Solvent permeation rates and ageing phenomena in polymer coatings

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The permeation rates of bulk solvents (SPR) into thin polymeric coatings can provide a sensitive measure for morphological changes. Measurements of SPR are easily made with a simple laser interferometer. As an example, this technique was applied to study the ageing of amorphous coatings below and above the glass transition temperature, T_g, a process that was accompanied by a significant decrease of SPR. This effect was particularly pronounced with poly(methyl methacrylate) (PMMA) spin-coated from dichloromethane (DCM), where the permeation rate of methyl ethyl ketone (measured at 25°C) was found to decrease by a factor of 30 when the coatings were heated to 140°C for several hours. Slower changes occurred at lower temperatures. A gradual decrease of SPR was even observed when the coatings were baked for many hours at 10–20° above T_g. Exposure of unheated PMMA coatings to DCM vapour, which was slowly attenuated, also caused a lowering of SPR. Solvent penetration into polystyrene was faster by several orders of magnitude, but the SPR changed only by a factor of less than 3 upon prolonged baking near T_g. The SPR decrease could not be explained by the removal of residual coating solvent (DCM). Also, heating of the PMMA coatings did not seem to cause a significant change of density. The ageing, as reflected in the changes of SPR, is interpreted as a local stress relaxation in the coatings.

(Keywords: solvent permeation rates; ageing phenomena; morphological changes; poly(methyl methacrylate))

INTRODUCTION

The development of lithographic images has generated considerable interest in the dissolution rates of polymeric coatings[1,2]. Beyond this commercially important application, dissolution rates and rates of solvent permeation can be used to probe morphological changes in coatings.

Typically, solvent permeates into a thin coating of a glassy polymer at a constant rate (Case II diffusion). The rate depends on the solvent power and, very extensively, on the molecular size of the permeant[3,4]. The solvent permeation rate (SPR) decreases with increasing molecular weight of the polymer[5], but a rate limit is approached at high molecular weights ($M_n > 10^5$)[6,7].

Polymer tacticity also seems to influence the SPR[3,5]. Rates of a given penetrant into different polymers may vary by several orders of magnitude, even if the thermodynamic interactions are comparable. An example, to be discussed later, is poly(methyl methacrylate) (PMMA) and polystyrene (PS) with MEK as the penetrant. Plasticizer in the polymer enhances the SPR. It has also been observed in dissolution rate studies with mixed solvents[8], that even the presence of a small amount of non-solvent may increase the SPR. An example is the dissolution rate of PMMA in methyl ethyl ketone (MEK) containing small amounts of water or methanol. This has been interpreted as a 'preplasticizing' effect of the smaller molecules moving ahead of the MEK front[7,8].

In lithographic applications the effect of high-energy electron beams on polymers such as PMMA has been the object of several studies. An increase of SPR upon exposure has been observed, which has been explained by polymer degradation[9,10] and, more recently, by an increase of free volume in the polymer because of gas formation[5]. Of particular interest have been observations that baking the polymeric coatings generally decreased the SPR. Greeneich[9] ascribed this effect to the removal of residual (high-boiling) solvent from PMMA. However, Ouano[5], who also used high-boiling solvent, observed a further decrease of SPR beyond the heating time required for the complete removal of the solvent, and he suggested the closing of micropores left by the departing solvent molecules.

We studied in some detail the effect of ageing at various temperatures below and above the glass transition point on the rate of MEK penetration into PMMA coated from a low-boiling solvent. Although a sharp decrease of SPR was observed upon baking the PMMA coatings, no other physical change consistent with this decrease could be demonstrated. Our explanation in terms of localized relaxation in the coatings is therefore only tentative.

Solvent permeation rates can be measured by laser interferometry with a rather simple and inexpensive apparatus[11]. This technique can be applied to coatings ranging in thickness from a fraction of a micrometre to several micrometres. The coatings must be optically smooth over the cross-section of the probing laser beam, and a reflecting substrate is generally required. The only major drawback is the destructiveness of the tests.

EXPERIMENTAL

Materials

PMMA samples used were a Dupont Elvacite 2010 (referred to as PMMA1) with $M_w = 81\,000$, $M_n = 42\,000$ and a (mid-point) $T_g = 109$°C, and Elvacite 2041 (referred to as PMMA2) with $M_w = 400\,000$, $M_n = 212\,000$ and $T_g = 123$°C. The molecular weights were determined by size-exclusion chromatography of tetrahydrofuran solutions.

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Also used was a commercial polystyrene (referred to as PS1) with $M_w = 212\,000$, $M_n = 86\,000$ and $T_g = 105$°C.

PMMA2 was purified by precipitation from dilute dichloromethane (DCM) solution in an excess of petroleum ether, followed by drying in a vacuum oven at 85°C. Similarly, PS1 was precipitated from DCM solution in methanol and dried at the same temperature.

The solvents used were reagent grade (Eastman Chemicals).

Silicon ('monitor') wafers (Pensilco Corp.) were of the p-boron type with diameters of ≈ 50 mm.

