Stress cracking behaviour of poly(methyl methacrylate) and a poly(methyl methacrylate–ethyl acrylate) copolymer

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Many organic fluids behave as stress cracking agents on polymers above a critical stress level, while remaining completely inert to the polymer below the critical stress. Because of this property, the proper selection of a stress cracking fluid and testing temperature can provide a non-destructive quality control test. Since many injection moulded parts will perform unacceptably when moulded with residual stresses above a certain level, this type of test is desirable. In this study, the effect of several organic fluids on the stress cracking behaviour of poly(methyl methacrylate) was studied. The experiments were conducted at two temperatures in order to generate a range of critical stress determining conditions. A homopolymer and copolymer of PMMA, having different molecular weight, were investigated and found to have significantly different responses to the stress cracking fluids.

INTRODUCTION

The ideal quality control test is one which has no effect on 'good' parts, yet readily indicates unacceptable parts. Many liquids cause stressed polymers to crack or craze at specified stress levels. Some act in a completely non-destructive manner below the critical stress level. Unfortunately, there are few guidelines to use in selecting a suitable stress cracking fluid. Solubility theory has been used to provide general indications of the ability of a liquid to dissolve a material. While solvents will not be acceptable non-destructive quality control agents, solubility theory can provide information on which fluids are not likely to be solvents. These fluids can then be investigated as stress cracking fluids.

Van Krevelen showed that two solubility parameters can be used to provide information of the solubility, and crazing tendency of liquids on stressed polymers[1]. These two solubility parameters are δ_H, the hydrogen bonding parameter, and δ_V, where

$$\delta_V = \delta_d^2 + \delta_p^2$$

δ_d and δ_p are the disperse and polar force solubility parameters, respectively. *Figure 1* is the presentation used by Van Krevelen to correlate a large quantity of data presented by Vincent and Raha[2]. Solvents with solubility parameters similar to that of the polymer (centre of the circles) will readily dissolve the polymer. The further the liquids solubility parameters are from that of the polymer the less likely it is to dissolve the polymer, and the more likely it is to crack or craze it in a stressed condition. The circles drawn on *Figure 1* do not demarcate solubility or crazing tendencies. Boundaries cannot be drawn to delineate solvents from non-solvents, nor can the critical stress level for a given stress cracking fluid be predicted.

MATERIALS

Four fluids were used in this program to study residual stresses in PMMA; N-methyl formamide, ethyl acetate, methanol, and a 50/50 mixture of ethylene glycol and N-methyl formamide. Ethyl acetate was chosen as a reference material. Since it is a known solvent it cannot be used in a non-destructive quality control test. As shown in *Figure 1*, ethyl acetate has solubility parameters similar to that of PMMA. N-methyl formamide was chosen because Haven and Sung showed that it will stress crack PMMA parts with a residual strain above 0.3%[3,4]. Below that strain level they reported that N-methyl formamide has no effect on the polymer. Unfortunately, they did not present any molecular weight data on the polymer they studied (VS-811 supplied by Rohm and Haas). The solubility parameter data presented in *Figure 1* shows that N-methyl formamide has only a slightly lower tendency to dissolve PMMA than ethyl acetate. Therefore, it is important that the molecular weight of the polymer be considered in developing a non-destructive quality control test using this fluid.

Methyl alcohol has an even lower tendency to dissolve PMMA, but has a higher critical crazing stress level than N-methyl formamide[5]. It was also appropriate to investigate the mixture of ethylene glycol and N-methyl formamide. Ethylene glycol is not a solvent for PMMA, while N-methyl formamide induces crazing at very low stresses.

In this study two grades of PMMA were investigated; Rohm and Haas VS-100, which is an injection mouldable methyl methacrylate–ethyl acrylate copolymer, and American Cyanamid based Polycast*, a homopolymer available in sheet form. The molecular weight characteris-

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* Sheet stock was supplied by Polycast Technical Company

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tics and glass transition temperatures of these polymers are presented in *Table 1*. The reduction of the glass transition temperature by random copolymerization is directly proportional to the copolymer content. Assuming that poly(ethyl acrylate) has a glass transition temperature of $-24°C^5$, and poly(methyl methacrylate) has a transition temperature of 115°C, the ethyl acrylate content of VS-100 is $\sim 25\%$.

