JOURNAL OF MATERIALS SCIENCE 11 (1976) 199–205

The surface cracking of glassy polymers under a sliding spherical indenter

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Glassy polymers crack under a sliding hard spherical indenter in a way that is observed in other brittle materials. A series of curved cracks concave to the wake of the indenter are formed and these can penetrate to a depth of a few hundredths of a millimetre. With polystyrene the additional stress imposed by sliding reduces the critical load to fracture under normal loading conditions by 95% and the presence of an active environment, methanol, reduced the critical fracture load for sliding by 83%. Other glassy polymers which are generally considered tough, cracked in the presence of agents which could promote environmental stress cracking. The stress necessary to cause cracking and the crack size obeyed laws pertaining to fracture under elastic stress conditions. Although the flaws observed are referred to as cracks it is recognized that they could possibly be crazes. The introduction of surface damage in the form of cracks or crazes is important practically, since the inadvertent scratching or abrasion of the polymer surfaces may introduce flaws which under normally acceptable stress-environmental conditions could lead to failure. It is also noted that the flaws are detrimental to the polymer's optical properties.

1. Introduction

The symmetrical stress field formed in a plane surfaced body indented by a normally loaded sphere becomes distorted when a tangential force is applied. Normal loading gives a stress field containing a compressive volume adjacent to and beneath the area of contact, surrounded by a region containing tensile stresses. These tensile stresses are greatest at the surface and reach a maximum at the contact boundary between the sphere and the flat. If the plane surface is brittle and the indenter hard then a ring crack will be produced at the periphery of the contact region when a critical load is applied. Further loading will cause the crack to extend down into the material forming a truncated cone crack. The application of a tangential force to the normally loaded surfaces decreases the tangential stress at the front of the sliding sphere and increases it at the rear. The result of this is to decrease the critical normal load for cracking and produce in the sliding track a series of parallel curved cracks concave to the wake of the indenter.

The principles and application of indentation fracture has recently been reviewed by Lawn and Wilshaw [1]. It clearly illustrates the importance of the stress system occurring under a sliding spherical indenter as it is basic to many tribological processes such as abrasion, erosion, polishing, scratching and wear. Surface cracking under laboratory conditions using a sliding indenter has been observed in a number of brittle materials, inorganic glasses [2–6], diamond [7–9] and various ionic single crystals [8–11].

In this investigation the surface damage produced during sliding contact has been extended to a class of materials that can be brittle, the glassy polymers. When subjected to the normal tensile test polystyrene and polymethylmethacrylate fracture in a brittle fashion while polyvinylchloride, polycarbonate and polysulphone suffer from plastic instability and neck. These latter tough polymers are, however, notch sensitive and are susceptible to environmental stress cracking so that they can fail by brittle fracture. Because of the importance of fracture in any commercial material, considerable effort has been made to understand the mode of fracture in glassy polymers and establish the principles involved. It has emerged from these studies that fracture in the glassy polymers is associated with plastic deformation on a microscopical scale in the form of bands of microvoids. These bands, termed crazes, form at right angles to the principal tensile stress and it is along these that the fracture crack travels. One of the most serious problems encountered practically is the promotion of craze formation in active environments of organic solvents at stresses very much lower than in air. The introduction of surface flaws is of considerable importance as it is from these surface stress raisers that crazes can nucleate and under the combined action of stress and environment extremely small cracks can grow leading to catastrophic failure.

2. Experimental details

The apparatus used in these tests was a modified Hounsfield Tensometer. In this, the lower polymer specimen is mounted on a carriage which can be slid horizontally at a constant velocity, 1.5 mm min^{-1} and the upper spherical indenter is fixed via a hinged arm to a spring beam. Prior calibration of the spring beam for deflection versus load allows the tangential force exerted on the indenter to be measured continuously throughout the tests. Steel ball-bearing indenters (1.5, 3.2, 4.7, 6.3 mm radius) were directly loaded against the lower sample. Polymer samples, 6 cm × 1 cm, were cut from 0.6 cm thick sheets of polystyrene (G. P. Carinex, Shell Chemical Industries Ltd), polymethylmethacrylate (Perspex, Imperial Chemical Industries Ltd), polycarbonate (Lexan, General Electric), polyvinylchloride (Darvic, Imperial Chemical Industries Ltd) and polysulphone (Union Carbide Corporation). The highly polished as-received surface of the polymer samples were repolished with wet gamma-alumina, to remove contamination, washed in water and dried with warm air. The steel balls were thoroughly degreased and cleaned ultrasonically. For tests involving a liquid environment a metal bath is inserted between the polymer sample and the sliding carriage; in this, 5 cm^3 liquid was sufficient to cover the polymer surface to a depth of 3 mm. Examination of the track produced by the sliding indenter was made with transmitted light optical microscopy and scanning electron microscopy. Specimens examined in the scanning electron microscope were coated with a thin layer of vacuum-deposited gold–40% palladium alloy to prevent charging.

