

THE DAMAGE MECHANISMS IN RUBBER TOUGHENED PMMA  
(Polymethylmethacrylate)

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Mechanical damage was investigated in polymethylmethacrylate toughened with core-shell (hard core) rubber particles. During a tensile experiment, volume changes, light absorption, light scattering and the small strain elastic modulus were recorded. Light scattering was quantitatively related to the number of damaged particles and a fast partial unloading technique allowed determination of the non elastic part of these changes in material properties. Experiments performed between  $10^{-5}$  and  $10^{-1} \text{ s}^{-1}$  and between 20 and 70 °C showed time-temperature transitions. Three types of microstructural damage were observed: pure matrix plasticity at very low strain rates or high temperatures, rubber cavitation at correlated locations at medium strain rates and temperatures, and disordered cavitation, rubber tearing and matrix plasticity at high strain rates or low temperatures.

INTRODUCTION

Glassy polymers are mainly rather brittle materials and if used for structural applications, are modified to behave in a more ductile manner and to develop large damage zones before breakage. The techniques employed to toughen such polymers vary depending on the nature of the material. Inclusion of small rubber particles in glassy polymer matrix is one very common way of achieving a high degree of toughness. The particles may consist of pure rubber, or may have an inner structure as in the so-called « core-shell », « onion » or « salami » particles. Toughening mechanisms in this type of polymer blend have given rise to a large number of experimental studies in many different polymers [1 - 4]. Recently, it has been experimentally demonstrated in several materials, that rubber particles cavitate and that this cavitation may be the precursor triggering the other mechanisms of damage [5 - 10]. A first theoretical analysis of cavitation in pure rubber [11, 12, 13] showed that particles may cavitate even under low mean tensile strain. A more refined model has now been proposed, discussing the nature and the mechanism of onset of the void and including a volume conservation criterion [14]. In this paper, the mechanical definition of damage (a decrease in modulus) was

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used to characterise changes in the inner structure of rubber toughened polymethylmethacrylate (RT-PMMA) during the deformation process. Unrecoverable volume changes, Poisson's ratio, lost energy and light transmission and scattering were recorded simultaneously. Techniques of measurement were developed to allow experiments over wide ranges of strain rate ( $10^{-5}$  to  $10^{-1}$  s $^{-1}$ ) and temperature (20 to 70°C). A partial fast unloading technique was used to estimate the non elastic volume change, while light transmission was found to be quantitatively related to the number of damaged rubber particles. Time-temperature transitions were carefully examined and experimental results compared with predicted values.

### EXPERIMENTAL TECHNIQUE

#### Material

The polymer was a low molecular weight PMMA ( $M_w = 120\ 000$ ) containing 40 % core-shell rubber particles, referred to as Altuglas EI-CH 60 (ATOHAAS Company). In this material, the particles have a hard core (PMMA), a crosslinked rubbery shell (butyl-acrylate-styrene) and an outer PMMA shell, the particle diameter is about 200 nm and the rubber content is 15% (Figure 1).

#### Mechanical measurements

As shown in Figure 2, the sample was a simple tensile sample, about 100 mm long, 10 mm wide and 2 mm thick of strictly constant cross section along its entire length in order to ensure homogeneous damage. Cross section was recorded by means of a transverse strain gage and the longitudinal strain was recorded with an identical strain gage. Volume changes were calculated using the simple equation for small strains. Correction for the elastic part is particularly important for volume changes. The total volume change is always positive, (including the elastic volume change as Poisson's ratio is lower than 0.5), showing small « ticks » at each unloading. Using these ticks extrapolated as on Figure 3 it is possible to calculate the mechanical damage and also the elastic part of the volume change. The remaining non elastic volume change (Figure 6) is almost zero during first damage (0 to 7 % strain), and subsequently depends on strain rate and temperature. The threshold strain below which the volume remains constant depends on strain rate and temperature. At low strain rates, the volume remains constant for any strain or level of damage. Above the critical rate, the volume increases with strain above the threshold with a slope also increasing with strain rate and can reach up to 50% of the theoretical increase in the case of a purely dilatational strain.

