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Antiplasticization of polyvinyl chloride in relation to crazing and fracture behaviour

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Experiments were carried out to study the effects of small amounts (10 p.h.r) of tricresylphosphate in polyvinylchloride on the crazing behaviour and fracture toughness over a wide range of temperatures. Crazing was induced by water/methanol mixtures and the critical crazing strain was measured as a function of immersion time and methanol concentration. Fracture toughness was measured on single-edge notched specimens in tension over three decades of strain rate in the temperature range −80 to 60° C. The 60 sec isochronous critical crazing strain displayed a minimum at around room temperature in an approximately parabolic fashion; the plasticized polymer exhibiting lower trough values, while the two curves intersected at both low and high temperatures. The fracture toughness curves, on the other hand, exhibited intermediate peaks, associated with β relaxations. The addition of plasticizers to the polymer reduced considerably the heights of the peaks and, once more, the two curves intersected at high temperature and merged at low temperature. From a comparison of the two sets of data, it is suggested that embrittlement due to antiplasticization is associated with a reduction in stability of the crazes as a result of the depression of β relaxations.

1. Introduction

Antiplasticization phenomena, caused by small amounts of plasticizers (i.e. < 15%), in polyvinylchloride (PVC) and other glassy polymers have been widely reported [1–7]. Antiplasticization is generally associated with a reduction in free volumes caused by strong interactions between plasticizer molecules and polymer chains [6–8]. The reduction in free volumes can be inferred directly from density measurements insofar as they show that density values calculated from additivity rules are lower than those obtained in practice [4, 6].

As a consequence of such densification, some physical properties, such as gas diffusion, thermal expansion, modulus, impact strength, etc., are affected in the opposite manner to that observed with plasticization phenomena (e.g. at high plasticizer concentrations), from which the term antiplasticization has been derived [2].

The most illuminating observations that have been reported to date on antiplasticization phenomena, however, are those made in relation to dynamic mechanical spectra. These have clearly revealed a depression in the β relaxation peak and a concomitant reduction in glass transition temperature without any apparent effect on the height of the α relaxation peak [5, 9]. Consequently, physical properties are affected by antiplasticization phenomena only over the temperature range which is influenced by the β relaxations. In other words a reversion from antiplasticization to plasticization takes place at both low and high temperatures, which can be conveniently called T_b and T_a threshold temperatures, respectively.

T_b and T_a threshold temperatures have been found also with respect to yield strength, measured by plain strain compression tests [9]. In the same study, the occurrence of brittle fractures in tensile tests at low temperatures have precluded direct observations on the T_b temperature but it clearly emerged that the threshold temperatures in tension are much more strain-rate dependent than in compression.

In tension, for instance, the T_a temperature for PVC containing 10 p.h.r tricresyl phosphate (TCP) increases from an estimated value of 5 to 10° C at 0.3 $\sec^{-1}$ to a measured value at 32° C at 2.2 $\sec^{-1}$.

Such a strong dependence of tensile deformation behaviour on strain rate has also been observed in creep experiments [10]. In this latter case it was shown that the upper threshold temperature, T_a, not only decreased with increasing duration time under stress, but also with the level of applied stress. It is worth noting that antiplasticization phenomena are quite distinct from physical ageing insofar as in the latter case the reduction in free volumes persists up the rubbery state of the polymer, causing a depression of both α and β relaxations [11].

Despite the widely reported embrittlement behaviour of lightly plasticized PVC, particularly in impact tests, very little attention has been paid to elucidation of the mechanism of fracture phenomena associated with antiplasticization.

There appears to be a variance, for instance, between

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fracture data derived from impact tests and those obtained from slow crack growth tests using compact tension specimens. For tests carried out at room temperature the slow crack growth fracture toughness shows a maximum at 10% wt/wt with increasing plasticizer concentration (di-isooctyl phthalate), while the impact fracture energy displays a minimum at the same concentration [12]. It is interesting to note that the calculated value for the crazing stress at the crack tip decreased monotonically with increasing plasticizer concentration for both tests.

