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Environmental effects of silicone oil on mechanical properties of low and high molecular weight PMMA

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The influence of a silicone oil environment on deformation modes and tensile behaviour of poly(methylmethacrylate) were investigated. Tests were made on samples coated with oils of varying viscosity, ranging from 5 to 1000 cSt. To investigate the effects of polymer molecular weight on environmentally induced craze growth and stability, tests were conducted on an extruded grade of relatively low molecular weight and on a cast grade of high molecular weight. All of the silicone oils acted as crazing agents and tensile strength and ductility were reduced in value as the viscosity of the oil was lowered. The low molecular weight polymer failed in a brittle manner in all environments but developed earlier and more intensive crazing as the liquid viscosity was reduced. The high molecular weight material underwent a ductile–brittle transition when the environment was changed from air to low viscosity silicone oils. The flow of the oil into existing flaws and crazes was sufficiently impeded at 1000 cSt viscosity so that both necking and surface crazing were observed under these conditions. To illustrate the various deformation and fracture modes that were observed, micrographs of free and fracture surfaces are presented and discussed.

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1. Introduction

Liquids may act as crazing agents for glassy polymers subject to tensile or bending stresses even though, in the absence of stress, there is little if any sorption of the liquid upon prolonged immersion of the polymer in the environmental media [1, 2]. For example, even in a hydrophobic polymer like polystyrene (PS), a small amount of sorbed water can cause reduction in both crazing and fracture stress [3]. In the more polar polymer, poly(methylmethacrylate) (PMMA), tensile testing in a water environment [4], as well as testing of specimens containing various amounts of sorbed water [5], deleteriously affects the mechanical properties.

The extent to which a glassy polymer is affected by environmental media depends on the ability of the medium to penetrate and plasticize the tips of existing surface flaws and thus to initiate stress-induced crazing [1, 6, 7]. Once crazes have formed, and this apparently requires some minimum value, K_m, of the stress intensity factor [8], their porous structure will permit relatively easy access of liquids to the craze tip, provided the penetrant molecule is not too large or the liquid viscosity too great [8, 9]. The ability of the environmental agent to plasticise is, in turn, dependent to a large extent upon the solubility parameter of the fluid and the closeness of this value to that of the polymer [1, 10, 11]. However, even when the difference in solubility values is quite large, as is the case for the polystyrene/water system, there may still be some degree of local plasticization, particularly at points of high stress concentration as at surface flaws or craze or crack tips.

In the present study, we are concerned with the

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possible effects of silicone oil, a liquid frequently used as the pressure medium in study of the effects of pressure on the properties of polymers [12], on the crazing, deformation and fracture behaviour of PMMA. On the basis of solubility parameter considerations one would expect little interaction between silicone oil and this polymer. However, in another glassy polymer, PS, silicone oil was found to have a detrimental effect on both tensile and fatigue behaviour even though there is no absorption of the oil in unstressed samples even after immersion for hundreds of hours [13, 14]. Also, in polyethylene, the time to fracture of tensile creep samples is reduced when samples are tested in a silicone oil environment [15].

The effects of penetrant size on craze formation and fracture in PMMA are examined by carrying out experiments using silicone oils of varying viscosity as the environmental medium. The influence of alcohols and other liquids on the craze initiation stress in a commercial PMMA of unknown molecular weight has been reported [2]. In this investigation the solvents used had varying solubility parameters and varying viscosities. Hence the effect of each of these factors was difficult to determine. For example, the craze initiation stress of PMMA in ethanol was found to be approximately the same as that in methanol despite the higher molecular weight and higher viscosity of the ethanol. Evidently, the expected effect of a higher craze stress with a higher viscosity was more than compensated by the lower solubility parameter value and greater chemical compatibility of the ethanol.

The environmental effects of silicone oil on PMMA may also be affected by the polymer molecular weight. To investigate this possibility, tests have been carried out on both a low molecular weight (LMW) polymer and on a high molecular weight (HMW) polymer. Although certain properties, such as the glass transition temperature are little affected by molecular weight above some critical value, it is known that changes in molecular weight can appreciably affect other properties. For example it is reported to have significant effects on fracture behaviour [7, 16] and on the stability of both intrinsic crazes [17–19] and environmental crazes [20, 21].

2. Experimental details

Two grades of PMMA were investigated. One was an extrusion grade of low molecular weight and the other a cast grade of relatively high molecular weight. The various molecular weight averages of these two materials, as determined by gel permeation chromatography, are given in Table I. Also given for each material are the densities, as determined by a density gradient column, and Young's modulus, as determined from strain gauge and load measurements on an Instron servohydraulic apparatus. Both materials were received in the form of rods, 1.27 cm diameter and test specimens were machined from these rods. A few tests were made on cylindrical specimens having a gauge length of 1.27 cm and a diameter of 5.08 mm but most test specimens were rectangular in cross section, with the waisted gauge section having a length of 1.27 cm, a width of 6.3 mm and a thickness of 3.15 mm. No significant differences in behaviour of the two types of specimen were noted. Before testing, all specimens were carefully polished, washed in distilled water, and dried in a vacuum oven at 50° C for 2 h.