EXPERIMENTAL

Stress cracking experiments were performed on 1.27 cm thick Polycast samples and injection moulded VS-100 samples. Stress was applied to the sample in a continuously varying fashion by means of cantilever loading as shown in *Figure 2*. The threshold crazing stress was calculated at various time intervals by the formula shown at the bottom of *Figure 2*. The threshold crazing stress was determined from the distance along the cantilever sample at which the crazes stopped. This was usually a well defined line marking the critical stress below which the stress cracking fluid has no effect. Different weights were used to load the cantilever such that about half the sample exhibited stress cracking for various fluids. Most of the experiments were conducted in triplicate at 23°C. A few were performed at 50°C in an attempt to reduce the critical stress and/or equilibrium time. Ethyl acetate was not used at 50°C because it is a solvent for PMMA and its rate of dissolution at 50°C would be even faster than at 23°C, further reducing its utility. Prior to testing, the test samples were annealed at 95°C for 48 h in a vacuum to relieve any residual stresses which might be present. The samples were cooled slowly at 0.5°C min^{-1}. *Figure 3* shows the change in critical stress of the Polycast specimens with time using N-methyl formamide, ethyl acetate, and methanol. *Figure 4* presents the same information for the VS-100 samples.

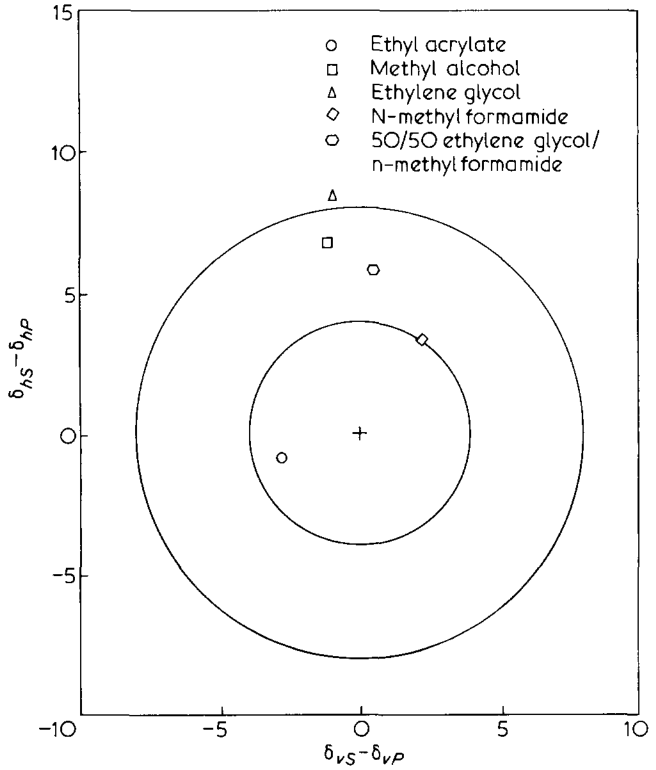

Figure 1 Solubility parameters of investigated fluids relative to PMMA (from reference 1, p 540, reproduced with permission of the publisher). Subscript *s* refers to the solvent and subscript *p* refers to the polymer

