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Spiral and other Crazing and Cracking in Polymers with Phenylene Groups in the Main Chain

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Examination of biaxially stressed films of certain polymers prepared on microscope slides showed, in addition to the normal cracking pattern produced on the application of liquids, that spiral cracks are also produced. Both single and multiple spirals occur and follow the logarithmic curve quite accurately. A single simple assumption is shown to account accurately for the phenomena and for the mathematical form of the curve.

1. Introduction

Previous study of the interaction of polymer films [1, 2], with liquids, showed a normal type of crazing and cracking, in lines perpendicular to the principal strain axes giving a pattern of rectangles, with an occasional triangle.

This study is concerned with stress cracking [3] either environmental [4-6] or solvent induced [7-9] It seems probable that in many cases, although caused by solvent, the phenomenon is nearer to environmental stress cracking and that the difference is usually marginal.

Spurr and Niegisch [10] and also Kambour [11] have shown that many cracks are really crazes, being up to 50% solid material. Kambour [12] states that discontinuities in crazes are submicroscopic, but present experience indicates a continuous gradation from almost invisible crazes up to coarse crazing and cracks.

Crazes and cracks normally occur together and crazes often develop into cracks. They require special experiments or study of subsequent behaviour to distinguish them. Here the term crack will be used for both phenomena.

2. Experimental

2.1. Polymeric Materials

Good quality commercial material in the form of granules for injection moulding was used.

Polyethylene terephthalate. The films were prepared from Arnite grade G.600.

Bakelite phenoxy resin. Q74. This resin is essentially a polymer of bisphenol A with glycerine (propane 1.2.3 triol).

Polycarbonate. The polycarbonic ester of 2,2-bis (4 hydroxyphenyl)propane. The grade used was Makrolon 3000W.

Polysulphone. This is the polycondensation product of 2,2-bis(4 hydroxyphenyl)propane with 4,4′dichloro-diphenyl sulphoxide manufactured by Union Carbide (Grade PL1700).

Polyphenylene oxide. The material used was poly(2,6-dimethyl-1,4-phenylene oxide) Grade PL500 CT1002.

2.2. Liquids

The best available laboratory reagents were used in all cases. They are listed in table I.

2.3. Film Preparation

Films were prepared as previously described [1], at 320°C for polycarbonate and 350°C for polysulphone.

2.4. Film Treatment

The glass slides containing films were placed on the microscope stage and small amounts of liquid were applied to the surface using an eye dropper. Control tests were carried out on unstressed polymeric material.

3. Results

3.1. General Morphological Changes

Polyethylene terephthalate and the phenoxy resin produced opaque crystalline spherulitic films in which the crystalline entitites were small and in most cases only just resolvable optically. The remaining films were amorphous and clear, and although crystal entities were observed on occasion [13] such films were not used in these experiments.

Treatment of unstressed polymer with various liquids either had no effect or wrinkling or crystallisation occurred (table I).

Treatment of stressed materials with liquids nearly always produced cracking, although occasionally no reaction could be observed. The cracking was often followed by crystallisation.

3.1.1. Cracking

Three distinct types of cracking were observed, rectangular, branched and spiral.

Rectangular cracking. Cracking perpendicular to the two principal directions of stress produces a rectangular crack pattern very rapidly (fig. 1). After the preliminary pattern has formed, if the residual stress is great enough new, slowly propagated cracks may further split the rectangles.

Branched cracking. This type of cracking occurs in biaxial stress conditions where the stress in the two directions differs greatly, near the edge of films and where there is a marked change of thickness, and once initiated appears to be the dominant form of cracking (fig. 2).

Spiral cracking. This refers to the very elegant spiral cracks which form within the rectangles and triangles of the original crack pattern (fig. 3). They are formed at a slow rate in comparison to the primary pattern but can form in under one second. These cracks were first reported for the system polycarbonate/carbon tetrachloride [14]; similar cracks have now been observed for about 20% of the systems investigated.