TABLE I Characteristics of the PMMA test materials

Property	LMW polymer	HMW polymer
$\bar{M}_n$	38 900	359 300
$\bar{M}_w$	79 300	665 300
$\bar{M}_z$	157 200	1 000 100
Density (g cm^{-3})	1.17	1.18
Elastic modulus (GPa)	2.93	2.93

Tensile tests were carried out at a displacement rate of 0.254 mm min^{-1} unless otherwise noted. Nominal stress–nominal strain curves were determined from the load displacement measurements. Tests were made on uncoated samples and on samples coated, prior to testing, with silicone oils of varying viscosity, ranging from 5 to 1000 cSt. For each test condition two or three separate samples were tested. Recorded values of yield and fracture stress, and of tensile elongation to fracture, are average values.

The stress for craze initiation was determined by shining a light source at an acute angle to the specimen axis and recording the light reflected by stress-induced crazes [22]. This reflected light was received by a photodetector set up on the opposite side of the specimen at the same angle to the specimen axis as the light source. The intensity of the reflected light was monitored as a function of time, or displacement, and the craze initiation stress σ_{ci}, was taken as that stress at which the intensity increased above its background value [23]. There was appreciable scatter in the values

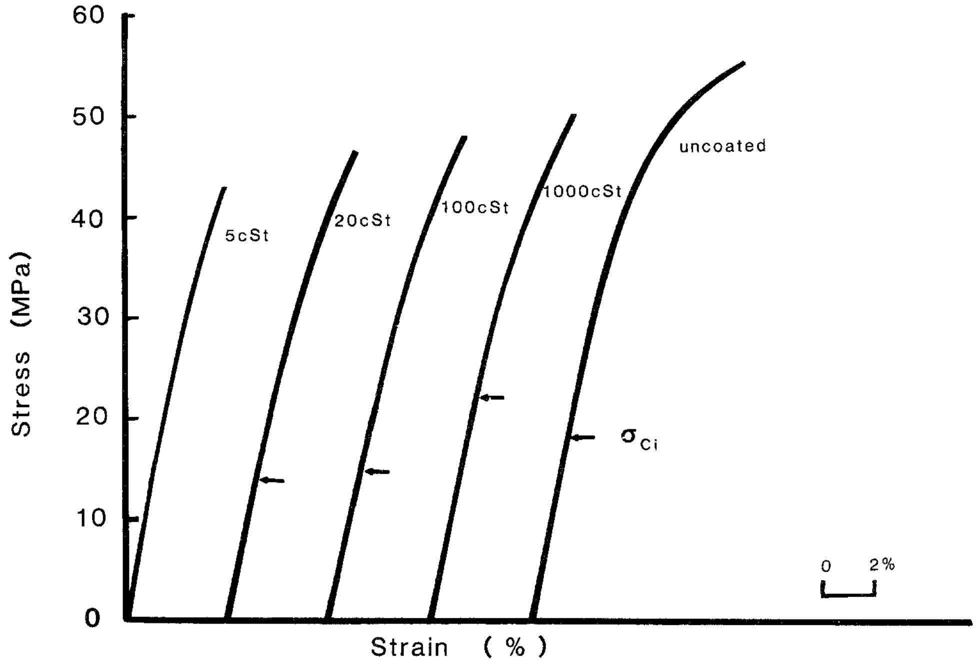

Figure 1 Stress–strain curves of LMW extruded PMMA; samples coated with silicone oils of varying viscosity.

recorded for individual specimens, due to variations in surface smoothness. Hence the tabulated values of σ_{ci} are only an approximate indication for the stress to nucleate crazes. Nevertheless, a comparison of the average values obtained from several measurements for each type of silicone oil environment should give some indication of the manner in which craze initiation is affected by the viscosity of the environmental medium.

Observations of the surface morphology for both lateral surfaces and fracture surfaces were made visually, by optical means, and by means of an Etec scanning electron microscope (SEM). Prior to SEM examination, the desired surfaces were coated with a thin film of gold–palladium.

3. Results and discussion

3.1. Environmental effects on low molecular weight PMMA

The results of the tensile tests are presented in Table II for both the LMW polymer and the HMW polymer. We discuss first the effects of the environmental media on the LMW extruded PMMA samples. All of these samples, whether coated or not, exhibited brittle fracture in the sense that they fractured prior to general yield. The stress–strain curves for these samples are shown in Fig. 1. It is evident from these graphs, as well as from the data of Table II, that all of the oils are environmentally damaging and they become more so as the oil viscosity is lowered. The situation is thus somewhat different in PMMA than in PS. In the latter material, no detrimental effect was observed on the tensile response when samples were tested in a 500 cSt oil environment [13].