Crack-growth data obtained from fatigue measurements on PVC of differing molecular weights containing up to 13% dioctyl phthalate (DOP) were also not conclusive on the effects of antiplasticization [13]. These data failed to reveal any difference in crack growth rate between the plasticized and antiplasticized specimens, while the K_c values were found to decrease in all cases, except one, with increasing plasticizer concentration. Fatigue studies at lower frequencies, on the other hand, showed a faster crack growth rate for the plasticized samples up to 20% DOP [14].

Observations on crazing phenomena in fatigue tests revealed the formation of perpendicular craze bands ahead of the crack tip, which increased in size with increasing plasticizer concentration.

It is evident from the foregoing discussion that there is a clear lack of understanding of time (or strain rate) and temperature effects on crazing and fracture toughness for lightly plasticized polymers. The purpose of this paper, therefore, is to throw some light on the inter-relationship between crazing and fracture toughness for lightly plasticized PVC materials, with respect to the change over from antiplasticization to plasticization by varying the ambient temperature.

2. Experimental procedure

2.1. Materials and specimen preparation

The polymer and plasticizer selected for this investigation were, respectively, a low molecular weight PVC homopolymer (ISO viscosity no. = 87) and tricresyl phosphate at 10 p.h.r. level. This particular combination and concentration was chosen in view of the pronounced antiplasticization behaviour displayed with respect to modulus and yield strength [7, 9–11]. The full details of the formulations are shown in Table I. The ingredients were premixed in a high-speed vortex mixer and compounded on a two-roll mill at 170° C. Plaques, 0.3 to 0.5 and 2.5 mm, respectively, were compression moulded at 180° C using a pressure of ~7 MPa and cooled under pressure. These were stored in a refrigerator to minimize physical ageing prior to testing.

TABLE I PVC formulations

	Unplasticized PVC	Plasticized PVC
Polyvinyl chloride Homopolymer, suspension grade (ISO viscosity no. = 87)	100.0	100.0
Tricresyl phosphate Plasticizer (Reomol TCP ex Ciba-Geigy)	–	10.0
Stearic acid (ex BDH)	2.0	2.0
Dibutyl tin didodecanoate (Stanclere TL, ex Akzo Chemie)	2.5	2.5

2.2. Testing procedure

2.2.1. Crazing experiments

Rectangular strips 10 mm wide were cut from 0.3 to 0.5 mm thick plaques, and wound around a series of cylindrical steel mandrels, ranging in diameter from 10 to 130 mm, in order to induce varying levels of axial strains into the specimens. The specimens were secured on to the mandrels by fastening the two ends by means of a staple, as shown in Fig. 1. The axial strain was calculated according to the Equation 1 [15]

$$\varepsilon_a \equiv -\varepsilon_b = \frac{1}{2(R/h)+1} \tag{1}$$

where ε_a is the strain at the outer surface, ε_b the strain at the inner surface, R the radius of the mandrel, and h the thickness of the specimen.

The mandrels were immediately immersed in a 1 : 1 mixture of distilled water and methanol maintained at constant temperature. The use of such a water/methanol mixture made it possible to carry out tests over a wide range of temperatures varying from −50 to +60° C.

The specimens were removed from the liquid bath after a predetermined period of time (normally 60 sec) wiped dry and examined under an image amplifier to detect the formation of crazes in the width direction.

The level of imposed strain at which crazes were observed was recorded as the "critical crazing strain", ε_c.

