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Osmotic cracking nucleation in hydrothermal-aged polyester matrix

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Abstract

In wet environments, unsaturated polyester based composites perish generally by blistering/cracking due to an osmotic process, characterised by an induction time t_{ind}. This article focuses on the mechanism of crack initiation in order to understand the relationships between the network structure and its stability expressed by the t_{ind} value. The proposed mechanism is based on the demixing of the polyester/small organic molecule system. By simulating the presence of glycols in the network, the dependence of crack induction time on glycol fraction is effectively demonstrated. Water then enters the micropockets induced by the phase separation and crack propagation results from the increase of osmotic pressure in the micropocket. A simple kinetic model for small organic molecule formation is proposed. This allows to explain the difference in behaviour between the two networks under investigation and some previously reported effects of catalyst residues.
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Keywords: Polyester; Hydrolysis; Osmotic cracking

1. Introduction

Glass fibre reinforced polyester composites are widely used as structural materials for boat hulls because of their ease of manufacturing and low cost It is however well known that polyester matrices are sensitive to humidity through water absorption leading to chain scission by ester hydrolysis and thus to embrittlement [1,2]. They also undergo plasticisation and swelling [3]. However, in practice, the most important ageing process is disk cracking, originally described by Ashbee for polyester matrices and composites exposed in hot water [4,5]. Cracking appears after an induction time which seems to obey the Arrhenius law until 40°C with an apparent activation energy of 100 kJ/mol [6]. This phenomenon was also observed in polycarbonate and polyetherimide [7] and even in vulcanised rubbers containing water soluble inclusions [8]. As any cracking phenomena, this process can be described in terms of initiation (defect nucleation), propagation and arrest. The mechanism of propagation is relatively well understood: it results from osmosis linked to the difference in chemical potential of water in the cracks and in the bath. The polymer layer separating the crack from the bath behaves as a semi-permeable membrane and, as initially described by Van't Hoff [9], one observes the build-up of an osmotic pressure Π in the cavity.

$$\Pi = \mathrm{k}T \sum_i C_i, \tag{1}$$

where k is the Boltzmann constant, T, the temperature, and C_i, the concentration of solute i in the cavity. If Π becomes higher than a critical value depending on the polymer toughness, the crack propagates. The nature of solutes has been often investigated, especially on the basis of chemical analysis of the liquid contained in blisters in aged samples. It was first supposed that they are essentially initially present impurities such as inorganic salts [4], or unreacted monomeric species, catalyst residues [10], etc. Thus, matrices containing 5% glycol excess exhibit microcracking more rapidly than does the control material. Other substances such as dimethylformamide appear even more efficient. Therefore, designing polyester with the minimum amount of residual substances was the solution proposed to prevent the material from cracking. It is however difficult to explain why cracking appears after a more or less long induction time [13].

If the crack propagation is, in our opinion, almost entirely elucidated, this is not the case for crack initiation which remains as in common fracture mechanics one of the most difficult problems. Many authors have aimed at resolving

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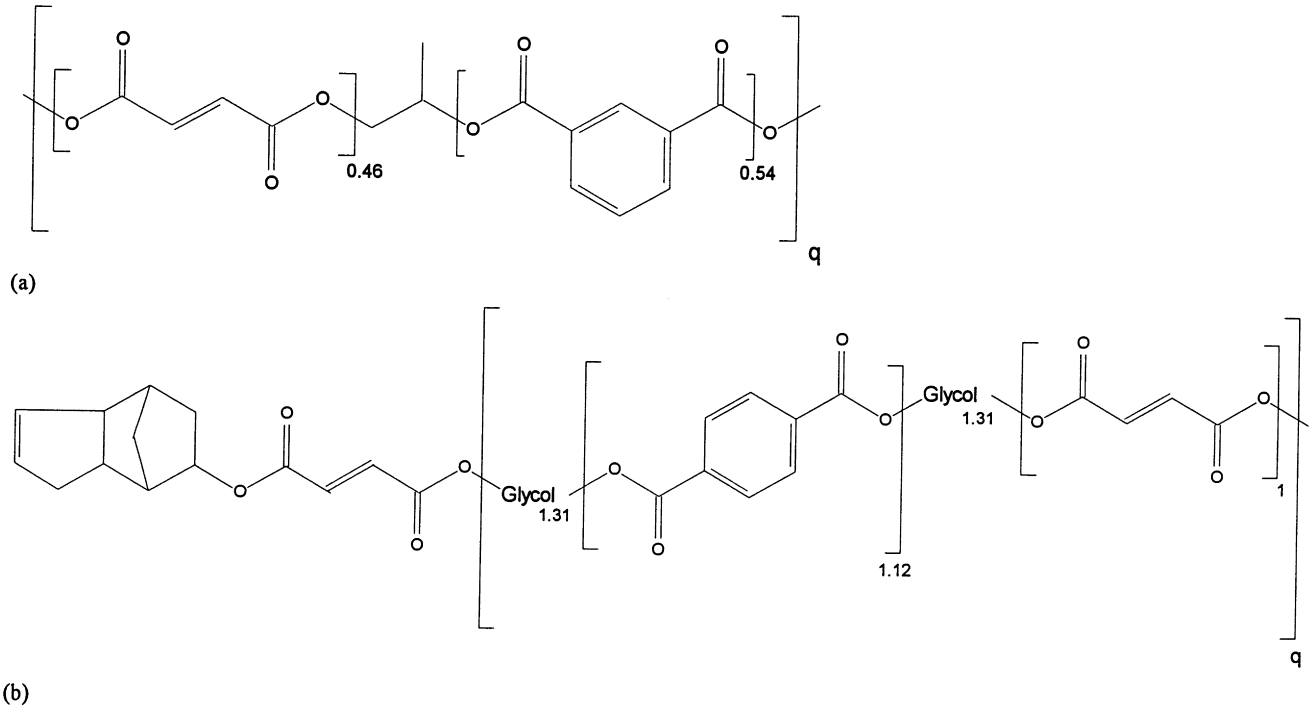