The arrows on the stress–strain curves of Fig. 1 depict the average value of the craze initiation stress, as determined by the light reflection method. These craze initiation stresses fall below the stress value where crazes are first visually observed, as well as below the stress value where non-linearity is noted. The light reflection method is thus a more sensitive indicator of the onset of crazing in PMMA than either of these other methods. A similar conclusion was drawn from tests on PS [14, 23]. The test results of Fig. 1 show that the

TABLE II Tensile properties of LMW and HMW grades of PMMA tested in various silicone oil environments

Viscosity of oil coating (cSt)	Maximum tensile stress		Strain to fracture	
	LMW (MPa)	HMW (MPa)	LMW (%)	HMW (%)
5	43.0	55.3	4.4	7.6
20	46.7	55.7	5.2	8.6
100	48.1	59.4	5.5	11.8
1000	50.4	59.6	5.6	16.9
Uncoated	55.2	61.2	8.9	64.1

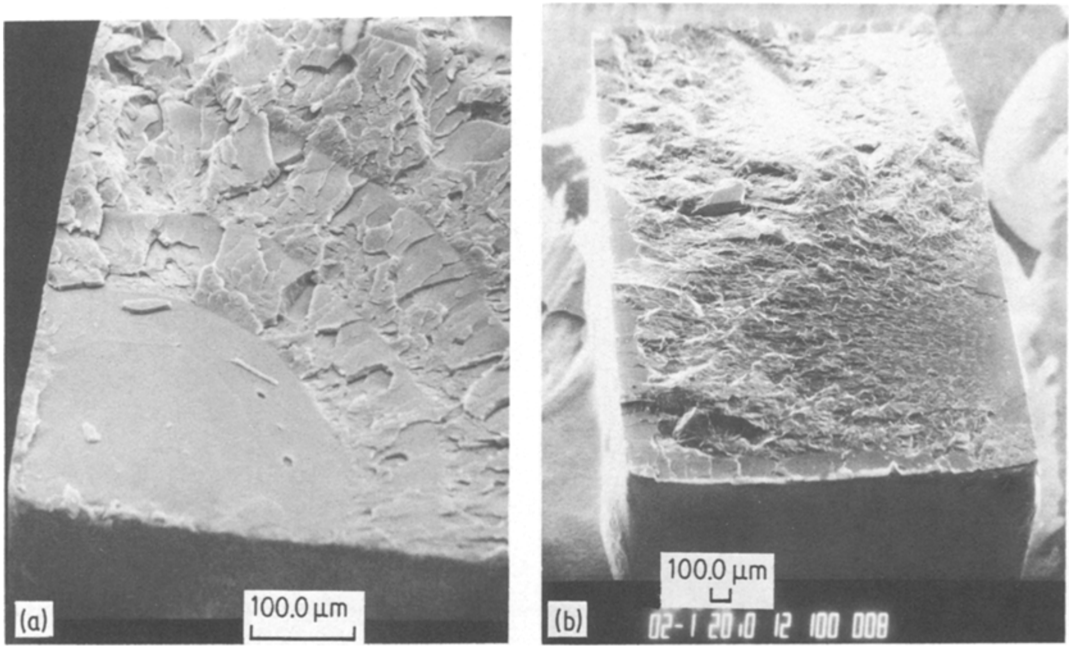

Figure 2(a) Portion of the tensile fracture surface of uncoated LMW polymer; sample tested at 0.508 mm min^{-1}. (b) Fracture surface of sample of LMW polymer coated with a 5 cSt silicone oil.

craze initiation stress, as well as the fracture stress, is sensitive to the surface environment; and, as the viscosity of the oil is increased, the craze initiation stress rises.

The higher σ_{ci} value for the samples coated with the 1000 cSt oil as compared to uncoated samples may be an artifact, in view of the limited number of samples investigated and the difficulty of obtaining uniform surfaces even after careful polishing. Another possibility is that the high viscosity coatings may themselves provide, at least at low stress amplitudes where crazing is first noted, some degree of protection against other possible contaminants or crazing agents in the air. This possibility was invoked in connection with the action of high viscosity oils on craze initiation in polystyrene [14].

Our test results appear to be in general accord with the ideas of Williams and co-workers [2, 8, 24]. They predict, on the assumption that a craze could be modelled as a uniform porous material, that craze velocity should be inversely proportional to the viscosity of the fluid medium. In our experiments where solubility parameter considerations are not the determining factor, the viscosity of the liquid medium appears to be the governing parameter in assessing environmentally induced changes in mechanical properties. As the viscosity is lowered, craze initiation occurs at lower stress values, more surface crazes are developed, and craze growth is fostered. Also, due to plasticization effects of the liquid on the craze fibrils, craze strength is lowered and fracture strength is reduced.