3. Experimental observations

3.1. Surface cracking in air

At low loads no permanent damage to the polymer surfaces occurred. As the load was increased surface damage began to appear in a form dependent on the individual polymer. Only with polystyrene was the surface roughening followed by the formation of cracks. When the load was sufficient to give a continuous track of surface roughness curved cracks often appeared at the start of the track. At loads just in excess of this a continuous row of parallel cracks concave to the wake of the indenter was formed throughout the length of the track (Fig. 1). As the cracks are formed at the rear of the sliding indenter, they are seen to start at the outer edge of contact at the beginning of the track and finish at the inner edge of contact at the end of the track. Increasing the load above the critical level necessary to produce cracking increases the crack breadth only slightly but the distance between cracks decreases significantly. A measure of crack depth was obtained by polishing away the damaged surface until the cracks become invisible and then measuring the decrease in specimen thickness. For a normal load of 18.5 kg on a 6.3 mm radius ball the depth of the cracks was 60 μm. Repeated uni-

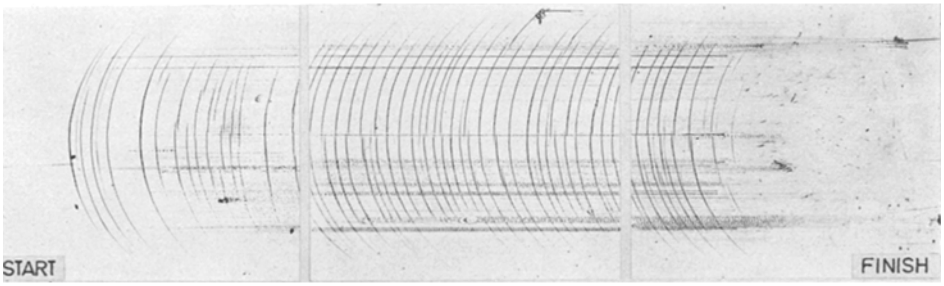

Figure 1 Track produced by 6.3 mm radius steel ball on polystyrene in air. Load 18.5 kg. Track width 1.2 mm.

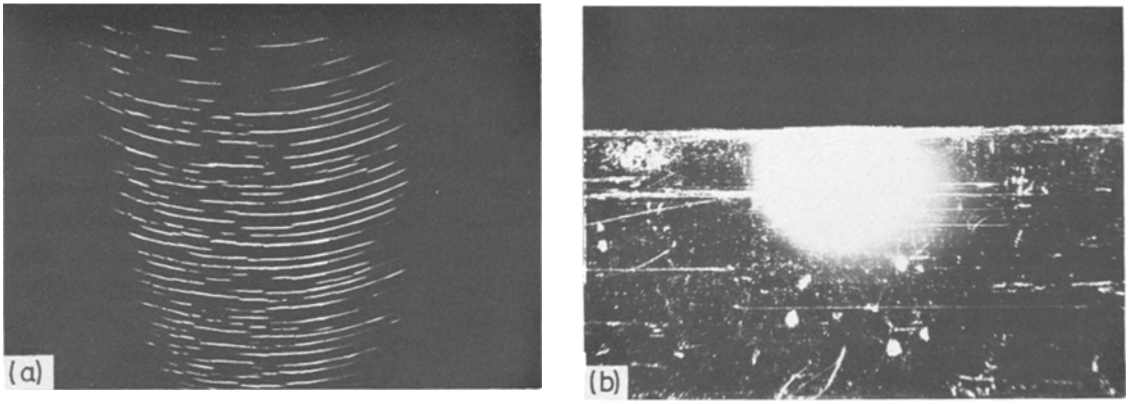

Figure 2 Track produced by 6.3 mm radius steel ball on polystyrene in air. Load 18.5 kg. Track width 1.2 mm. (a) Oblique illumination. (b) Transverse cross-section, dark field.

directional sliding over the same track increased the crack penetration, and for ten passes at the above load their depth was 90 μm. Crack penetration becomes visible with oblique illumination (Fig. 2a), and dark-field microscopy of polished transverse cross-sections (Fig. 2b) illustrated their ability to scatter light.

