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Analysis and properties of some commercial poly(methylmethacrylate)-based materials

P. J. BURCHILL, G. MATHYS, R. H. STACEWICZ
Materials Research Laboratories, Defence Science and Technology Organisation, Department of Defence, Melbourne 3032, Australia

Four commercial crosslinked poly(methylmethacrylate)-based materials have been analysed, and the differences in some of their physical properties from those of the unmodified polymer have been related to the variation in chemical structure. These co-polymers, which are about 95% methylmethacrylate, have different co-monomers which introduce crosslinks and hydrogen bonds into the polymer. The modifications have changed the craze resistance relative to the homopolymer, with in some cases improvements of over 50%. This change in craze resistance is not uniform with change in crazing agent, so showing that the responses of the materials with the change in solubility parameter of the agents are not the same. Likewise the water absorption behaviour shows wide variation, the solubility ranging up to twice that of the homopolymer. Measurements of the fracture properties show that three of the polymers are significantly less ductile than the homopolymer, though this is masked by an increase of the elastic modulus in two.

1. Introduction

The most demanding application of poly(methylmethacrylate) (PMMA) as a structural material is probably its use for aircraft windows. Here, the material must have good optical properties, withstand the loads due to pressurization at high altitudes, and be resistant to degradation by sunlight. At the same time, the material will experience temperature changes of nearly 100 K, and wide variations in relative humidity. During its service life, the window will also suffer exposure to organic fluids. The usual reason for removal of a window is loss of optical clarity due to crazing and scratching. To improve the properties of the base polymer as cast sheet it is modified during polymerization by addition of small amounts of comonomers to crosslink the polymer.

For a PMMA plastic item to have good mechanical properties, the molecular weight needs to be greater than 100 000 [1–3]. Crosslinking the polymer would ensure that these properties are realized for any batch in which the item is also formed during polymerization. However, the decreased chain mobility caused by crosslinks has significant effects on mechanical properties even in glassy polymers [4, 5]. Crosslinks inhibit the ease with which plastic deformation occurs, so increasing yield strength and craze resistance. Fracture toughness decreases due to reduced ductility at crack tips, but this may be partly offset by the increase in yield strength and elastic modulus. Similarly, brittle strength decreases with increasing crosslink density. A change in tensile failure mode at a given temperature from ductile to brittle may occur; for PMMA this occurs near room temperature. Thus, manufacturers of modified PMMA have to strike a balance between increases in desirable physical properties without embrittlement and a great loss in toughness. Fortunately these properties appear to vary at different rates with crosslinking.

Modified PMMA materials from four manufacturers have been analysed to determine the crosslinking process and crosslink density. Some physical properties have been measured and the difference related to the chemical changes made to the base polymer.

2. Experimental details

2.1. Materials

Four modified poly(methylmethacrylate) polymers (A to D) from different manufacturers (Table I), and an unmodified PMMA (U) were obtained as sheets nominally 6 mm thick. Test fluids for craze resistance were reagent grade acetone, isopropanol and N-methylformamide of better than 99% purity.

2.2. Analysis

Infrared powder spectra were recorded on a Perkin-Elmer 580B spectrophotometer, and difference spectra obtained by subtraction of the spectrum of Material U from those of the other materials. The absorption at 860 cm^{-1} was used for normalization of the spectra for subtraction. The materials (~ 5 g) were pulverized and then extracted with dichloromethane in a soxhlet. Concentration of the dichloromethane solution, followed by thin-layer chromatography on Kieselgel GF254 using mixtures of petroleum ether (40 to 60° C) and ethyl acetate as eluant was done to obtain the residual monomers and stabilizers in the polymers. In addition Material D as powder was hydrolysed with 5% aqueous sodium hydroxide solution in a pressure vessel at 200° C for 14 h. The hydrolysate was extracted with ether via a continuous liquid–liquid extraction

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TABLE I Poly(methylmethacrylate) cast sheets and their manufacturers

Code	Manufacturer	Material
A	Polycast Corp. (USA)	Polycast 76
B	Rohm and Haas (USA)	Plexiglas 55
C	Roehm GmbH (FRG)	Plexiglas 249
D	Swedlow Inc. (USA)	S-708
U	Roehm GmbH (FRG)	Plexiglas 201

and this ether solution concentrated for analysis. The separation components were identified by infrared and mass spectrometry.