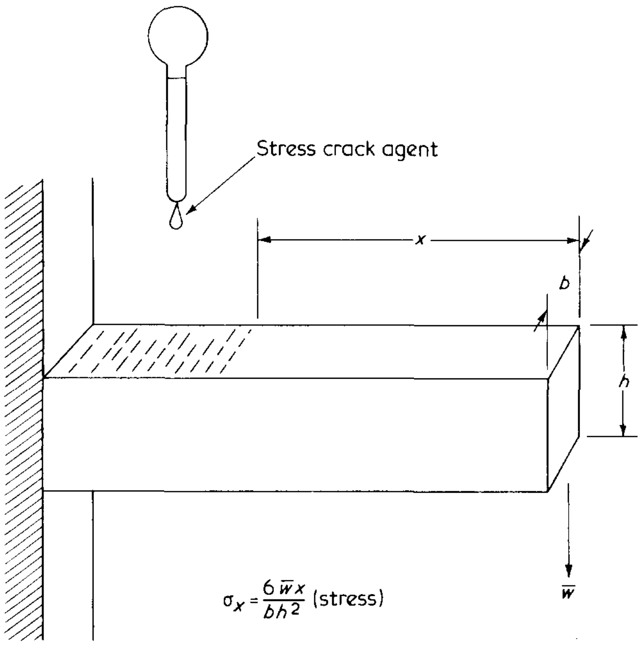

Figure 2 Schematic drawing of stress crack testing experiment

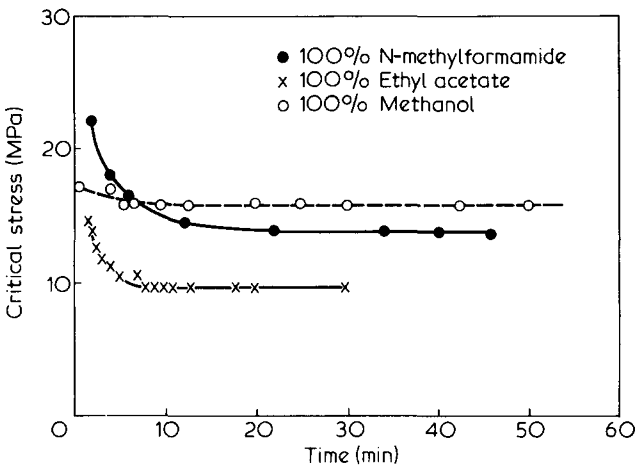

Figure 3 Effect of N-methyl formamide, ethyl acetate, and methanol on the critical crazing stress *versus* exposure time of Polycast PMMA

Table 1 Molecular weight characteristics of resins investigated

Material	Chemical nature	T_g, C	$M_n(10^4)$	$M_w(10^4)$	$M_z(10^5)$	M_w/Mn
Polycast	PMMA	105	30.0	135.6	37.7	4.52
VS-100	P(MMA-EA)	81	3.15	7.04	1.20	2.24

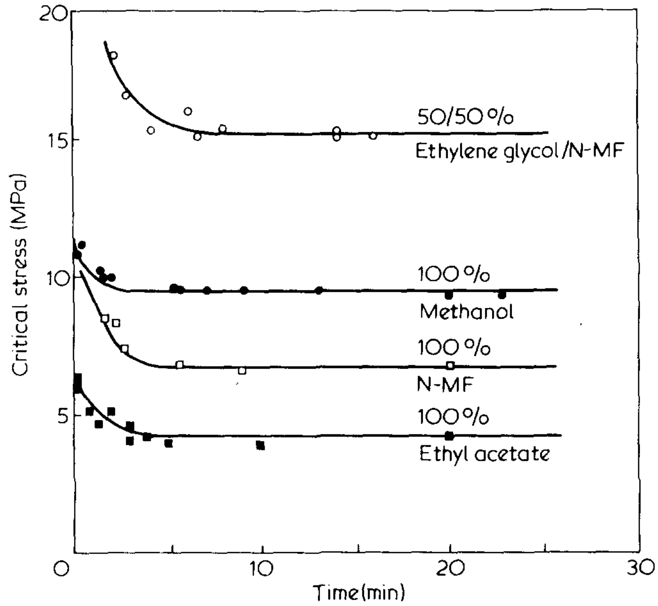

Figure 4 Effect of ethyl acetate, N-methyl formamide, methanol, and 50/50 ethylene glycol/N-methyl formamide on the critical crazing stress *versus* exposure time of VS-100 PMMA

Table 2 summarizes the results of the stress cracking experiments. The two grades of polymer show different threshold stresses. The lower molecular weight VS-100 copolymer has a lower critical stress than the higher molecular weight Polycast due either to the lower molecular weight or to the copolymer nature of the VS-100. Further experiments are needed to delineate which affect is predominant. The effect of molecular weight is probably more significant than the presence of ethyl acrylate. Poly(ethyl acrylate) has solubility parameters that are almost the same as poly(methyl methacrylate)[5]. Ethyl acetate produces the lowest threshold stress of the stress cracking fluids examined. Unfortunately, it is also a solvent for PMMA and causes the test samples to lose their optical clarity. N-methyl formamide has the next lowest threshold stress, ~50% higher than those recorded for ethyl acetate. The critical strain for VS-100, assuming a tensile modulus of 2.62 GPa, is 0.25%. Assuming a tensile modulus of 3.4 GPa for the Polycast gives a critical strain of 0.4%. These values closely agree with the value of 0.4% reported by Vincent and Raha and the value of 0.3% reported by Haven and Sung. N-methyl formamide has no effect on the optical properties of Polycast, making it a non-destructive test for identifying residual stresses above 13.8 MPa. N-methyl formamide did cause the VS-100 to surface whiten, thereby destroying its optical clarity. Because poly(ethyl acrylate) has solubility characteristics similar to those of PMMA, the copolymer nature of the VS-100 should not be influential in the formation of crazes. Solubility parameters however, are affected by molecular weight. Higher molecular weight polymers are more difficult to dissolve, and logically less likely to stress crack.