Fig. 1. Chemical structures of prepolymers A (a) and B (b).

this problem. The easiest way consists in assuming that microcavities preexist before any ageing (air bubbles, impurities, porosity), but it then becomes hazardous to explain why an initially homogeneous polymer-like polycarbonate presents microcracks after water immersion. One can also imagine that the ageing process, as for instance thermal quenching [11], induces spatial fluctuations of the water concentration responsible for phase separation. The problem is quite different when isothermal ageing is concerned. According to Robeson et al. [7], microcrack nucleation sites in polycarbonate are regions of higher water concentration (clustering) and of increased hydrolytic attack. The byproducts of PC hydrolysis are indeed CO_2 and polymer chains with polar end groups leading to further localised water solubility. Therefore, the microcavity formation would be due to potential build-up in internal pressure in those loci of high water concentration. However, the water diffusion is sufficiently fast (compared to the ageing timescale) to eliminate these fluctuations. It has also been suggested that ageing could shift the equilibrium towards lower water concentrations and then an initially saturated polyester–water system would become oversaturated [12]. However, here also, this phenomenon should be slow and water diffusion should easily eliminate the water excess. Further, ageing generally leads to an increase in hydrophilicity [2], and the equilibrium would therefore shift rather towards higher water concentrations.

Until now, all the theories proposed to explain crack initiation by a polymer–water demixing, but it was difficult or impossible to build a consistent mechanistic scheme. Thus, it seemed of utmost importance to investigate another hypothesis: crack nucleation would result from a demixing of the polymer–organic solutes system, the organic solutes coming essentially from the polyester hydrolysis. Their rate of accumulation can be related to the intrinsic stability of the ester functions present in the polymer, to their concentration and to the concentration of dangling chains [1]. The purpose of this study is to monitor the inherent hypotheses and to validate the proposed mechanism. Model systems in which glycols (an water soluble organic molecule) were incorporated into the matrix were chosen for the study, and their effect on cracking was observed.

2. Experimental

Unsaturated polyester resins were supplied by Cray-Valley Total company. Resin A is a classical polyester resin with isophthalic acid, maleic acid and propylene glycol (PG) (styrene weight fraction of 0.45), whereas B is a resin under development designed to reduce styrene weight fraction to 0.34 by using dicyclopentadiene as chemical intermediate (DCPD) and with orthophthalic and maleic acid and a mixture of PG, ethylene glycol (EG) and diethylene glycol (DEG) (Fig. 1). The resin was polymerised with conventional curing agents (0.5% (w/w) cobalt octoate and 1.2% (w/w) methylethyketone peroxide) for 24 h before being post-cured 10 h at 80°C and 4 h at 120°C to avoid any residual exotherm. The cast matrices were then machined into $\varnothing 32 \times 1$ mm specimens using a Unitom saw and polished using abrasive papers (800–2400) and diamond pastes (6 and 1 μm) in order to get transparent

samples. Three kinds of samples were then tested under hydrothermal ageing:

- *Virgin samples*
- *Swollen samples:* samples were exposed to a glycol saturated atmosphere in an oven at 50°C. The glycols under study were PG, EG and DEG. Their absorption was gravimetrically determined using a laboratory balance with a relative precision of 10^{-4}. The quantity of absorbed glycol is expressed by $P1$

$$P1 = \frac{m_1 - m_0}{m_0} 100, \quad (2)$$

where m_0 is the initial sample weight and m_1, the sample weight after glycol sorption.

- *Doped samples:* The styrene–prepolymer mixture was stirred with different weight fractions of PG, EG and DEG ranging from 1 to 7%, and was then cured and cast as before.

Differential Scanning Calorimetry was carried out with a Perkin–Elmer DSC 4 apparatus to determine the matrix glass transition temperature. The thermogram of a 10 mg sample is scanned from 20 to 180°C at a heating rate of 10°C/min. The glass transition temperatures of the post-cured matrices A and B are 369 K (96°C) and 355 K (82°C), respectively.

