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Fracture of slightly plasticized polyvinyl chloride

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Impact tests and fracture toughness tests using compact tension specimens were carried out on a number of slightly plasticized PVC compositions. These measurements, together with calculations from the craze thickness profile were used to determine the fracture mechanisms operating in the various tests. The marked decrease in the impact strength of PVC on addition of small amounts of a conventional plasticizer was found to be due to the plasticizer decreasing the stress intensity necessary to nucleate a craze at the notch tip of the impact specimen. The fracture toughness of the compact tension specimens which failed by a crazing mechanism increased with increasing plasticizer content. It is thought that the fracture of these specimens is controlled by the stress intensity necessary to propagate the pre-existing crack/craze system through the material.

1. Introduction

Several conventional plasticizers, which would normally be incorporated in PVC at concentrations greater than 20 wt%, are known to cause an increase in elastic modulus and a decrease in impact strength when used at low concentrations (less than 15 wt%) [1]. This phenomenon has been called antiplasticization and has been observed also in bisphenol polycarbonates [2]. The work described in this paper examines the relationship between the effects of small quantities of plasticizer on the impact properties and the crazing properties of PVC.

Crazing and fracture of amorphous polymers has been the subject of two recent review articles [3, 4] and for a fuller introduction to this subject the reader is referred to these articles.

The stress required to initiate and propagate crazes in a given polymer is generally decreased by the presence of an organic fluid [3–7]. The fluid is thought to work by both reducing the surface energy of the crazed matter and softening the uncrazed material close to the craze tip [8]. Recent work [3–6] has shown that small amounts of dichlorobenzene in polystyrene lower the crazing resistance of the polymer but have little effect on the modes of flow (creep and shear yielding) which normally compete with and retard crazing.

The relation between crazing and fracture has been examined for a clear grade of rigid PVC by Mills and Walker [9]. Non-crazing failure modes in rigid PVC have also been reported [10, 11]. Theories of crazing have been proposed by Gent [12] and also by Argon [8, 13] and co-workers.

2. Experimental

2.1. Specimen preparation

Suspension polymerized PVC (Geon 110 × 233), a product of B.F. Goodrich Co. Ltd., with an average degree of polymerization of 640 was used. The PVC powder was blended with varying amounts of di-isooctyl phthalate (DIOP) (Corflex 880), a product of CSR Chemicals Pty. Ltd., and one or other of the organo-tin stabilizers (Mark 465 or Mark 292), which were obtained from Steetley Chemical Co. Ltd.

Ten samples were prepared with the following compositions: 3, 5, 7, 10 and 15 wt% DIOP with 1 wt% of an organo-tin stabilizer (either Mark 465 or Mark 292).

The powder blends were compounded for 10 min on a polymer mill at 150 to 160° C. Subsequently, the compounded sheet was compression moulded into 6.2 mm thick sheets, on a platen press at 170° C for 5 min. The temperature of the press was then lowered to room temperature by allowing cooling water to pass through it. The pressure on the specimen was maintained during cooling to prevent the sheet from buckling.

2.2. Extraction of plasticizer

A series of experiments were carried out in which the amount of plasticizer in the final specimen sheets was determined by the method described by Haslam *et al.* [14].

2.3. Impact tests

Four bars (45 mm x 6.2 mm x 3.0 mm) were cut from each of the ten sheets of material. These bars were all notched to a depth of 2.1 mm with a jewellery file (notch tip radius 0.24 mm) before being used in a series of impact tests on a Hounsfield Plastics Impact Tester.

2.4. Fracture toughness tests

Four razor notched compact tension specimens were prepared from each specimen sheet. These specimens were tested under monotonic loading conditions in an Instron Tensile Testing Machine, with a cross-head speed of 0.05 mm min^{-1}. As the crack began to move, both the load and crack length were recorded simultaneously until the specimens failed catastrophically.

2.5. Optical microscopy of crazes

Rectangular specimens of PVC (approximately 20 mm x 15 mm) were cut from the remains of the compact tension specimens and notched along three sides.

They were then put in a vice which was designed to fit on the stage of the optical microscope. A razor blade was slowly forced into the material, propagating the crack in a horizontal plane.

The crack and craze were photographed using the microscope in both transmission and reflection modes. However, reflection microscopy gave better interference fringes for the craze. When the craze had been photographed in its loaded state, the razor blade was removed and it was re-photographed in its unloaded state.