2.3. Irradiation

Shavings (~ 0.2 g) of the four modified polymers were placed in enclosed extraction thimbles and irradiated with γ-rays from a Co^{60} source at a dose rate of 1.68×10^{18} eV g^{-1} h^{-1}. The thimbles were removed at appropriate time intervals and extracted for 3 days with acetone in a soxhlet, and dried for a further 3 days at 105° C. The gel contents of the irradiated polymers were obtained from the weights as dry polymer before and after irradiation and extraction.

2.4. Craze resistance

Bars (180 mm × 25 mm × sheet thickness) were cut from the sheets and conditioned by heating at 120° C for 2 h, and then cooling slowly to room temperature. The bars were then stored over phosphorus pentoxide or in water until required for testing. The craze resistance was measured by loading the bars as cantilevers in a procedure similar to those in standard test methods [6, 7]. The load was applied for 10 min before placing the test fluid on the tensile surface, which was kept wet for a further 30 min before examination for crazing. The stress at the craze closest to the load point was calculated by linear interpolation from the maximum stress at the fulcrum [8] to give the minimum stress to craze the material.

2.5. Water absorption

This was measured as the increase in weight of plates of these materials immersed in water at 25° C. The weight increase with time showed that the absorption was Fickian.

2.6. Mechanical properties

The flexural properties were determined in three-point bending at a test speed of 20 mm min^{-1}. Specimens were bars 25 mm × 180 mm × sheet thickness and had been annealed at 120° C for 2 h, followed by slow cooling and storage in a dry environment for a month before testing.

Fracture properties were investigated using a double torsion test procedure as outlined by Kies and Clark [9]. The specimens were plates 30 mm × 80 mm cut from sheet material and with a sharp central longitudinal groove about 2 mm deep. They were conditioned as above. A compliance calibration curve was established for each material for the determination of the strain energy release rate at a test speed of 0.2 mm min^{-1}.

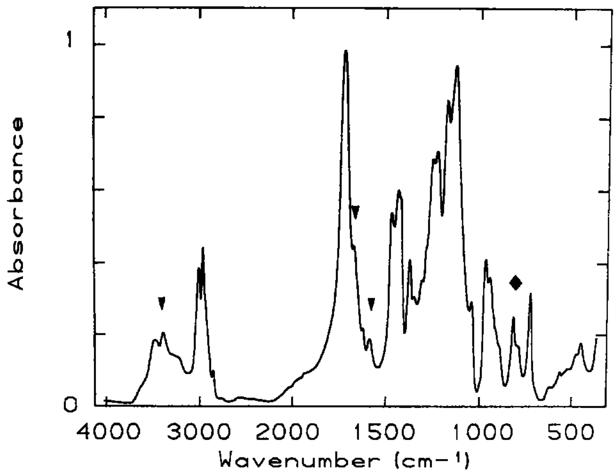

Figure 1 Infrared spectrum of Material A; the arrowed absorptions are additional to a PMMA spectrum. The peak (◆) was used for spectral normalization.

3. Results and discussion

3.1. Chemical properties

Infrared spectra of all the modified materials showed that they were largely PMMA; the spectrum for Material A is given in Fig. 1 with the absorptions not found in the homopolymer U indicated. By numerical subtraction of the spectra for A and U the difference spectrum in Fig. 2 was obtained, and the additional absorptions assigned to amide groups. In a similar manner the other modified materials revealed that B contained amide groups, C contained the symmetrical triazine, while D showed no extra absorptions but only changes in relative intensity.

Separation and analysis of the low molecular weight components of the polymers and of the hydrolysate of D by infrared and mass spectroscopy revealed the nature of the co-monomers and stabilizers used:

A : methacrylamide
B : methacrylamide and
N-methoxymethylmethacrylamide
C : 2,4,6-trisallyloxytriazine
D : 2,2-dimethyl 1,3-propanediol dimethacrylate

In all the materials the same UV stabilizer was found:

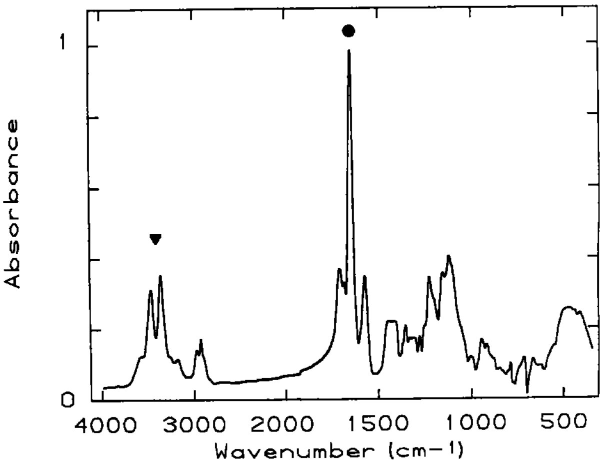

Figure 2 Difference spectrum obtained from the spectra of Materials A and U. The identified additional absorptions are (▼) N–H stretching vibration, (●) amide I band.