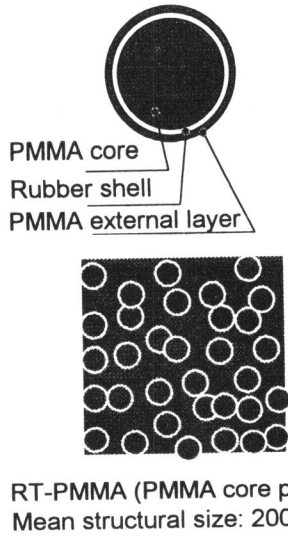


Figure 1 Rubber toughened PMMA with hard core (PMMA) and rubbery shell.

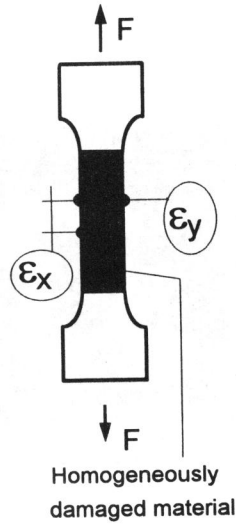


Figure 2 Standard tensile sample about 100 mm long, 10 mm wide, 2 mm thick.

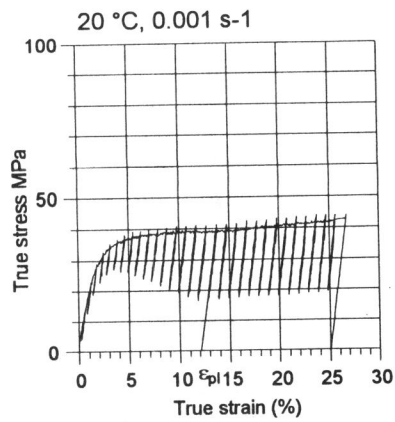


Figure 3 True stress-strain curve. Unloadings at high strain rate ( $0.5 \text{ s}^{-1}$ )

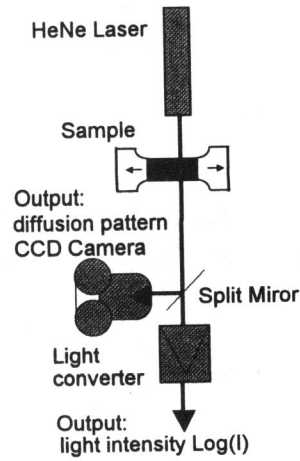


Figure 4 Light absorption and light scattering setup.

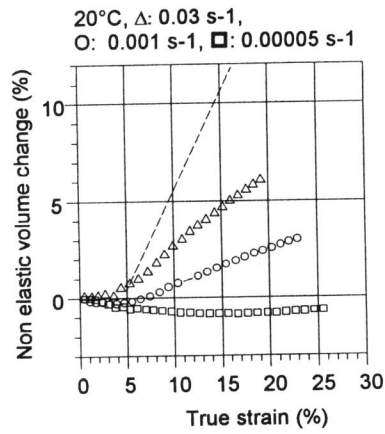
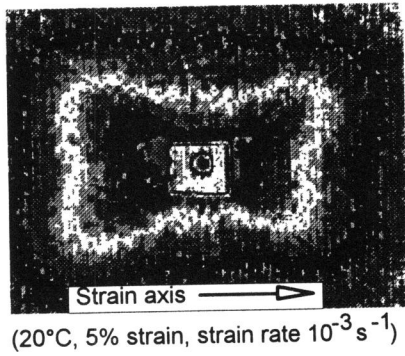


Figure 5 Light diffraction gives a cross like pattern.

Figure 6 Volume change corrected for elastic changes.

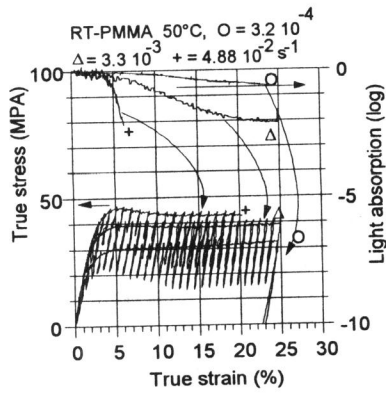
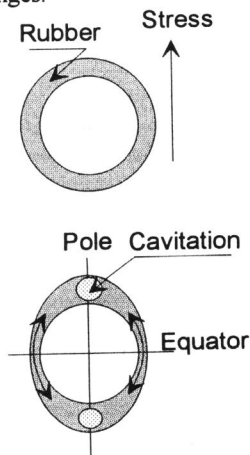


Figure 7 Light absorption and stress-strain curves.