Extraction studies were carried out on the post-cured samples in order to identify and quantify the residual molecules. Pulverised samples were placed in cellulose thimble for extraction in dichloromethane for 2 days. The organic phase was then analysed by gas chromatography with a mass spectrometer detector (GC/MS). Experiments were performed on a 610 series ATI Unicam GC with the following oven program: from 80 to 280°C at a heating rate of 20°C/min and a plateau at 260°C for 5 min. The injector temperature was 250°C. The Unicam type Automass MS detector was set in electronic impact at 70 eV (ionisation source temperature of 160°C, mass scanning from 29–400 uma). Two microlitres of the solution was injected into the Supelcowax 10 column (length 30 m, diameter 25 mm). For quantitative analysis, xylene and butanediol were used to determine the response factor for styrene and glycols, respectively. The same procedure was followed for the immersion bath analysis after extraction in 100 ml dichloromethane and evaporation to 10 ml.

Sample UV/VIS spectra were recorded on a spectrophotometer Perkin–Elmer Lambda 9 at wavelengths ranging from 300 to 800 nm. An auto-integrating sphere was used to perform global transmission analysis.

The samples were first vacuum dried for 1 week at 50°C before immersion in water at 30, 50, 70 and 100°C. Weight changes were recorded periodically on a 10^{-4} precision balance. The apparent weight gain corresponding to water concentration was calculated using Eq. (2) with m_1 being the weight after water immersion. The P1 evolution curves were plotted as a function of reduced co-ordinates (square root of time normalised by thickness).

Initially and after glycol or water sorption, samples were observed with a NIKON optical microscope.

3. Results and discussion

3.1. Osmotic cracking development

Samples exposed at various temperatures ranging from 50 to 100°C were regularly weighed and observed with an optical microscope. A saturation plateau can be observed on kinetic curves of mass gain, but after a time t_1, the mass gain re-increases until a maximum and then decreases rapidly (Fig. 2). Microscopic observations allow to detect the time (t_{ind}) at which cracks of size larger than 40 μm appear. The cracking induction time (t_{ind}) corresponds to the time when cracks were detected under the optical microscope at a critical size of 40 μm. There exists however a shift between the induction time (t_{ind}) and the onset time shown on the P1 curve (t_1). The microcracks were disk shaped and characterised by a nucleation locus from which radial lines are developed as shown in Fig. 3(a). Cracks may also have an ellipsoidal shape as reported by Sargent et al. [14] (Fig. 3(b)). In fact, observations on thick specimens (3 mm) show that both shapes correspond to a single crack geometry.

These remarks can be explained as follows:

Cracking kinetics display an induction time of the order of t_{ind} but presumably lower. The cracks increase the sorption capacity of the polymer which induces the mass re-increase at t_1. t_1 is higher than t_{ind} owing to the relative insensitivity of the chosen gravimetric method to relative mass variations of about 10^{-3}, which corresponds to crack volume fractions of the same order. It should be noted that, in the case of Fig. 2, the whole crack volume fraction at the

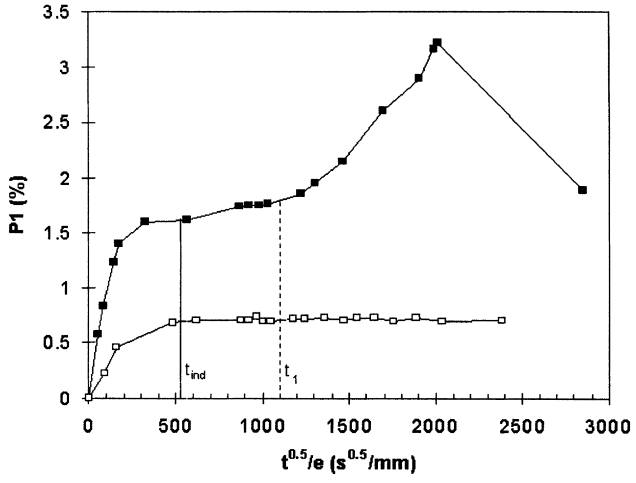

Fig. 2. Apparent weight gain evolution curves of matrices A (□) and B (■) at 70°C.

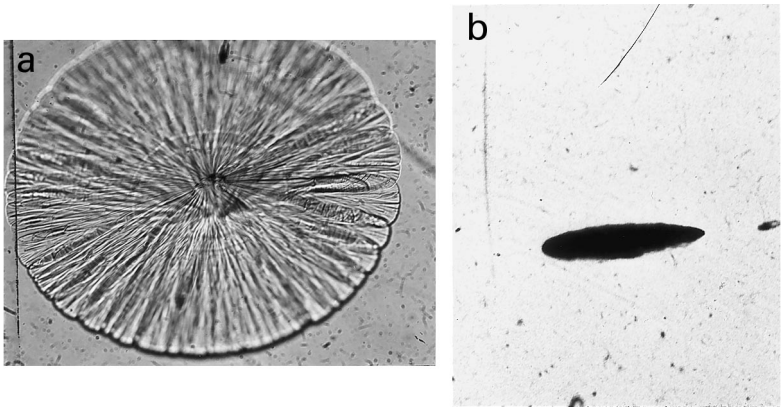

Fig. 3. Microscopic observations of disk cracks (a) and lenticular cracks (b).

maximum of the mass gain curve is of the order of 2%. The maximum corresponds to the percolation of the crack network and its opening at the sample surface. Then the organic molecules trapped inside the cracks migrate rapidly in the bath, which explains the observed weight loss.

