Critical energy for crack initiation in rubber-toughened poly(methyl methacrylate)

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A single specimen J-integral method has been used to evaluate the critical energy for crack initiation in rubber-toughened poly(methyl methacrylate). An abrupt transition is observed in the evolution of J_{Ic} as a function of particle volume fraction and the sudden increase in toughness appears to be directly related to a comparable change in the materials's ability to nucleate plasticity.

(Keywords: rubber-toughened PMMA; fracture toughness; plasticity)

INTRODUCTION

The fracture toughness of rubber-toughened poly(methyl methacrylate) (RT-PMMA) has recently been evaluated as a function of particle volume fraction, and the observed behaviour was related to the capacity of the material to nucleate plasticity. The latter property is characterized by a work-hardening parameter measured in the early stages of the non-elastic deformation (preyield zone of the stress–strain curve) during a constant strain-rate compression test. Values of critical stress intensity factor K_{Ic} obtained by slow rate single-edge notched bend tests exhibit a striking variation with particle volume fraction, i.e. a sudden increase in toughness occurs for a particular fraction $V_f \approx 0.3$ in the case of particles of the core–shell type and outer diameter of 270 nm. On both sides of this critical fraction, the stress intensity factor, taken at the onset of non-linearity of the load–displacement curve, remains fairly constant at a lower or upper value in the low or high volume fraction range respectively. The work-hardening rate displays the same kind of behaviour, the abrupt drop in K when V_f is increased beyond 0.3 implying a transition from difficult to easy plasticity nucleation. This approach thus provides a semi-quantitative correlation between plasticity and resistance to crack initiation[1].

The fact that the polymer systems under investigation showed increasing ductility as the particle fraction was increased was a strong incentive to check toughness by the J-integral approach[2]. Its application to polymers proves to be rather difficult and questions arise about the reliability of the crack blunting line concept to determine the J-integral value for crack initiation[3–5]. Also, the method requires a large number of specimens to establish the resistance R-curve, and we were not able to consider it for this reason. A single specimen J-integral method was recently proposed as an alternative to the standard method[6] and its use in the case of RT-PMMA is presented below.

EXPERIMENTAL

Fracture toughness

The single specimen J-integral method considers a single-edge notched bend (SENB) specimen which obeys the usual geometrical requirements. One of the basic steps of the method is to express the plastic component of the displacement Δp through the following empirical equation[6]:

$$\Delta p = A[P/B(W-a)^2]^m \qquad (1)$$

where P is the load reached at the point considered, B and W are the specimen thickness and width, respectively, and A and m are fitting constants.

The next step is to obtain the plastic displacement at the critical point for crack initiation Δp_C. Differentiating equation (1) yields[6]:

$$\Delta p_C = \Delta p_S/[1 + m(P_S - P_C)/P_C + 2m\,\Delta a/(W-a)] \qquad (2)$$

where Δp_S is the plastic displacement at point S up to which the specimen is loaded and Δa is the apparent crack growth. The curve corresponding to equation (2) is superimposed on the load–displacement curve and their intersection gives the critical point. The critical J-value, J_{Ic}, is then computed from the area U under the load–displacement curve up to point C, according to the classical formula:

$$J = 2U/B(W-a) \qquad (3)$$

Plasticity

During a compression test at constant strain rate, plasticity is viewed as the nucleation and propagation of

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localized shear defects in the chain arrangement. Beyond yielding, stationary plastic flow is associated with the thermally activated propagation of these micro-shearbands, whereas the early stages of the non-elastic deformation behaviour predominantly refer to the nucleation stage. The latter is characterized by work-hardening rate measurements; the relevant parameter used here is the slope of the plot of the applied stress σ_a as a function of non-elastic strain ε_p. We thus introduce

$$K' = \left(\frac{\partial \sigma_a}{\partial \varepsilon_p}\right)_{\dot{\varepsilon}_t} \tag{4}$$

which is related to the number of shear nuclei produced per unit stress[7]. The transition from difficult to easy plasticity nucleation has been quantified with this parameter in RT-PMMA samples of various particle sizes. This behaviour could be rationalized in terms of a single critical interparticle distance τ_c, independent of the particle diameter[8]. On the basis of a percolation approach[9], it is proposed that this transition implies connectivity of plastically active matrix ligaments of thickness less than τ_c

The PMMA matrix has a number-average molecular weight $M_n = 0.65 \times 10^3$ g mol^{-1} and a polydispersity index $I = 2$, as determined from gel permeation chromatography in tetrahydrofuran with a polystyrene calibration. The particles have a soft rubber core and a rigid grafted PMMA shell. Inner and outer diameters are 241 and 271 nm, respectively. Details of material elaboration and preparation have been given elsewhere[1,10].