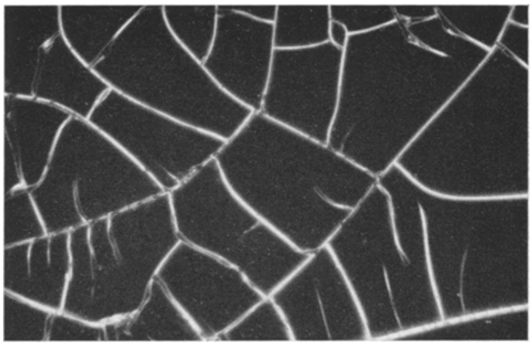

Figure 1 Rectangular cracking. Acetone on polysulphone. Dark field (×140).

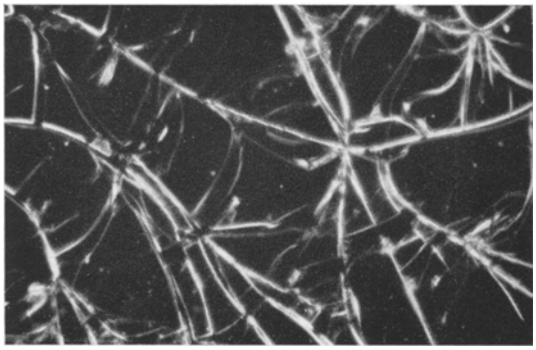

Figure 2 Branched cracking. Acetone on polysulphone. Dark field (×140).

Polycarbonate with carbon tetrachloride,

TABLE I Liquids showing reactions with unstressed polymer surfaces

Polymer*		
Polycarbonate	Polysulphone	Polyphenylene oxide
		Methanol, W*
Acetone, X	Acetone, Cr, G	
		Ether, Cr
Anisole, X		Anisole, sX, sCr
n-Butyl halides, W	*n*-Butyl halides sW	*n*-Butyl halides, Cr, Q
Xylene, X	Xylene, E	Xylene, W
Chlorbenzene, X		Chlorbenzene, W
Dimethyl aniline, sX		Dimethyl aniline, W
	Cyclohexanone, E	Cyclohexanone, sX
		n-Diamyl ether, sCr

W = surface wrinkles produced. Cr = crazing. G = surface granulated. X = surface crystallisation occurs. E = edge of film etched. Q = cracks produced in surface. s = slight.

*Polyethylene terephalate and the phenoxy resin showed no reaction with any of the liquids used.

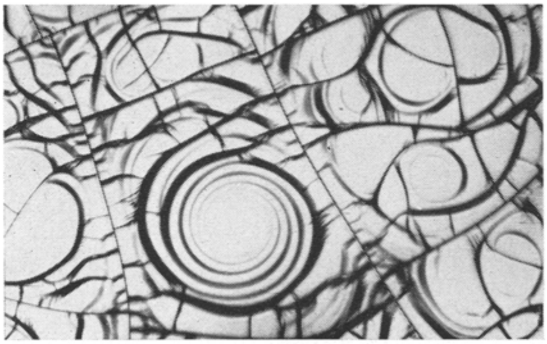

Figure 3 Spiral cracks. Xylene on polyphenylene oxide. Polarised light, no analyser (×140).

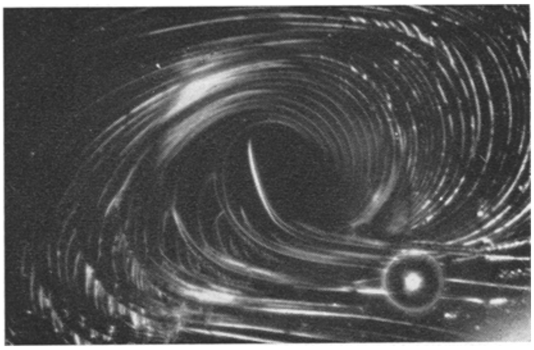

Figure 4 Multiple spiral cracks. Carbon tetrachloride on polysulphone. Dark field (×140).

xylene, diethyl ether, di-*n*-amyl ether, diphenyl ether and very rarely acetone.

Polysulphone with methanol ethanol, xylene, carbon tetrachloride (fig. 4), *n*-butyl halides, chlorbenzene, diethyl ether, di-*n*-amyl ether, diphenyl ether and acetone.