The influence of temperature on induction times (t_{ind}) is shown in Fig. 4. It appears that network B is less stable than network A. At 100°C, when the two materials are in the same rubbery state, the crack induction time in matrix B is lower than in matrix A. No cracking was observed on samples A exposed 10 000 h at 70°C, whereas cracks appeared even at 50°C after about 3000 h in samples B. The fact that only matrix B undergoes microcracking at 70°C may be due to its lower glass transition temperature (82°C in the dry state but reduced by water absorption).

3.2. Osmotic cracking nucleation mechanism

The proposed mechanism can be summarised as follows:

Hydrolysis events on dangling chains (initially present or created by hydrolysis on elastically active chains) generate small organic molecules such as monomeric glycols or acids [1]. The latter accumulate in the network because of a very low diffusivity (compared to water diffusivity and to their build-up rate). As they are considerably more polar than the polymer, their equilibrium concentration S_∞ must be low. Thus, after a certain time, depending on the hydrolysis rate, the system becomes oversaturated and undergoes a phase separation. The excess of organic molecules therefore leads to the build-up of micropockets. According to water affinity for those hydrophilic solutes, a water flux will enter the microcavity up to a

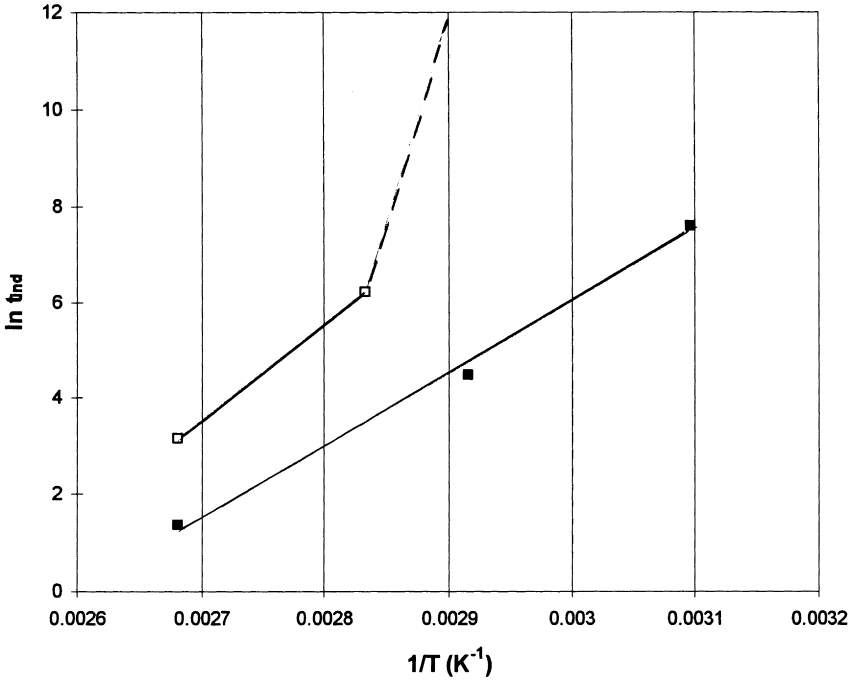

Fig. 4. Influence of temperature on crack induction time in matrices A (□) and B (■).

certain limit thus increasing the osmotic pressure, and osmotic crack propagation then occurs.

This mechanism is based on two major assumptions which have to be experimentally checked:

- the generation from hydrolysis of sufficient quantities of organic monomeric species to induce demixing;
- the low diffusivity of these organic molecules into the polyester which must act as a semi-permeable membrane.

3.2.1. Organic solute formation

A kinetic model for the formation of small organic molecules can be based on the following simple assumptions:

(i) Polyester hydrolysis obeys a second-order kinetic law:

$$\frac{dn_t}{dt} = kEW, \tag{3}$$

where n_t is the number of hydrolysis events per volume unit at time t, E, the ester concentration and W, the water concentration and k, a rate constant obeying the Arrhenius law. At low conversions, in nondiffusion controlled conditions, W can be considered constant (hydrophilicity changes due to hydrolysis are neglected), so that we can write

$$\frac{dn_t}{dt} \approx KE_0, \tag{4}$$

where K is a pseudo-first-order constant ($K = kW$) and E_0 is the initial ester concentration.

(ii) Each hydrolysis event creates two chain ends. A small molecule results from a hydrolysis event close to the chain ends. In a first approximation, let γ be the number of these molecules per volume unit, we can write

$$\frac{d\gamma}{dt} = 2k\varphi Wn_t = 2\varphi Kn_t, \tag{5}$$

where the constant φ is of the order unity linked to the mean number of ester functions in a dangling chain (it expresses the probability of a chain scission event in a dangling chain).

(iii) The integration of Eq. (4) gives

$$n_t = n_0 + KE_0t \tag{6}$$

with n_0 being the initial number of dangling chains per volume unit. It is a hyperbolic function of the initial molecular weight of the polyester prepolymer.

(iiii) By replacing n_t in Eq. (4) and after integration one obtains

$$\gamma = \gamma_0 + 2\varphi K\left(n_0t + \tfrac{1}{2}KE_0t^2\right). \tag{7}$$

The first term corresponds to the small molecules initially present inside the network, the second term refers to the small molecules generated by hydrolysis in initially present dangling chains and the last one is related to the small molecules generated by the attack of elastically active segments.

