Water-induced nucleation of disc cracks in selected thermosets

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Orthophthalic polyester, isophthalic polyester and vinyl ester resins exposed to water and to saturated salt solutions at 40, 65 and 90°C were studied to determine if disc cracks formed. The time of initiation of disc cracks was determined and related to the water absorption curves. The morphology was studied by optical and scanning electron microscopy. Disc cracks were found in orthophthalic and vinyl esters but not in isophthalic resins. The two-component phase diagram of polymer and water is the key to the prediction of behaviour. A new mechanism for disc crack initiation is presented. It states that disc cracks are the result of a thermodynamically driven phase separation that results in nucleation of a water phase within a supersaturated polymer. The mechanism is supported by the observation that, when the temperature of a nearly, but not completely, water-saturated polymer is reduced, bringing the polymer in to a region of supersaturation, massive disc crack initiation results. The reverse process—the disappearance or healing of disc cracks—predicted by the phase diagram and reported earlier in the literature, was confirmed in this work when a water-saturated, heavily disc-cracked specimen was placed into an environment of lower relative humidity. The growth rate and ultimate coalescence of disc cracks depend on the nature of the polyester. The hydrolysis of the polyester by the disc crack liquid with chain breakdown by de-esterification at the water–polymer interface is a key step in blister formation. It results in a concentrated solution, which generates osmotic pressure. The orthophthalic polyester is susceptible to hydrolysis; the other two resins are more resistant. Examples are noted of disc crack formation in polymers not saturated. This is explained by the presence of a water-soluble second phase, which was present initially or is generated in the polymer during heat treatment. The ability of the water–polymer phase diagram to predict the appearance and disappearance of disc cracks strongly supports the interpretation of disc cracking as a thermodynamic process.

(Keywords: disc cracking; thermosetting resins; water absorption; polyesters; scanning electron microscopy; optical microscopy)

INTRODUCTION

The economic impact of boat hull blistering

Boat hulls fabricated of fibre-reinforced polyester (FRP) sometimes develop external surface defects below the water line that have the appearance of blisters. They are fluid-filled cavities and may eventually enlarge sufficiently to crack the gel-coat overlayer. This phenomenon has been described and studied by various authors since the late 1970s[1–6]. Blistering is at best a cosmetic problem and at worst a defect that destroys the hull.

Relationship of disc cracks to blistering

During experiments that exposed unsaturated polyester resins to hot water, disc-shaped or penny-shaped cracks were observed to form spontaneously after an initiation period[8,9]. These cracks, which can range in diameter from less than a micrometre to several millimetres, fill the interior volume of the polymer, and appear to be randomly oriented. Other investigators have reported disc cracks in other polymers, and their presence in polyesters has been reported for a variety of environmental conditions[10–13]. Rockett *et al.*[6,7] showed that disc cracks were related to and preceded blisters in FRP boat hulls.

Literature of disc cracks

Several studies show the importance of osmotic pressure for the growth of disc cracks, but the nucleation mechanism is not well understood. Steel[9] hypothesized that water uptake swells the resin and strains molecular bonds to cause internal rupture of the resin. Ashbee *et al.*[8] and Abeysinghe *et al.*[13] concluded that water-soluble impurities or unreacted residual glycol interacted with dissolved water to generate pockets of solution, which caused osmotic pressure and led to the initiation of disc cracks. They also found that the disc cracking onset was delayed or eliminated in polyester resins exposed to potassium chloride or sodium chloride solutions, which have relative humidities below 100. The disc crack initiation time was progressively delayed as the solution concentration increased. Sargent and Ashbee[14] also

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observed that, upon drying, disc cracks in a polyester can disappear or heal.

The aims of this study

An investigation of the initiation and growth of disc cracks, and the effects of the casting initiator, post-curing treatment and polymer type of cracking was made. During the study, observations of crack healing were also made in an attempt to define the conditions of crack stability in a polymer. The results have led to a new theory of initiation of the cracks. They are seen to be a new phase formed when a polymer becomes supersaturated with water.

EXPERIMENTAL MATERIALS AND METHODS

Materials

Three different thermosetting resins were used for this study. They were a general-purpose orthophthalic polyester resin, a two-stage cooked isophthalic polyester and a vinyl ester modified epoxy resin. The resins were cast and cured at room temperature using two curing systems: (1) benzoyl peroxide (BPO) as the initiator and *N,N*-dimethylaniline (DMA) as the promoter; (2) methyl ethyl ketone peroxide (MEKP) and cobalt naphthanate (CN). Sample designations and the curing conditions for orthophthalic polyester are given in *Table 1*. The isophthalic polyesters were cured with 2 wt% BPO/0.3 wt% DMA and 2 wt% MEKP/0.3 wt% CN, respectively. A 2 wt% BPO/0.3 wt% DMA system and a 2 wt% MEKP/0.3 wt% CN/0.1 wt% DMA system were used for curing vinyl ester.

Sample preparation

Polyester sheets were cast between Mylar film (Dupont$^{\text{TM}}$) lined glass plates separated by shims to give a sheet thickness ranging from 0.4 to 1.3 mm. Resins were cured at room temperature for 48 h, and half of each casting was post-cured at 120°C for 2 h.

Absorption procedure

One-inch square ($\sim 2.5 \times 2.5\,\text{cm}^2$) samples were immersed into distilled water, potassium sulphate, potassium chloride and sodium chloride solutions maintained at 100%, 95%, 83% and 75% relative humidity (r.h.) and 65°C, respectively. Other experiments were made at 40 and 90°C. Temperature was held to ±0.5°C.

Table 1 Sample designation and curing conditions for orthophthalic polyesters tested[a]

Designation	Initiator	Promoter	Curing
Polymer 1	BPO 1%	DMA 0.3%	AC
Polymer 2	BPO 1%	DMA 0.3%	PC
Polymer 3	BPO 2%	DMA 0.3%	AC
Polymer 4	BPO 2%	DMA 0.3%	PC
Polymer 5	MEKP 1%	CN 0.3%	AC
Polymer 6	MEKP 1%	CN 0.3%	PC
Polymer 7	MEKP 2%	CN 0.3%	AC
Polymer 8	MEKP 2%	CN 0.3%	PC

[a] AC, as cast; PC, post-cured at 120°C for 2 h; see text for other abbreviations

Data collection

Immersed samples were periodically removed, weighed to ±0.0001 g, and examined under the optical microscope to determine initiation time. Initiation could then be related to saturation time and post-saturation weight changes. Details of disc crack morphology were studied in a scanning electron microscope. Samples for SEM examination were fractured through disc cracks and the surfaces were gold coated to prevent charging in the electron beam.

RESULTS AND DISCUSSION

The microscopic appearance of disc cracks

Figure 1a shows a scanning electron micrograph of the inner surface of a disc crack. The polymer was fractured and the disc crack was exposed for microscopic examination. *Figure 1b* is an enlargement of the centre of the disc crack. The circular structure at the centre of the disc crack may be related to the initial water cluster at which the disc crack begins to form. The structure around the circle is present in many disc cracks. It represents a fast fracture or a mirror zone. At the crack tip, there is a zone of crazing. *Figure 1c* shows the crazing zone as seen in the transmitted light microscope. This zone is strongly birefringent in crossed nicols (polarized light), proving that a high degree of residual stress exists at the crack tip. Many absorption isotherms show an anomalous increase in the weight per cent of water absorbed by a polymer as the 100% r.h. point is reached. This anomalous absorption has been described as water clustering. These clusters are not a second phase but are the precursors to nucleation of a second phase. Woo and Piggott[15] found that 60–75% of the absorbed water in saturated epoxy resin was concentrated in disc-shaped clusters, which may be precursors to disc cracks. These findings are consistent with the observations of this study that disc cracks never form until a polymer is in equilibrium with water or saturated vapour at 100% r.h.