SENB fracture tests and compressive deformation experiments have all been performed at room temperature. In both sets of experiments the crosshead speed of the Instron machine was set at 100 μm min^{-1}. In the fracture experiments, the ratio of the span to the width of the specimen, S/W is equal to 4, while a/W was kept close to 0.5. Compression testing was done on cylindrical samples (diameter 8 mm, height 16 mm). K' work-hardening parameter data are accessible over the entire preplastic range of the stress–strain curve[8].

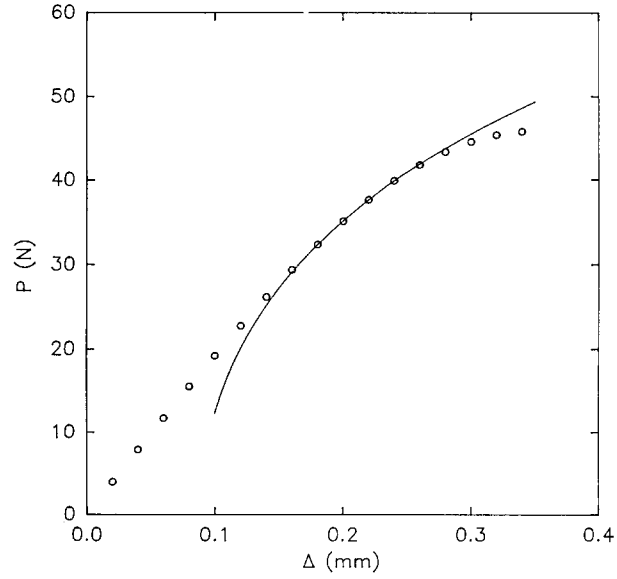

Figure 1 Load–displacement curve for the blend with 20% particle volume fraction: O, data points; ——, equation (2)

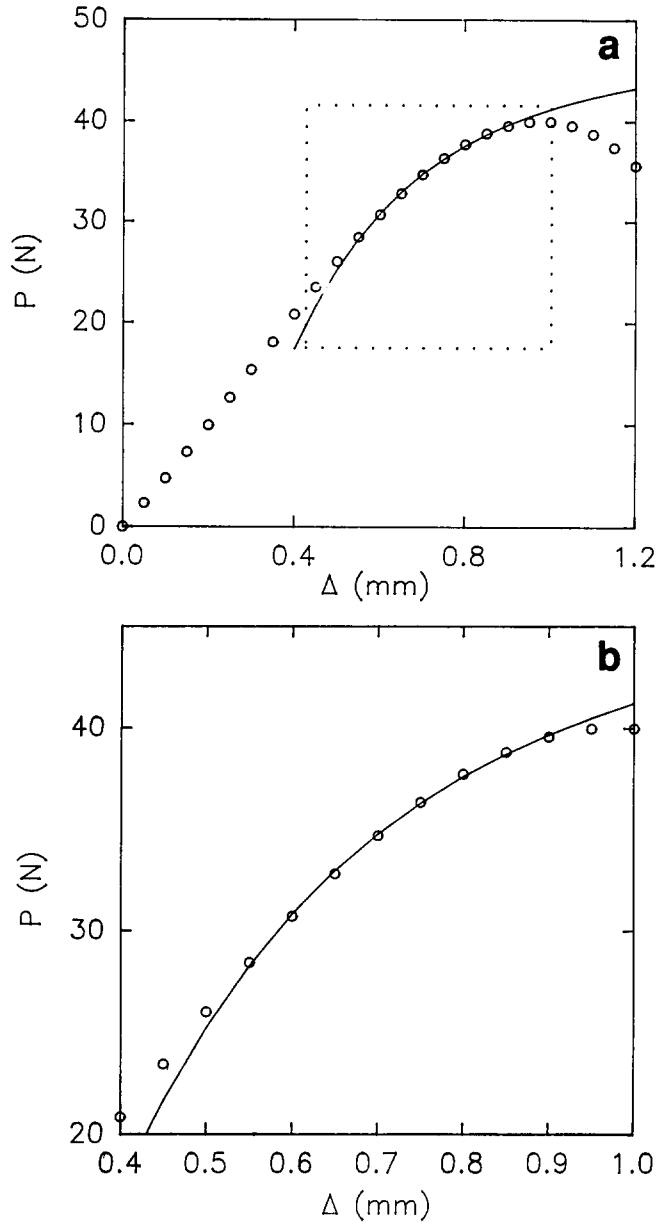

Figure 2 (a) Load–displacement curve for the blend with 40% particle volume fraction; (b) enlargement of the area outlined with dots in (a). O, Data points; ——, equation (2)

