JOURNAL OF MATERIALS SCIENCE 25 (1990) 2866–2868

The propagation of cracks and crack-like defects in thin adhered polymer films

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The strain energy release rate G of a through-thickness crack in a thin film that adheres to a rigid substrate is shown to vary linearly with the film thickness at constant film stress. G is normally small, so adhered polymer films are only expected to crack in the presence of an aggressive environmental agent unless the polymer is very brittle. A minimum film thickness for cracking is likely to be observed. The propagation of crack-like defects in a polyimide in the presence of xylene was examined experimentally. The defects grew at a constant rate (independent of their length) that increased rapidly with film thickness. The minimum film thickness for defect growth was found to be about $2\,\mu$m.

1. Introduction

The formation and propagation of cracks or crack-like defects (in polymers, crazes or deformation zones) can be understood as a reaction of the material to a particular mechanical situation. In most circumstances the mechanical situation required for crack or craze initiation and craze propagation is adequately described in terms of the local stresses in the material. Often the mechanical situation relevant for crack propagation is best described by fracture mechanics in terms of a value of the stress intensity factor $K_{\rm I}$ or, equivalently, the strain energy release rate G. The aim of the work described here has been to examine the mechanical criteria required for the propagation of crack-like defects that can be observed in thin films of some polymers that have been adhered to a rigid substrate. The morphology of these defects has already been described [1] in a previous publication.

Polymers have been used for many years in the form of thin films adhered to a rigid substrate. Paints are a particular example of this usage. More recently, thin polymer films have found use in the electronics industry as dielectric layers that are deposited on the top of silicon or ceramic substrates. In all these cases the stress state of the polymer film tends to be one of biaxial tension in the film plane. The tensile stress is caused by the contraction of the polymer film relative to the substrate that occurs during processing. Hence the stress can be caused by both solvent loss during the drying of the polymer film on the substrate and differential thermal contraction between the polymer and the substrate that happens as they are cooled from the drying or curing temperature. Significant stress, in the range of 20 to 60 MPa, has been measured in high-T_g polymer films [2]. The stress is controlled mainly by the thermal expansion coefficient of the polymer and is, in general, independent of film thickness [2] and is of such magnitude that it might be expected to cause cracks or defects in free-standing films, particularly in the presence of aggressive environments. The main purpose of this paper is to show that adhered films often survive without cracks or crack-like defects mainly because they are thin. As long as the adhesion of the film to the substrate is good, the important crack dimension for fracture mechanics analysis is its length normal to the film plane, which can be assumed to equal the film thickness, not its length in the film plane. It follows that the crack driving force (G or $K_{\rm I}$) is, at constant film stress, a function of the film thickness but independent of the maximum length of the crack in the film plane.

2. Fracture mechanics of thin adhered films

We wish to find the strain energy release rate for the propagation of a crack in a film of thickness h that is bonded to a rigid substrate and experiences a remote equibiaxial tensile stress σ_0. The situation is shown in Fig. 1 with the crack assumed to be long with respect to the film thickness. We shall first consider the form of the relationship between G and the sample dimensions using dimensional analysis then obtain the numerical factors from a published fracture mechanics solution.

It is evident that the crack opening at the film surface remote from the crack tip is independent of the crack length as long as the adhesion to the substrate is good. It follows then that the stress pattern round the crack tip must be independent of crack length, so the average strain energy release rate for propagating the crack in the film plane $\tilde{G}$ is also independent of crack length. However, $\tilde{G}$ must be a function of the elastic strain energy in the film so from dimensional considerations must be given by an expression of the form

$$\tilde{G} = A\frac{\sigma_0^2 h}{E} \qquad (1)$$

where A is a constant containing a numerical factor and Poisson's ratio ν. The situation is very similar to the case of interface failure where, from the stored

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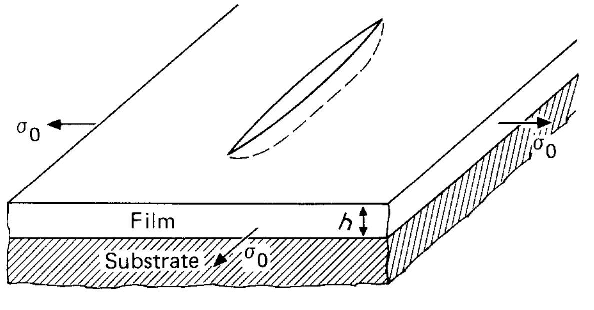

Figure 1 A sketch of a crack in a thin layer of material that is bonded to a rigid substrate.