Resistance among different materials to disc cracking

Isophthalic polyester. The isophthalic polyester resin did not develop disc cracks after exposure to water at 65°C for 6 months. Both curing systems gave the same results and they were independent of the amount of post-curing. It will be shown that the nucleation of the second phase in the polymer matrix results in a disc crack. The polymer exposed to water reaches saturation but must not develop supersaturation, a condition necessary for second phase formation. One possible explanation of the resistance is that the isophthalic resin has a much higher exotherm on curing, which essentially post-cures the resin before absorption, so no solubility shift (a requirement for disc cracking) takes place during water absorption. The measured peak exotherm for the isophthalic resin was 190°C *versus* 180°C for vinyl and 115°C for orthophthalic resin. Also, the glass transition temperature of isophthalic resin is higher than that of orthophthalic resin, so absorption at 65°C may be well below the anneal range for the sample, and therefore no structural relaxation is possible at the exposure temperature. The measured heat distortion temperature for isophthalic resin was 112°C *versus* 68°C for orthophthalic resin and 90°C for vinyl. Further, the isophthalic structure may be inherently stronger than the orthophthalic one, so that even if supersaturation takes place the residual

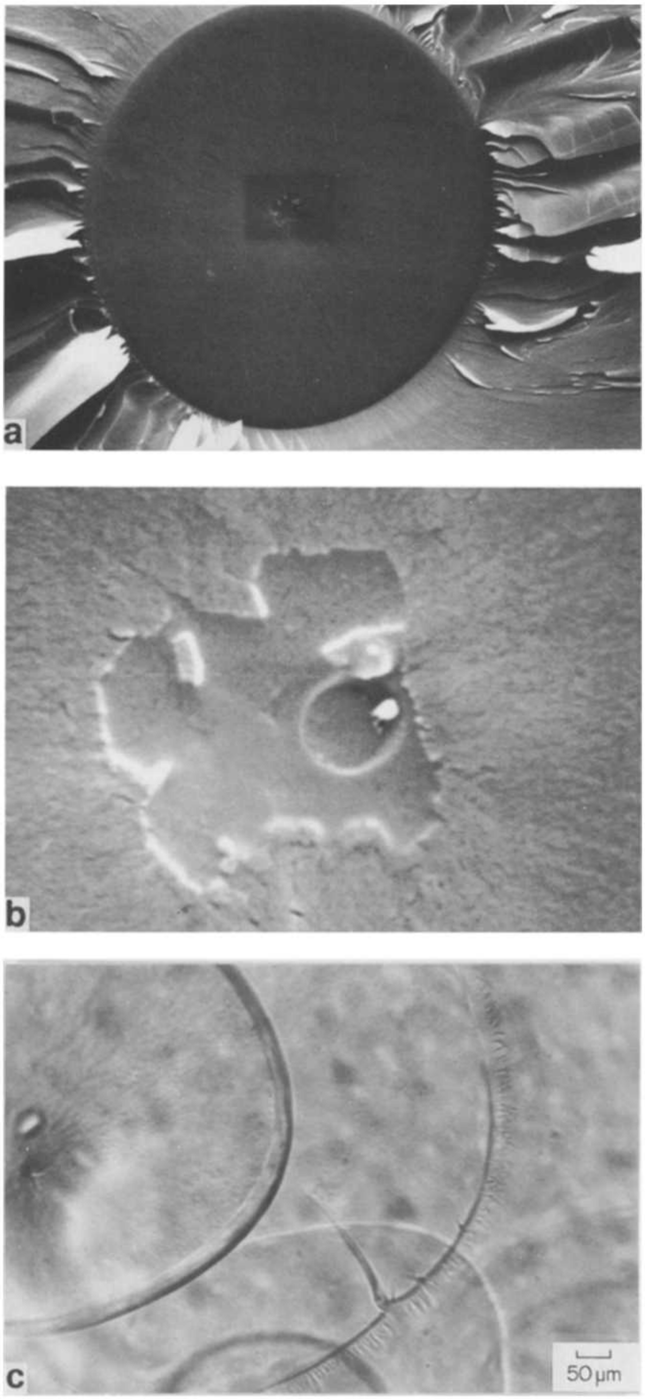

Figure 1 Micrographs of the surface of a disc crack; note the structure at the centre and at the edges of the crack. (a) Low-magnification SEM, (b) high-magnification SEM; (c) transmitted light micrograph

stresses developed by water clustering are not sufficient to cause disc crack nucleation, i.e. the cracking of the polymer network to make room for the new phase.

Vinyl ester. No disc cracks were observed in a vinyl ester resin cured with MEKP after exposure to water at 65°C for 6 months. Small disc cracks, less than 80 μm and uniformly dispersed, formed in a vinyl ester cured with BPO after 1 day of immersion in water at 65°C. These small disc cracks did not grow after an additional 65 days. *Figure 2* shows the disc cracks in vinyl ester after 1 day and 65 days. The pictures were taken at an identical position. This lack of growth is attributed to the hydrolytic stability of the vinyl ester. While nucleation is due to a solubility shift or the presence of an impurity, growth that is due to osmosis demands a reaction between the disc crack solution and the polymer. The vinyl ester exhibits no hydrolysis and, therefore, no partial pressure difference exists between the inside solution and water on the outside, and no osmosis is possible.

Orthophthalic polyester. Disc cracks were readily formed in the orthophthalic resin (polymer 3 in *Table 1*) at 65°C. The disc cracks first appeared after 8 h immersion in water. After 8 days, the number and size of the disc cracks had increased, filling the resin. The dramatic growth is illustrated in *Figure 3* with photomicrographs taken sequentially at an identical position at 4, 8 and 14 days.

The orthophthalic polyester resin showed a distinct difference in disc cracking behaviour related to the curing system used. *Figure 4* shows the difference in size and density of disc cracks in MEKP and BPO cured samples. The MEKP samples resisted the initiation of disc cracks substantially better than the BPO samples. Initiation time and growth rates are listed in *Table 2*. Once initiated, disc cracks are slower growing in the MEKP sample by a factor of 3. Two types of BPO were also used for curing. Paste BPO and emulsion BPO showed basically the same results for disc cracking.

Post-curing delayed the initiation time of disc cracking and reduced the density in both the MEKP and BPO

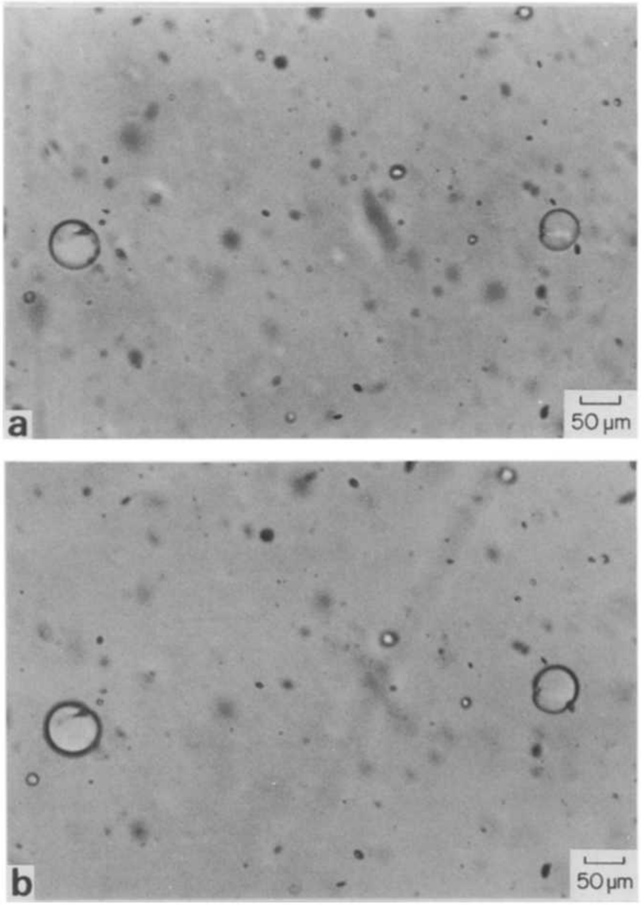

Figure 2 Disc cracks formed in vinyl ester at 65°C: (a) after 1 day, (b) after 65 days