Equipment

The interferometric device for measuring the rate of solvent permeation was similar to an apparatus described in the literature[11]. The light source was a He–Ne laser (631 nm, unpolarized; Uniphase model 1105, Newport Research Corp.). The light, attenuated to 10%, was guided through a fibre optic cable (Dolan-Jenner micro-optic scanner, random bifurcated, Kapitol instrument sales). We encased the end of the fibre bundle, with its small right-angle window, in an 18 cm long glass tube, sealed at one end, which we mounted on a 5 × 12 cm Teflon frame. The silicon wafer was held against the Teflon frame with a spring, allowing solvent to enter through a gap of about 2 mm between the reflecting surface and the window of the optical fibre. The reflected light with the interference signal was guided through the second branch of the bifurcated cable to a Pin-6DP photodiode (with a 20 mm^2 area). The electrical signal, after amplification by a 101 A amplifier (United Detector Technologies) was displayed on a strip-chart recorder or, for high permeation rates, on a storage oscilloscope. The Teflon holder with the silicon wafer in place was plunged into a beaker of thermostatted solvent from a release mechanism which also triggered the oscilloscope.

Depending on the polymer coating and on the solvent, the permeation times ranged from 50 ms–15 h.

The coatings on the silicon wafers were made with a Photoresist spinner model 1-EC 101-R485 (Headway Research Inc.). To obtain uniform coatings with low-boiling solvents, such as DCM, we placed a glass sleeve, 15 cm high, with an i.d. of 15 cm over the bowl containing the spinning stage. Inside the sleeve, surrounding the rim of the bowl, was a circular glass trough, 3 cm deep, to contain the volatile solvent. For better evaporation, the solvent was allowed to rise in a sheet of filter paper resting in the circular trough. The polymer solution was introduced by means of a pipette through a small hole in a lid that covered the glass sleeve.

Measurements of refractive index and of coating thickness were made with a Metricon Corp. PC-200 prism coupler[12].

Procedures and evaluation of data

The thickness of the coatings was controlled by the proper choice of polymer concentration and of the revolutions per minute of the spinning stage. (The results of Flack *et al.*[13] served here as a guide.) For most of our experiments we chose a (dry) coating thickness between 1 μm and 1.5 μm. A solution of 6.8 g of PMMA2 in 100 ml of DCM, for instance, gave a coating thickness of approximately 1.2 μm when spun at 2000 rev min^{-1}.

In addition to DCM, we considered acetone as an alternate low-boiling solvent for PMMA, but trace amounts of DCM were found easier to remove from the coatings.

The amount of residual solvent in the spin coatings was determined in parallel experiments by head-space gas chromatography[14] with a Hewlett–Packard 19305 automatic sampler. Typically, one-half of a coated wafer was broken up and sealed in a small vial with a Teflon-lined silicone rubber septum. After heating to 120°C, part of the gaseous head-space in the vial was sampled and injected into the gas chromatograph.

In most experiments the coatings were aged by placing the silicon wafers on thermostatted hot plates. The hot-plate temperatures were monitored with surface thermometers and checked with thermocouples pressed against the surface. To assure that the temperature measured in this manner corresponded to that on the surface of the silicon wafers, the melting of small benzoic acid crystals (122.1°C), placed on the wafer surface, was observed. The results indicated that the temperature at the wafer surface differed by approximately 1°C. We concluded that the error in the assigned temperatures was always less than 2°C.

The rate (R) of solvent permeation was calculated from the spacing of the interference peaks (S) on the time axis as

$$R = \lambda/(2nS) \qquad (1)$$

where λ is the wavelength of the laser light and n is the refractive index of the polymer. Examples of interferograms are shown in *Figure 1*. Generally, we calculated S as an average over four to five periods, although in practically all cases S was constant over the thickness of the coatings. The latter can be calculated from the total width (W) of the interferogram (*Figure 1*) as equal to WR.

RESULTS AND DISCUSSION

Solvent permeation rates

Coatings of PMMA2 in DCM were stored in laboratory air for 1–3 weeks before the first measurement

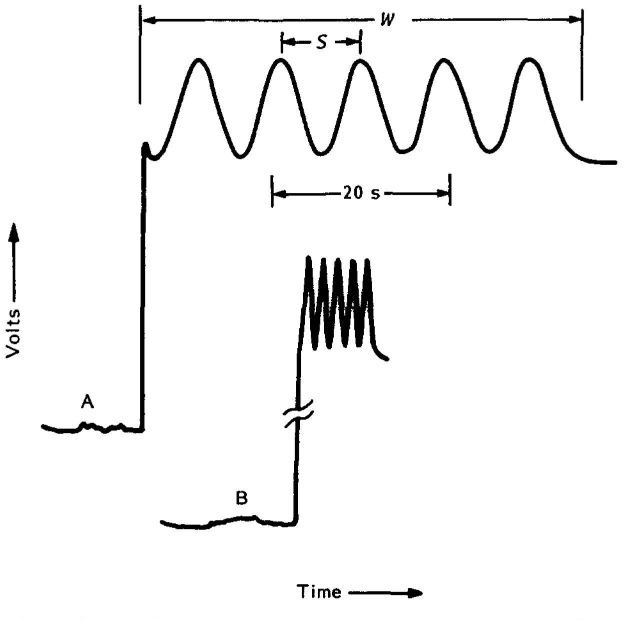

Figure 1 Interferograms showing penetration rate of MEK into PMMA at two different stages of ageing: 49 h at A, 112° and B, 68°C