Polyphenylene oxide with methanol, ethanol, xylene (fig. 3), *n*-nutyl halides, diethyl ether and diphenyl ether.

Spiral cracking has not been observed in the polyethylene terephthalate or phenoxy resin.

All the cracking results are summarised in table II. Nucleation and propagation mechanisms may well be closely related since slow nucleation

TABLE II Cracking* and morphological changes in polymer/liquid systems

Liquid	Polymer				
	Arnite	Phenoxy resin	Polycarbonate	Polysulphone	Polyphenylene oxide
Methanol	M	—	?	M P	F P
Ethanol	M	S	?	S P	F P
Hexanol	—	S → M	M	M	S—M
Decanol	—	—	SS	SS	S
Cyclohexanol	M	—	—	—	S
Xylene	S	S	S P X	F P	M P
n-Hexane	—	—	S	—	—
n-Decane	—	—	SS	SS	—
Cyclohexane	—	—	S	—	—
Methyl cyclohexane	—	—	—	—	—
Carbon tetrachloride	?	S	F P P	F P	—
n-Butyl chloride	?	SS	F	F P	M P
n-Butyl bromide	?	SS	F	F P	M P
n-Butyl iodide	?	SS S	F	F P	M P
Chlorobenzene	S	M	F X	F P	M (X)
Diethyl ether	F	F	FF P	FF P	F P
Di-*n*-amyl ether	F	—	S P	F P	—
Methyl phenyl ether	SS	S	M→F	M→F	M→F
Diphenyl ether	?	SS	S P	M P	S P
Acetone	M	—	M—F (P) X	F P	M→F X
Methyl ethyl ketone	S	S	M—F X	FF B	S X
Cyclohexanone	M	—	M—F	—	—
Dimethyl aniline	S	S	S X	S (P)	S
Ethyl acetate	M	S	F X	—	—

FF = Very fast
F = Fast
M = Primaryc racking Medium
S = Slow
SS = Very slow

B = Branched cracking
P = Spiral cracking
X = Crystallisation at surface

*Unless otherwise stated the cracking is rectangular.

seems to produce a crack which propagates slowly and vice versa.

3.1.2. Crystallisation

Certain liquids induce crystallisation under stress, but all these used except anisole also caused slow crystallisation in the absence of stress. The stress crystallisation may cause crazes to develop into cracks. The spirals formed as a result of the application of a liquid which does not cause crystallisation, can be converted to the most beautiful spiral spherulites by subsequent application of a liquid causing rapid crystallisation, such as acetone. The spherulites are most perfectly produced using an acetone/chloroform 20/80 by volume mixture. The crazes act as crystallisation nuclei, and the material between the turns of the spiral rapidly becomes crystalline. Fig. 5 shows a completed spiral spherulitic disc showing the typical Maltese cross under crossed polaroids. The fully formed spiral spherulites when treated with a solvent do not break up either along the lines of the original crazes or along the lines where crystal growth from adjacent segments meet, but random areas of material become detached piecemeal as the solvent eats into material.

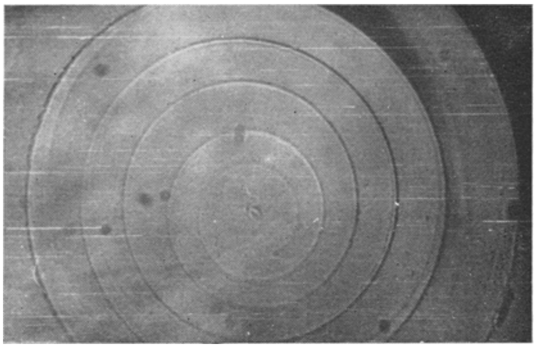

Figure 6 Single arm spiral. Carbon tetrachloride on polycarbonate (×1000).

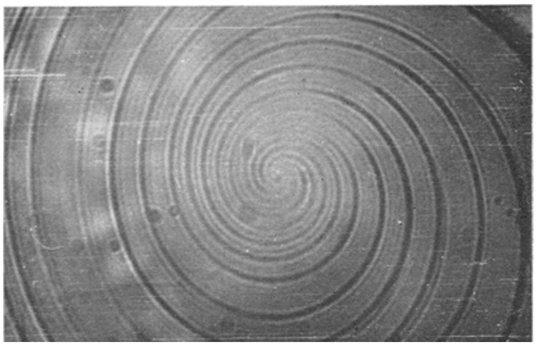

Figure 7 Five arm spiral. Carbon tetrachloride on polycarbonate (×1000).