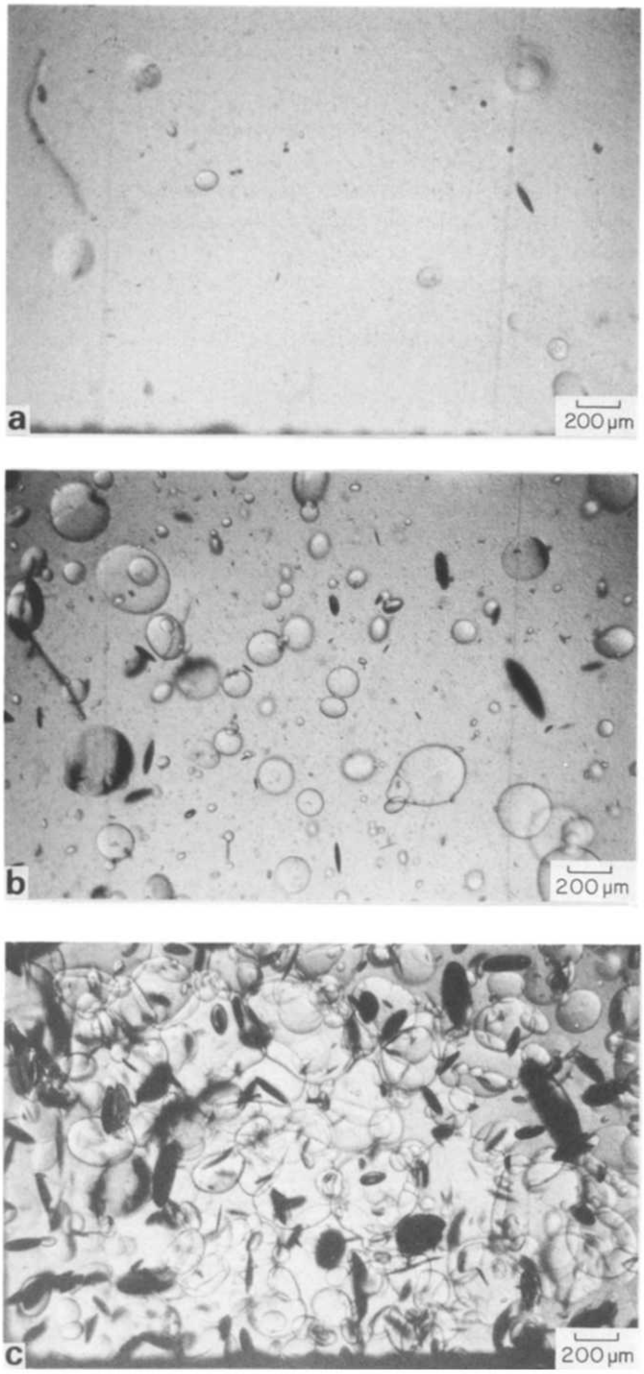

Figure 3 Disc crack growth in polymer 3 exposed to water at 65°C. Each picture is taken at the same position in the sample. (a) After 4 days, (b) 8 days, (c) 14 days

cured resins. *Figure 5* shows the disc cracks in post-cured samples. The 'as-cast' behaviour is shown in *Figure 3*. The growth rate of disc cracks was not affected by the post-curing. The growth rates did show some dependence on the type of initiator used for curing. These observations suggest that, of the two mechanisms, i.e. post-curing and relaxation, which play a role in disc crack formation, delayed post-curing during water absorption is more significant.

Water absorption and disc crack initiation

Figure 6 shows the water absorption curves for four orthophthalic polyesters, the curing conditions of which are given in *Table 1*. They were immersed in distilled water and three different saturated salt solutions at 65°C. Maximum water absorption increases as water vapour partial pressure increases from sodium chloride solution (75% r.h.) to water. The orthophthalic resin designated in *Table 1* as polymer 3 loses weight after reaching the maximum water pick-up. The weight loss is due to the release of residual styrene[16]. The loss rate depends upon the water content of the polymer. At the highest water saturation value, the loss rate is a maximum. The amount of loss is related to the degree of cure and is reflective of the hydrolytic stability.

Table 2 gives disc crack growth rates and initiation times; compare the time at which disc cracking initiated with the time at which the water maximum was reached as shown in *Figure 6*. In this study or in associated studies on water absorption in polyesters and vinyl esters[16], hundreds of experiments were made and there was never

Table 2 Average disc crack growth rate and initiation time for eight orthophthalic polyesters

	Growth rate ($m\,s^{-1} \times 10^{10}$)	Initiation time (days)
Polymer 1	2.88	Within a day
Polymer 2	3.10	2
Polymer 3	3.88	Within a day
Polymer 4	2.39	2
Polymer 5	1.07	14
Polymer 6	1.10	34
Polymer 7	1.47	14
Polymer 8	1.10	21

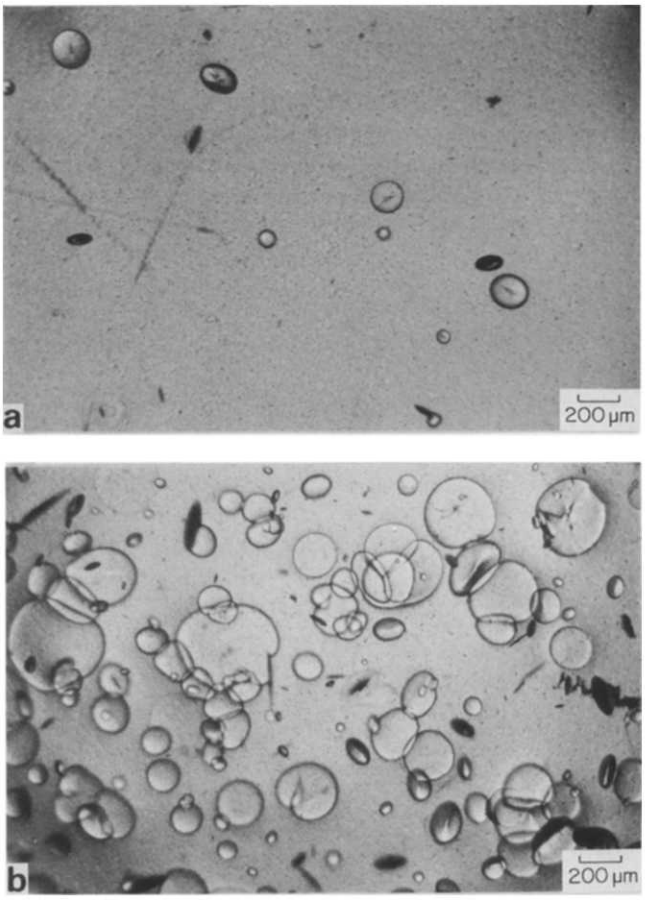

Figure 4 Disc crack size and density difference in polymer cured with BPO and MEKP. All samples were exposed to 65°C water. (a) Polymer 7 after 31 days; (b) polymer 1 after 14 days

