly plastic yield property, is reported as a function of load and exposure time. The following specific conclusions are drawn from this study.

- (1) Plasticization of PMMA by methanol takes place by the Case II diffusion process. It follows in two stages; plastic gelation followed by partial restructuring which conveys a more elastic character.
- (2) The scratch hardness of PMMA changes from *ca* 1000 MPa in the dry state to a steady state value of *ca* 200 MPa for a fully plasticized PMMA surface. The scratch hardness values show a dependence upon the normal load for dry PMMA; the origin of this effect is not resolved. However, the same data are more scattered for the plasticized PMMA surface. This is probably because of the change in the structure of the polymer due to the plasticization process. However, the depth dependence hardness data are consistent with the measured rates, or extents, of the solvent diffusion front.
- (3) The deformation mechanism, in scratching, shows that the plasticization of PMMA by methanol induces

gelation of the surface followed by a partial restructuring. The mechanism of the scratch deformation changes from that of a brittle fracture, in the dry state, to that plastic and finally to viscoelastic rubber-like, quasi-brittle behaviour as the exposure time of methanol is increased.

Finally, this work has demonstrated that scratch hardness method is a very convenient technique for the study of the plasticization and deformation behaviour of PMMA-methanol systems, which can presumably be adopted for other polymer/solvent combinations.

ACKNOWLEDGEMENTS

The authors are grateful for the financial help provided by Unilever, UK for this study. One of the authors (FR) is thankful to the Erasmus Project of the European Community for providing sponsorship for the study visit to Imperial College, UK. The authors would also like to thank the Dow Chemical Company (USA) and Dr Willem deGroot for the provision of a bursary for E. Pelillo.

REFERENCES

1. Briscoe, B. J., Stuart, B. H. and Arvanitaki, A., in *Proc. Int. Trib. Conf.*, Yokohama, Japan, 1995, Han Lim Wong, Korea, 1996.
2. Ruan, L., Norton, P. R. and Wan, W. K., *Tribology Letters*, 1996, **2**, 189-197.
3. Crank, J. and Park, G. S., *Diffusion in Polymers*, Academic Press, London, 1968.
4. Chalmers, J. M., Gaskin, W. G. and Mackenzie, M. W., *Polymer Bull.*, 1984, **11**, 433.
5. Nguyen, H. X. and Ishida, H., *Polymer*, 1986, **27**, 1400.
6. Briscoe, B. J., Stuart, B. H., Thomas, P. S. and William, D. R., *Spectrochemical Acta*, 1991, **47A**, 1299-1303.
7. Briscoe, B. J. and Stuart, B. H., in *Proc. Leeds/Lyon Conf.*, ed. D. Dowson *et al.* 1995.
8. Briscoe, B. J., Evans, P. D., Pelillo, E. and Sinha, S. K., *Wear*, 1996, **200**(1-2), 137-147.
9. Briscoe, B. J., Evans, P. D., Biswas, S. K. and Sinha, S. K., *Trib. Int.*, 1996, **29**(2), 93-104.
10. Johnson, K. L., *Contact Mechanics*, Cambridge University Press, Cambridge UK, 1985.
11. Briscoe, B. J., Sebastian, K. S. and Sinha, S. K., *Phil. Mag. A*, 1996, **74**(5), 1159-1169.
12. Briscoe, B. J., Pelillo, E. and Sinha, S. K., *Polym. Eng. Sci.*, 1996, **36**(24), 2996-3005.
13. Windle, A. H. and Thomas, N., *Polymer*, 1978, **19**, 255.
14. Billmeyer Jr., F. W., *Textbook of Polymer Science*, Wiley-Interscience, New York, 1984.
15. Collins, E. A., Bares, J. and Billmeyer Jr., F. W., *Experiments in Polymer Science*, Wiley-Interscience, New York, 1973.
16. Alfred, T., Gurnee, E. F. and Lloyd, W. G., *J. Polymer Sci. (c)*, 1996, **12**, 249.
17. Windle, A. H. and Thomas, N., *Polymer*, 1981, **22**, 627.
18. Windle, A. H. and Thomas, N., *Polymer*, 1982, **23**, 529.
19. Sarti, G. C., Costoli, C. and Masoni, S., *J. Memb. Sci.*, 1983, **15**, 181.
20. Stilwell, N. A. and Tabor, D., *Proc. Phys. Soc.*, 1961, **78**, 169.
21. Briscoe, B. J. and Sebastian, K. S., *Proc. R. Soc. Lond. A*, 1996, **452**, 439-457.