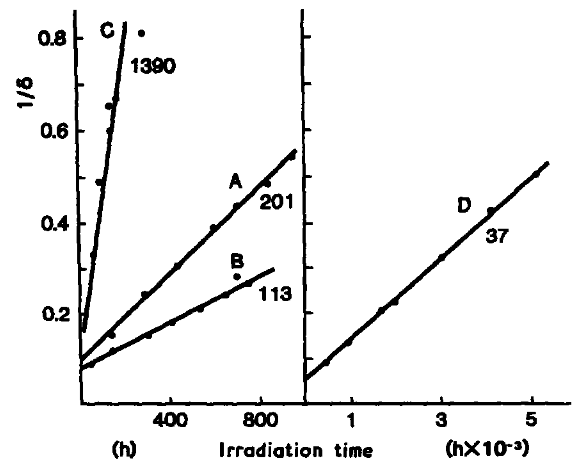

Figure 3 Crosslinking coefficient ($1/\delta$) against irradiation time (h). Lines for each material (A to D) are shown with their average number of monomer units between crosslinks.

2(2'-hydroxy-5'-methylphenyl)-benzotriazole (Tinuvin P). Material A was also found to contain carboxylic acid groups through changes in the infrared spectra of powder on treatment with dilute sodium hydroxide solution, and both A and B evolved ammonia when heated with strong alkali. The infrared spectra of the polymers A to C indicated that the co-monomers were less than 5% of the material, while the recovery of 2,2-dimethyl 1,3-propanediol from the hydrolysis of D indicated at least 1% co-monomer.

The crosslink is formed in Material B by elimination of methanol between the polymerized co-monomers. The same crosslink would be produced in Material A if formaldehyde were used, though no evidence was found of this substance; formaldehyde is widely used to crosslink such acrylic co-polymers [10], and the reaction is usually catalysed by acid.

Crosslink density was determined by the method developed by Shultz for crosslinked methacrylate polymers [11]. The polymers were irradiated with γ-rays from a Co^{60} source, and the gel content for different radiation doses measured. From the gel content (g), a function (δ) is calculated from the equation

$$1 - g = (1 + \delta g/2)^{-2}$$

The reciprocal of δ is related to irradiation time by

$$\frac{1}{\delta} = \frac{1}{\delta_0} + \frac{It}{2AE}$$

in which I is the radiation intensity ($eV\,h^{-1}$), t is time (h), A is the number of crosslinked units per gram and E is the efficiency of reaction (eV per scission). The results of irradiating these modified polymers are shown in Fig. 3 in which the slopes of these linear plots are inversely proportianal to the crosslink density (A). Indicated on this figure is the average number of monomer units between crosslinks for each polymer, showing there is a large difference in crosslink density between these materials.

Assuming the crosslinking efficiency of 2,2-dimethyl 1,3-propanediol dimethacrylate is similar to that of 1,2-ethanediol dimethacrylate, which has been determined [11] to be about 50%, then the co-monomer content of D must be about 5%. The very low crosslink density of C is probably due to the very low reactivity of the triallyloxytriazine in co-polymerization with methylmethacrylate [12]. The crosslinking by condensation reactions in A and B would not be expected to be very efficient. From the evidence of the infrared spectra and the crosslink densities, most of the amide groups are not participating in this way which is demonstrated by the evolution of ammonia on treatment with alkali.

TABLE II Minimum stress to craze (MPa)

Material	Test fluid*		
	Isopropanol	Acetone	N-Methylformamide
A	22	21	18
B	25	19	18
C	18	10	17
D	26	15	26
U	17	10	22

*Solubility parameters ($(J\,m^{-3})^{1/2}$): PMMA 19.4, isopropanol 23.4, acetone 20.3, N-methylformamide 32.9.