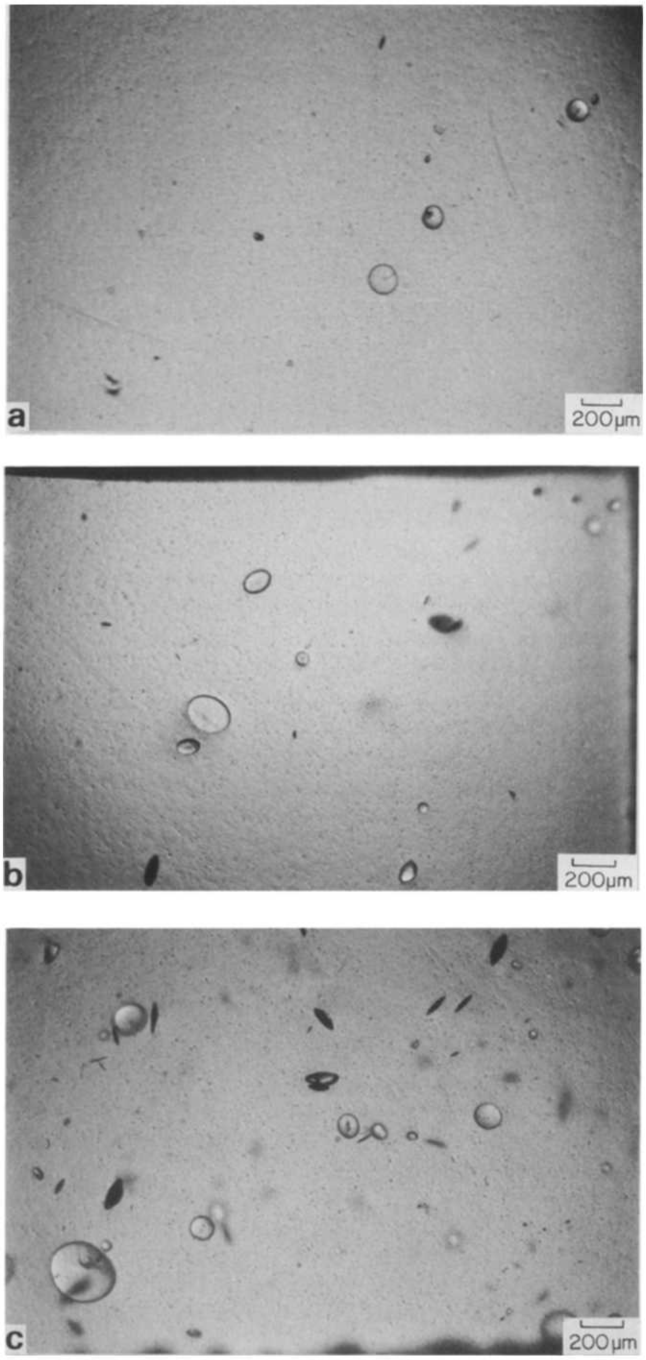

Figure 5 Disc cracks formed in post-cured polymers at 65°C. Compare with as-cast samples in *Figure 3*. (a) Polymer 8 after 30 days; (b) polymer 2 after 14 days; (c) polymer 4 after 14 days

a case in which disc cracking began before the polymer was saturated with water. If a polymer swells severely during absorption of a solvent, then cracks caused by the swelling stresses will develop between the swollen zone and the rest of the polymer. If such swelling stresses played a role in the nucleation of water-filled disc cracks, the cracking would begin when swelling stresses are at a maximum before saturation. The observation that initiation always follows saturation shows that swelling stresses do not cause nucleation. Residual stresses in the polymer can, however, affect the direction of disc crack growth[17].

Forcing disc crack initiation by dropping temperature

The following experiment was done to confirm the hypothesis that disc cracking is a phase-separation phenomenon. Polymer 3 was immersed into potassium sulphate solution (95% r.h.) at 90°C for 1 day. The sample is essentially disc-crack-free. The few cracks that formed were small and had impurities associated with

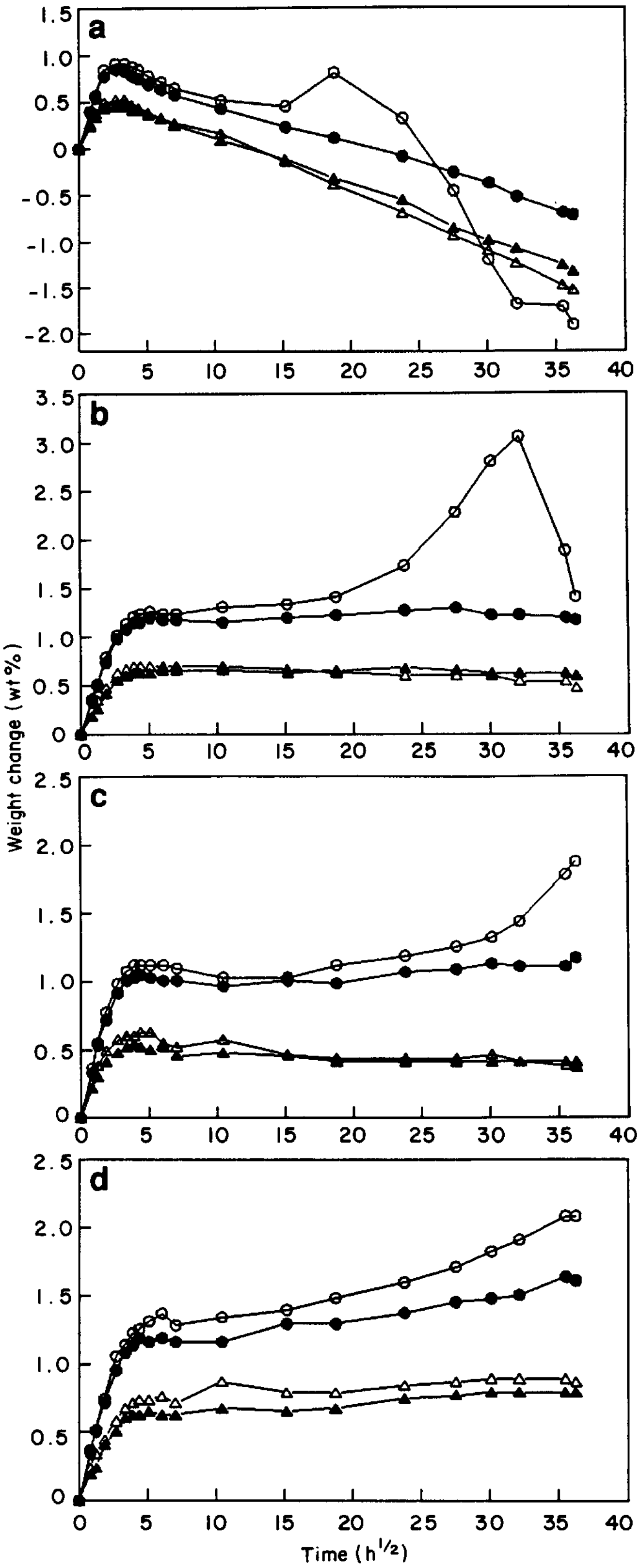

Figure 6 Absorption curves for four orthophthalic polyester resins exposed to liquids with relative humidities 100% (○), 95% (●), 83% (△) and 75% (▲). The temperature was 65°C for all runs. (a) Polymer 3, (b) polymer 4, (c) polymer 5, (d) polymer 6

them. The sample was transferred into a potassium sulphate solution (r.h. = 95%) at 65°C. Disc cracks in the cooled sample were observed after 2 h and are shown in *Figure 7*. Cooling led to supersaturation of the polymer (*Figure 8*, S to S′) and formation of a second phase.