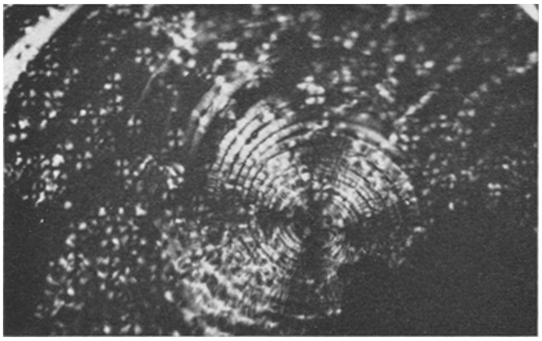

Figure 5 Spiral spherulite produced by acetone/chloroform treatment of spiral craze/crack system. Polarised light, polaroids crossed. Polycarbonate (×90).

4. Discussion

The spiral cracking of polymers has not previously been observed. The ring crazes observed by Tomikawa and Kaji [15] seem quite different requiring "several hours" treatment and raised temperature to produce instead of seconds in the present case. The spirals are left or right handed in about equal numbers and may have from one (fig. 6) to nine arms although four, or five (fig. 7) are the commonest. Occasionally a great number of incomplete arms are formed (fig. 4). The spirals are logarithmic, obeying an equation of the form $r = k^{\theta}$ where r is the length of the radius vector, θ the angle of rotation and k a constant. Fig. 8 is the plot of log r against θ for a one armed spiral and fig. 9 a similar plot for a five-arm spiral. The value of k will obviously

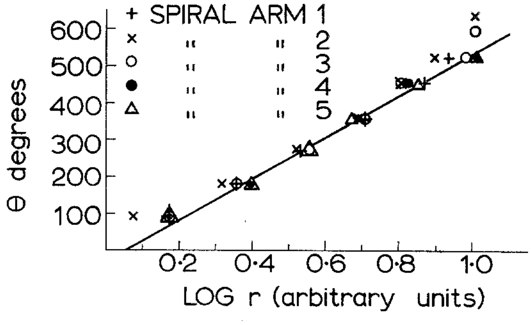

Figure 8 Plot of logarithm of radius vector against angle of rotation for single-arm spiral.

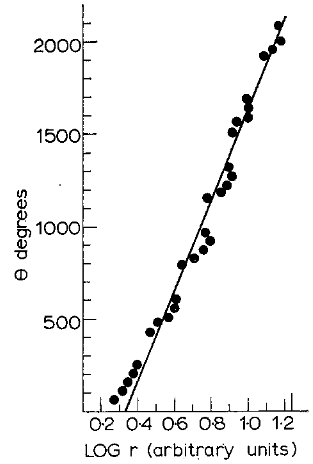

Figure 9 Plot of logarithm of radius vector against angle of rotation for five-arm spiral.

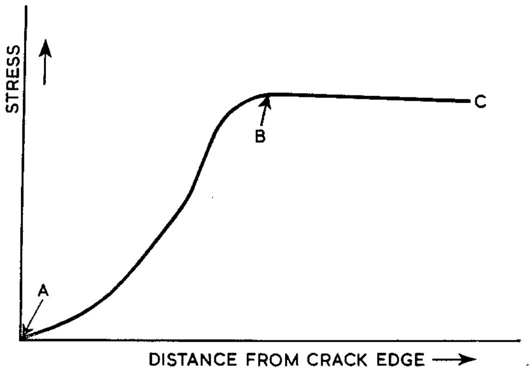

Figure 10 Stress profile adjacent to a rectangular crack.

depend on the stress in the material and the area of the quadrilateral or triangle in which the spiral is formed.