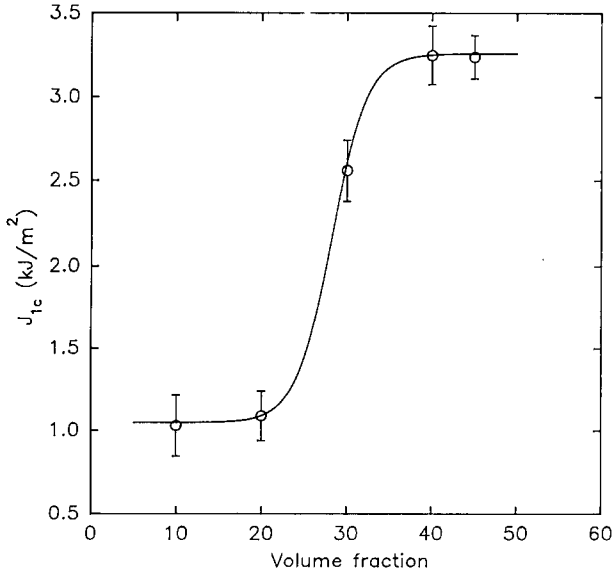

Figure 3 Evolution of J_{1c} as a function of particle volume fraction

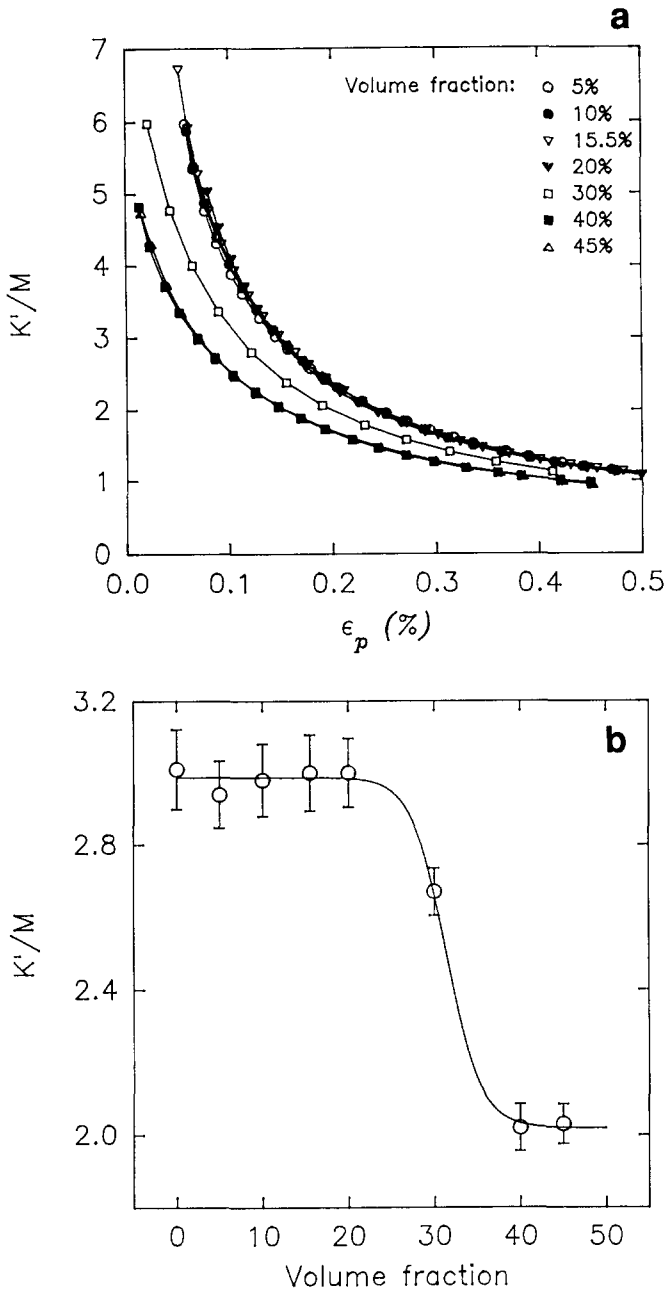

Figure 4 Evolution of the work-hardening parameter as a function of (a) the non-elastic deformation in the preplastic range; (b) particle volume fraction for $\varepsilon_p = 1.5 \times 10^{-3}$