Conditions for disc crack healing

If disc crack formation is a thermodynamically reversible phase separation, then water resident in cracks, formed on supersaturation, will redissolve in the continuous phase when the polymer is no longer saturated. If the temperature is at or above the polymer glass transition temperature, the cracks then disappear (heal).

This effect was demonstrated in the following experiments. Samples of polymer 3 immersed at 65°C in water until extensively disc-cracked were placed in air at the same temperature but at lower humidities (75% and 0% r.h.). Cracks penetrating the specimen surface remain open and appear black in microscopic observations as air displaces the water; cracks not open to the surface close up and disappear. Similarly, samples equilibrated at saturated conditions at 90°C (*Figure 9a*) and then exposed at 83% r.h., still at 90°C, exhibit identical behaviour of crack closure (*Figure 9b*). Saturated samples placed in 75% r.h. and even at 95% r.h., still keeping temperature constant at 90°C, exhibit the crack closing behaviour. SEM micrographs showed open cracks intersecting the fracture plane for saturated specimens (*Figure*

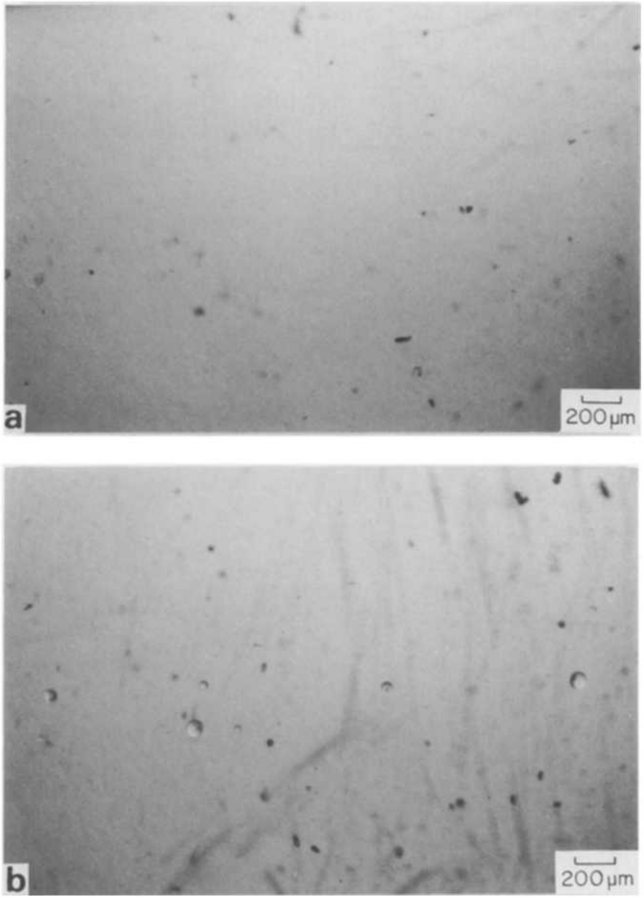

Figure 7 Disc cracks formed in polymer 3 by cooling an unsaturated sample from 90°C to 65°C and exceeding the solubility limit. (a) At 90°C and 95% r.h. after 24 h; (b) cooling from 90°C and 95% r.h. to 65°C and 95% r.h. after 2 h

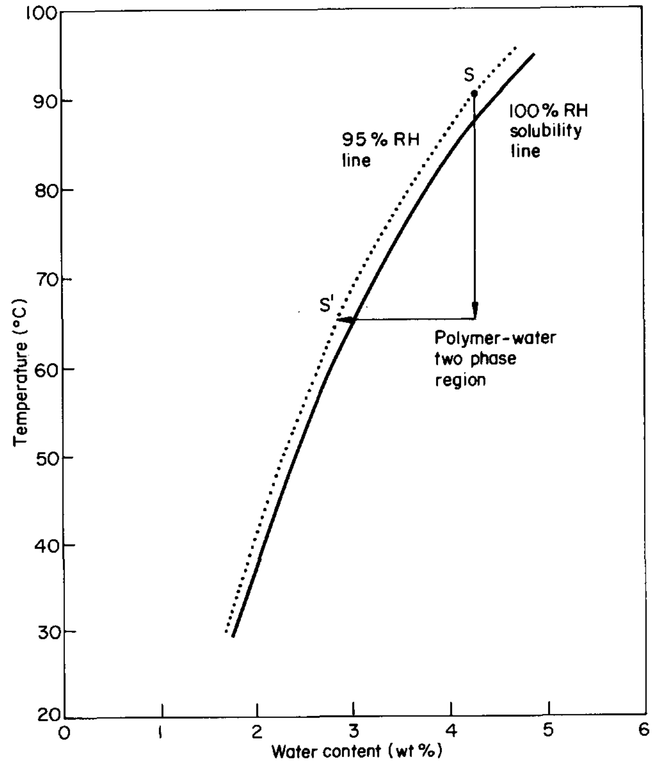

Figure 8 The hypothetical phase diagram shows the change produced by cooling an unsaturated polymer from one state to a second state. The second state is reached when the supersaturated polymer, which exceeds the solubility limit, forms two phases

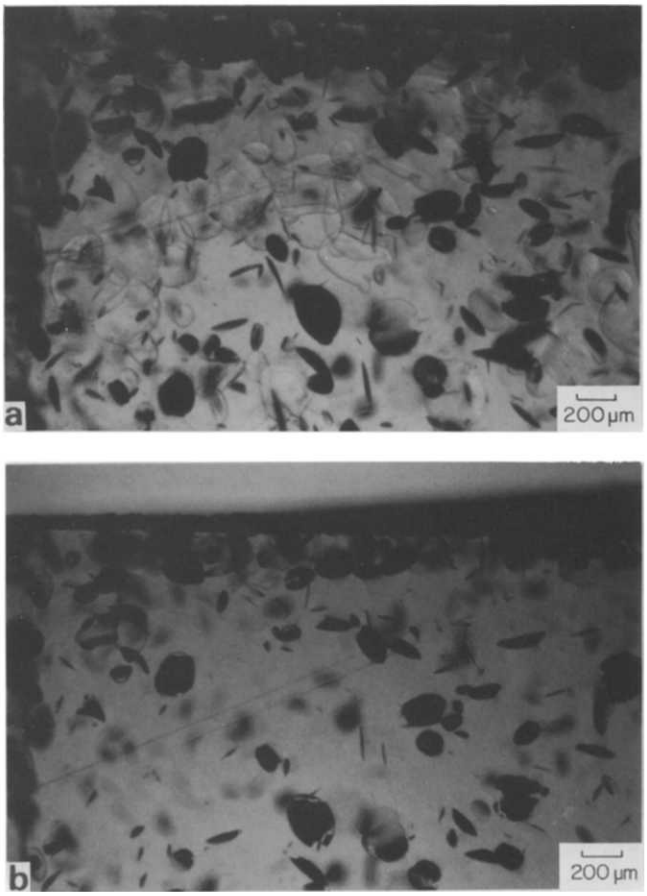

Figure 9 Micrographs taken at identical places in polymer 1 showing the healing of disc cracks. Black disc cracks intersect the surface and lose the liquid phase. (a) Disc cracks in polymer 3 at 90°C water; (b) the same place after healing at 90°C and 83% r.h.