Observations of the external surfaces of the extruded PMMA samples during testing and after fracture reveal that the only observable mode of deformation is crazing. For the uncoated samples surface crazes were generally few in number while for the samples tested in the silicone oil environment there was a higher density of crazes and the average craze length was greater as the viscosity was reduced. Fracture occurred when a microcrack formed in one of the crazes, after some critical level of damage had been reached. The crack then rapidly propagated through the remaining material.

The tensile fracture surface morphology in the region near the fracture source is shown in Fig. 2a for an uncoated rectangular sample; similar features are observed in cylindrical samples. The fracture surface morphology does not differ significantly from that shown in Fig. 2a for the oil-coated samples. However, for the very low viscosity oils, there is some evidence, as shown by Fig. 2b, of a thin penetration layer extending in from all side surfaces. This feature was also noted in PS [14].

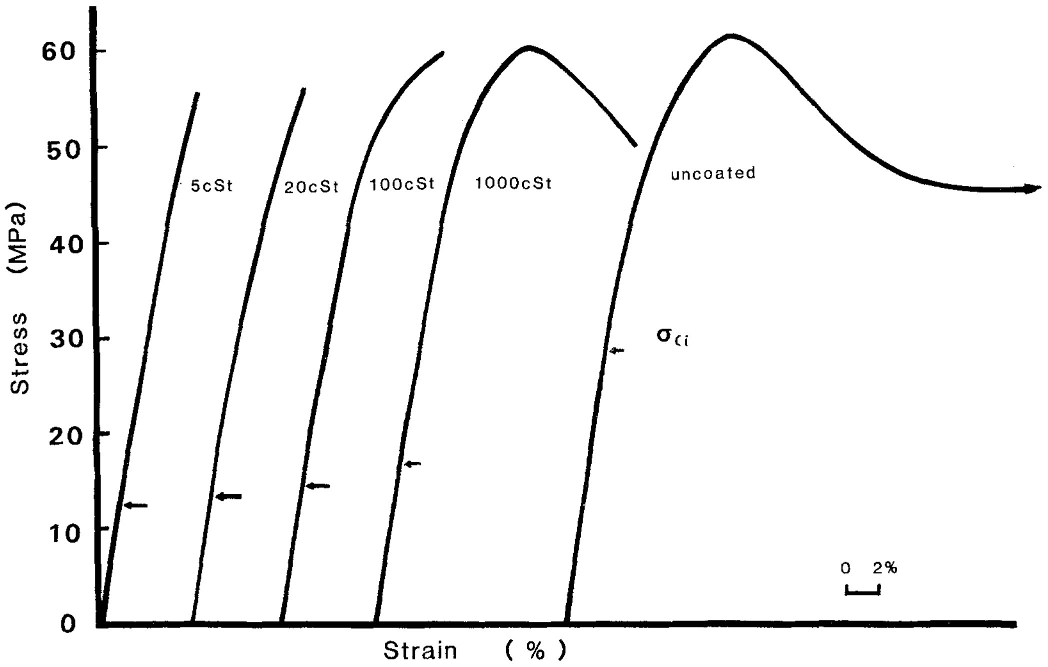

Figure 3 Stress–strain curves of HMW cast PMMA; samples coated with silicone oils of varying viscosity.

The principal features of the fracture morphology of these low molecular weight PMMA samples are: a small, relatively smooth, mirror zone surrounding the surface source, followed by several broad bands of varying texture, and then a rough mottled region. The smooth region represents the extent of craze growth prior to craze breakdown and rapid crack propagation. The broad bands of varying texture arise from the development of craze branching ahead of the crack tip once the crack velocity becomes high [25]. In these low molecular weight samples there is little evidence of parabolic markings on the fracture surface. Due, however, to increased craze branching and crack bifurcation as the crack advances, a definite widening of the damage layer in the direction of crack advance has been observed in most samples. These findings are in accord with the ideas of Chudnovsky and Moet [26] who suggest that growing cracks produce a surrounding damage zone that has a given width and shape rather than merely a given length.

It is concluded that the principal effects of the silicone oil environment on the LMW polymer are to cause earlier craze nucleation, more rapid craze growth, reduced craze stability and lower strains to fracture. These results arise from penetration and plasticization of the craze matter by the liquid environment. It is interesting to note that low viscosity silicone greases have been used as a shield against penetration of an environmental liquid in studies of stress and solvent crazing in notched PMMA specimens [21, 24]. From the results of the present study, it is suggested that such silicone coatings may themselves have an environmental effect on the stressed PMMA samples.