This simplified model gives us essential experimental information such as parameters which promotes the osmotic cracking of the matrix, for instance:

- Excess of initially present small molecules, especially catalyst residues, unreacted monomers (high value of γ_0) promotes cracking.
- The short length of polyester prepolymers (high value of n_0) decreases the network stability.
- The high reactivity of ester function towards hydrolysis (high value of K) is responsible for accelerated cracking.

In an attempt to quantify the amount of free molecules initially present, an extraction method followed by GC/MS analysis was carried out. The results in Table 1 confirm the existence of many residual monomers which may come from either polyester prepolymer, styrene decomposition or initiating mixture. Nevertheless, the residual weight fractions of styrene or glycols (corresponding to γ_0) turn out to be very small (less than 1% (w/w)) and can be considered as negligible.

Let us now evaluate the exact nature and the respective amount of molecules resulting from hydrolysis. There is hardly a way to identify molecules trapped inside the network except when osmosis forms blisters at the surface [10]. One way to overcome this problem is to analyse the immersion baths before and after the appearance of osmotic cracks. The identified molecules are reported in Table 2 as well as the initial prepolymer characteristics useful for the estimation of molecule build-up. The concentration of ester functions in dangling chains is determined from the concentration of acidic and alcoholic chain ends as described by Bellenger et al. [15]. The recovery of nonnegligible amounts of organic molecules would suggest that the contribution of molecules produced by hydrolysis is much higher than that of the residual monomer. The high percentage of ester functions present in dangling chains may be the weak point of matrix B even though the reactivity of ester function in the sequence (DCPD-O-MAA) should be low.

Table 1
Qualitative and quantitative analyses of residual molecules present initially in matrices A and B

Substances	Possible origin	Monomer concentration (10^6 mol/g)	
		Matrix A	Matrix B
Hydroperoxide	Initiator	Present	Present
PG	Unreacted monomer	1.3	5.2
EG	Unreacted monomer	[a]	3.2
DEG	Unreacted monomer	[a]	4.7
Styrene	Unreacted crosslinking	11.5	48
Benzaldehyde	Styrene oxidation	Present	Present
Phthalate	Initiator and catalyst	Present	Present
DCPD derived	Unreacted monomer	[a]	Present

[a] Not present.

Table 2
Qualitative and quantitative estimations of molecule formation by hydrolytic process (IPA: Isophthalic acid, MAA: Maleic acid, FUM: Fumaric acid)

Matrix	Molecular weight (g/mol)	Initial ester concentration E_0 (10^3 mol/g)	Initial ester concentration in dangling chains (10^3 mol/g)	% of ester functions in dangling chains	Substances analysed in immersion baths by GC/MS
A	2150	10.9	1.5	13	IPA, MMA, FUM, PG, phtalate, benzoic acid, styrene derived products
B	630	9.7	1.98	20	IPA, MAA, FUM, PG, EG, DEG, phthalate, benzoic acid, styrene derived products, DCPD-OH, DCPD derived products

3.2.2. Semi-permeable membrane

A semi-permeable membrane can be defined as a barrier that lets water penetrate but prevents or at least delays the entering of solutes. This property was studied for both matrices with regard to glycols as solutes. Fig. 5 shows that glycol solubility in matrix A at 50°C is hardly null. As far as matrix B is concerned, glycols were absorbed in a nonnegligible amount, but there existed yet an induction period during which the matrix remains impermeable to glycols.

3.3. Study of model systems

In an attempt to check the proposed mechanism, it seems interesting to us to study the behaviour of model systems in which known quantities of small organic molecules (glycols) are introduced in the network. Glycols were chosen as small organic molecules as they fulfil two main conditions:

- They are infinitely soluble in water, and therefore potential promoters of disk cracking through an osmotic process.
- They are liquid organic molecules, and therefore can be introduced in the prepolymer or in the network by absorption.

As a matter of fact, two ways were compared for the introduction: a “swelling” method in which glycols were incorporated into the network by diffusion and a “doping” method in which glycols were introduced into the reactive mixture (prepolymer styrene) before crosslinking.

3.4. Swelling

Several swelling degrees were achieved by the exposure of polyester samples in glycol saturated media (Table 3). Cracking occurs only in matrix B within 5 h immersion at 50°C only when the swelling degree exceeded 0.5%. It appears that the swelling degree does not influence the crack induction time, but that it influences only the crack