Methyl alcohol affects the test samples in much the same manner as N-methyl formamide. The threshold stress levels are slightly higher, while the equilibrium times are lower. In particular, the equilibrium time for the Polycast sample is much lower than that required using N-methyl formamide.

The 50/50 mix ethylene glycol and N-methyl formamide did not whiten the VS-100 test sample. However, the threshold stress level was the highest of any of the stress cracking agents investigated.

The effect of testing temperature was substantial. The threshold stress of Polycast was reduced by ~50% by increasing the test temperature from 23 to 50°C for both N-methyl formamide and methyl alcohol. Because of the whitening of the VS-100 samples by these agents this material was not tested at 50°C. It is expected that the critical stress would be reduced by a similar amount for the VS-100 at 50°C.

CONCLUSIONS

The amount of residual stress (or strain) in an amorphous polymer can be determined by stress cracking in specific fluids. The experiments reported in this paper were conduced on samples in which residual stresses were removed such that the critical stress level–fluid sensitivity could be established. Different fluids cause stress cracking at different levels of stress so that the exact level of residual stress in a moulded part can be determined by testing in several fluids. However, the critical stress level at which a specific fluid causes cracking cannot be determined *a priori*. Many fluids are available which act as stress cracking agents above a critical stress, but are completely inert to the polymer below the critical stress. Such fluid–polymer combinations can be used in non-destructive quality control testing. It was discovered that many aspects of stress cracking, including the non-destructive nature of some fluids, is dependent on the nature of the polymer. N-methyl formamide and methyl alcohol were inert to a high molecular weight homopolymer PMMA below their critical stress levels, yet caused whitening to a low molecular weight PMMA copolymer. The higher molecular weight homopolymer required a longer time for the stress cracking fluid to cause cracking at the minimum residual stress level, and also stress cracked at a higher minimum threshold stress.

Ethyl acetate produced cracking at the lowest residual stress level. However, because it is a solvent, it cannot be used in a non-destructive test. The low molecular weight VS-100 copolymer could only be non-destructively tested with the 50/50 mix of ethylene glycol and N-methyl

Table 2 Summary of stress cracking experiments

Stress cracking agent	Material	Temp. (°C)	Threshold stress (MPa)	Equilibrium time (min)
Ethyl acetate[a]	VS-100	23	4.3	5
Ethyl acetate[a]	Polycast	23	9.6	8
N-methyl formamide[a]	VS-100	23	6.6	5
N-methyl formamide	Polycast	23	13.8	20
N-methyl formamide	Polycast	50	6.6	13
Methyl alcohol[a]	VS-100	23	9.7	4
Methyl alcohol	Polycast	23	15.9	6
Methyl alcohol	Polycast	50	10.0	6
50/50 Ethylene glycol/N-methyl formamide	VS-100	23	14.7	8

[a] Surface whitening observed within 5 s of immersion in stress cracking agent in unstressed areas

formamide. The critical stress for this fluid is 14.7 MPa. The higher molecular weight, Polycast, can be non-destructively tested with N-methyl formamide with approximately the same critical stress of 13.8 MPa. Testing at 50°C will reduce the critical stress by $\sim 50\%$.

Characterization of the VS-100 polymer indicates that it contains $\sim 25\%$ ethyl acrylate. Since the ethyl acrylate content effects the glass transition temperature, it will also effect the degree of residual stresses induced in injection moulded parts.

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REFERENCES

1 Van Krevelen, D. W. 'Properties of Polymers', Elsevier, New York, 1976
2 Vincent, P. I. and Raha, S. *Polymer*, 1972, **13**, 283
3 Haven, R. E. and Sung, N. H. 'Science and Technology of Polymer Processing', (Ed. N. P. Suh and N. H. Sung), M.I.T. Press, Cambridge, 1979, 734
4 Haven, R. E. and Sung, N. H. 'SPE Technical Papers' 1978, **24**, 406
5 Miller, M. L. 'The Structure of Polymers', Reinhold, New York, 1966