3.2. Physical properties

3.2.1. *Craze resistance and water absorption*

The observation of crazing in polymers or the alternative deformation mode shear yielding has been correlated with entanglement density by Donald and Kramer [13]. Henkee and Kramer [14] have further shown that when crazing is the yielding process as in polystyrene then crosslinking the polymer increases the critical strains required, though the molecular weight between crosslinks has to be similar to that between entanglements for an effect to be observed. For PMMA the average number of monomer units between entanglements is about 90 [15, 16]; hence the crosslinking in A, B and D is expected to influence the craze resistance but not in C. Table II gives the minimum stresses required to produce crazes when the polymers are exposed to various test fluids. Material D, which can be considered to be a crosslinked PMMA in which no new chemical groups have been incorporated, shows the effect of crosslinking alone with large increases in craze resistance relative to U. The results for A and B, however, appear anomalous.

Many studies of crazing in polymers have shown that the craze resistance is lowest towards those fluids which have a solubility parameter close to that of the polymer [17–20]. The values of these parameters for PMMA and the test fluids are given in Table II, and the order of craze resistances for D and U is as expected. Materials A and B show much greater resistance towards acetone than expected. The increase in solubility parameter for these polymers due to the presence of the polar co-monomer would be no more than $1\,(J\,m^{-3})^{1/2}$. Hence hydrogen bonding between polymer chains (so decreasing chain mobility) must be adding to the effect of crosslinking. With N-methylformamide as test fluid, A and B are less resistant than U and even less resistant towards this fluid than acetone despite the much greater difference in solubility parameters. Here the fluid must be disrupting the hydrogen bonds between chains through its ability to be an acceptor and donor of these bonds. Crazing is a

TABLE III Water absorption at 25° C

Material	Diffusion coefficient ($m^2 sec^{-1} \times 10^{13}$)	Solubility (%)
A	3.2	4.9
B	3.0	3.7
C	4.7	2.4
D	5.5	2.4
U	5.1	2.4

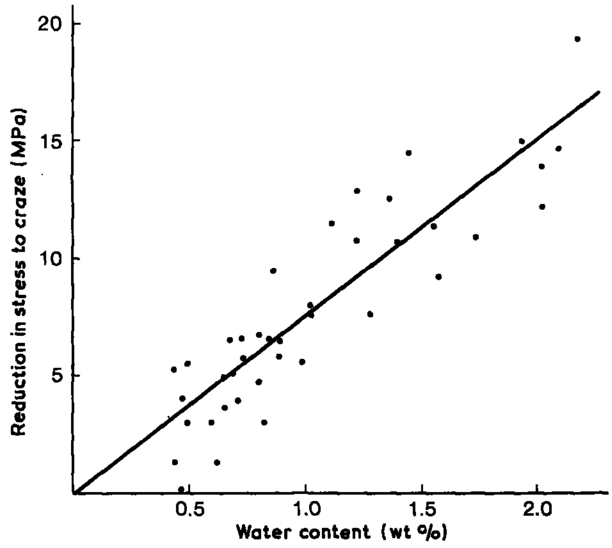

Figure 4 Reduction in craze resistance (MPa) against water content (wt %) for all materials.

localized event induced by defects in structure whether physical or chemical, and these hydrogen-bonded regions are now acting as detrimental defect groups.

The water absorption properties of these polymers are given in Table III. Their diffusion coefficients are similar, with the crosslinking appearing to have no effect on diffusion or solubility when D and U are considered. Materials A and B, though, show much greater water solubility due to their amide content through hydrogen bonding. This bonding may also be responsible for the slightly smaller diffusion coefficients in A and B in reducing polymer chain or diffusant mobility.

A previous study [21] has shown that the craze resistance of PMMA is reduced if it contains water. Fig. 4 shows the reduction in resistance towards crazing by isopropanol for all these materials at different water contents. The scatter in the data is mainly due to experimental error in measuring the minimum stress required to produce a craze, and so the materials have not been distinguished. A good approximation of the reduction in craze resistance by absorbed water for all the materials is given by the line shown, which has a slope of $8\,MPa/(0.01\,g\,g^{-1})$.

While water is being steadily absorbed, the time required to reach a specific reduction in craze resistance is not the same for each material. From the absorption data (Table III), A will reach a 1% water content in about a third of the time that D requires. For even larger water contents, when the absorption is no longer linear with $t^{1/2}$, the ratio of the times will be even greater.