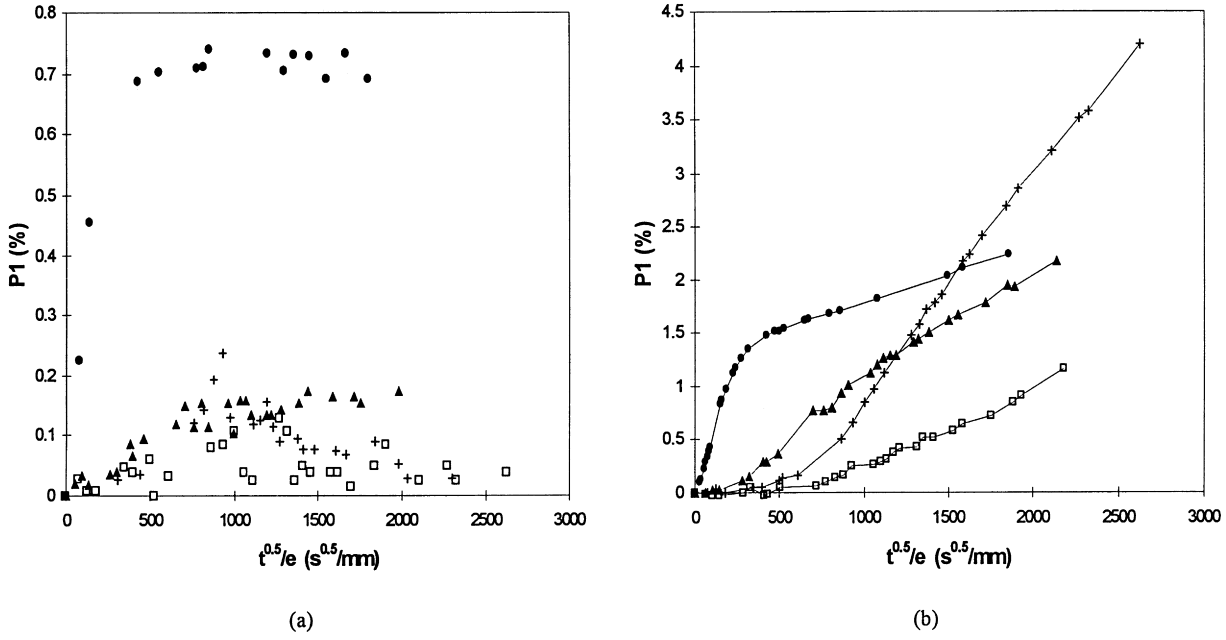

Fig. 5. Water solubility (●) and PG (□), EG (▲) and DEG (+) solubility in matrices A (a) and B (b).

Table 3
Swelling degrees (in (w/w)%)

Matrix	PG	EG	DEG
A	0.04	0.17	0.03
A	0.4		
B	0.48	0.25	0.23
B	1.16[a]	1[a]	1.2[a]
B	3[a]	2.1[a]	4.2[a]

[a] Samples where disk cracks were observed within 5 h immersion at 50°C.

Table 4
Miscibility thresholds (with prepolymer A, $\delta = 23\ J^{1/2}\ cm^{-3/2}$)

Glycol	Solubility parameter $\delta(J^{1/2}\ cm^{-3/2})$	Glycol weight fraction (%)	
		Matrix A	Matrix B
EG	33.4	1.5	1.5
PG	30.3	3	11
DEG	29		50

initial size. For example, a 1% EG swelling gives rise to a 180 μm crack, whereas the crack size reaches 300 μm for a 2% swollen matrix and 500 μm for a 4% DEG swollen matrix. It may depend on the initial size of the glycol-rich phase before water immersion.

3.4. Doping

Different glycol weight fractions were incorporated into the initial mixture before crosslinking during which a limited fraction (considered as negligible) could evaporate. The first remark to make is that glycols are not infinitely soluble in the prepolymer–styrene solution. The cloud point method enabled us to determine the miscibility threshold of the different glycols at an ambient temperature in both matrices, knowing that it increases with temperature (Table 4). The hierarchy in glycol concentration is in good agreement with the Van Krevelen solubility parameter [16]. The main result reported in Fig. 6 is the dependence of crack induction time with glycol weight fraction. The fact that the crack induction time is reduced by the introduction of glycols confirms positively our mechanism. The curves in Fig. 6 look very similar to the lower critical separation temperature polymer–solvent phase diagram (LCST) where the critical factor would be the immersion time and not the temperature. Therefore, the conclusion can be drawn that the observed cracking is the result of phase separation between the polyester network and the aqueous solution of glycols.

4. Discussion

It is nevertheless important to distinguish two cases in the previous experiments: either glycol introduction induces phase separation before water immersion, or the mixture glycol–polyester network can be considered as homogeneous initially.

In the first case, glycol-rich micropockets preexist to water immersion. The cracking is therefore only water diffusion controlled. Optical properties were chosen as a tool to detect phase separation induced by glycol incorporation. Fig. 7 represents the transmission and extinction UV spectra of matrix C swollen with different glycol fractions, whereas the case of “doping” is presented in Fig. 8. The transmission