The rubber must flow from the equator to the poles.

Figure 8 Deformation of the core relative to that of the hole in the matrix.

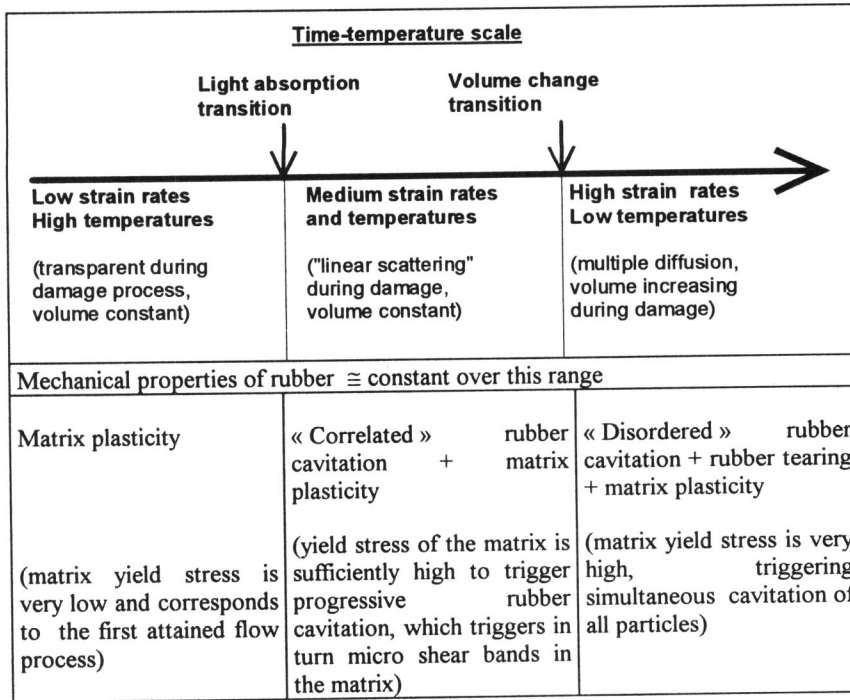


Figure 9 Position of light absorption and volume increase transitions on the time-temperature scale, with the plausible micromechanisms of damage.

Optical measurements

A mechanical definition of damage does not provide any information about its nature at the microscopic level. In this study, the procedure was the simultaneous measurement of light scattering at the beginning of the damage and light absorption at high strain and damage, when multiple scattering occurred (Figure 4). The diffraction pattern of Figure 5 indicates that the damaged sites are not randomly distributed throughout the material, but located in organised layers, which points to the existence of particle interaction. On this image, the angle between the strain direction and the cross is about 35°. Light scattering would therefore appear to be much more sensitive than light absorption to detect first damage. The angle at which plasticity develops in the matrix around a ruined particle depends on the material properties [13] and the ruined particles align along « dilatational bands » or « croids » [10], located on a cone around the stress direction. At high strain (above 10%) and low temperature, multiple light scattering occurs and the scattering pattern becomes blurred.

As the light absorption due to particles cavitation depends strongly on time and temperature, its detailed time and temperature behaviour was investigated. Figure 7 shows experimental results for three different strain rates at 50°C. The yielding behaviour of the material appears to be closely linked to the particles cavitation. When examined on an Arrhenius plot, the onset of light absorption and hence of cavitation may be seen to follow a linear law with an activation energy of about 22 kcal/Mol, equal to the activation energy for plastic flow below the glass transition of pure PMMA. This confirms the dominant role of the plasticity of the matrix in the mechanism of the particle cavitation.

Discussion and conclusions : microscopic mechanisms (Figure 8 and Figure 9)

The most relevant factor is the very low shear modulus of the rubber relative to that of the matrix, as opposed to the bulk modulus of the rubber which is of the same order of magnitude as that of the matrix. Hence no significant shear stress is transmitted from the bulk matrix to the particles, and almost pure hydrostatic pressure dominates in the rubber. A rubber particle may then cavitate, lowering the inner hydrostatic pressure to nearly zero and inducing a micro shear band in the surrounding matrix. This shear band may in turn trigger cavitation in a neighbouring particle.

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