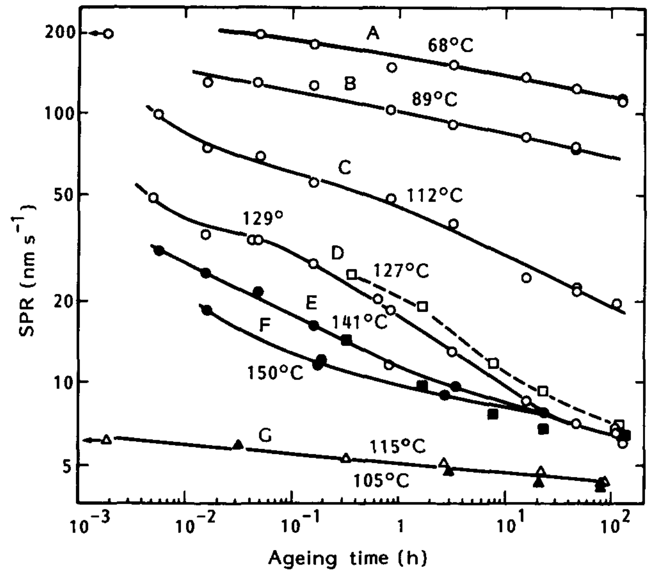

Figure 2 Ageing of PMMA2 at different temperatures. Rates of MEK permeation at 25°C: ○, ●, heating on hot plate; □, ■, heating in oven; △, ▲, coatings had been previously kept for 1 week at 141°C. Arrow in top left indicates SPR before heating

of SPR was made in MEK at 25°C. The initial value of 200 nm s^{-1} is indicated in the log–log plot in *Figure 2* by a horizontal arrow. Samples were subsequently heated on hot plates to 68, 89, 112, 129, 141 and 150°C for various lengths of time, ranging from less than 1 min to 1 week. As shown in *Figure 2*, a very significant drop of SPR occurred, with a low value around 6.3 nm s^{-1} after 1 week of heating at the high temperatures. Agreement between different coatings was found to be very good after heating, but differences within 10% were noted with unheated PMMA2 coatings. Analysis in a gas chromatograph/mass spectrometer showed no degradation of PMMA2 up to 150°C.

The spacing of the interference peaks, from which the SPR values were calculated, indicated uniform rates of solvent penetration. Included in *Figure 2* are a few experimental points obtained with samples that had been heated in ovens at 127 and 141°C. The agreement with the results from hot-plate heating was satisfactory.

Analogous results were obtained with PMMA1 coatings which we studied in less detail. The initial MEK permeation rates for this polymer, after keeping at room temperature for 10 days, was 400 nm s^{-1}. Subsequent ageing at 127°C for 63 h gave a value of 28 nm s^{-1}. The higher SPR values for PMMA1 are consistent with the lower molecular weight. Some differences of tacticity, reflected in the lower T_g, may also contribute[3,5].

The penetration of MEK into PS at room temperature was too fast to be measured ($>3\times10^4$ nm s^{-1}). We therefore chose methyl isobutylketone (MiBK) as the permeant. The initial SPR into 16-day-old coatings was 3.1×10^4 nm s^{-1}. Heating for 1 week to 114°C (9° above T_g) gave a decrease to 1.3×10^3 (*Figure 3*). Within experimental error, heating to 102 and 114°C gave the same results, while a slower decline of SPR values was found at lower temperatures. The rather modest change of SPR with PS1 made this material less rewarding for further studies than PMMA2, where a decrease by a factor greater than 30 was observed.

The striking difference of permeation rates for comparable solvents into these polymers is interesting. MEK penetration into unannealed PS1 could be measured at 13.5°C as 1.1×10^4 nm s^{-1}. The corresponding rate for PMMA2 was 1.06 nm s^{-1}. A small decrease of SPR because of the higher molecular weight of PMMA2 should be more than compensated for by the somewhat greater (thermodynamic) solvent power of MEK for PMMA. We can conclude that under fully comparable conditions, permeation into PS is faster by four orders of magnitude than into PMMA. The lower T_g of PS cannot explain this vast difference, as MEK penetrated into PMMA1 (with T_g close to that of PS1) only about twice as fast as into PMMA2, despite the much higher molecular weight of the latter. The slow penetration into PMMA may be connected with the higher density of this polymer as compared with PS, but we cannot offer an explanation in terms of molecular structure.