In order to determine the effects of methanol concentration on the critical crazing strain, experiments were also carried out at room temperature over the

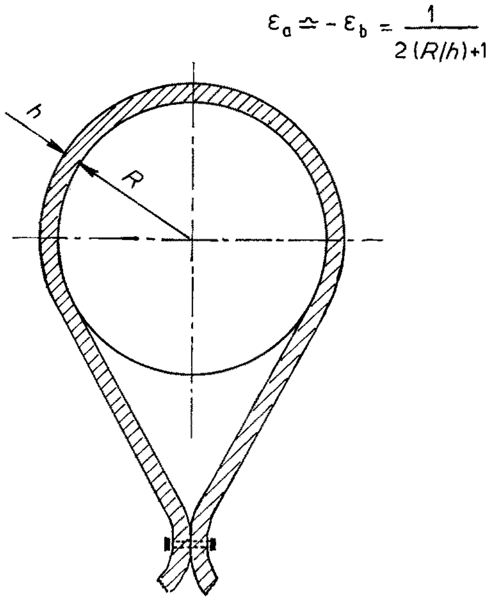

Figure 1 Axial strain in rectangular strips wrapped around cylindrical mandrels.

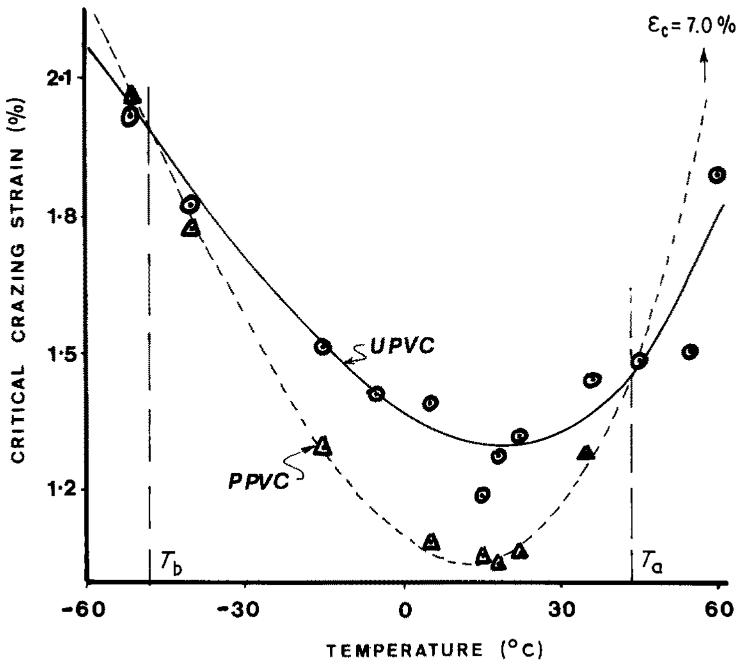

Figure 2 Isochronous critical crazing strain (60 sec) as a function of temperature.

entire range of water/methanol ratios. Experiments were also carried out using the standard 1 : 1 water/methanol mixture at room temperature to determine the relationship between critical crazing strain and immersion time. In all cases a total of four specimens were tested to determine the range value of the critical crazing strain.

2.2.2. Fracture toughness measurements

Rectangular strips 20 mm wide and 60 mm long were machined from the 2.5 mm thick plaques and a slit 5 mm long was cut out by means of a 1 mm thick precision diamond wheel to produce single-edge notched (SEN) type specimens. A sharp cut about 0.25 mm long was subsequently introduced at the tip of the notch by means of a razor blade.

Unnotched rectangular strips, 15 mm wide and 120 mm long were also machined from the same plaques for modulus measurements. The SEN specimens were tested to fracture in a tensile testing machine, fitted with an environmental chamber, over the temperature range -80 to $+60°$ C at five nominal strain rates ranging from 0.0028 to $0.28\,\text{sec}^{-1}$ and both the peak load and total fracture energy were recorded. The unnotched rectangular specimens were also tested at the same temperatures and strain rates and the slope of the initial part of the load/grip separation curve was used to calculate the "nominal" modulus, E'. From the fracture data, the "nominal" critical stress intensity factor, K_c, was calculated using the compliance analysis [16], i.e.

$$K_c = \frac{Y\hat{P}}{BW^{1/2}} \tag{2}$$

where Y is the compliance calibration factor, $\hat{P}$ the peak load, B the thickness of the specimen, and W the width of the specimen.