3. Results and observations

3.1. Extraction of plasticizers

Since discrepancies [7] in the crazing behaviour of polystyrene have been attributed to the evaporation of the plasticizer during compounding, it was decided to check the concentrations of plasticizer in the PVC sheets after all processing had been completed. The plasticizer loss during the compounding operations was found to be less than 0.5 wt%, which was within the accuracy of the extraction technique.

3.2. Impact tests

Results from the impact tests are plotted in Fig. 1. These were converted to fracture toughness values using the method suggested by Brown [15] and Williams *et al.* [16]. In obtaining the values of K_{IC} given in Fig. 2, the moduli of the various

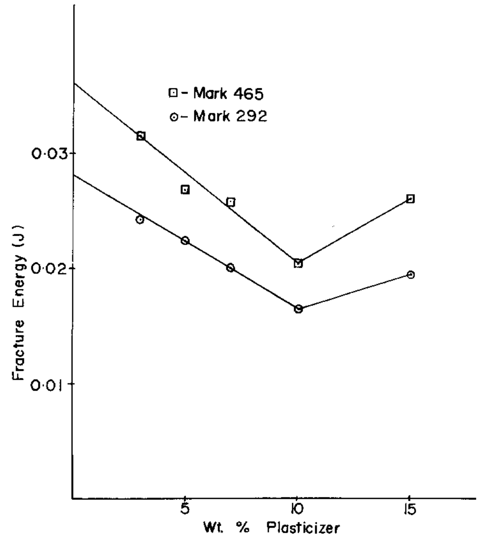

Figure 1 Measured impact fracture energies.

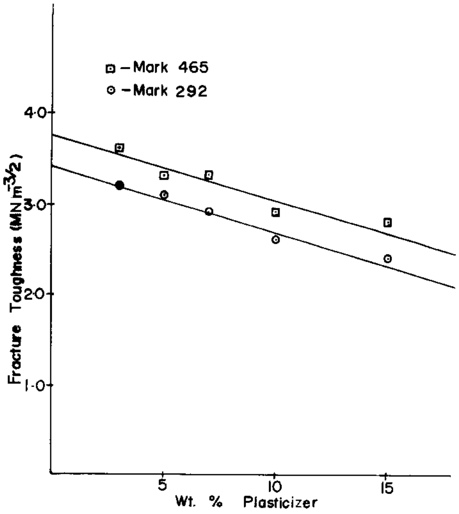

Figure 2 Fracture toughness from impact tests.

specimen compositions were estimated from the graph [1] of modulus versus wt% DOP. Poisson's ratio was taken as 0.32 (the value for polystyrene).

3.3. Fracture toughness tests using compact tension specimens

Most of the compact tension specimens were found to undergo a small amount of slow crack growth before they failed catastrophically. However, both 15 wt% plasticizer compositions showed considerable plastic deformation and no tendency to fail in a brittle manner. The values of load and crack length, together with the compliance function from Knott [17], were used to calculate the fracture toughness of all the compact tension specimens during the period of slow crack propagation. The average values of the fracture toughness for catastrophic failure for the 3, 5, 7 and 10% DIOP materials are shown in Fig. 3. The value for the 15% material is that at which gross yielding was first apparent.

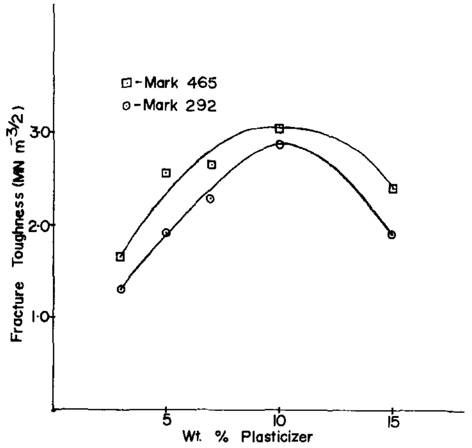

Figure 3 Fracture toughness from compact tension specimens.