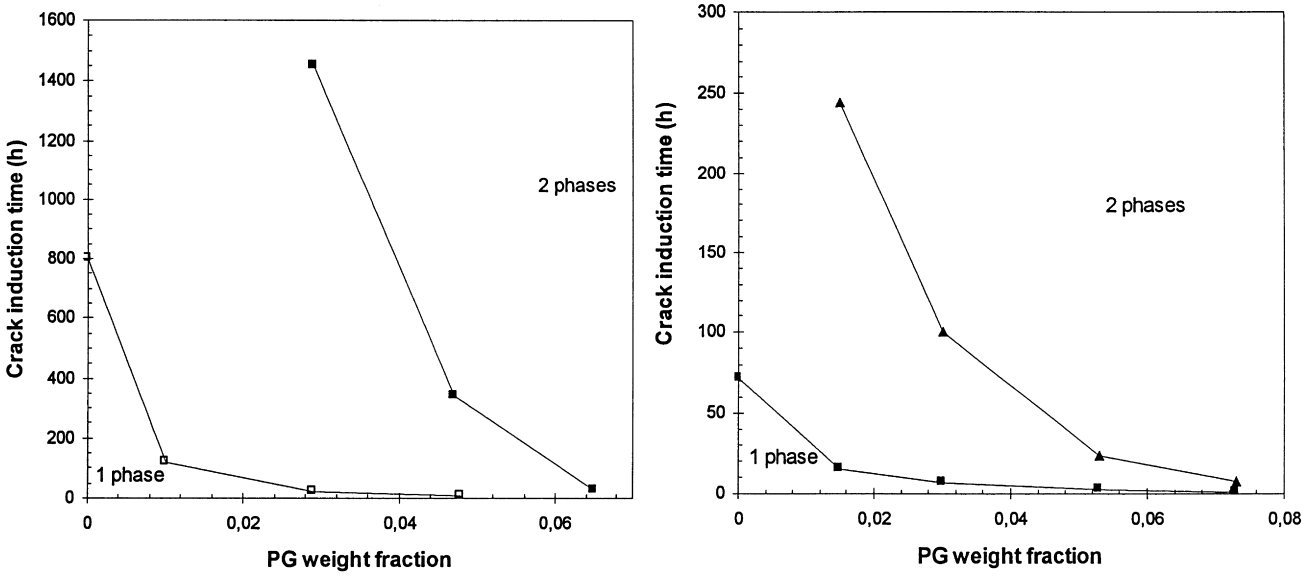

Fig. 6. Phase separation diagrams of polyester–PG systems at 50°C (▲), 70°C (■) and 80°C (□) for matrices A (a) and B (b).

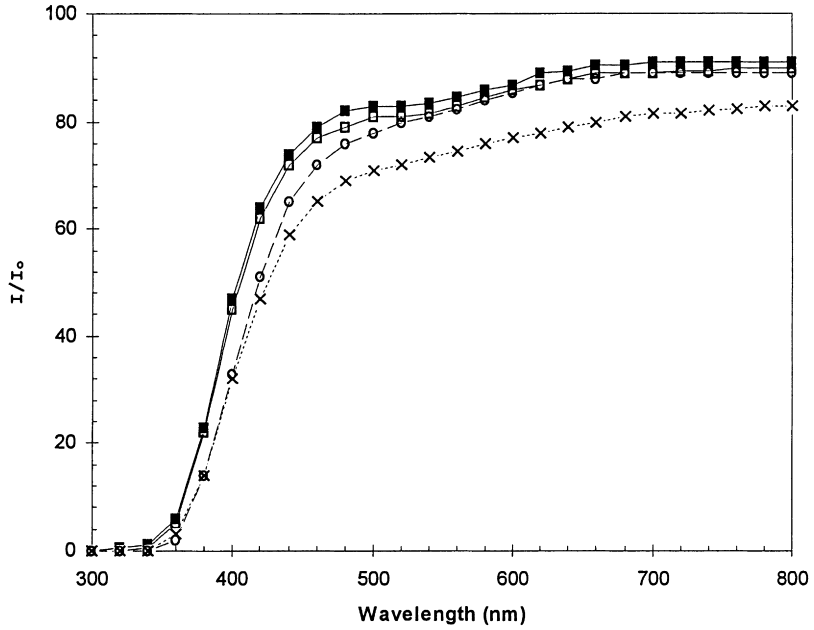

Fig. 7. Transmission (■) and extinction spectra of glycol swollen B matrix: 1.1% PG (□), 2% EG (○) and 4% DEG (×).

spectrum does not evolve with glycol swelling or doping, but the extinction spectrum is strongly influenced by the glycol ratio. The difference between the transmission and extinction spectra reveals the presence of diffusing heterogeneities.

For doped homogenous samples, the microcavitation origin is obviously different as the cracking timescale is superior to the diffusion timescale. Using gravimetric analysis, we found a correlation between crack induction time and water absorption: water concentration values at the induction times are reported in Table 5. This result is to be interpreted with caution in that apparent weight gain measurements do not take into account an eventual molecule extraction. As a consequence, water concentration may be underestimated, and it would explain why the higher the crack induction time is, the lower is the water concentration. Nevertheless, the following scheme can be put forward: glycol molecules incorporated into the prepolymer mixture remain soluble in the network until a critical concentration. Their hydrophilic character increases the water absorption