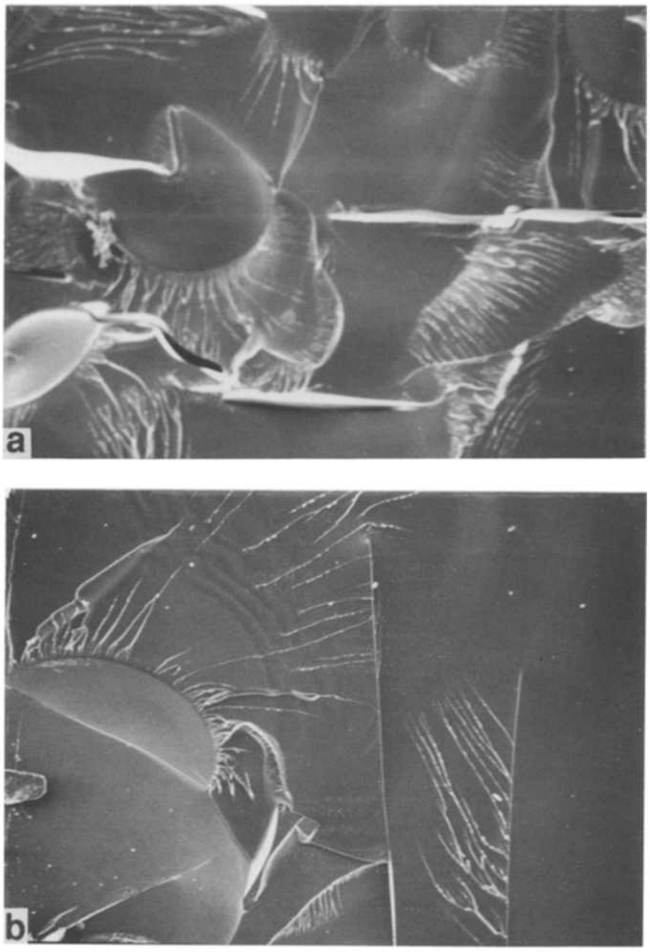

Figure 10 Scanning electron micrograph of disc cracks and healed disc cracks. (a) Unhealed open disc cracks in polymer 3; (b) healed disc cracks—the two vertical lines were open before crack healing

10a) and closed cracks intersecting the fracture plane for unsaturated specimens (*Figure 10b*).

Crack closure (healing) requires not just unsaturation exposure, but polymer mobility. Disc cracks in samples exposed to unsaturated conditions at 40°C do not heal. Instead vapour gradually replaces the liquid water, as illustrated in the photomicrograph of a gas bubble in the centre of a partially dried disc crack in *Figure 11*. While the crack closes at a temperature near the glass transition temperature, welding and interdiffusion processes, which would be expected in thermoplastic materials[18–20], probably do not happen in the highly crosslinked polyester. The closed crack remains as a defect or weakness in the structure.

Sargent and Ashbee[14] observed the healing of cracks and explained this phenomenon as being caused by elastic recovery following the loss of osmotic pressure in the crack. If this explanation were the case, then surface-connected cracks should also close or heal, and closure should happen even at room temperature. That it does not shows that the displacement is a plastic deformation that depends on the internal pressure of the disc crack (positive for opening and negative for closing) and sufficiently high polymer mobility.

The crack healing phenomenon is entirely consistent with the supersaturation theory of disc crack formation in that, when the matrix water concentration becomes unsaturated, the second-phase water dissolves in the matrix, the pressure drops and the two crack surfaces reconnect. If solute is present in the second-phase water, the critical water partial pressure required for crack closure is reduced. The pressure drop in the disc crack leads to closure if the polymer is mobile. If not, a vapour phase fills the crack volume when the internal pressure drops below the vapour pressure.

A thermodynamic theory of disc crack formation

Disc cracking is a result of the nucleation of a second phase within a supersaturated polymer. The second phase has the requisite properties defined by J. W. Gibbs, i.e. a chemically homogeneous and physically distinct unit of matter that is mechanically separable from a neighbouring phase at an interface[21]. *Figure 12* shows the hypothetical phase diagram for a binary system in which

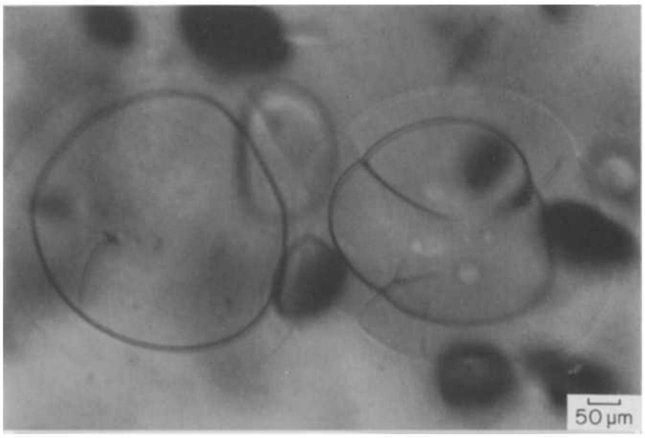

Figure 11 Gas bubble formation in a disc cracked after partial drying at room temperature

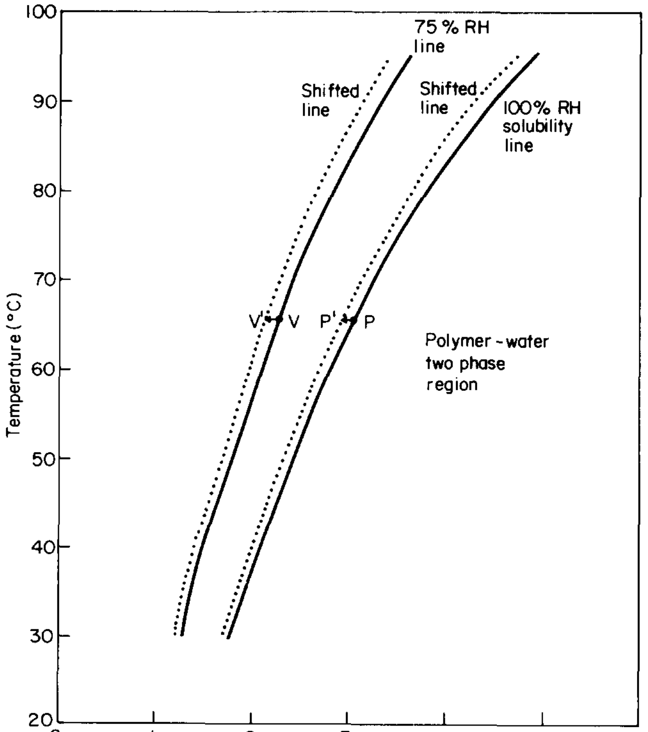

Figure 12 The hypothetical phase diagram for a binary polymer–water system showing the solubility limit of water in the polymer at 100% and at 75% r.h. The dotted curves represent the solubility limit of water in the aged polymer

the two components are neat resin and water. Exposed to water or saturated air, the polymer absorbs water to form a single-phase solid solution until it reaches the solubility line, P. The solubility line represents the composition of the saturated polymer in equilibrium with water in the liquid phase. The percentage of water at line P is the M_∞ value of an absorption experiment. The other solid saturation lines represent equilibrium between the polymer and a vapour phase of 75% relative humidity.

