

## **TITLE**

Damage mechanisms in a toughened acrylic resin: effect of temperature and thermal history

## **AUTHORS**

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## **ABSTRACT**

The effect of temperature on the damage mechanisms occurring in a toughened acrylic resin was investigated by studying volume changes during tensile tests, analysing the reversibility of the damage after applying proper thermal histories and by direct Transmission Electron Microscope observations. It was found that an increase of temperature, from 0 to 60 °C, shifts the predominant mechanism from crazing to cavitation and shear yielding. When the latter occur, the material response is very susceptible to previous thermal treatments, and in particular to the cooling rate from above glass transition temperature. Crazing on the other hand is not influenced by the thermal history of the material.

## INTRODUCTION

Acrylic resins are widely appreciated for their properties such as stiffness, transparency and good weather resistance but they tend to yield by crazing showing a brittle fracture and this is a major drawback for their adoption for structural purposes. Hence, this class of materials is fit for toughening, as many examples from literature demonstrate [1-6].

Toughening is nowadays a common practice to improve the fracture resistance of brittle glassy polymers by the addition of a rubbery phase in the rigid matrix. The result is a material with a slight decrease in stiffness but tough, displaying different deformation mechanisms that contribute to energy dissipation during fracture. Generally, the mechanisms occurring in toughened polymers are multiple crazing, shear yielding and cavitation of the rubbery domains. Cavitation promotes shear yielding of the surrounding matrix, therefore these two mechanisms are often present together. The presence of one mechanism or another or their simultaneous occurrence is related to rubber particle shape and size, rubber content and distribution, type of matrix, interfacial properties and temperature and loading conditions [2], [7-11].

A quite well-established method to investigate and distinguish the different damage mechanisms in toughened polymers is to study their dilatometric behavior during tensile tests [12-16]. Typically, volumetric strain vs. strain curves present an initial portion related to the elastic behavior of the material up to a point from which a change occurs in the slope which gives information on the mechanism acting. Shear yielding occurs with no changes in volume, since it is a flow process, therefore in the ideal case of pure shear yielding the slope of the volumetric strain vs. strain curve is equal to zero. Crazing on the other hand is a process in which voids nucleate and grow and the slope of the resulting curve should be ideally equal to one, since crazing is supposed to occur without lateral contraction. Cavitation is a voiding process too, hence a change in volume cannot be related straightforward to crazing. However, the volume change is generally lower in the case of cavitation.

In the real case, since the different mechanisms can be present at the same time, curves usually have intermediate slopes between zero and one.

Preliminary tensile tests at different temperatures were carried out following the same approach as in [15]. Results are shown in Fig. 1 as stress vs. strain and anelastic volumetric strain vs. strain curves. The curves show a clear effect of the testing temperature on the response of the material, with the maximum stress decreasing with increasing temperature as expected. Further, while at 0 and 23°C the maximum occurs at about 3-4% strain at 60°C it occurs at about 6-7%. Regarding the anelastic volume variation (overall minus elastic volume change), at all three temperatures it remains very close to zero and then at a strain near to the maximum stress a major change in the volume strain curves slope occurs. At 0 and 23°C the slope becomes nearly one while at 60°C the slope is much lower suggesting that crazing is the main deformation mechanism at 0 and 23°C and that cavitation and shear yielding give a significant contribution at 60°C.

These results well agree with those regarding fracture in [15], where toughness was observed to increase with temperature, as it is commonly accepted that cavitation and shear yielding cause higher energy dissipation than multiple crazing [8], [10].

In the present work the damage mechanisms occurring in the material were further investigated. In fact, information on the damage mechanism may be drawn with the application of complex thermo-mechanical histories to the material. The basic assumption is that crazing and shear yielding are reversible mechanisms [17], in the sense that if the material is brought to a temperature above glass transition, the mobility of the molecular chains is sufficient to “heal” crazes and shear yielded material. Cavitation of the rubber on the other hand is not reversible: the thermal treatment would recover the deformation around the particles and close the cavities, but the rubber would remain torn. Thus, in this research the identification of the deformation mechanisms active in the toughened acrylic resin was made applying a combination of thermal and mechanical cycles to test specimens

and using dilatometry during tensile tests. Also, direct observation via Transmission Electron Microscopy (TEM) was made.