Figure 4 shows Arrhenius plots for PMMA2/MEK and PS1/MIBK, with the respective activation energies of 1.0×10^5 and 5.6×10^4 J mol^{-1}. The coatings were baked for 15 h at 138 and 110°C, respectively. It is of interest that our activation energy for PMMA2/MEK agrees with the result obtained by Thomas and Windle[15] for the penetration of methanol into PMMA. Methanol only swells the polymer without dissolving it. By our technique, we found slightly distorted interferometric peaks for the permeation of methanol into PMMA2, which abruptly disappeared at a penetration depth of about 0.4 μm, presumably because of optical distortions in the methanol-swollen top layer. The SPR for the unheated coating was 14 nm s^{-1}. Thomas and Windle[15] found approximately 1.2 nm s^{-1}, but their sample had been annealed at 130°C for 1 h. Baking of our coatings at 140°C for 24 h lowered the SPR to 0.24 nm s^{-1}.

In further experiments with PMMA2/MEK, we heated the coatings in an oven at 141°C for 1 week. At this point the MEK penetration rate was 6.2 nm s^{-1}, in very good agreement with the previous results. Subsequent annealing at 105 and 115°C gave a further, albeit small, decrease of SPR, with very little difference between the two temperatures (curve G in *Figure 2*). After 85 h a value of 4.1 nm s^{-1} was reached.

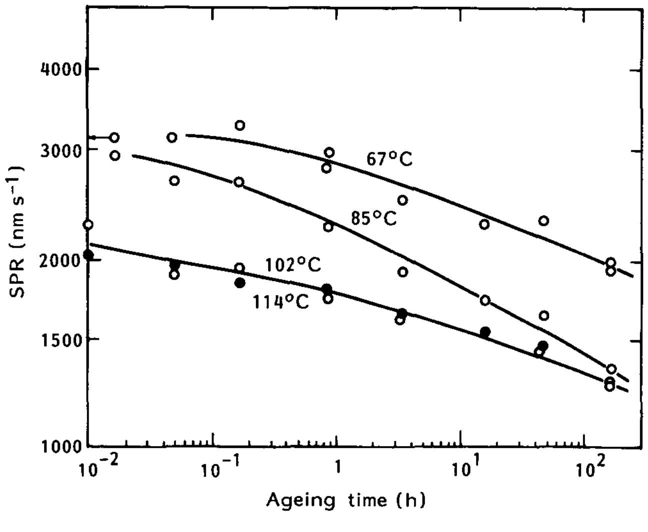

Figure 3 Ageing of PS1 at different temperatures. Rates of MiBK permeation at 25°C. ○, 102°C; ●, 114°C. Arrow on left indicates SPR before heating

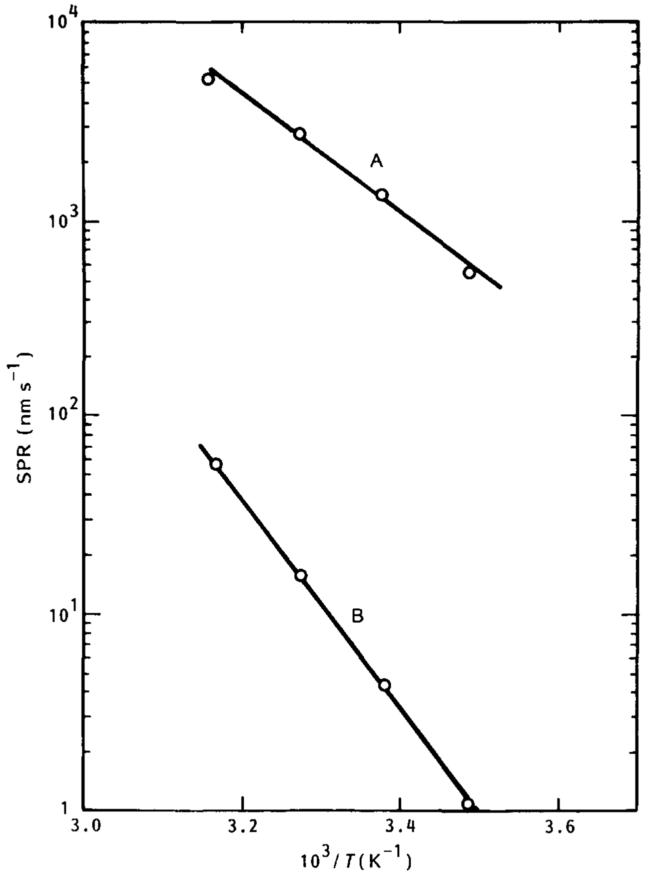

Figure 4 Arrhenius plot of penetration rates for MiBK into PS1 (A) and MEK into PMMA (B). The respective activation energies are 56 and 100 kJ mol^{-1}

Curve G follows the familiar annealing path of a polymer below its glass transition which is accompanied by a decrease of enthalpy and of specific volume[16,17]. However, this consolidation of the polymer matrix had only a minor effect on the SPR, in contrast to the changes in the polymer which are reflected in the results given by curves A–F in *Figure 2*.