An "equivalent" fracture toughness parameter was also calculated from the specific fracture energy, $\overline{G}_c$ (i.e. total fracture energy/crack ligament area) and the nominal modulus, E', and expressed as $(E'\overline{G}_c)^{1/2}$. This approach implies that in the absence of gross plastic deformations a non-linear load/extension curve resulting from the viscoelastic nature of the material can be linearized on account of the recoverability of strain energy.

Obviously the "equivalent" fracture toughness parameter, $(E'\overline{G}_c)^{1/2}$, may well depend on the a/W (crack length/specimen width) ratio, because the specific fracture energy ($\overline{G}_c = U/A$) is not equal to the true critical strain energy release rate ($G_c = \partial U/\partial A$), but it will provide more realistic values for the fracture toughness of polymers than those calculated from linear elastic fracture mechanics (LEFM).

3. Results and discussion

3.1. Crazing studies

Fig. 2 shows plots of the 60 sec isochronous critical crazing strain ε_c, as a function of temperature for both plasticized and unplasticized PVC, fitted to a third degree polynomial. Both materials display a minimum for the critical crazing strain in the temperature range between the β and α relaxation temperatures.

The lightly plasticized samples, however, show much lower critical crazing strain values in this region than the unplasticized samples, while the two curves display the typical T_a and T_b threshold temperatures associated with antiplasticization phenomena in relation to modulus and yield strength, as discussed in Section 1. It is instructive to note that at room temperature, i.e. within the antiplasticization region, the methanol concentration in the environmental medium and the incubation time for crazing do not display any interactive effects with the plasticizer in the formation of crazes (Figs 3 and 4). This can be deduced from the observation that the difference in the critical crazing strain values between the unplasticized and plasticized polymer is approximately constant in all cases. Furthermore, extrapolating the crazing strain curve in Fig. 4 to very short times, i.e. equivalent to the duration of the load in impact tests, suggests that fracture induced at very high strain rates may occur without

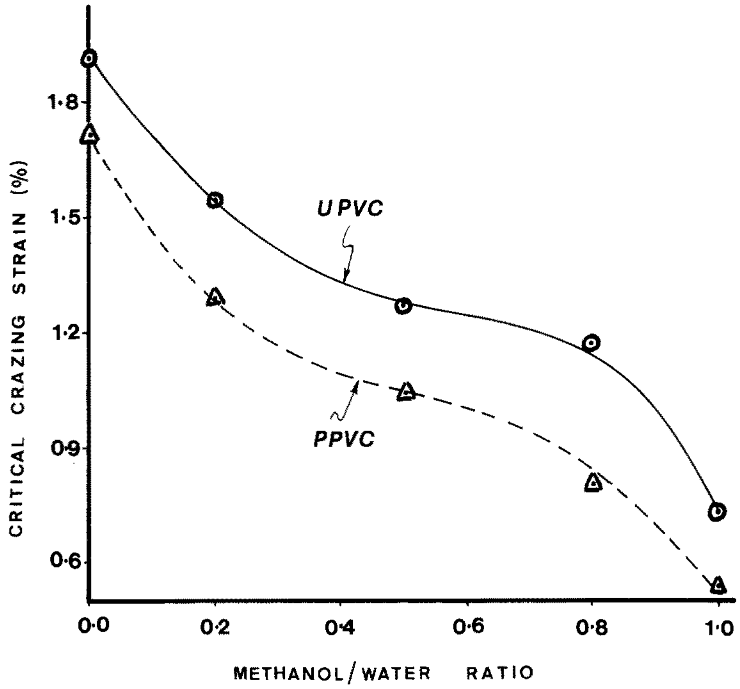

Figure 3 Effect of methanol/water volumetric ratio on the isochronous critical crazing strain.

the formation of visible crazes, owing to the very high values for the critical crazing strain expected under these conditions.

Consequently, the delayed formation of crazes would increase the level of strain energy in the specimen at their incubation stage, rendering them less stable and, therefore, inducing catastrophic fracture prior to their reaching the dimensions required to make them visible.