## **MATERIALS AND METHODS**

The material studied in the present work is a novel toughened resin produced by Arkema under the commercial tradename of Elium Impact®. It is a thermoplastic acrylic resin in which the addition of an acrylic block copolymer (Nanostrength®) produces nanometric inclusions. Samples about 0.1 µm thick were microtomed at room temperature and Transmission Electron Microscopy (TEM) observations were carried out on a FEI CM120 microscope operating at 80 kV. Fig. 2 shows TEM observations of the morphology of the nanometric inclusions. Glass transition temperature,  $T_g$ , of the glassy matrix, found via Differential Scanning Calorimetry performed on a Mettler DSC 30 machine, is 123 °C.

The material is made by “in situ” polymerization and was provided by Arkema under the form of 3 mm thick plates, from which dumbbell specimens, having an 18x5 mm gauge, were machined. Before tensile tests, the specimens were prepared for Digital Image Correlation (DIC) analysis [18]: since the material is transparent, the specimens were first painted white with a powder suspension which is usually adopted in non-destructive testing. This solution was adopted to avoid any “skin” effect of the paint and truly measure the deformation of the underlying specimen. Once this first layer dried, a fine black speckle pattern was airbrushed over the gauge length.

Uniaxial tensile tests were carried out at a constant displacement rate of 1 mm/min at 0, 23 and 60 °C, up to a nominal strain of 10-15%, then the specimens were unloaded at the same rate. The strains measured with DIC were used to evaluate the volume changes occurring in the material. In fact, under the assumption of transversal isotropy and neglecting higher order terms, the volumetric strain is

$$\left(\frac{\Delta V}{V_0}\right) = (1 + \varepsilon)(1 + \varepsilon_l)^2 - 1 \quad (1)$$

where  $\varepsilon$  and  $\varepsilon_l$  are the longitudinal and lateral strain respectively. The volumetric strain can be considered as the sum of an elastic component that can be calculated as

$$\left(\frac{\Delta V}{V_0}\right)_{el} = (1 - 2\nu) \frac{\sigma}{E} \quad (2)$$

In which  $\sigma$  is the applied stress,  $\nu$  the materials Poisson ratio, and E its young's modulus, and an anelastic one

$$\left(\frac{\Delta V}{V_0}\right)_{anel} = \left(\frac{\Delta V}{V_0}\right) - \left(\frac{\Delta V}{V_0}\right)_{el} \quad (3)$$

The anelastic component is made of a viscoelastic component which recovers with time and a plastic component which is permanent unless the material is taken to temperatures above the glass transition. In all cases the elastic volumetric component was determined by considering E and  $\nu$  equal to 2704 MPa and 0.3942 respectively. These values are relevant to the initial part of the stress-strain curve at 0°C. This choice was made considering that the elastic modulus is not temperature dependent and that at 0 °C the viscoelastic strain component can be neglected.

All the tests were performed on a Instron 1185 dynamometer, equipped with a 10 kN load cell and a thermostatic cabinet. For each testing condition, at least two specimens were tested but only one curve is shown in the plots. The results showed very good repeatability in all cases.

During this work the specimens were tested as received (in the following called “pristine”) and following different thermo-mechanical histories. Specimens were labelled as reported in Tab. 1: the combination of different labels describes the complete thermo-mechanical history. The pristine material has an unknown thermal history in the sense that it is cooled from the polymerization temperature which is above 125°C but the cooling rate was not specified by Arkema.

## **RESULTS AND DISCUSSION**

## Effects of thermal treatments

As mentioned in the introduction, to identify the type of damage mechanism its reversibility was considered. To this end the specimens, once loaded, had to be thermally treated above  $T_g$ . As the thermal history can affect the mechanical behavior of a glassy polymer, and more specifically its yielding behavior, a preliminary study on these effects was carried out.

To this end, all the four different thermal treatments described in Table 1, were applied to pristine specimens which were then subjected to a loading cycle at 23 and 60°C.

Fig. 3 and Fig. 4 show the stress-strain and anelastic volumetric strain-strain curves obtained at 23 and 60°C respectively.

For the tests at 23°C (Fig. 3) both stress-strain and anelastic volumetric strain-strain curves from the pristine specimens and those that underwent the different thermal treatments are very similar. The maximum stress is slightly lower for the quenched specimens. Regarding the anelastic volumetric strain, it can be observed that at 3-4% longitudinal strain, where the maximum in the stress-strain curve occurs, the slope changes from a very low value to a value near to one, indicating that crazing is probably occurring and that this mechanism is fairly insensitive to the thermal history applied to the sample before the test.