It is also of interest that the SPR slowly decreased over many hours while the coatings were held at temperatures of up to 27°C above T_g (curves D–F in *Figure 2*). A change of a diffusive nature, originating either at the polymer/air or the polymer/substrate interface can be ruled out since the equidistant peak spacings in the interferograms indicated a uniform morphology throughout the depth of the coatings.

Ouano[5] inferred from his data on PMMA, coated from chlorobenzene, that upon baking at 160°C, the SPR continued to decrease well beyond the time (>20 s) required for the complete removal of the solvent. Since this temperature is nearly 30° above the boiling point of the solvent, Ouano suggested that the rapidly evaporating solvent leaves behind a highly porous matrix with a large free volume, so that an additional time at elevated temperatures was required for consolidation.

Residual solvent

It seems reasonable to suspect residual coating solvent in the polymer to enhance the SPR. If such solvent is removed by heating of the coatings, the SPR should decrease. This suggestion has been made by Greeneich[9], in an earlier study of solvent permeation into PMMA that had been coated from high-boiling solvents (MiBK or trichloroethylene).

We deliberately chose a low-boiling solvent that could be removed at temperatures well below the T_g of the polymer. Quantitative information about residual DCM was obtained by head-space gas chromatography[14]. Residual DCM in PMMA, expressed as volume per cent, is shown in *Figure 5* as a function of time at room temperature (~23), 45 and 68°C, respectively. After 2–3 weeks at room temperature, the PMMA2 coatings still contained 0.1–0.2 vol% DCM. The same level was reached after 6 h at 45°C, and in less than 1 h at 68°C. Only a few minutes were required at 89°C (not shown in *Figure 5*). To reach a level of 0.01% required approximately 20 h at 45°C, 2–3 h at 67°C and less than 30 min at 89°C. The results at these low concentrations were rather erratic, which may at least in part have been caused by traces of DCM in the laboratory air (0.01% corresponded to only 100 ng DCM per vial which contained the fragments of one-half of a coated wafer).

PS1 lost DCM at a much faster rate. A level below 0.1% was reached within less than 30 min at room temperature.

The loss of residual DCM from PMMA2 coatings cannot be correlated with the decrease of the SPR upon heating. We started our annealing experiments with coatings kept at room temperature for 2–3 weeks when the residual DCM level was not greater than 0.2%. Heating for 2 h at 67°C reduced the DCM content by a factor of 10 (*Figure 5*), while the SPR decreased only slightly from 200 to 160 nm s^{-1} (*Figure 2*). Subsequent heating at 140°C for 100 min lowered the SPR to 11 nm s^{-1}. This much larger drop of SPR was accompanied by the loss of only trace amounts of solvent, of the order of 0.01%, or less.

Refractive index measurements

The results of the previous section suggested that the decrease of the SPR was a sensitive indicator for the ageing of PMMA. It was of interest to measure some other physical property that reflected this process.

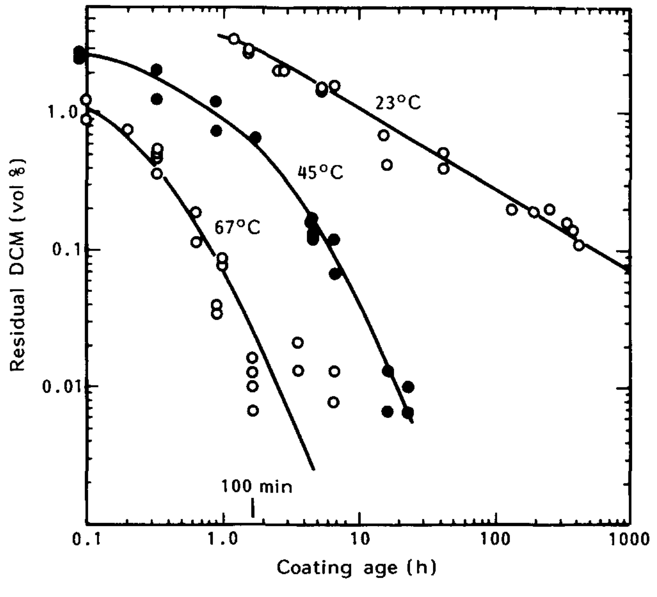

Figure 5 Residual solvent (DCM) in PMMA2 coatings at indicated keeping temperatures

Measurements of enthalpy relaxation in a differential scanning calorimeter[18] did not seem promising with thin coatings, a sample format which we considered important in all our experiments.

The data of Curro and Roe[19] and of Greiner and Schwarzl[20], indicate a specific volume loss of the order of 0.1% when quenched PMMA is annealed for 100 min at temperatures 5–30°C below T_g. We have seen that annealing of pre-heated PMMA2 gave only very small changes of SPR (*Figure 2*, curve G). By comparison with the substantial decrease of SPR in the regime of curves A–E, we may expect volume contractions well in excess of 0.1% within a few minutes when the coatings are heated to 140°C, provided micropores (or free volume) are an important factor that determines the rate of solvent permeation.