3.2. Environmental effects on high molecular weight PMMA

The influence of a silicone oil environment on the mechanical properties of the HMW polymer is shown by the stress–strain curves of Fig. 3 and by the tensile strength and tensile ductility data of Table II. The arrows on the curves represent the estimated craze initiation stresses. The observed effects of the oil environment on the HMW polymer are somewhat different than for the LMW polymer, although in both cases there is a decrease in the craze nucleation stress, in the maximum tensile strength, and in the strain to fracture with a decrease in viscosity of the oil. The percentage change in strength in going from the uncoated polymer to samples coated with the lowest viscosity oil is less than for the HMW polymer (9.6%) than for the LMW polymer (22%) but the reduction in strain to fracture is much greater for the HMW material. Nevertheless, for any given coating condition, the strain to fracture is greater for the high molecular weight material despite its higher tensile strength. This is clear evidence for a greater resistance of the HMW polymer to craze breakdown. The craze nucleation stresses, though clearly influenced by the oil viscosity, are not appreciably affected by the molecular weight (with the possible exception of the uncoated samples).

A striking effect in the testing of HMW polymer in the presence of silicone oils of varying viscosity is a change in deformation mode as the oil viscosity is reduced. Uncoated HMW samples, at the low speed of testing used in this investigation, are ductile and both necking and cold drawing are generally observed. Neither of these phenomena are found in the testing of the LMW polymer. Generally, PMMA is regarded as a semibrittle material with strains to fracture of 4 to 8% [27–29] although, in one study, onset of necking and plastic strains to about 20% were reported for a PMMA of unknown weight [47].

The observed change in deformation mode from brittle to ductile with increase in molecular weight is attributed to the greater degree of entanglement of the molecular coils in the high molecular weight material. This leads to an increase in craze stability, a decrease in craze velocity and a higher craze breakdown stress [21, 30]; as well as to a decrease in craze fibril extension ratio and an increase in the volume fraction of fibrils [31]. As a result shear modes of deformation become operative and tend to limit craze growth [4, 30]; hence large strains can be developed prior to fracture.

The ductile behaviour of the HMW polymer changes to a brittle mode when samples are tested in relatively low viscosity silicone oil environments. Transitions from a ductile to a brittle response in glassy polymers are frequently a result of lowering temperature or of increasing strain rate but here it is a result of the environmental fluid penetrating surface crazes, reducing their strength by plasticization, and causing earlier crack nucleation and fracture. As the viscosity of the liquid medium is lowered, interaction between molecular chains is reduced and this results, as noted by others [19, 32], in easier slippage of molecular entanglements. The driving force for liquid penetration into the porous craze is capillary pressure [21, 33].

As the viscosity of the liquid environment is raised, penetration and plasticization become less efficient; the resulting increase in craze stability may then be sufficient to overcome early craze breakdown and crack formation and permit shear modes of deformation to come into play. For the 1000 cSt oil, Fig. 3 shows that a yield maximum is reached and necking begins. However, failure occurs before the neck has stabilized indicating that even with this high viscosity oil coating there is some penetration into and weakening of the craze fibrils. Under the conditions of this experiment, and also for the uncoated samples, there is a close competition, at the temperature and strain rate of testing, between craze breakdown to form a crack and shear yielding to give plastic deformation. A higher strain rate or a slightly lower temperature could readily induce a ductile–brittle transition [4] and even small changes in the amount of water present in the samples could have an effect [5]. The greater durability of the HMW cast PMMA, as the data of Table II show, is attested by the fact that even when it is tested in a silicone oil environment having a viscosity of 100 cSt or more, it develops superior strength and ductility than the low molecular weight PMMA tested in an air environment.

The silicone oil environment induces in the cast PMMA some changes in surface deformation modes and in fracture surface morphology. In the uncoated material, an interesting plastic deformation mode, aside from the necking, is the development in the necked region of diamond shaped cavities on the surface of the specimen. Fig. 4 shows an SEM micrograph of such a cavity that developed in the cast PMMA on straining beyond yield. The cavity is quite large, with a width of about 15 μm. The inside walls are relatively smooth and the sides of the cavity have apparently separated by a tearing action. At higher magnification, flow lines are visible on the cavity walls. It is also evident, from the distortion of the machine and polishing lines in the vicinity of the cavity, that extensive shear deformation has occurred in this region. Other cavities, of generally similar shape but varying size, are also present in the drawn sample and eventually one of these becomes the fracture origin.