Under high strain rates the addition of plasticizer is not likely to decrease substantially the critical crazing strain, thus it must be the further reduction in craze stability that is responsible for the embrittlement behaviour through antiplasticization.

3.2. Fracture data

Fig. 5 shows plots of K_c values obtained from the LEFM equation against the equivalent fracture toughness parameter, $(E'G_c)^{1/2}$, calculated from the specific energy. Excluding the data at 60° C for all PPVC specimens and two values (at the lower strain rates) for UPVC specimens, the correlation between the two sets of fracture data, is remarkably good, the correlation coefficients being, respectively, 0.96 for UPVC data, and 0.92 for PPVC data. The fracture mode for the specimens that did not produce data falling in the range of such correlation was clearly identified as a "plastic-tearing" type, while the anomalous behaviour for the two PPVC specimens at lower strain rate was associated with a strain-rate related tough/brittle transition.

Figs 6 to 8 show plots of the equivalent fracture toughness, $(E'G_c)^{1/2}$ against temperature in the range -80 to $+60$° C at three strain rates. The shape of these curves was determined by a fourth degree polynomial fit using the data at low strain rates. Fig. 6 shows a displacement of the peak of the curves to higher temperatures with increasing strain rate for the

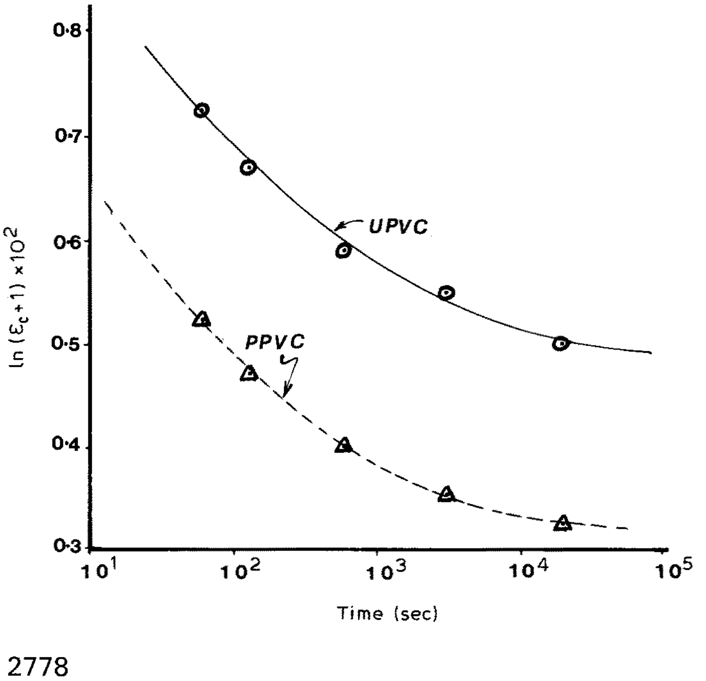

Figure 4 Effect of incubation time on the "true" critical crazing strain (ln (ε_c + 1), where ε_c is the "engineering" strain).