Direct measurements of small density changes in the thin PMMA coatings could not be made. However, the disappearance of pores upon annealing should cause a detectable increase in the refractive index. The Metricon apparatus measures the refractive index of thin coatings on silicon wafers to four decimal places at a wavelength of 632.8 nm. We tried to extend the precision by the averaging of multiple data.

To relate refractive index (n) to volume changes we used a simple mixing rule[21], $n^2=\Sigma\phi_i n_i^2$, where ϕ_i is the volume fraction of component i. When applied to a mixture of polymer matrix and voids, this rule can only be expected to serve as a rather crude approximation. The superior Lorenz–Lorentz equation, giving similar results is also not truly quantitative[21,22]. A precise estimate of volume change is not needed, however.

According to the above mixing rule, a loss of voids with a volume fraction, ϕ_0, causes a change of refractive index of

$$\Delta n=\phi_0(n_2^2-n_0^2)/(2n_2^2) \qquad (2)$$

where $n_0=1.0$, and $n_2=1.485$ is the refractive index of PMMA. For $\phi_0=0.001$, Δn is 0.0004.

Two complications must be dealt with, however. One is the contribution of residual DCM. Heating the coatings to 67°C for 100 min reduced the residual solvent to $\phi_1=0.0003$. Complete removal of this amount of solvent leads to two limiting cases: the solvent molecules with $n_1=1.42$ are replaced by voids (pores). Then, $\Delta n=\phi_1(n_0^2-n_1^2)/(2n_2)=-0.00010$ for $\phi_1=0.0003$; or the polymer shrinks without void spaces being formed, so that

$$\Delta n=\phi_1(n_2^2-n_1^2)/(2n_2)=1.9\times 10^{-5} \qquad (3)$$

A second complication arises from water ($n_w=1.33$) in the polymer. According to Miyagi and Tanaka[23], the water content of PMMA at 35% r.h. (the upper limit of humidity in our laboratory during these experiments) is $\phi_w=0.004$, the water molecules taking up sites in pores rather than causing the polymer to swell. Emptying the pores without shrinking should then cause a change of refractive index

$$\Delta n=\phi_w(n_0^2-n_w^2)/(2n_2)=-0.0010 \qquad (4)$$

This substantial decrease is comparable in magnitude to the effect of the expected change of specific volume. It is a more serious interference than the presence of residual DCM.

Preliminary measurements indicated an increase of refractive index by approximately 0.001 when unannealed coatings that had been stored in laboratory air lost their water content by drying in a desiccator over Drierite. This change was found to be reversible. We then kept a set of five coatings of PMMA2 for 48 h over Drierite before making the first refractive index measurement. This was followed by a sequence of keeping conditions, as indicated in *Figure 6*, with intervening measurements. After each stage the refractive index of each sample was measured 10 times, concurrently with the refractive index of two PS1 coatings (which were always stored at room temperature in a desiccator), to monitor small fluctuations (mostly due to temperature changes) in the Metricon apparatus. The percentage changes of these values were then used to correct the average of 10 readings on the PMMA2 samples. The standard deviations of the results for the five samples are indicated by error bars in *Figure 6*.

The changes in refractive index, in the course of the experimental sequence, somewhat exceeded the standard deviations. Heating for 100 min at 67°C caused a significant rise of refractive index (*Figure 6*) but only a slight decrease of SPR (*Figure 2*). Subsequent heating to 141°C for 100 min, which produced a large drop of SPR, did not cause the expected rise in refractive index. On the contrary, as shown in *Figure 6*, a drop in refractive index, equal to 0.00023, was observed. (Consecutive heating of PMMA coatings, first to 67°C and then to 141°C, each for 100 min, produced a drop of SPR by a factor of 15, in agreement with the values shown in *Figure 2*.) This was followed by a rise in refractive index after the samples had remained at room temperature for 42 h. Subsequent annealing at 105°C, with the attendant thermal expansion, again lowered the refractive index. This was followed by a recovery at room temperature. When at this point the sample was exposed to 33% r.h., only an

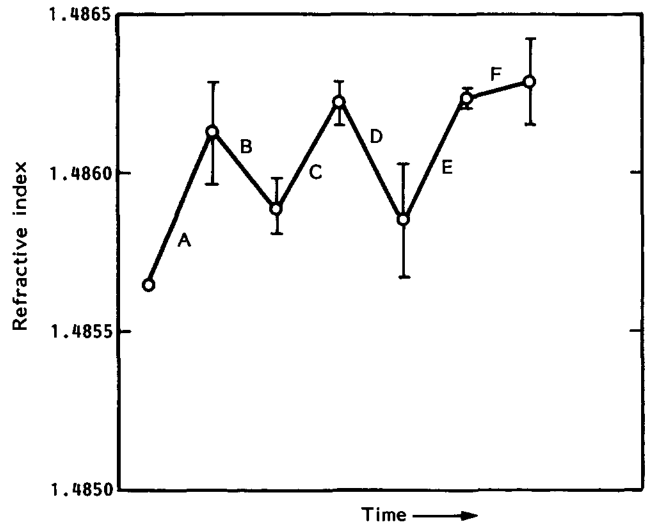

Figure 6 Refractive index of PMMA coatings. The segments A–F indicate the sequence of environmental conditions to which the coatings were subjected before each measurement: A, 100 min at 67°C; B, 100 min at 141°C; C, 42 h in vacuum desiccator at room temperature; D, 22 h at 105°C; E, 72 h in vacuum desiccator; F, 48 h at room temperature and 33% r.h.