The spirals are only formed after the primary crack pattern has been established and only when there is biaxial stress in the material. The spirals always grow inward and the "eye" is usually close to the centre of the original area concerned.*

Because of the method of preparation, the film is biaxially stressed and stuck to the substrate so that when a crack forms stress is only relieved locally in an area adjacent to the crack, and rapidly builds up to the original value at a short distance from the crack. If σ_r and σ_θ are the polar components of major stress in a small rectangle formed by the initial crack pattern, then σ_r, the stress perpendicular to the crack edge, will have a profile of form of fig. 10 rising to a plateau at B where the stress is equal to that originally present. σ_θ however, is constant, so that there is no driving force turning the crack into the plateau area. Thus a crack initiated in the plateau area will, in general, pass across the area in a straight line merely dividing the original rectangle into two new rectangles. If, however, the critical stress for cracking is below the value at B a crack can form in the area of the stress gradient between the crack at the edge of the rectangle and the edge of the plateau B. Such a crack will follow the gradient contour of critical stress and would be expected to have a circular path. But the new crack will result in a stress relaxation which may extend through a considerable area of material, and if the speed at which this relaxation spreads is sufficient to affect the material just ahead of the crack tip, then the critical stress contour will shift slightly towards the centre of the area and so subsequently will the crack tip. Then if r_1, r_2, r_3 etc. are the radii of curvature of successive points on the crack from the area centre then $r_1 > r_2 > r_3$. Then provided that the rate of propagation of the relaxation due to the crack and the rate of crack growth are approximately constant or remain in the same ratio

$$\mathrm{d}r = Q\mathrm{d}l$$

where dr is the change in radius of curvature, dl the change in crack length and Q is a constant.

Let P_1 P_2 be two points very close together on the crack (fig. 11). Let the radius of curvature at P_1 and P_2 be r_1 and r_2 and dθ the angle between them.

Then

$$r_1 - r_2 = \mathrm{d}r = Q\mathrm{d}l = Qr\mathrm{d}\theta$$

Integrating

$$\log r = Q\theta + C = Q\theta + \log K$$

or

$$r = K^{Q\theta}$$

which is the form of a logarithmic spiral (C is the integration constant). Not all the curves take the form of perfect spirals and every possible variation of straight line and spiral crack interaction can be observed. Spirals may be unable to complete their formation, because straight line cracks block the formation. and because spirals may only be partially formed. The spiral generation may also stop if the stress relaxation near the crack tip is sufficient to lower the stress below the critical value for crack propagation. Such cases appear to occur in the polysulphone/

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*This is not always accurately so since straight cracks may still form during and after the spinal formation.

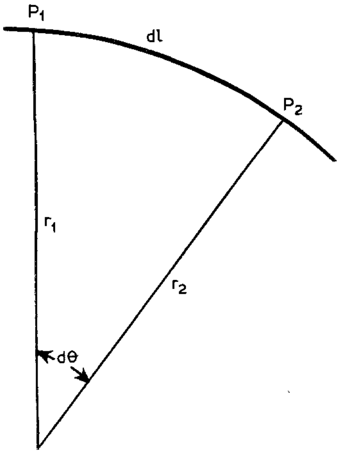

Figure 11 Diagram of short portion of curved crack.

chlorbenzene system when the spirals can often be reduced to the form of hooks.

A further phenomenon has been observed in these experiments. When the liquid applied is rapidly absorbed at the polymer surface, the normal craze pattern appears at first, but shortly afterwards, due to stress relaxations resulting from liquid penetration, the lines develop a "wobble" and some crazes may appear to heal.

The results shown in table II indicate that small molecules tend to be more efficient in cracking polymers than large ones, but it is also clear that this is far from supplying the whole answer to the problems. The question as to why polycarbonate does not seem to crack or craze with methanol and ethanol, whereas polysulphone and polyphenylene oxide do, is still unanswered. No doubt the solubility parameter and molecular shape, both of the polymer and the liquid, must be taken into account. These will be discussed in a future paper. Chlorocompounds appear to be efficient cracking agents as do the ethers. Although the crystalline polymers polyethylene terephthalate and phenoxy resin crack with liquids they are in general more resistant. They never show spiral cracking probably because the crystal structure prevents rapid spread of stress relaxation caused by cracks.

Acknowledgement

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