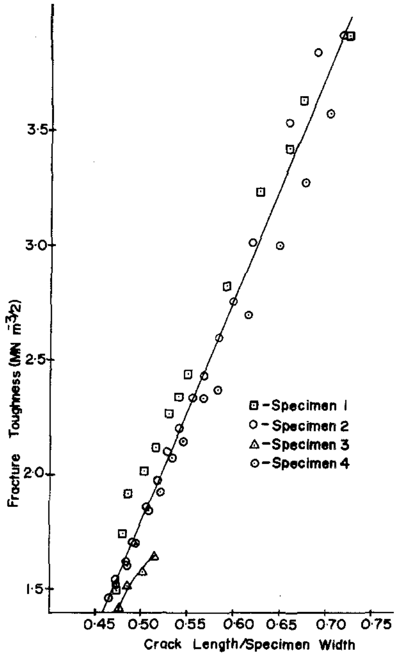

Figure 4 Plot of fracture toughness against crack length for 3% plasticizer Mark 465 specimens.

The 3 wt% plasticizer specimens (stabilized with Mark 465) demonstrated a far greater degree of slow crack growth than that of any other specimen composition and only one of the specimens of this composition failed catastrophically (specimen 3). An unexpected result was the linear dependence of fracture toughness upon crack length (see Fig. 4) found in the other specimens of this material.

3.4. Optical microscopy results

3.4.1. Qualitative observations

The crack tips of all the Mark 465 stabilized materials were examined under the optical microscope. Crazes were sometimes seen at the crack tips for all the materials. However the 3 wt% DIOP (465) specimens could also show a non-crazing failure mode which gave a rough fracture surface. The fracture surface from crazing failure was much smoother than that resulting from the non-crazing failure mode. In the 3% DIOP (465) material, the failure mode was apparently controlled by the initial razor notching rate, crazing being encouraged by a high notching rate.

The fracture surfaces of the impact and compact tension specimens were also examined in the optical microscope. The impact specimens were all found to show smooth fracture surfaces. It was therefore assumed that they probably failed by a crazing mechanism. All the compact tension specimens with 10 wt% or less of DIOP showed smooth fracture surfaces except for specimens Nos. 1, 2 and 4 of 3 wt% DIOP (465) where the fracture surfaces were quite rough. It was assumed that these latter three specimens failed by a non-crazing mechanism. In these three specimens, in addition to the general surface roughness, steps on the surface were visible which were oriented along the crack growth direction and increased steadily in size as the crack grew.

3.4.2. Craze shapes

Craze shapes were measured from the interference patterns on the optical micrographs for all the

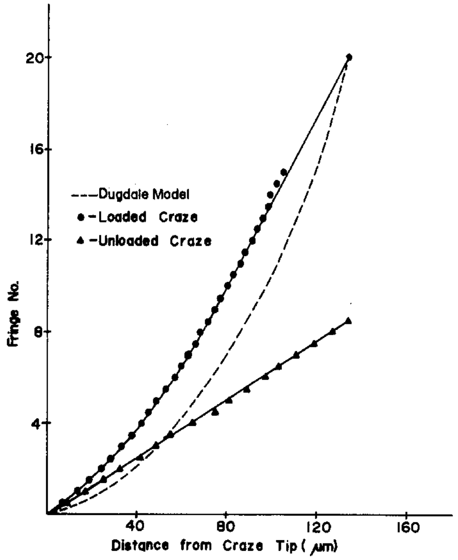

Figure 5 Craze shapes for a 10% plasticizer Mark 465 specimen.

Mark 465 stabilized materials. The shapes were qualitatively very similar for all plasticizer levels but the craze dimensions increased with an amount of plasticizer. The craze shape for the 10 wt% DIOP material is shown in Fig. 5 where the craze thickness is plotted in terms of the interference fringe number. This can be converted to actual craze thickness using the method of Brown and Ward [18] if one assumes a value of 1.30 (as measured by Mills and Walker [9]) for the refractive index of an unloaded craze in PVC. Also shown on Fig. 5 is shape predicted by the Dugdale model when fitted to the same craze length and maximum thickness. The measured craze shapes are very similar to those found by Mills and Walker [9] in a different PVC compound.