The optical examination of the polystyrene samples was made with transmitted light because it was found that the cracks were not visible on the roughened surface and it was necessary to focus the microscope a little below the surface to see them. This was verified in the scanning electron microscope examination which revealed no cracks in the considerably roughened surface of the sliding track. An examination by scanning electron microscopy of scratches produced on the polymer surface by a sharp point showed that in the case of polymethylmethacrylate, cracks which curved concave to the direction of scratching were produced (Fig. 3).

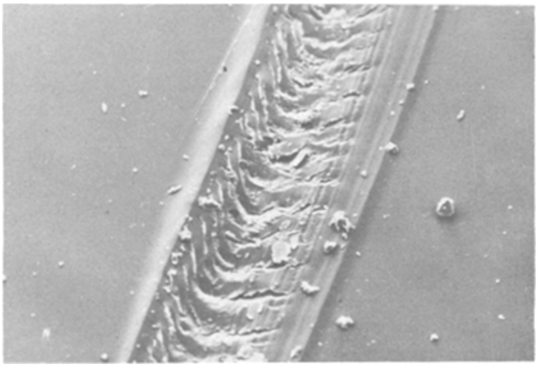

Figure 3 Scanning electron micrograph of a scratch. 1.4 μm width, on polymethylmethacrylate. Scratch direction ↑.

3.2. Surface cracking in an active environment

In these tests organic liquids which are known to promote environmental cracking were chosen for the individual polymers. Surface cracking was promoted in polystyrene in the presence of methanol and the critical cracking load was 83% lower than that in air (Table I). Cracking was also observed in the other four polymers when the appropriate environment was present (Fig. 4). The coefficients of friction obtained were similar to those in air, except in the case of polyvinylchloride which was reduced by 60%. Scanning electron microscopy of the sliding tracks showed that the curved cracks were only visible on the surfaces of polymethylmethacrylate and polysulphone (Fig. 5). The surfaces of the rest were considerably roughened and that of polyvinylchloride was also covered by a large amount of fine debris.

3.3. The critical stress necessary for surface cracking

The modified elastic stress field produced in a plane surface when indented by a sliding hard sphere has been solved analytically by Hamilton and Goodman [12]. From this the largest tensile stress occurring at the rear of the indenter has been expressed by Gilroy and Hirst [4] in the form:

$$\sigma = \frac{3P}{2\pi a^2}\left[\frac{1}{3}(1-2\nu_1)+\mu\pi\frac{(4+\nu_1)}{8}\right] \quad (1)$$

where P is the normal loaded, ν_1 is Poisson's ratio for the indented material and μ is the coefficient of friction. The radius of the circle of contact, a, is

TABLE I Critical conditions for the surface cracking of glassy polymers indented by a 6.3 mm radius steel ball sliding at a speed of 1.5 mm min^{-1}

Polymer	Environment	Critical load (kg)	Coefficient of friction	Track width (mm)		Calculated fracture stress (MN m^{-2})
				Measured	Calculated	
Polystyrene	Air	2.4	0.27	0.70	0.64	54
Polystyrene	Methanol	0.4	0.33	0.44	0.34	30
Polymethylmethacrylate	Methanol	2.4	0.39	0.62	0.64	60
Polyvinylchloride	Toluene	22.8	0.04	1.48	1.32	21
Polycarbonate	Carbon tetrachloride	1.1	0.42	0.58	0.56	37
Polysulphone	Diethyl ether	0.7	0.33	0.52	0.48	22

Critical load for cracking polystyrene in air under a normally loaded 6.3 mm radius steel ball = 45.6 kg.