When the solubility limit of a constituent dissolved in a phase is exceeded by a change in either composition or temperature, the system changes from state I, single phase, to state II, a mixture of two phases, and the free energy of the system (G) decreases[22]. Thus, if ΔG is negative, the transformation takes place. The free-energy change for water nucleation from the saturated polymer is related to the equilibrium constant (K) by the relationship:

$$\Delta G = -RT \ln K \tag{1}$$

where K is related to the concentration of water in the polymer at the saturation point by the activity (a) as follows:

$$K = \frac{[a_{\mathrm{H_2O}}^{(\mathrm{water})}]}{[a_{\mathrm{H_2O}}^{(\mathrm{in\,polymer})}]} \tag{2}$$

where R is the gas constant and T is the temperature in kelvins. Since the activity of pure water is 1 and since the concentration of water in the polymer ($C_{\mathrm{H_2O}}^{\mathrm{polymer}}$) is less than 2 wt%, the solution can be considered a dilute solution, giving, as a first approximation, $a_{\mathrm{H_2O}}^{\mathrm{polymer}} = C_{\mathrm{H_2O}}^{\mathrm{polymer}}$. Combining equations (1) and (2) gives:

$$\Delta G^\circ = RT \ln C_{\mathrm{H_2O}}^{\mathrm{polymer}} \tag{3}$$

Using 632 g mol^{-1} as the molar mass of the polymer, a value arrived at by taking the molar mass of each repeat unit, and converting the weight per cent of water in the polymer to mole fraction, a value of $C = 0.175$ is obtained for a 0.6 wt% saturation. The free-energy change associated with nucleating water in the polymer is -1.03 kcal mol^{-1}. Since

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{4}$$

and by combining this relationship with equation (3), the following is obtained:

$$\ln C = \left(\frac{\Delta H^\circ}{R}\right)\frac{1}{T} - \frac{\Delta S^\circ}{R} \tag{5}$$

By plotting ln C against $1/T$, values of ΔH° and ΔS° for the formation of a disc crack can be obtained[23]. A value of ΔH° of -4.1 cal mol^{-1} was obtained. Hence, the heat of formation of a disc crack is negative. An entropy change of -9.84 cal mol^{-1} °C^{-1} is a measure of the ordering resulting from the disc crack formation.

If by some process the polymer becomes supersaturated, a second phase can nucleate throughout the polymer. The process causing supersaturation may be a drop in the temperature, a relaxation of the polymer network, or a continuation of the curing process. The last two processes will result in a shift of the solubility line in the phase diagram to the left. This is shown by line P′ in *Figure 12*. If the solubility shift is caused by relaxation it can only take place near the glass transition temperature. Absorbed water may accelerate relaxation or post-curing and thereby aid in the solubility limit shift. Precipitation of disc-shaped units of a second phase results in disc crack formation. In time, the water in the disc cracks may extract residual water-soluble materials from the polymer or attack the polymer network and hydrolyse reaction products. Both of the reactions will form a solution inside the disc crack. The decreasing partial pressure of water in the solution then generates osmotic pressure, which drives the growth of the cracks. Since the initial phase in the disc crack is pure water, no osmotically driven growth is possible until one of the two above reactions takes place.

Striking similarities exist between disc crack initiation and known phase-separation processes. For example, age hardening of metal is caused by phase separation from a solid solution by supersaturation[24]. The mechanism has been shown to take place in three steps. On lowering temperature, the solubility limit of one constituent in the parent phase is exceeded. During an incubation period the supersaturated atoms diffuse through the matrix and begin to agglomerate or cluster. Precipitation regions that are richer in the diffusing species form in the parent phase. These Guinier–Preston zones can cause major changes in the metal properties by straining the matrix, even though no new phase has yet been nucleated. When nucleation begins, some strains are relieved, and overageing, with a reduction in strength, takes place. Analogously, disc cracking in neat resins also shows the stages of saturation, supersaturation, diffusion, residual stress build-up and nucleation. Heat treating polymer blends can lead to supersaturation and precipitation of a second phase by spinodal decomposition.

Osmotically driven growth of disc cracks

Osmosis cannot take place in the absence of a second liquid phase inside a polymer or on the other side of a polymer membrane. Osmosis occurs when a pure solvent is separated from a solution by a semipermeable membrane[25]. The chemical potential of a pure solvent is higher than that of a solvent in a solution. Diffusion commences and continues until a balance is reached between the chemical potential of water outside the polymer and the chemical potential of water in the solution, which increases with pressure:

$$\mu_A^* \text{ (at } P) = \mu_A \text{ (for } x_A \text{ and } P + \pi)$$

$$\mu_A(x_A; P + \pi) = \mu_A^*(P + \pi) + RT \ln x_A$$

$$\pi = \frac{n_B}{V} RT$$

where μ_A^* is the chemical potential of a pure solvent A, μ_A is the chemical potential of component A in solution, π is the osmotic pressure, R is the gas constant, T is temperature, x_A is the mole fraction of solvent, n_B is the mole fraction of solute and P is the external pressure on the system.

In a saturated neat polymer there is no second liquid phase. All of the water is present as discrete molecules absorbed in the polymer, and therefore part of the polymer. The liquid phase inside a polymer must form by supersaturation and nucleation or by chemical reaction with a soluble second phase before osmosis can begin. As an example of the latter process, Ashbee and Abeysinghe *et al.* formed disc cracks by adding water-soluble second phase to a neat resin[8,11]. When the diffusing water reaches an included salt crystal or droplet of another constituent, it interacts to form a solution within the polymer. The partial pressure of water in this highly concentrated solution is much lower than that of the external solution and osmosis draws water into the internal second phase. The growing internal pressure in the polymer causes growth of the disc crack. Notice that the nucleation step was performed by the experimenter upon inserting the salt crystal or droplet into the polymer.

There is one additional mechanism for disc crack formation. If a neat resin is heat treated, a soluble constituent may separate from the base resin. If this phase is water-soluble, it acts as a nucleus for a disc crack when diffusing water interacts with it. *Figure 13* is a flow chart summarizing the steps that lead to the formation of the included second phase known as a disc crack.