elastic energy in the film, it is evident that

$$G_{\text{in}} = \frac{\sigma_0^2(1 - \nu^2)h}{2E}$$

The constant A in Equation 1 can be obtained from a knowledge of K_1 for a long crack of depth b in a film of thickness h adhered to a rigid substrate. Such a situation has been studied by Gecit [3], who showed that

$$K(b) = f\left(\frac{b}{h}\right)\sigma_0(\pi b)^{1/2}$$

where the function $f(x)$ is presented in graphical form in Gecit's paper. But

$$G = (1 - \nu^2)K^2/E$$

The average value of G, $\tilde{G}$, for the propagation of the crack in the film plane is hence given by

$$\tilde{G} = \frac{1 - \nu^2}{Eh}\int_0^h K^2(b)\,\mathrm{d}b$$

From Gecit [3] one can estimate that

$$\int_0^1 xf^2(x)\,\mathrm{d}x \simeq 0.36$$

so that

$$\tilde{G} \simeq 0.36(1 - \nu^2)\sigma_0^2\pi h/E$$

It is useful to consider typical values of $\tilde{G}$ that might be experienced in thin polymer films used in electronic applications. Glassy polymers typically have a tensile modulus E of about 3×10^9 Pa, and Poisson's ratio ν of about 0.3. We shall assume a large value of σ_0 of 7×10^7 Pa and film thickness of 20 μm and 1 μm covering the range from packaging to on-chip applications. The values of $\tilde{G}$ obtained are 33 and 1.65 J m^{-2}. These are very low values; G_c for crack propagation in air for glassy polymers varies between about 300 and 400 J m^{-2} for brittle thermoplastics such as polymethylmethacrylate or polystyrene to about 60 J m^{-2} for crosslinked unsaturated polyesters [4]. It would appear that, even for 20 μm films, cracking in air is not likely to be a problem unless a very brittle polymer is used.

Polymers are susceptible to cracking in a variety of aggressive environments which can be divided into two groups, organic fluids which plasticize the polymer and chemically aggressive materials that cleave the chains. Crack propagation has been observed to occur in polymers at very low G values, i.e. G_c drops dramatically, in the presence of materials from either of the two groups. Also it is observed that in general the crack does not grow below a critical value of G, and for G values higher than this the crack growth rate is a rapidly increasing function of G. From the analysis given above it may be concluded that thin polymer films that adhere well to a rigid substrate are only likely to crack in the presence of an aggressive environment, and the crack growth rate is expected to be a rapidly increasing function of film thickness as long as the thickness is above a critical value.

3. Experimental techniques

The polymer used in these experiments was the thermoplastic polyimide XU293 obtained from Ceiba-Geigy. The thin films were spin-coated on to glass slides from a solution of the polymer in γ-butyrolactone. The films were dried at 85° C for 15 min, 150° C for 30 min then 230° C for 30 min. Deformation zones formed and propagated when the polymer-coated slides were placed in xylene at room temperature. The deformation zones normally initiated at flaws (dust particles or scratches), so often the film was scratched in a number of places to help initiation before placing in the xylene. The slides were periodically removed from the xylene and examined rapidly in the optical microscope to measure the lengths of the deformation zones and then reimmersed in the xylene. The deformation zone propagation stopped when the slide was removed from the xylene as the residual xylene on the film dried quickly. More details of the film preparation techniques and the structure of the deformation zones have been published [1].

4. Experimental results and discussion

Fig. 2 shows the length of a number of deformation zones length as a function of immersion time. Clearly the zones were growing at a constant speed; different zones initiated at different times but on one slide they all grew the same velocity. The zone growth rate was measured for a series of samples which differed only in the film thickness. In all cases the zones grew at

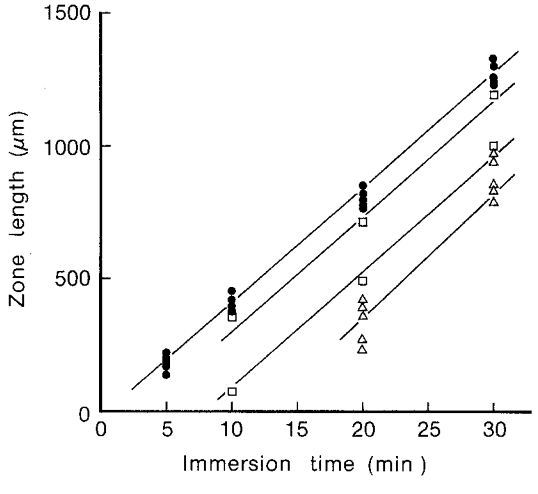

Figure 2 The variation of deformation zone length with immersion time for a number of deformation zones in one sample: different symbols indicate groups of defects initiated at different times. Film thickness 10 μm.