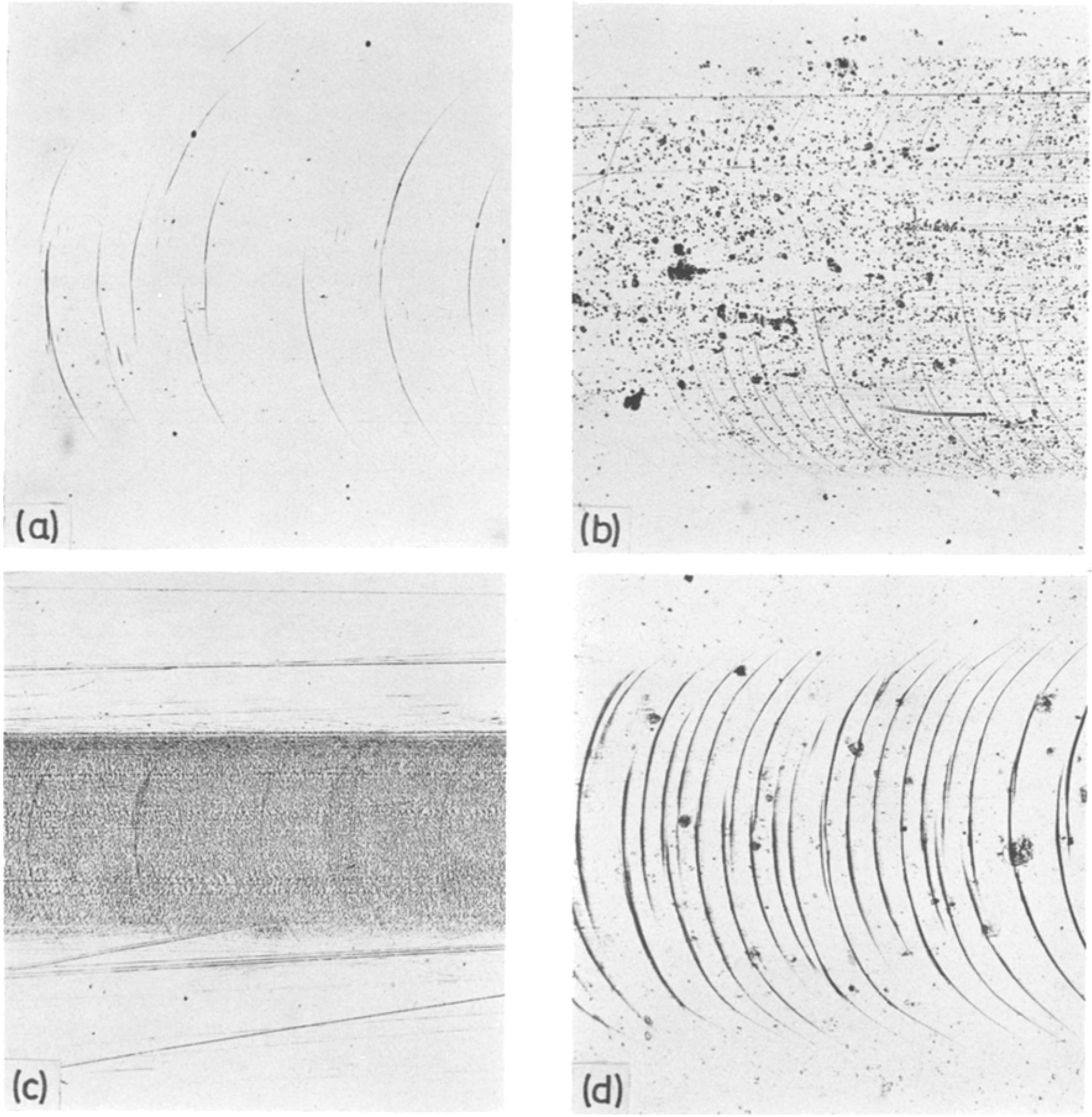

Figure 4 Track produced by 6.3 mm radius steel ball on glassy polymers under liquid environments. (a) Polymethylmethacrylate under methanol. Load 21.6 kg. Track width 1.2 mm. (b) Polyvinylchloride under toluene. Load 22.8 kg. Track width 1.5 mm. (c) Polycarbonate under carbon tetrachloride. Load 1.1 kg. Track width 0.5 mm. (d) Polysulphone under diethyl ether. Load 6.6 kg. Track width 1.1 mm.