Although the fit of these craze shapes to the Dugdale model is not very good, it is still reasonable to use it to calculate the fracture toughness of the craze/crack system and the stress across the craze. This is because the main interest is in variation of craze stress and toughness between the different plasticizer levels rather than absolute values. They are obtained from the measured craze opening displacements and lengths using the expression derived by Rice [19].

$$\sigma_0 = \delta \frac{\pi E}{8R}$$

$$K_1^2 = \frac{\delta^2 \pi E^2}{8R}$$

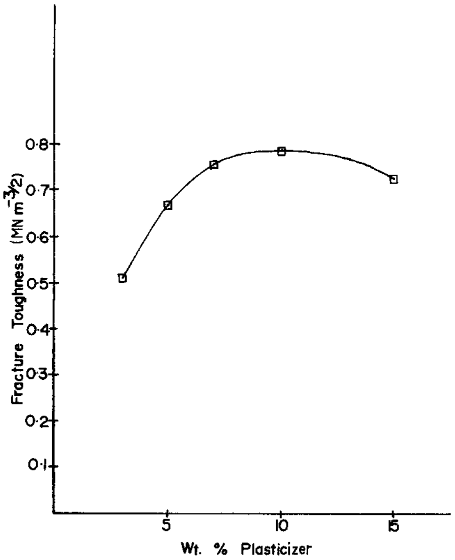

Figure 6 Fracture toughness calculated from craze shapes for Mark 465 specimens.

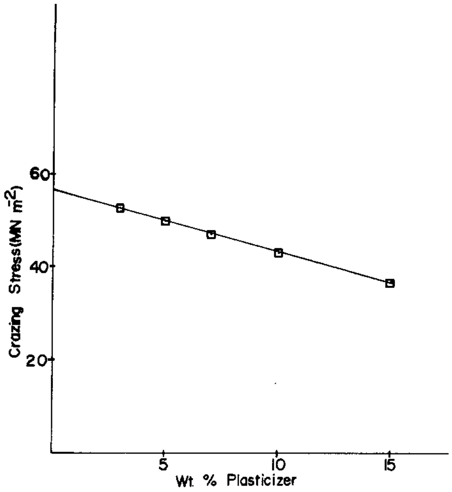

Figure 7 Craze stress calculated from craze shapes for Mark 465 specimens.

where δ = craze opening displacement
R = craze length
σ_0 = craze stress
K_1 = fracture toughness

and are shown in Figs. 6 and 7.

4. Discussion

4.1. Impact failures

The impact energies shown in Fig. 1 clearly exhibit the minimum in impact strength which is normally ascribed to antiplasticization. The calculated stress intensity factors for impact failure, Fig. 2, show only a monotonic decrease with increasing plasticizer content suggesting that the minimum impact energy is caused by a combination of a monotonic decrease in some failure stress together with a maximum in the modulus.

Frazer and Ward [20], working with PMMA, have shown that a critical failure stress criterion works well in blunt notched impact tests. In addition they showed that the stress was that required to initiate a crack by producing a craze. Plati and Williams [21] have used what is in essence the same critical stress criterion and found that they were able to predict the variation of impact energy with notch tip radius in a number of materials including PVC.

4.2. Craze stress

It is possible to calculate the stress at the root of the notch, σ_r, in the impact specimens using the normal stress concentration factors assuming small notch tip radii. For simple tension

$$K_1 = \sigma\sqrt{(\pi a)}$$

$$\sigma_r = \sigma[1 + 2\sqrt{(a/\rho)}] \simeq 2\sigma\sqrt{(a/\rho)}$$

$$\sigma_r \simeq \frac{2}{\sqrt{(\pi\rho)}}K_1$$

where σ is the remote stress
a the crack length
ρ the notch tip radius

Values of σ_r, calculated in this way are compared with values of craze stress, σ_0, obtained from craze shapes, in Table I.

Gotham [22] has measured the crazing stresses as a function of time for a number of polymers and finds that in PVC these stresses are very time dependent. The results in Table I are therefore consistent with the idea that σ_r is a high speed crazing stress.

It may be suggested that the failure criterion in these impact tests is that the stress at the root of the notch should equal a high speed crazing stress.

TABLE I

wt % DIOP	σ_0 (MN m^{-2})	σ_r(MN m^{-2})	σ_r/σ_0
3	53	260	4.9
5	50	240	4.8
7	47	240	5.1
10	43	211	4.9
15	37	205	5.5

4.2. Craze shapes

We shall consider next the results obtained from the measurements of craze shapes. The values of craze stress found using the Dugdale model are similar to those found by Mills and Walker. They used the same model but measured craze length and applied stress intensity factor rather than the craze lengths and crack opening displacement used in this work. The values of craze stress are also similar to Gotham's [22] directly measured 10 second crazing stresses.