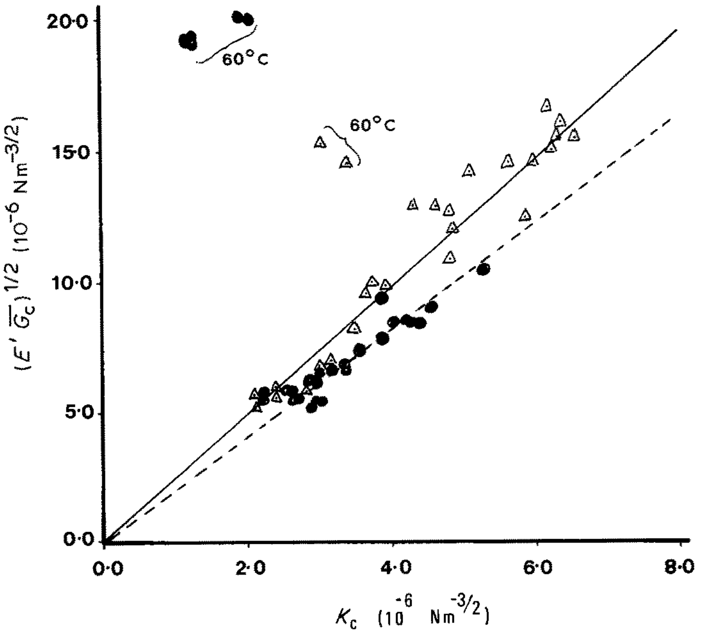

Figure 5 Correlation between the equivalent fracture toughness parameter, $(E'\bar{G}_c)^{1/2}$, and the values of K_c calculated from the load to fracture.

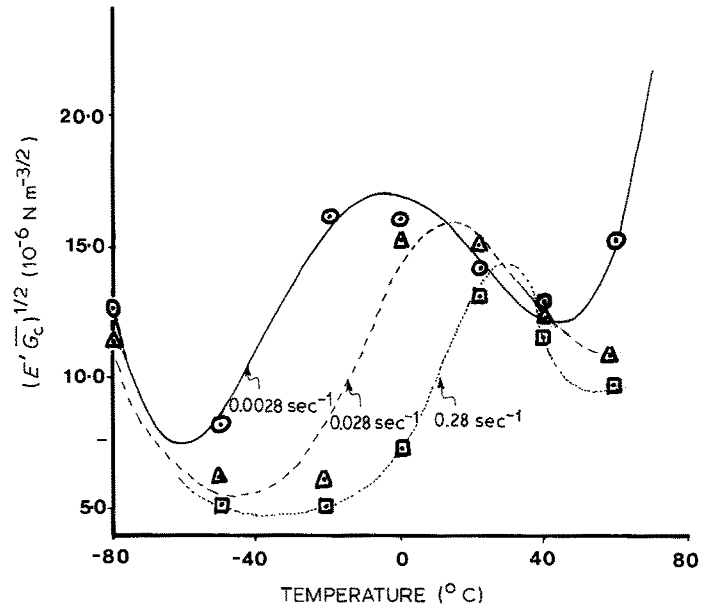

Figure 6 Equivalent fracture toughness for unplasticized polyvinyl chloride (UPVC), at different strain rates, as a function of temperature.

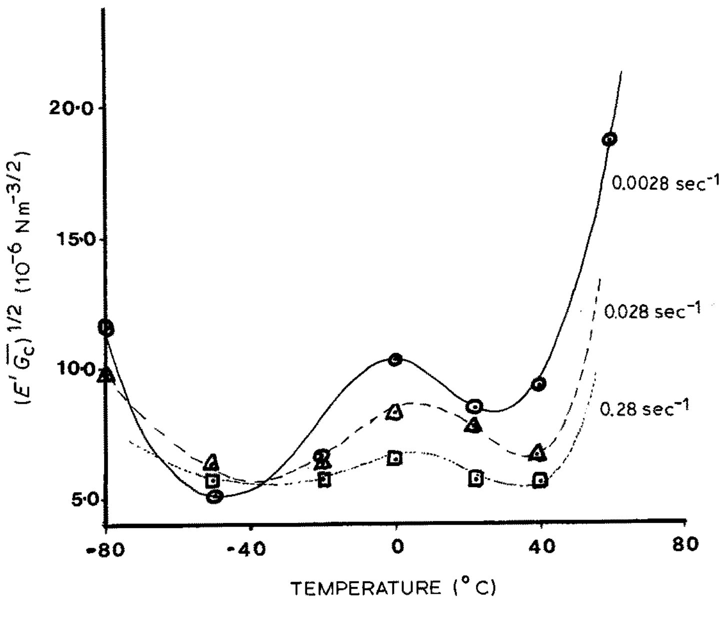

Figure 7 Equivalent fracture toughness for plasticized polyvinyl chloride (PPVC), at different strain rates, as a function of temperature.