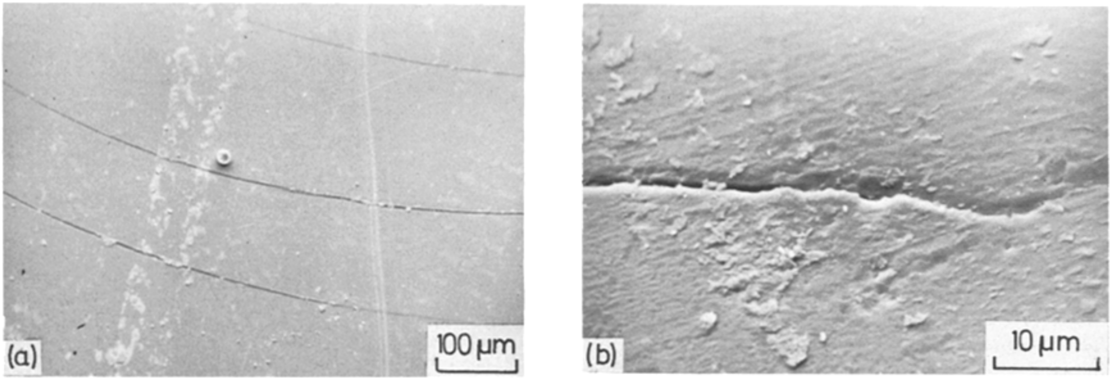

Figure 5 Scanning electron micrograph of a track produced by 6.3 mm radius steel ball on: (a) polymethylmethacrylate under methanol. Load 18.5 kg; (b) polysulphone under diethyl ether. Load 6.6 kg. Specimen tilt angle 45°.

given by Hertz' classical analysis as:

$$a^3 = \frac{3}{4} Pr \left(\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right) \tag{2}$$

where r is the indenter radius and E_1, ν_1 and E_2, ν_2 are Young's modulus and Poisson's ratio of the solid and the indenter respectively. Calculated values of the maximum tensile stress and track widths at the critical loads for crack formation are given in Table I.

The critical loads required to cause surface cracking in polystyrene in air were measured for indenters of various radii. These results, presented in Fig. 6, show the critical load to be directly proportional to the radius of the indenter up to a radius of 6.3 mm.

4. Discussion

The curved cracks formed behind a sliding spherical indenter on the surface of the glassy polymers investigated have the same configuration as those produced on inorganic glasses subjected to the same stress system. It has been predicted theoretically by Lawn [3] that the introduction of a sliding motion to a normally loaded spherical indenter on a brittle surface significantly lowers the normal load required to produce cracking. This prediction has been verified experimentally on glass [4, 6], titanium carbide [13] and in this work on polystyrene. Polystyrene was the only polymer tested which cracked in air under both normal and sliding loads. Sliding reduced the critical load for cracking by 95% of that under normal loading for the 6.3 mm radius indenter. This reduction in critical load is of

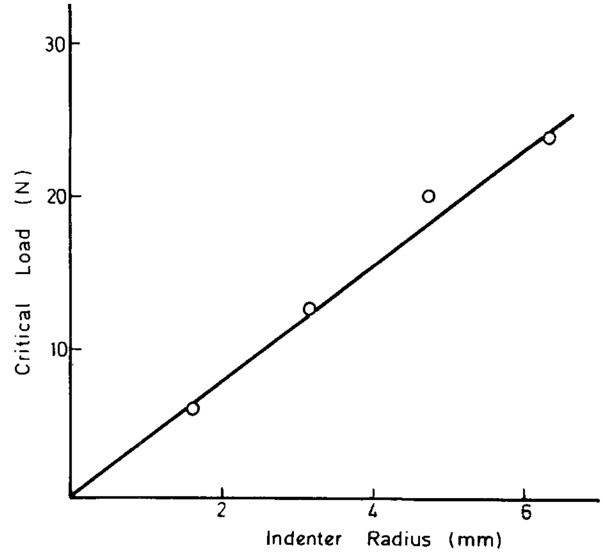

Figure 6 Critical load to produce cracks on the surface of polystyrene in air plotted against the radius of the indenter.

the same order as that observed with inorganic glass by Gilroy and Hirst [4] when the coefficient of friction between the glass and the sliding steel ball was 0.3.