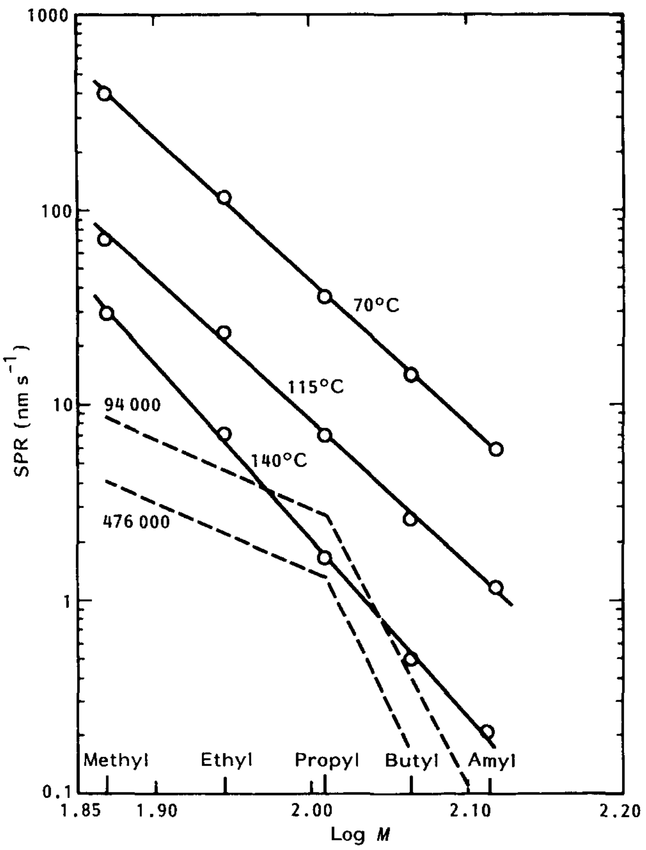

Figure 7 Penetration rates of acetic acid esters into PMMA2 at 25°C. The coatings were aged for 100 min at the indicated temperatures. The broken lines give the results of reference 3 for atactic PMMA fractions of molecular weight (M) = 94 000 and 476 000, which are to be compared with the 140°C line

insignificant change, well within the experimental error, was observed.

These variations in refractive index correspond to changes of specific volume of less than 0.1%. The pattern of change is more consistent with 'ordinary' annealing of a polymer than with the expected, greater volume changes in coatings that had not previously been heated above T_g (curves A–F in *Figure 2*).

We conclude that the observed changes of refractive index, if interpreted as a measure for loss of porosity, cannot explain the sharp drop of SPR when PMMA coatings were heated to 141°C.

Pore size distribution

The apparent absence of a significant change of specific volume upon heating of the PMMA coatings, as discussed earlier, was unexpected. A net volume contraction, too small to be detected by our measurements, accompanied by a change of pore size distribution remained as a possible, although not very plausible, explanation. However, changes of randomly distributed pore sizes in the course of conventional annealing (sample quenched after heating above T_g) have been inferred by Curro and Roe[19] by a comparison of results from dilatometry and from X-ray scattering.

Gipstein *et al.*[3] and Ouano[4] reported the SPR values of the homologous series of alkyl acetates with PMMA of different molecular weight and tacticities. Plotting the logarithms of the SPR values against the molecular weights of the respective esters, these authors obtained a curve with a distinctive break at propyl acetate (as indicated by the broken line in *Figure 7*), and they discussed their results in terms of the SPR being affected by pores of different sizes, taking into account differences with respect to the free energy of mixing within the homologous series[4]. We repeated these measurements with PMMA2 coated from chlorobenzene and heated for 1 h at both 145 and 150°C using our interferometric technique. We did not find a break in the plot at propyl acetate. The lack of agreement between results is difficult to explain, except perhaps by differences in the measuring technique. Gipstein *et al.*[3] followed the stepwise dissolution of PMMA by monitoring the decreasing thickness of the dried-down samples from the displacement of a stylus (Rank Talystep instrument).

It was of interest whether PMMA coated from DCM and heated for 100 min to temperatures of 70, 115 and 140°C would give plots of log SPR *versus* log molecular weight (M) with significantly different slopes (we followed the practice of the earlier authors of choosing the molecular weight rather than the more size-related molar volume as the variable). Within experimental error, the slopes were identical for 70 and 115°C (*Figure 7*). A slightly steeper slope resulted from heating to 140°C, indicating that the coatings had become somewhat more discriminating against the larger permeants. This is consistent with a loss of larger pores, provided the free energies of mixing remained unchanged by the sample. We re-plotted the results of Gipstein and coworkers[3], with the break at propyl acetate in *Figure 7*. This plot is to be compared with our 140°C results (with coatings from DCM). These were nearly identical with our earlier results from chlorobenzene coatings, none of which showed the break at propyl acetate.