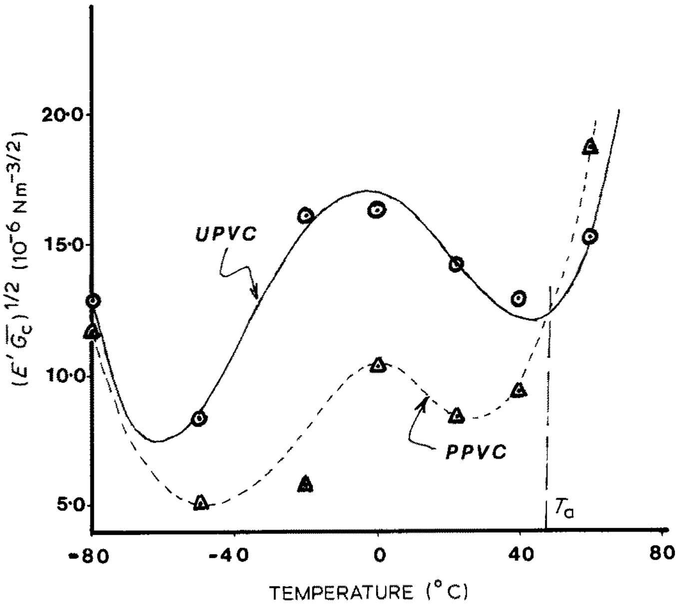

Figure 8 Equivalent fracture toughness parameter as a function of temperature (strain rate = 0.0028 $\sec^{-1}$).

case of UPVC. Extrapolation to much higher strain rates is expected to result in the merging of such peaks with those arising from the α transition, as already established from impact tests [17].

A comparison with the plots in Fig. 7 for PPVC clearly reveals a substantial depression of such peaks, at all strain rates, as a result of antiplasticization. A clearer illustration of antiplasticization with respect to fracture data is shown in Fig. 8 by comparing the $(E'\overline{G}_c)^{1/2}$ curves for UPVC and PPVC. It is interesting to note that these curves are remarkably similar to those for tan δ obtained from dynamic mechanical tests, suggesting that the flattening of the peaks in the fracture curves must be associated with the depression of β relaxations.

A comparison of the effects of antiplasticization on crazing and fracture data is also very instructive insofar as while the general reduction in critical crazing strain is matched by a lowering of fracture toughness, the occurrence of minima, in the first case and peaks in the second, suggest that the enhancement of nucleation of crazes resulting from antiplasticization cannot be solely responsible for the observed embrittlement. The peaks in the fracture data in Figs 6 to 8 may point to an increased stability of crazes from β relaxations.

The shallower and smaller peaks for the plasticized samples, therefore, must be responsible for the lower stability of the crazes and for the observed reduction in fracture toughness. Furthermore, increasing the strain rate would flatten these β relaxation peaks much sooner than for the unplasticized samples and produce a more pronounced embrittlement through antiplasticization, as suggested earlier with respect to the inferences on impact fracture behaviour.

4. Conclusions

The main conclusions that can be drawn from this study are, firstly, that the presence of a small amount of plasticizer in PVC compositions reduces the critical crazing strain over a distinct temperature range confined by the typical T_a and T_b threshold temperatures associated with antiplasticization. Secondly, that the variation of fracture toughness as function of temperature displays the typical strain-rate dependent peaks associated with β relaxations, which are drastically reduced in the presence of small amounts of plasticizers. A definite T_a threshold temperature exists at high temperatures also with respect to fracture behaviour, while the merging of the curves at low temperatures for the plasticized and unplasticized samples suggests that a T_b threshold from antiplasticization is possible, albeit the increase in fracture toughness resulting from the addition of plasticizer may be rather small. Furthermore, the data suggest that the embrittlement due to antiplasticization may arise from the decreased stability of the crazes as a result of the depression in β relaxations.

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