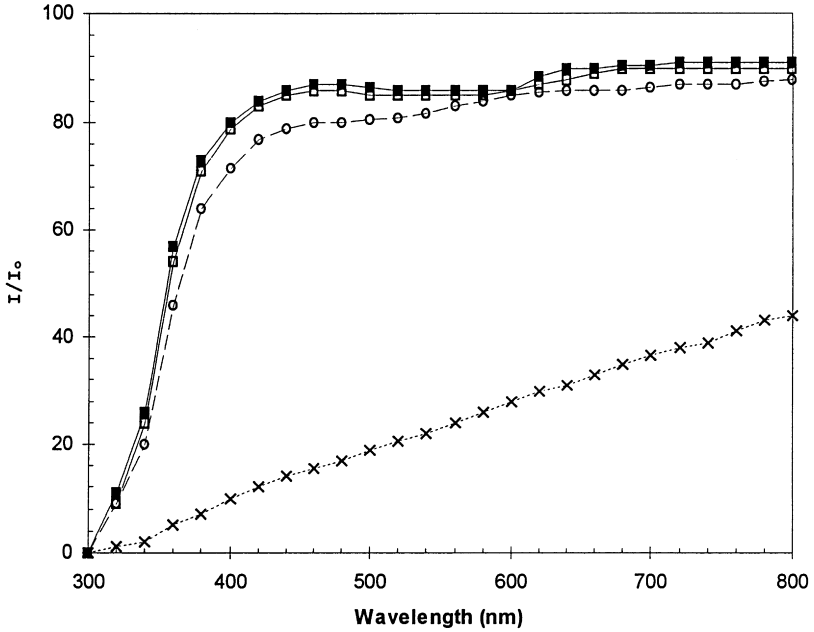

Fig. 8. Transmission (■) and extinction spectra of A virgin matrix (□) and doped with 5% PG (○) or with 7% PG (×).

Table 5
Water concentration (in (w/w)%) at crack induction times (crack induction times (h) are placed in italics in brackets)

Matrix	Temperature	PG content in (w/w)%			
	(°C)	1	3	5	7
A	70	[a]	1.5 (*1450*)	2.2 (*340*)	2.5 (*24*)
B	80	1.3 (*120*)	2.7 (*24*)	3.6 (*7*)	[b]
	30	2.5 (*2500*)	3.6 (*816*)	4.3 (*168*)	5 (*72*)
	50	2.3 (*245*)	3.6 (*100*)	4.2 (*24*)	4.5 (*8*)
	70	2.1 (*15*)	2.8 (*7*)	3.8 (*2.5*)	4 (*1*)

[a] No microcracking.
[b] Not determined.

in localised regions thus inducing matrix swelling in those particular glycol-rich sites leading finally to matrix cavitation. The more the glycol incorporated, the more does the matrix swell, and the lower the induction time is. To summarise, free glycol molecules associated with a certain amount of water act as an internal stress inside the network leading to matrix cracking. The influence of temperature is shown in Fig. 9 where glycol weight fractions are plotted as a function of the logarithm of crack induction time. It leads to a linear relation where intercept A is temperature dependent but not slope B. This is as follows:

$$t = 2.3 \exp\left(-\frac{\mathrm{PG}(\%) - A(T)}{B}\right). \quad (8)$$

The slope value, which is a temperature independent parameter, is higher for matrix A than for matrix B. It expresses the lower stability of matrix *B* towards osmotic cracking.

5. Conclusion

The degradation of polyester matrices in water at different temperatures involves water uptake, swelling, ester hydrolysis, osmotic cracking and leaching of small molecules. The osmotic cracking nucleation is produced by a phase separation between the polymer and water soluble organic molecules resulting from hydrolysis. Once some assumptions were verified, the nucleation mechanism was validated by simulating the presence of glycols inside the network. Depending on the initial state of the polymer–glycol system (heterogeneous or homogeneous), the osmotic cracking is instantaneous or crack induction time is observed depending on the glycol fraction and temperature. Major parameters promoting matrix cracking were identified:

1. high fraction of monomeric and catalyst residues;

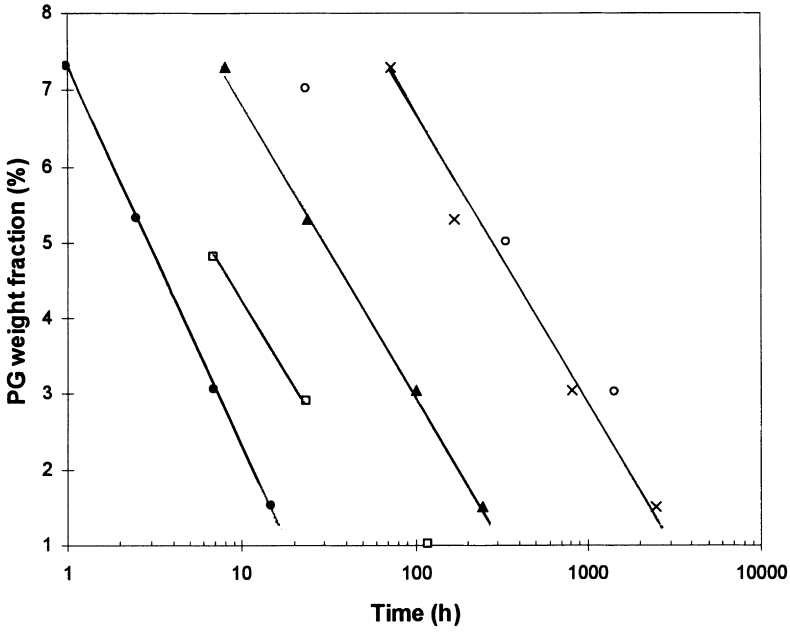

Fig. 9. Influence of glycol weight fraction on logarithm of crack induction time at 80°C (□) and 70°C (○) for matrix A and at 70°C (●), 50°C (▲) and 30°C (×) for matrix B.

2. high fraction of ester functions in dangling chains;
3. high reactivity of ester functions.

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