At 60°C (Fig. 4) the response is different. The time elapsed above glass transition temperature has no effect (1M and 1H curves are almost coincident), while the response is strongly affected by the cooling rate. Specifically:

- the shape of the stress-strain curves is different for annealed specimens in comparison to that of quenched ones, as in the former case the curves show higher values of the maximum in the stress-strain curve and more evident strain softening. It is known that when an amorphous material is rapidly cooled from above glass transition temperature, the free volume is larger than in the case of a slow cooling [19, 20]. The increased mobility of the molecular chains lowers the shear yielding

threshold as reported in [21-23] in studies of aging effects on shear yielding in uniaxial compression tests, where crazing is obviously suppressed and only shear yielding occurs. Therefore, this change in the stress-strain curve can be an indication that shear yielding is promoted by quenching the specimen from above  $T_g$ .

- the slope of the anelastic volumetric strain vs. strain curves up to about 5.5% strain is low and the same for slowly cooled and quenched specimens, after this strain the slope increases slightly for the quenched material and is near to one for the material cooled at  $1\text{ }^\circ\text{C}/\text{min}$ . The pristine material shows an intermediate slope, allowing to infer that the cooling rate imposed during production was higher than  $1\text{ }^\circ\text{C}/\text{min}$  but slower than quenching (it is reasonable to assume that it was cooled in air to room temperature). This difference in the slope of the curves suggests that when the material is rapidly cooled from above  $T_g$  it cavitates and shear yielding takes place while if it is slowly cooled mainly crazing occurs.
- the qualitative observation of the specimens after unloading, shown in Fig. 5, seems to confirm this hypothesis. The specimens quenched and then tested at  $60\text{ }^\circ\text{C}$  (1HQ-60L and 1MQ-60L) show only a very slight whitening, probably due to cavitation; the pristine and slowly cooled specimens show intense whitening. All the specimens tested at  $23\text{ }^\circ\text{C}$  (Fig. 6), on the other hand, show the same intense whitening in the gauge section.

The above results show that the deformation mechanisms occurring at  $60\text{ }^\circ\text{C}$  are dependent on the previous thermal history of the material and that high free volume seems to suppress crazing in favor of cavitation and shear yielding.

### **Reversibility of the damage mechanisms**

The scope of analyzing the reversibility of the damage occurring during loading was to identify the relevant mechanisms. To this end a first loading-unloading cycle is applied to the specimens, then a thermal treatment above  $T_g$  is applied and finally a new loading-unloading cycle is carried out.



At first specimens with a known thermal treatment before the first loading were considered. In particular specimens 1HSC-60L and 1HQ-60L, after unloading underwent the same thermal treatment already received (1HSC and 1HQ respectively) and then they were subjected to another loading/unloading cycle at 60 °C.

Fig. 7 shows the specimens at the different stages: after the first loading, after the thermal treatment and after the second loading. It can be observed that the second thermal treatment was able to fully recover the transparency of the material. Moreover, it is evident that the difference in the amount of whitening after the first loading between the annealed and quenched specimens, already discussed above, is not present anymore after the second loading/unloading cycle as all the specimens show intense whitening of the gauge.

Fig. 8 and Fig. 9 show the stress and anelastic volumetric strain vs. strain curves obtained for the two different cooling rates. The second loading of the quenched samples (1HQ) (Fig. 8), after the thermal treatment above  $T_g$ , is very different from the first one: the stress-strain curve shows a maximum around 5% strain and at this strain the slope of the anelastic volumetric strain increases and becomes close to one. This change in the deformation mechanism indicates that the damage after the first loading is not completely recovered with the thermal treatment confirming that cavitation took place during the first loading and further, that during the second loading shear yielding does not seem to occur. Regarding the slowly cooled specimens (1HSC) (Fig. 9) both the first and the second loading are similar in shape: the stress strain curves show a maximum and at the strain at which the maximum occurs the slope of the anelastic volumetric strain vs. strain curve becomes near to one indicating that crazing occurs. Nevertheless, the maximum of the second loading is lower and occurs at a lower strain, suggesting that probably some cavitation occurred during the first loading.

Aim of this work was to further investigate and confirm the results found in [15] in which the effect of previous thermal history was not taken into account and both tensile and fracture tests were

carried out on the as received specimens (pristine). Hence, the effect of the two thermal treatments 1HQ and 1HSC was examined. After a first loading at 0 and 60 °C the specimens underwent the thermal treatment (1HQ or 1HSC) and they all recovered their transparency, as in the cases described above. Then they were re-loaded: Fig. 10 and Fig. 11 show the comparison of the curves obtained before and after the thermal treatment.