3.2.2. Strength and toughness

The flexural properties are given in Table IV. The methacrylamide copolymers (A, B) have a significantly higher modulus than the other materials, with a probability that these observations are due to chance of less than 1%. Flexural strengths of A and B are also significantly greater than that of the unmodified polymer (U) with a probability of less than 5% that there is no difference. These properties indicate that increases in modulus and strength in these materials are due more to intermolecular hydrogen bonding than to crosslinking, since Material D is no different to U.

The toughness of these materials was measured under conditions of slow, steady crack growth using the double-torsion test method [9] which has been extensively used by many others in studying crack growth in acrylic materials [22–24]. A compliance (C) against crack length (a) relation was determined for each material at a test speed of $0.2\,mm\,min^{-1}$ and the strain energy release rate G_c calculated from the relation

$$G_c = \frac{P^2}{2B_c}\left(\frac{dC}{da}\right)$$

P is the load required to propagate the crack at a steady rate, and B_c is the thickness of the double-torsion specimen at the crack plane. Values of G_c are given in Table IV and these show that the most highly crosslinked material (D) gave the lowest G_c; for A and B the G_c values are only marginally less than that of the uncrosslinked material U, the G_c of which is the same as that obtained by Atkins *et al.* [25] for crack growth at 296 K and at a speed of $2 \times 10^{-4}\,m\,sec^{-1}$.

Table IV also gives the fracture toughness, K_c, which was calculated from the expression

$$K_c^2 = \frac{P^2}{2B_c}\frac{6(1+\nu)\,l^2}{WB^3} = G_c E$$

TABLE IV Physical properties

Property	Material				
	A	B	C	D	U
Flexural strength (MPa)*	143	146	139	132	125
Flexural modulus (GPa)*	3.67	3.69	3.44	3.40	3.33
$G_c (J\,m^{-2})$†	314	362	408	246	381
$K_c (MN\,m^{-3/2})$†	1.00	1.07	1.08	0.83	0.99
$(ue_y) \times 10^8 (m)$	10	11	14	9	15

*Measured according to ASTM 790-81 at a loading rate of $20\,mm\,min^{-1}$.

†Slow crack growth toughness, crack speeds within the range 0.25 to $0.45\,mm\,sec^{-1}$.

in which B and W are the thickness and width of the specimen, respectively, l is the moment arm used to apply the load in the double torsion apparatus and v is Poisson's ratio and E is the elastic modulus. Apart from D, all the materials have essentially the same value of K_c. The larger elastic modulus of A and B compensates for the reduced strain energy release rate G_c. The values of K_c are the same as those recorded by Marshall *et al.* [22] and furthermore the variation in crack speed is insufficient to account for the difference in K_c values. The crack speed in Material D was almost twice that in U, whereas from the K_c values it would have been expected to be an order of magnitude lower. These results reflect the lower ductility of D.

Marshall *et al.* [22] have given an analysis which relates K_c to the crack opening displacement u, the yield strain e_y, the crack speed $\dot{a}$ and modulus E_0:

$$K_c = (ue_y)^{1/2}\left(\pi \frac{e_y}{u}\right)^n E_0\dot{a}^n$$

The constant, n, is related to the mechanical loss factor. In the same way an expression for G_c can be obtained:

$$G_c = (ue_y)\left(\pi \frac{e_y}{u}\right)^n E_0\dot{a}^n$$

From the measured values of G_c and K_c, values for (ue_y) can be determined and are given in Table IV. This quantity is a measure of the change in ductility of each material brought about by the modification to the polymer. Through elimination of the effect of modulus the ductility change is seen more clearly in these values, which are equivalent to the distance moved in performing the work necessary to propagate the crack. The conclusions of Berry [4] and of Broutman and McGarry [5] on the effect of crosslinks on the fracture properties of PMMA are confirmed. In their work there is no indication of the degree of crosslinking or the role of hydrogen bonds.

4. Conclusions

In these methylmethacrylate polymers the presence of crosslinks and hydrogen bonds are seen to have a dramatic effect on the craze resistance of the plastic. However, there is a reduction in ductility and hence in toughness. It appears that hydrogen bonds are a more effective means of improving craze resistance than chemical bonds in these polymers without sacrificing toughness, but not against all crazing agents. A reduced craze resistance is observed where specific interactions with the fluid can disrupt these bonds. Furthermore, the presence of the polar co-monomer has rendered the plastic more susceptible to degradation of its properties by absorbed water. The choice of material will obviously be governed by the humidity of its service environment.

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