It is interesting to note that the craze stress decreases monotonically with increasing plasticizer level although the modulus and yield stress go through a maximum at ~ 7% plasticizer. The steady decrease of craze stress with plasticizer concentration has also been observed by Kambour [6, 7] in polystyrene-based systems and is evidence that craze stress and yield stress are not directly related. These observations are in agreement with Gent's [12] theory of crazing as the glass transition temperature similarly decreases monotonically with plasticizer level [7]. It is however hard to see how these observations could be predicted from Argon's [8] theory of crazing as yield stress increases initially with plasticizer level and there is no reason to expect a change in surface tension.

4.3. Fracture toughness tests

The fracture toughness tests showed three different types of failure. These were the non-crazing failure of the 3% DIOP (465) specimens 1, 2 and 4, the crazing failure of all the other materials with 3, 5, 7 and 10% DIOP and a macroscopic yielding type of failure in the 15% DIOP specimens.

The observation of the crazing type failure is in accord with Mills and Walker [9] who observed craze material on the fracture surfaces of their compact tension specimens. They also found values of fracture toughness similar to those found in this work. The stress intensity values calculated from the craze shapes, shown in Fig. 6, differ by about a factor of 3 from those found experimentally. Both sets of data do however change in the same way with plasticizer level. The reason for this discrepancy is not clear, it was however also observed by Mills and Walker who suggested that it might be caused by yielding above and below the craze. Alternatively the discrepancy might be caused by the use of the

Dugdale model. It can be seen from Fig. 5 that this model is not a very good fit to the data and hence values of craze stress and fracture toughness obtained from it will not be very accurate. The shapes of the crazes for all the materials were very similar and only the actual size varied with plasticizer level. The Dugdale model should therefore give a reasonable estimate of the variation of the craze stress and fracture toughness between the materials although the actual values might be wrong. It is therefore reasonable to conclude that the measured fracture toughness for the crazing type failures is that necessary to propagate the crack/craze system through the material.

If the non-crazing failure of the 3 wt% DIOP (465) material is considered it may be noted that its behaviour was similar to that of the other specimens known to fail by a crazing mechanism. The fact that specimen 3 failed by a crazing mechanism, at a far lower applied stress intensity than the other three specimens, shows that the craze propagation mechanism of failure is the most energetically favourable mechanism for the 3 wt% DIOP (465) material.

The absence of a craze at the tip of the razor notch may be a reason for compact tension specimens 1, 2 and 4 (3 wt% DIOP (465)) failing by a non-crazing mechanism. As mentioned before, during optical observations of the crazing behaviour of all the specimen compositions used in this work, it was noticed that the faster the razor blade was pushed into the optical specimens the more likely a craze was to nucleate at the crack tip. This is in accord with the general observation [3] that crazing failure is more likely the faster the loading rate. Hence the probable reason that a craze was nucleated at the tip of the razor notch in specimen 3, but not in specimens 1, 2 and 4 (3 wt% DIOP (465)) is that specimen 3 happened to be notched at a faster speed than the others.

This non-crazing failure mode is probably the same as that described by Cornes and Haward [10] and by Tormala *et al.* [11] when discussing the formation of diamond shaped cavities. The former authors discussed the longitudinal steps which were observed on the fracture surface while the latter showed that this failure mode did not require a craze. The steady increase of stress intensity with crack growth may have been caused by the increase in size of the steps as larger steps would require a high energy shear failure.

The 15 wt% plasticizer materials showed considerable plastic deformation around the notch tip. Since it is known [3] that plastic deformation inhibits crazing, it seems likely that this inhibited the propagation of the craze that probably existed at the tip of the razor notch in all the 15 wt% plasticizer specimens. The marked decrease in the stress intensity necessary to start a yielding failure in the 10 to 15 wt% DIOP range could be due to the large decrease in modulus [1], which occurs over this composition range.

5. Conclusions

The conclusions to be drawn from this work are, firstly, that in lightly plasticized PVC compound the crazing stress decreases monotonically with increasing plasticizer concentration. Secondly, that in blunt ($\frac{1}{4}$ mm radius) notched impact tests, failure is controlled by the stress necessary to initiate a craze at the crack tip and this criterion, together with the variation of modulus with plasticizer level gives a minimum in impact energy at $\sim 10\%$ plasticizer. Thirdly, that three failure modes are possible in fracture toughness tests on these materials; these are a non-crazing but macroscopically brittle mode at low plasticizer levels, a crazing mode up to 10% plasticizer and a non-crazing ductile mode at 15% plasticizer.

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