Diamond cavities, or truncated diamond cavities similar to those shown in Fig. 4, were first observed in polyvinylchloride (PVC) [34]. They were also observed in PMMA by Haward and co-workers [35] but only when tensile tests were carried out at elevated temperatures in the neighbourhood of 60 to 70° C. Evidently, the high molecular weight material used in the present study provides sufficient craze stability to permit

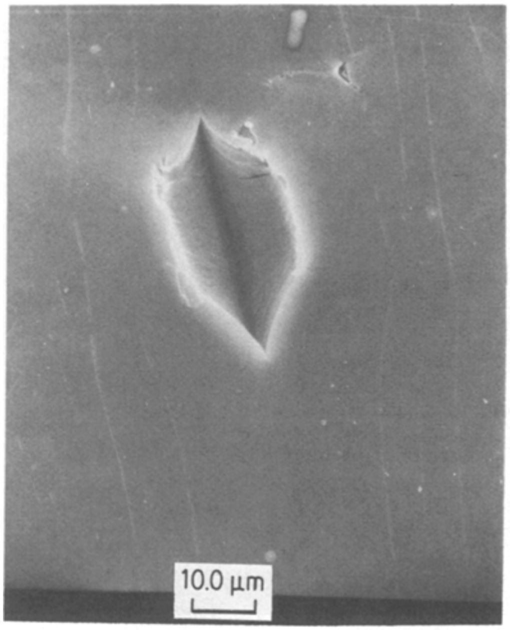

Figure 4 Free surface near to the fracture plane of uncoated HMW polymer; sample tested at 0.508 mm min^{-1}.

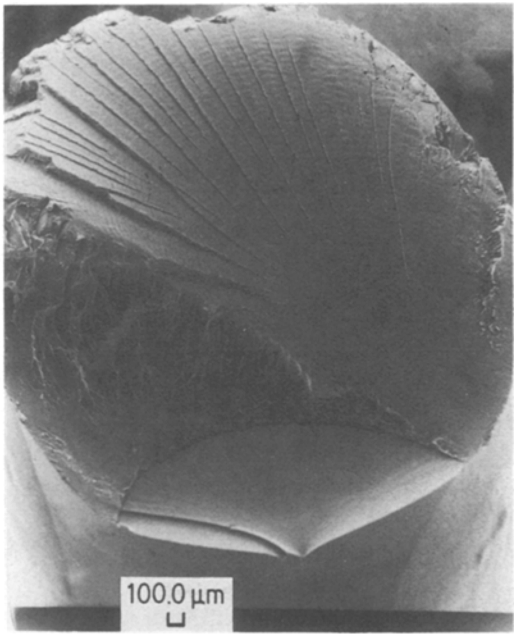

Figure 5 Fracture surface of uncoated HMW polymer; sample tested at 0.508 cm min^{-1}.

shear yielding and diamond cavity formation even at ambient temperature. Similar shaped cavities have been observed by Shen *et al.* [36] in a cast PMMA subject to fatigue loading. Here, however, the stress amplitude and the test frequency were sufficiently high to induce hysteresis temperature rises of 60° C or more.

For the uncoated HMW samples that fractured only after extensive plastic deformation, the fracture surfaces usually showed two distinct regions, one transverse to the load axis and one inclined to the load axis. A typical tensile fracture surface, in this instance for a round sample, is shown in Fig. 5. The principal features are the same for rectangular specimens. The source of the fracture is one (or more) of the surface diamond cavities and the comparatively smooth transverse region is indicative of fracture through a craze extending ahead of the diamond cavity. The inclined portion of the fracture surface, indicative of shear type failure, developed later. Views of the lateral surface of these specimens show the presence of shear deformation bands intersecting the inclined portion of the fracture surface.

In the presence of a silicone oil environment, the dominant deformation mode of the HMW polymer becomes crazing. For tests made with an oil coating of viscosity 100 cSt or less, the fracture surface, as depicted by Fig. 6 for a sample coated with a 5 cSt oil, was transverse to the stress axis and there was no indication of necking or of diamond-shaped surface cavities. The fracture morphology, is quite different from that of the LMW material tested in a similar environment. In the HMW material, the entire fracture surface is much smoother and much of the fracture surface is covered with numerous parabolic or conic features. These arise from interaction between the primary crack and secondary cracks nucleated at heterogeneities ahead of the primary crack [1].

For the cast PMMA samples tested in the high viscosity oil of 1000 cSt, it was observed that shear deformation and necking, as well as crazing, were present. An SEM picture of a free surface region near to the fracture surface is shown in Fig. 7. Many surface crazes and many small cavities are visible. The cavities appear to develop near the centre of existing crazes and gradually, as strain is increased, they widen and take on the characteristic diamond, or truncated diamond, shape. Sometimes several cavities form adjacent to one another and coalesce. Crazes nearby these cavities are distorted by the localized stress fields. Eventually, fracture occurs by crack propagation from one of the larger cavities. Features similar to these noted here in HMW-PMMA have also been observed in PVC samples tested in an air environment at ambient temperature [34]. In the high molecular