In the case of the tests performed at 0 °C (Fig. 10) the stress and anelastic-volumetric strain vs. strain curves of the two loading cycles overlap almost perfectly. The slope of the anelastic-volumetric strain vs. strain close to one and the complete recovery of the damage above  $T_g$  suggest that the mechanism acting is only crazing.

For the tests carried out at 60 °C (Fig. 11) the behavior of the material before and after the thermal treatments is different. During the second loading after both thermal treatments (1HQ and 1HSC) the stress strain curves show a maximum as the pristine material did: for the pristine material the maximum occurs at about 6-7% strain, for the slowly cooled specimen the maximum is slightly lower and occurs at about 4% strain, for the quenched specimen the maximum is much lower and occurs at about 5% strain. After the maximum the slope of the anelastic-volumetric strain vs. strain curves have a slope more indicative of crazing but before the maximum, in the case of the pristine material and the quenched one the change in slope occurs within a relatively wide range of strains probably indicating that some shear takes place while for the slowly cooled material it is sudden suggesting that only crazing takes place. In any case the second loading after either thermal treatment is different from the first loading confirming the occurrence of cavitation on the pristine material during the first loading.

### **Transmission Electron Microscopy**

An attempt of direct observation of the damage mechanisms was made via TEM. Samples were cut from the plastically deformed gauge portion of the tensile specimens after tensile testing. Thin slices (thickness about 0.1  $\mu\text{m}$ ) were microtomed at room temperature in such a way that the slice

plane (i.e. the plane of observation) is parallel to the tensile stress direction. No staining was applied to the specimens. The images obtained in the region close to the fracture surfaces of the specimens tested at 0 and 60 °C are shown in Fig. 12 and Fig. 13 respectively.

No remarkable distinct features can be observed from Fig. 12, as the morphology is very similar to that of material analyzed before mechanical testing and reported in Fig. 2. On the contrary, a clear evidence of cavitation of the rubbery inclusions is observable in Fig. 13. Moreover, in this case the un-cavitated rubber appears to be stretched, suggesting a shear flow of the surrounding matrix.

Hence, direct observation of the specimens confirms the presence of cavitation and shear yielding in the specimens tested at 60 °C, while for those tested at 0 °C there is not clear evidence of crazing. If the crazes took place, as expected considering the volume strain measurements and the fact that the damage was recovered after the thermal treatment on the deformed specimen, they may have closed after unloading.

## **CONCLUSIONS**

To investigate the damage mechanisms active in the considered toughened acrylic resin observation of volume variation during strain application and direct Transmission Electron Microscopy of deformed samples were considered. At the different temperatures, different mechanisms were hypothesized and then confirmed on the basis of their reversibility after a thermal treatment in which the material after a first loading is taken above  $T_g$ , cooled to room temperature and then reloaded.

A first part of the research regarded the effect of the thermal treatment alone on the tensile response of the material. From this part it was concluded that:

- At 23°C the response is not influenced by the thermal treatment above  $T_g$ . The stress and volumetric strain vs. strain curves were practically the same irrespective of the cooling rate from temperature above  $T_g$ . The volume changes observed are in agreement with what is expected from

crazing. Lower temperatures are expected to promote crazing. Indeed, at 0°C at which only one condition was examined, the slope of the volumetric strain vs. strain curve confirms the occurrence of crazing.

- At 60 °C the response depends on the rate at which the sample was cooled from above T<sub>g</sub> before mechanical tests. From the volume changes, a change in mechanism from crazing to cavitation and shear yielding seems to be fostered as cooling rate increases.

Then, to confirm these hypothesized mechanisms, the reversibility of the damage was examined. It was found that:

- At 0 °C, the material shows exactly the same tensile behavior when the specimen is reloaded after the thermal treatment. This confirms that crazing occurs at this temperature, as this type of damage is expected to heal above the glass transition.
- At 60 °C the stress-strain curve of the first loading of the pristine sample and that of the second loading after the thermal treatment differ. The results confirm that when the volumetric strain vs. strain curve shows a low slope an irreversible mechanism, i.e. cavitation takes place. As cooling rate decreases, the volumetric strain vs. strain curve slope becomes higher and also the difference between first and second loading becomes less significant, as expected when crazing becomes the dominant mechanism.

TEM micrographs confirmed cavitation on specimens tested at 60 °C.

The results from the present work evidence the effect of thermal history on the deformation mechanisms in toughened polymers and confirm those hypothesized in a previous research on the same material [15], in which the increase of fracture toughness with temperature is due to a change in damage mechanisms from crazing to cavitation and shear yielding.

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## TABLES

Table 1 Loading and thermal treatments labels. The name of each specimen is the combination of the labels describing the complete thermo-mechanical history.