RESULTS AND DISCUSSION

The experimental procedure of the single specimen J-integral method is illustrated in *Figures 1* and *2* for 20% and 40% particle volume fractions, respectively. *Figure 3* gathers the J_{Ic} data which exhibit a striking evolution for a critical volume fraction around 30%, as already seen on the K_C data mentioned previously. It is worth noting that the critical point C obtained with this method is close to the onset of non-linearity of the load–displacement curve, which validates the choice of the latter point in the K_C determination[1].

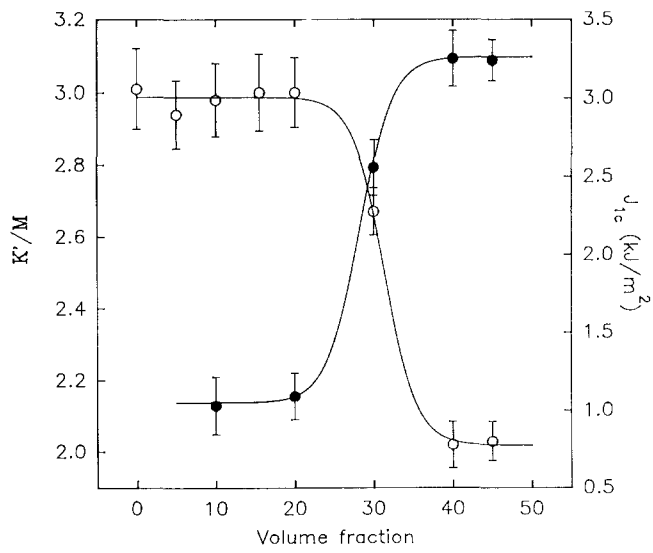

Figure 5 Comparison of variations of J_{Ic} (●) and K'/M (○) as a function of particle volume fraction

Work-hardening rate measurements are presented in *Figures 4a* and *b*. The quantity K'/M (where M is the apparent elastic modulus of the sample) is used and its variation as a function of particle volume fraction is given for a non-elastic strain $\varepsilon_p = 1.5 \times 10^{-3}$. The peculiar shape of the curve in *Figure 4b* does not depend on the choice of ε_p as seen from *Figure 4a*. For volume fractions below 30% the capacity of the blends to nucleate plasticity remains fairly stable. Then, the occurrence of a sudden drop in K'/M indicates an improved ability to shear nucleation.

The correlated evolutions of toughness (J_{Ic}) and capacity of the material to develop plasticity (K'/M) are illustrated in the plot of *Figure 5*. Both parameters, although referring to different stress fields, show the same response of the materials' morphology to energy dissipation processes. Based on our previous work on shear nucleation with particles of various diameters[8], we may therefore suggest that percolation of ductile matrix ligaments is a necessary requirement in both aspects of the observed mechanical response of these systems.

REFERENCES

1 Gloaguen, J. M., Steer, P., Gaillard, P., Wrotecki, C. and Lefebvre, J. M. *Polym. Eng. Sci.*, in press
2 Rice, J. R. *J. Appl. Mec.* 1968, **35**, 379
3 Hashemi, S. and Williams, J. G. *Polym. Eng. Sci.* 1986, **26**, 760
4 Narisawa, I. and Takemori, M. T. *Polym. Eng. Sci.* 1989, **29**, 671
5 Huang, D. D. and Williams, J. G. *Polym. Eng. Sci.* 1990, **30**, 1341
6 Zhou, J., Yin, J., Liu, W. and Li, B. *Polym. Commun.* 1991, **32**, 423
7 François, Ph., Melot, D., Lefebvre, J. M. and Escaig, B. *J. Mater. Sci.* 1992, **27**, 2173
8 Gloaguen, J. M., Heim, P., Gaillard, P. and Lefebvre, J. M. *Polymer* in press
9 Margolina, A. and Wu, S. *Polymer* 1988, **29**, 2170
10 Wrotecki, C., Heim, P. and Gaillard, P. *Polym. Eng. Sci.* 1991, **31**, 213