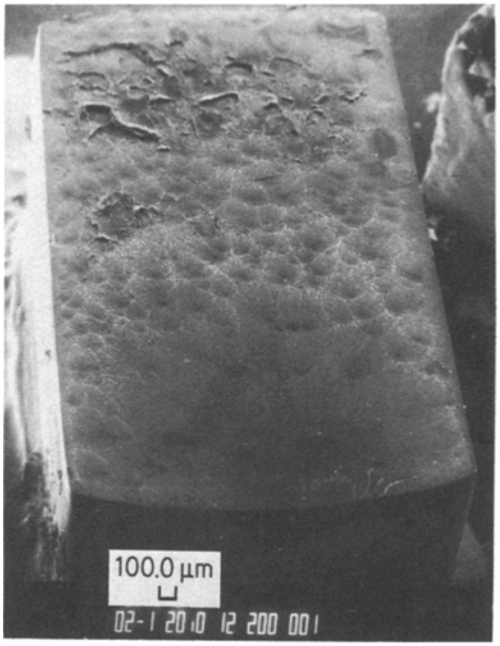

Figure 6 Fracture surface of sample of HMW polymer coated with a 5 cSt silicone oil.

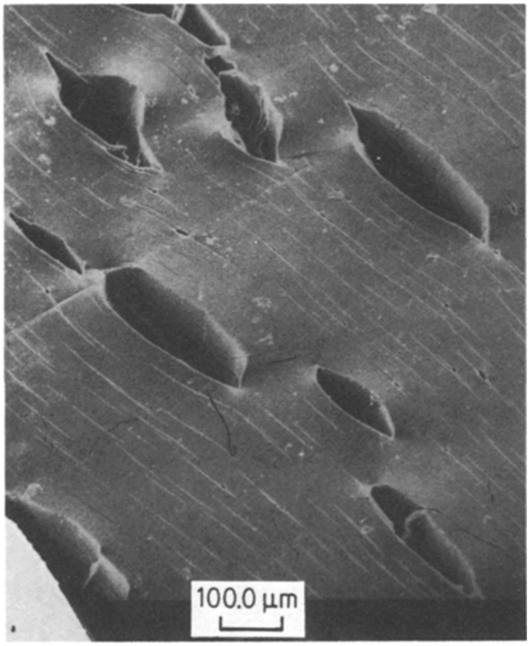

Figure 7 Free surface in drawn region of a sample of HMW polymer coated with a 1000 cSt silicone oil.

weight PMMA the cavities form even when samples are tested in the 1000 cSt oil environment. This occurs because the extent of local penetration and plasticization is relatively small as a result of the high silicone oil viscosity; and early craze breakdown is prevented by the high degree of chain entanglement in the cast PMMA. Hence shear deformation and necking occur and these are the essential requirements for the development of diamond-type cavities [35, 36].

As already noted, the craze initiation stress for the HMW polymer (Fig. 3) is above that recorded for the LMW polymer (Fig. 1). It is generally assumed that the craze initiation stress in glassy polymers is independent of molecular weight, based on results obtained on PS [30, 37]; however, a rise in the craze formation stress with molecular weight has been observed in a styrene–acrylonitrile copolymer [38]. An observed increase in craze initiation stress with increase of molecular weight may reflect a greater degree of homogeneity in the stress field as molecular weight is raised, chain entanglement increased, and density of chain ends reduced. A greater stress field homogeneity with increasing molecular weight has been suggested as a contributing factor to the occurrence of longer and finer crazes in high molecular weight material [7]. Additional information, involving tests on a much larger number of samples, is needed in order to resolve this question of a relation between molecular weight and craze nucleation.

To investigate the influence of applied strain on craze development in the HMW polymer, one test was run in which the reflected light intensity from developing crazes was followed to strains well into the plastic region. The greatest rate of craze development was found to occur at the yield strain. As strains were increased beyond yield, the rate of craze formation declined and a maximum was reached in the reflected light intensity. This occurred at a strain of about 12% as compared to a yield strain for this sample of about 7%. This effect of a decline in craze development with increased applied strain is attributed to a cessation of craze growth due to the development of shear bands at the tips of existing crazes [4, 30, 39]. It is interesting to compare these results obtained on HMW-PMMA with some recent reported results obtained on a high molecular weight PS [40]. In this latter investigation average craze density and average craze length were determined from direct observations of surface crazes taken at different values of applied strain. It was found, in keeping with the results of the present study on a different glassy polymer, that the rate of crazing began to decline at about the yield strain and that at somewhat higher strains both craze density and craze length became essentially independent of strain.

4. Conclusions

1. Silicone oils are stress-crazing agents for PMMA and the environmental effects of the oil on craze initiation stress, on tensile strength, and on strain to fracture become greater as the viscosity of the oil is lowered.

2. For any given silicone oil environment, the high molecular weight PMMA has a greater tensile strength and a greater strain to failure than the low molecular weight polymer.

3. A ductile–brittle transition is induced in high molecular weight PMMA by changing from an air environment, where shear flow, crazing, and diamond cavity formation are all observed, to a silicone oil environment.