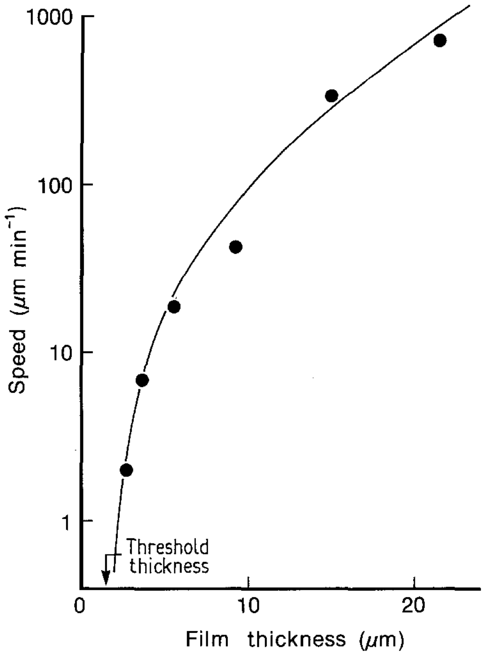

Figure 3 Growth rate (speed) of deformation zones as a function of film thickness.

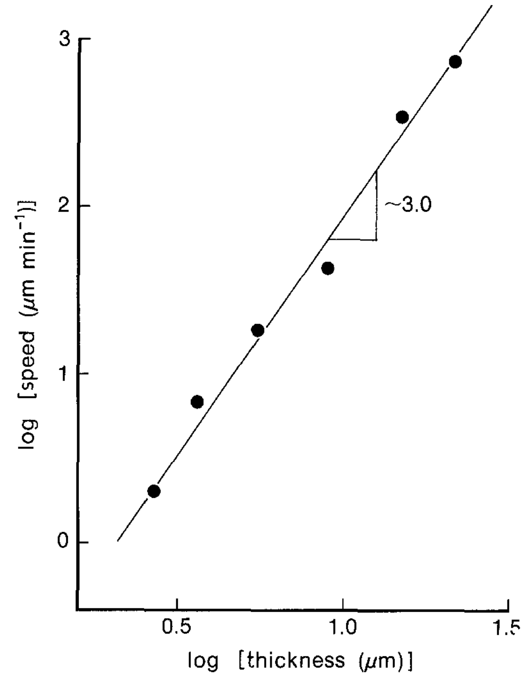

Figure 4 The same data as Fig. 3 plotted to show the power-law dependence of zone speed on film thickness.

constant speed with the speed a function of the film thickness, as shown in Fig. 3. The minimum (threshold) film thickness below which the zones did not grow was about 2 μm. From the analysis presented earlier it is evident that the zones growth rate was a function of $\tilde{G}$. This is consistent with the observation [1] that the opening of these zones on the film surface was independent of crack length. Also the fact that the width of the diffuse bright band along the zones (which was caused by photoelastic effects) was constant shows that the stress pattern round the zones was independent of crack length. There was a critical value of $\tilde{G}$ below which the zones did not grow, and above the critical value of the zone growth rate increased rapidly with $\tilde{G}$. Fig. 4 shows that over a considerable range of $\tilde{G}$ the zone growth rate went as $\tilde{G}^3$.

The results obtained here are very typical of environmental crack growth phenomena in polymers where, as mentioned above, the cracks often grow at a rate that increases rapidly with G as long as G is above a critical value. The deformation zones are not cracks but they do release a large portion of the stress in the film [1] so, not surprisingly, can be considered mechanically as very like cracks. In this way they are very different from crazes in free-standing sheets or films. A craze is mechanically quite unlike a crack in the sense that the stress across a craze is very similar to the stress in the uncrazed portions of the sample; crazes release very little of the stress in the sample. For this reason crazes tend to grow at a constant rate, that depends on the film stress, in free-standing films that experience a constant remote stress [5]. In a similar situation cracks grow at steadily increasing rates, as here G increases with crack length. Craze growth rates cannot be described by considering them as cracks, calculating the G relevant for the crack length and assuming that G controls the growth rate.

The analysis and experimental result presented above show that one would expect that a thin adhered film that is under tension is more likely to crack as the film thickness is increased. Thus a simple way to classify the aggressiveness of any environment for a particular polymer is to find the minimum film thickness in which cracks will propagate. It is assumed here that the substrate and film processing conditions are kept constant so that the film stress is independent of film thickness. Alternatively, given a polymer–substrate–environment combination one can find the maximum film thickness that is safe to use.

5. Conclusions

We have shown that the average strain energy release rate, $\tilde{G}$, in thin films that adhere to a rigid substrate is independent of crack length but a linear function of the film thickness at constant film stress. For typical film thickness $\tilde{G}$ is small and cracking is unlikely in polymer films, unless the film is very brittle or there is some environmental agent present. Crack-like deformation zones have previously been shown to occur in a thermoplastic polyimide when it is immersed in xylene. The growth rate of these zones was constant, independent of their length, but was found to increase rapidly with film thickness. These results are consistent with the growth rate being controlled by $\tilde{G}$.

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Received 22 March
and accepted 4 September 1989