The empirical relationship, discovered by Auerbach (1891), states that the critical load to fracture glass is directly proportional to the radius of the indenter and has been shown by Tillett [14] to be limited to indenters below 30 mm radius under normal loading conditions. When sliding of the indenter is involved, the limiting size of the indenter up to which Auerbach's law is obeyed is reduced. This reduction has been observed for glass [4, 6] and titanium carbide [13] to depend on the coefficient of friction of the sliding surfaces; the limiting size diminishes with increasing coefficient of friction. Gilroy and Hirst [4] found that for a steel indenter on glass the linear range proportionality was not observed above a coefficient of friction of 0.5. The results reported have shown that Auerbach's law is obeyed with a sliding steel indenter on polystyrene up to an indenter radius of 6.3 mm when the coefficient of friction was 0.27.

There is some evidence, even with inorganic glasses, of plastic deformation [2] on the surface of the sliding track which tends to invalidate the application of the Hertzian elastic stress field equation. The glassy polymers did show plastic grooving at high loads but at the critical loads for fracture only polyvinylchloride showed any appreciable indentation. On a micro scale, however, all the polymers exhibited some plastic deformation. This was particularly noticeable with polystyrene where a layer of polymer covered the surface cracks and a small amount of polymer was observed on the surface of the steel indenter. Calculations using Archard's equation [15] suggest that frictional heating increased the polymer surface temperature above its softening temperature, 80° C, allowing it to be readily deformed and also removed by adhesive transfer. The micro flow does not significantly affect the Hertzian analysis as good agreement was obtained between the measured and calculated track widths for all the polymers. The calculated maximum tensile stresses to cause fracture under the sliding indenter (Equation 2), are of the right order when compared to those observed under normal tensile tests. For example, the tensile test fracture stresses for polystyrene in air and methanol are 42 and 27 MN m^{-2} respectively while those calculated from these tests are 54 and 30 MN m^{-2} respectively. In the case of the stronger, tougher polymer, polysulphone, which has a tensile yield stress of 85 MN m^{-2}, an environment of diethyl ether induces brittle fracture and a failure stress of 28 MN m^{-2}. This compared favourably with a value of 22 MN m^{-2} computed from the sliding indenter tests.

One of the most important problems that has to be recognized in the use of glassy polymers is their susceptibility to environmental stress cracking in the presence of a wide variety of organic agents. The occurrence of environmentally induced brittle failures can drastically reduce the strength of the polymer well below the designed working stress. Experimental evidence [16] has shown that inherent surface flaws are extremely important in the brittle fracture of glassy polymers and it is suggested that possibly surface cracks a few hundredths of a millimetre in length can grow by the action of environment and applied or residual stresses. In the few results presented here it has been shown that cracking under tangential Hertzian stresses is promoted by the presence of an active environment. This embrittlement is due to the penetration of the environment into the polymer, inducing craze and crack formation at inherent stress raisers. The curved flaws observed in this work have been termed cracks because they are formed under elastic conditions which produce cracks in other brittle materials. It must, however, be recognized that brittle fracture in glassy polymers is preceded by craze formation so it is possible that the flaws are crazes. The important factor is that stress-raising flaws which are considerably larger than those present in the highly polished as-received surface have been introduced as potential nuclei for crack growth.

It is obvious that the absorption of the liquid environment will change the properties of the polymer surfaces. However, under the high normal loading conditions of these experiments, no significant change in sliding friction was observed by the introduction of the liquid environment. Polyvinylchloride was the exception, its test environment, toluene, induced the formation of excessive amounts of loose debris between the sliding surfaces reducing the coefficient of friction in air by 60%.

The transparency of the glassy polymers is often used to advantage particularly with polystyrene and polymethylmethacrylate which have excellent optical properties. They are, however, susceptible to scratching which can drastically reduce the light transmission through optical systems such as lenses and light pipes. These results have illustrated that the flaws nucleated in the scratch track, are extremely effective in scattering transmitted light.

Acknowledgement

I should like to thank Professor G.C. Wood for his help and encouragement throughout this work.

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Received 21 July and accepted 28 August 1975.