Label	Description
	<b>Loading</b>
<b>0L</b>	Tensile test, with loading and unloading, carried out at 1 mm/min and 0 °C
<b>23L</b>	Tensile test, with loading and unloading, carried out at 1 mm/min and 23 °C
<b>60L</b>	Tensile test, with loading and unloading, carried out at 1 mm/min and 60 °C
	<b>Thermal treatments</b>
<b>1HSC</b>	1 hour at 125 °C followed by slow cooling at 1°C/min
<b>1MSC</b>	1 minute at 125 °C followed by slow cooling at 1°C/min
<b>1HQ</b>	1 hour at 125 °C followed by quenching (in ice water)
<b>1MQ</b>	1 minute at 125 °C followed by quenching (in ice water)

## FIGURES CAPTIONS

Fig. 1 Stress,  $\sigma$ , and anelastic volumetric strain,  $(\Delta V/V_0)_{\text{anel}}$ , vs. strain,  $\epsilon$ , curves at different temperatures and at a displacement rate of 1 mm/min. The boxed scheme shows the ideal slopes for shear yielding and for crazing, equal to 0 and 1 respectively.

Fig. 2 Rubbery inclusions (dark) morphology. TEM images taken at two magnifications (a) and (b) on pristine material.

Fig. 3 Stress,  $\sigma$ , and anelastic volumetric strain,  $(\Delta V/V_0)_{\text{anel}}$ , vs. strain,  $\epsilon$ , curves at 23 °C. Pristine specimens (solid squares) and specimens after different thermal treatments (circles and triangles). Please refer to Tab. 1 for the complete description. The boxed scheme shows the ideal slopes for shear yielding and for crazing, equal to 0 and 1 respectively.



Fig. 4 Stress,  $\sigma$ , and anelastic volumetric strain,  $(\Delta V/V_0)_{\text{anel}}$ , vs. strain,  $\epsilon$ , curves at 60 °C. Pristine specimens (solid squares) and specimens after different thermal treatments (circles and triangles). Please refer to Tab. 1 for the complete description. The boxed scheme shows the ideal slopes for shear yielding and for crazing, equal to 0 and 1 respectively.

Fig. 5 Whitening in specimens tested at 60 °C after different thermal histories. Refer to Tab. 1 for the complete description.

Fig. 6 Whitening in specimens tested at 23 °C after different thermal histories. Refer to Tab. 1 for the complete description.

Fig. 7 Whitening in specimens tested at 60 °C after different stages of thermal and mechanical cycles. Refer to Tab. 1 for the complete description.

Fig. 8 Stress,  $\sigma$ , and anelastic volumetric strain,  $(\Delta V/V_0)_{\text{anel}}$ , vs. strain,  $\epsilon$ , curves at 60 °C for quenched specimens. Please refer to Tab. 1 for the complete description. The boxed scheme shows the ideal slopes for shear yielding and for crazing, equal to 0 and 1 respectively.

Fig. 9 Stress,  $\sigma$ , and anelastic volumetric strain,  $(\Delta V/V_0)_{\text{anel}}$ , vs. strain,  $\epsilon$ , curves at 60 °C for slowly cooled specimens. Please refer to Tab. 1 for the complete description. The boxed scheme shows the ideal slopes for shear yielding and for crazing, equal to 0 and 1 respectively.

Fig. 10 Stress,  $\sigma$ , and anelastic volumetric strain,  $(\Delta V/V_0)_{\text{anel}}$ , vs. strain,  $\epsilon$ , curves at 0 °C. Curves represents results from the first loading/unloading (open triangles) and the second loading/unloading after thermal treatment on the same specimens (solid triangles). Please refer to Tab. 1 for the complete description. The boxed scheme shows the ideal slopes for shear yielding and for crazing, equal to 0 and 1 respectively.

Fig. 11 Stress,  $\sigma$ , and anelastic volumetric strain,  $(\Delta V/V_0)_{\text{anel}}$ , vs. strain,  $\epsilon$ , curves at 60 °C. Curves represents results from the first loading/unloading (open triangles) and the second loading/unloading after thermal treatment on the same specimens (solid triangles and open squares. Please refer to Tab.

1 for the complete description. The boxed scheme shows the ideal slopes for shear yielding and for crazing, equal to 0 and 1 respectively.

Fig. 12 TEM images taken at two magnifications (a) and (b) on specimen tested at 0 °C and 1 mm/min.

Fig. 13 TEM images taken at two magnifications (a) and (b) on specimen tested at 60 °C and 1 mm/min.