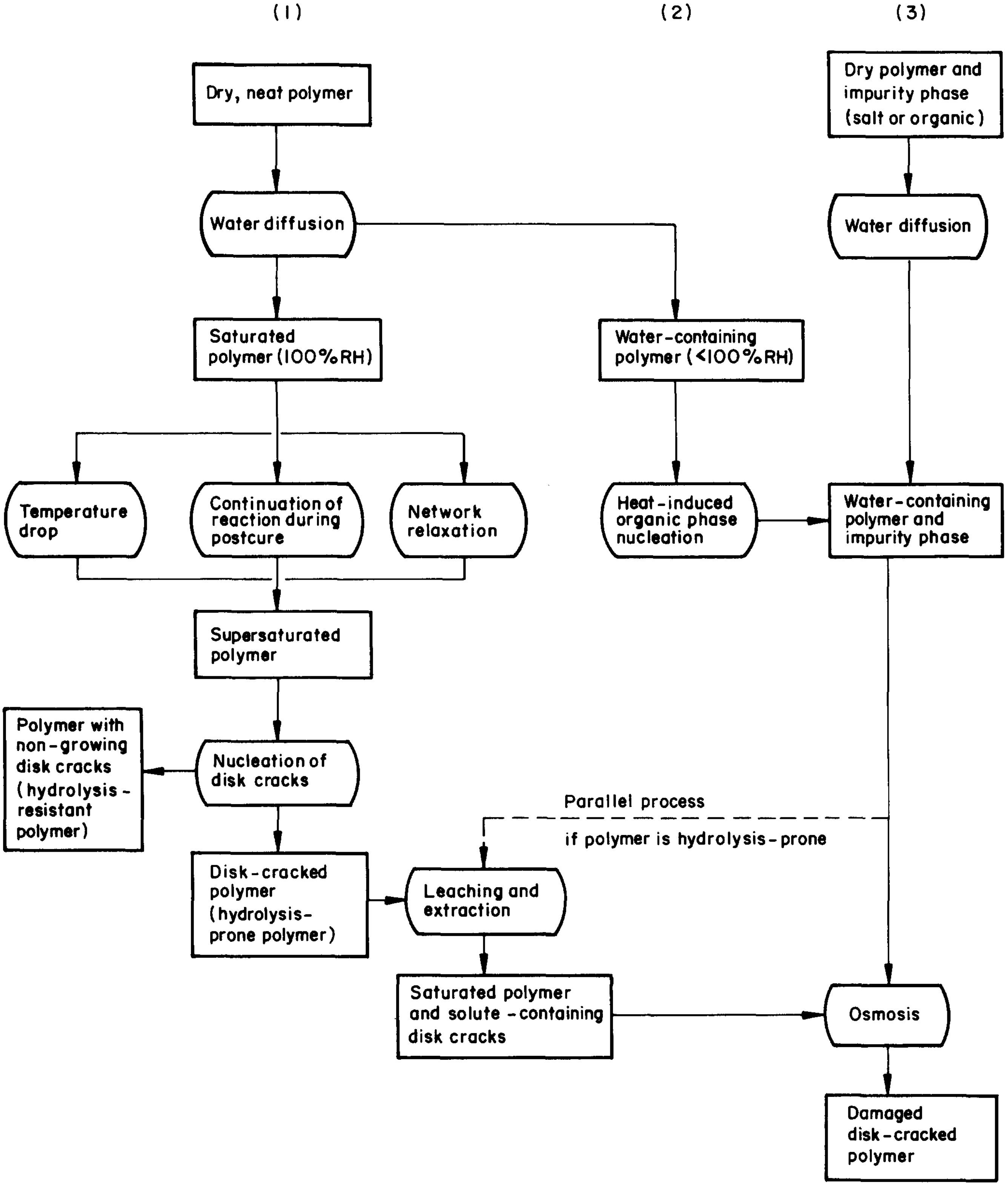

Figure 13 Flow chart summarizing the steps leading to water-induced disc crack initiation and growth in thermosets. Boxes are material states, ovals are processes

The water adsorption curve for polymer 3, shown in *Figure 6a*, gives further evidence that disc crack nucleation and growth are separate phenomena. The 100% exposure saturates in 9 h and shows disc cracks in 15 h. At 95%, saturation takes place in 9 h but disc cracks do not form. Weight loss is constant for both samples over the next 100 h. Osmosis draws water into the sample and must not be a factor until after 100 h of exposure, the point at which gain begins again. The weight loss of polymer 3, in water, after the secondary gain is due to solution loss as disc cracks break through the surface. Can absorbed water molecules create an inherent osmotic pressure in a polymer that will result in disc cracking? The data suggest not. Higher absorbed water contents at higher temperature do not result in disc cracks unless the relative humidity is 100%. There is more water in the polymer network at 90°C and 95% r.h. than 65°C and 100% r.h. and yet disc cracks form at 65°C but not at 90°C.

Anomalous disc crack formation

No disc cracks were found in the resin when immersed in saturated sodium chloride (75% r.h.) and potassium chloride (83% r.h.) solutions after 30 days. A few disc cracks, with large impurities associated with them, developed in the potassium sulphate (95% r.h.) solution. *Figure 14* shows the drastic difference in size and number between water and potassium sulphate exposure after 30 days. The weight gain whether in water or in potassium sulphate is virtually the same.

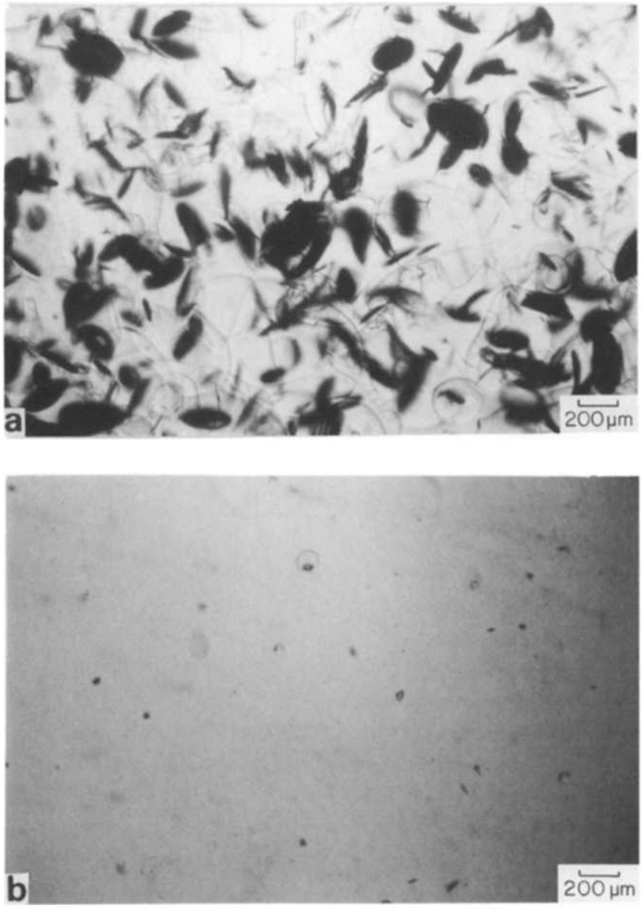

Figure 14 The size and density of disc cracks in polymer 3 after 30 days exposure to (a) 100% r.h., (b) 95% r.h. at 65°C. Note that the disc cracks in the 95% r.h. sample nucleate at an impurity. The neat resin portion of the sample shows no disc cracks

As mentioned above, the samples in equilibrium with vapour or solution with relative humidity less than 100% do not show disc cracking. Some exceptions were encountered at 95% r.h. but these did not show the same density, size, or growth rate as in samples at 100% r.h. At sample exposures less than 100% r.h. the water molecules inside the polymer remain as isolated molecules, and they are free to diffuse out of the polymer upon supersaturation and they do not form a condensed phase.

Formation of disc cracks at 95% r.h. in the resins is not a supersaturation effect and requires a different explanation even if the number and size of the disc cracks is very small. Some impurities exist as a separate phase even in relatively clean resins, which dissolve sorbed water to start osmosis and growth of the second phase. The interface between the polymer matrix and impurity is the disc crack initiation site. Also, 'heat treatment', associated with high-temperature absorption, may precipitate droplets or crystals of an organic second phase, which in turn dissolve sorbed water to create a solution with a lower partial pressure than 95% r.h. The observation that impurities can cause solution formation and therefore disc cracking at relative humidities less than 100% was observed in preliminary experiments performed using an impure orthophthalic polyester. It has also been reported in other studies[26]. In these cases, the disc cracking always begins near the surface and moves inwards with time as the water content increases inside the resin. In the neat resins, nucleation takes place throughout the sample thickness but never begins until the sample is saturated and equilibrium with a vapour or liquid at 100% r.h. is reached.

Steel[9] proposed that disc crack formation was controlled at all temperatures by the absorption of a critical amount of water. The following observations prove that this hypothesis cannot be true for the resins examined in this study. At 90°C and 95% r.h., polymer 3 gained 1.217 wt% but showed little disc cracking after 30 days. The same resin, at 65°C and 100% r.h., only gained 0.906 wt% and showed severe disc cracking. Therefore, absolute weight gain is not the critical factor in disc crack initiation.

SUMMARY

The chart shown in *Figure 13* sums up our current understanding of the conditions leading to disc crack formation and growth, including the basic condition of second phase formation under supersaturation conditions and various cases of anomalous formation and growth. The following rules emphasize various findings regarding disc cracks:

1. Disc cracks do not form before water saturation of pure polymers.
2. Disc cracks only form in pure resins saturated in 100% r.h. air or water.
3. Disc cracks form by forcing supersaturation of water in the resin, e.g. by reducing temperature.
4. In orthophthalic polyesters at constant temperature and 100% r.h., disc cracks form spontaneously.
5. Initiation and increased crack density is promoted in orthophthalic polyester by the choice of resin and by the degree of under-curing.
6. Disc cracks can be healed by reducing the water content below saturation in the matrix resin.

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