These results do not help to explain the changes of SPR in PMMA. It is even somewhat surprising that parallel plots were obtained for the 70 and 115°C samples, which means that the relative size discrimination remained unaltered, although the SPR values changed by a factor of >5.

Coating stresses and solvent vapour annealing

As we have shown, neither residual solvent nor microporosity could give a satisfactory explanation for the drastic decrease of SPR upon heating of the PMMA coatings. There remains the question of coating stresses.

One type of stress could be demonstrated by the use of 28 μm thick Kapton discs as the coating support. Strips cut from the circular discs that had been dried on a flat plate curled extensively, and maximum stresses (σ) of the order of 10^7 N m^{-2} were estimated from the radius of curvature (r) by means of the equation[24]:

$$\sigma = E(t+Rd)^3/[6rtd(1-p)] \tag{5}$$

where E is the Young's modulus of the Kapton support (3×10^9 Pa) of thickness t, d is the thickness of the coatings (1.2 μm), $R = E(\text{coating})/E(\text{support}) = 0.8$, and p the Poisson ratio of the support (assumed to be equal to 0.3). This equation is related to expressions derived by Brenner and Senderoff[25].

Heating to 140°C flattened the strips because of thermal expansion. Subsequent quenching and volume contraction restored the curvature to values similar to those of the unheated strips. These contractive stresses, therefore, cannot be correlated with the observed changes

Table 1 DCM vapour annealing of PMMA2. Effect on SPR of MEK at 25°C

Rate of vapour attenuation[a] $-(\mathrm{d}p/\mathrm{d}t)/p$ (1 h)	Coatings kept at room temperature	Coatings baked at 140°C for 4 h
–	200	–
1.7	97	94
0.4	57	56
0.013	38	37
–	–	7

[a] Nominal values only, based on the rate of solvent exchange

of SPR. However, the coatings could also be isothermally annealed by exposure to solvent vapour which was gradually attenuated. Effects of solvent vapour on enthalpy recovery in conventional annealing are known, an example being the study of Berens and Hodge[26] on poly(vinyl chloride).

Kapton strips spin-coated with PMMA2 lost their curvature at room temperature when exposed to DCM vapour. Upon slow attenuation of the vapour pressure, the strips remained flat, or nearly so. When we subjected PMMA2 coatings on silicon wafers to the same vapour treatment, we observed a significant lowering of SPR.

PMMA2 coatings on silicon wafers were kept for 4 h at room temperature in a closed chamber that contained a dish with a mixture of 55 g DCM and 45 g dibutylphthalate (DBP). Thereafter, pure DBP was pumped into the stirred mixture at a constant rate, while solvent mixture was removed at the same rate until all of the DCM had been replaced. Depending on the rate of solvent exchange, this treatment lowered the SPR of MEK at 25°C from 200 nm s^{-1} before treatment to values shown in *Table 1*. Coatings that were initially kept for 4 h in an oven at 140°C (which lowered the SPR to 7 nm s^{-1}) and were then subjected to solvent–vapour annealing gave nearly matching SPR values. This indicated that the heated and the unheated coatings approached the same state during the vapour treatment.

The results in *Table 1* are only semiquantitative because the delays in equilibration could not be estimated.

At this point, we can envisage what changes may occur in the coatings upon heating or during solvent-vapour attenuation. When fresh spin coatings are quickly dried and become glassy, polymer chains are locked into conformations that do not correspond to a free-energy minimum, and SPR values will be relatively fast. Heating or solvent-vapour annealing, in the course of which the vapour pressure is very slowly reduced, should then produce a better cohesive packing of the polymer chains with a lower free energy, giving rise to slower solvent permeation. This model implies the disappearance of microvoids (or pores) upon heating, which, however, we were not able to demonstrate. Local conformational changes over dimensions comparable to those of the permeating molecules should significantly affect the SPR.

CONCLUSION

The foregoing results show that rates of solvent permeation into thin coatings are a sensitive indicator for changes of polymer morphology. Verification of such changes by some other quantitative physical measurements is needed to correlate the SPR results with the processes on the molecular scale during the ageing process.

Three observations of the PMMA coatings do not readily fit the model of the conventional annealing of a glassy polymer:

(1) Slow changes occur at temperatures well above T_g.

(2) Annealing coatings at 10–20° below T_g (after heating above T_g and quenching) had only a very small effect on the SPR, in contrast to a very large decrease of SPR when 'fresh' coatings were heated.

(3) The heating regime that produced these decreases of SPR seemingly did not give the expected rise of density (with the concomitant change of refractive index).

The question also arises as to what extent the behaviour of thin coatings quantitatively differs from that of bulk polymers because of a preferential orientation of the polymer backbone in the plane of the coating, as has been suggested by Prest and Luca[27].

The ease with which SPR values can be measured by laser interferometry should stimulate a wider use of this technique for the study of coating morphology.

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