4. In the uncoated HMW polymer, the greatest degree of craze development occurs at the yield strain but, as strains are increased beyond yield, craze growth essentially terminates due to the development of localized shear bands at the craze tips.

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References

1. R. P. KAMBOUR, *Macromol. Rev.* **1** (1973) 7.
2. J. G. WILLIAMS, G. P. MARSHALL, I. GRAHAM and E. L. ZICHY, *Pure Appl. Chem.* **39** (1974) 275.
3. L. S. A. SMITH, C. C. CHEN and J. A. SAUER, *Polymer* **23** (1982) 1540.
4. Y. IMAI and N. BROWN, *J. Mater. Sci.* **11** (1976) 417.
5. J. SHEN, C. C. CHEN and J. A. SAUER, Abstract, IUPAC MACRO '83, Section IV, Bucharest, Rumania (1983) p. 279.
6. G. A. BERNIER and R. P. KAMBOUR, *Macromol.* **1** (1968) 393.
7. H. H. KAUSCH, "Polymer Fracture" (Springer, Berlin, 1978).
8. G. P. MARSHALL and J. G. WILLIAMS, *Proc. Roy. Soc. London A* **342** (1975) 55.
9. I. NARASAWA, *J. Polymer Sci. A-2* **10** (1972) 1789.
10. E. H. ANDREWS and L. BEVAN, *Polymer* **13** (1972) 337.
11. R. P. KAMBOUR, E. E. ROMAGOSA and C. L. GRUNER, *Macromol.* **5** (1972) 335.
12. K. MATSUSHIGE, E. BAER and S. V. RADCLIFFE, *J. Macromol. Sci. Phys.* **B-11** (1975) 565.
13. A. MOET and E. BAER, *J. Mater. Sci.* **15** (1980) 31.
14. C. C. CHEN, D. R. MORROW and J. A. SAUER, *Polymer Eng. Sci.* **22** (1982) 451.
15. M. E. R. SHANAHAN and J. SCHULTZ, *J. Polymer Sci. Phys. Ed.* **14** (1976) 1561.
16. J. P. BERRY, *J. Polymer Sci. A* **2** (1964) 4069.
17. S. WARTY, J. A. SAUER and A. CHARLESBY, *European Polymer J.* **15** (1979) 445.
18. G. W. WEIDMANN and W. DOLL, *Colloid Polymer Sci.* **254** (1976) 205.
19. P. PRENTICE, *Polymer* **24** (1983) 345.
20. J. F. RUDD, *J. Polymer Sci. B* **1** (1963) 1.
21. E. J. KRAMER and R. A. BUBECK, *J. Polymer Sci. Phys. Ed.* **16** (1978) 1195.
22. B. MAXWELL and L. F. RAHM, *Ind. Eng. Chem.* **41** (1949) 1988.
23. C. C. CHEN, N. CHHEDA and J. A. SAUER, *J. Macromol. Sci. Phys.* **B-19** (1981) 565.
24. G. P. MARSHALL, L. E. CULVER and J. G. WILLIAMS, *Proc. Roy. Soc. London* **A319** (1970) 165.
25. M. J. DOYLE, *J. Mater. Sci.* **18** (1983) 687.
26. A. CHUDNOVSKY and A. MOET, *ACS Preprints, Organic Coatings and Plastics Chem.* **45** (1981) 607.
27. P. BEARDMORE, *Phil. Mag.* **19** (1969) 389.
28. G. REHAGE and G. GOLDBACH, *Angew Makromol. Chem.* **1** (1967) 125.
29. J. A. ROETLING, *Polymer* **6** (1965) 311.
30. C. B. BUCKNALL, "Toughened Plastica" (Applied Science, London, 1977).
31. A. M. DONALD and E. J. KRAMER, *Polymer* **23** (1982) 463.
32. M. B. JAFFE and E. J. KRAMER, *J. Mater. Sci.* **16** (1981) 2130.
33. R. P. KAMBOUR and A. F. YEE, *Polymer Eng. Sci.* **21** (1981) 218.
34. P. L. CORNES and R. N. HAWARD, *Polymer* **15** (1974) 149.
35. P. L. CORNES, K. SMITH and R. N. HAWARD, *J. Polym. Sci. Phys. Ed.* **15** (1977) 955.
36. J. SHEN, C. C. CHEN and J. A. SAUER, *Polymer Commun.* **24** (1983) 167.
37. J. F. FELLERS and B. F. KEE, *J. Appl. Polymer Sci.* **18** (1974) 2355.
38. J. A. SAUER and C. C. CHEN, *Adv. Polymer Sci.* **52/53** (1983) 170.
39. J. SHEN, C. C. CHEN and J. A. SAUER, *Polymer*, to be published.
40. A. MORENO, A. MOET and E. BAER, Paper No. 16, 5th International Conference on Deformation, Yield and Fracture of Polymers, Churchill College, March (1982).

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