

# Hysteretic thermal behavior of amorphous semi-aromatic polyamides

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## Abstract

The hysteretic thermal behavior of two amorphous semi-aromatic polyamides, subjected to cyclic loading at high stress levels, has been investigated. The two polymers, called 1I and 1.8T, were selected with regards to chain mobility and plastic deformability considerations. This work reports the exothermal response of these materials to high level cyclic stress (of the order of  $\sigma_y$ ), with emphasis on the initial thermal peak, normally observed in commercial polycarbonate (PC) and not in commercial polymethylmethacrylate (PMMA). The investigated materials exhibit noticeable initial thermal peaks, which are similar, to some extent, to those observed in PC. The present results suggest that chain mobility may indeed be partially responsible for the initial exothermal peak, thus supporting the hypothesis that it may be related to the transition from shear deformation zones to chain disentanglement crazing.

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## 1. Introduction

Temperature rise in polymers subjected to cyclic loading, as a result of hysteretic behavior, is a well-known phenomenon. Energy dissipation results from internal friction in the material, due to its viscous nature, whether viscoelastic or viscoplastic [1,2]. Generally, a hysteretic loop is created during each cycle, as a result of the phase lag between the stress and strain. The mechanical energy enclosed in the loop is partly stored into the microstructure and partly dissipated as heat [3,4]. Although thermomechanical coupling is generally well defined for metals [5], for which several constitutive models have been developed [6], the phenomenon is not well understood in polymers in its microstructural aspects. For polymers, it is known that very low frequency loading may lead to conventional fatigue failure, exhibiting minimal temperature changes in the material. At higher frequencies, on the other hand, significant heating may develop, causing noticeable material softening until final failure [2]. This phenomenon has been modeled by Molinari and Germain [7], along with a few other references in the literature that deal with low cyclic stress, i.e. significantly below the yield stress ( $\sigma_y$ ) of

the material. However, very little information is available, regarding high stress cyclic loading, of the order of the yield stress of the material. Consequently, the customary reported pattern, for low stress cyclic loading in polymers, is of an initial rapid rise in temperature, followed by a well-defined plateau, ensued by a second rapid temperature rise leading to final failure [2].

Rittel [8] examined the behavior of commercial polycarbonate (PC) and polymethylmethacrylate (PMMA) under high stress cyclic loading. Both materials were tested at high stresses, yet avoiding premature failure; the maximum applied stress (normalized by the yield stress) was near unity for the PC and 0.45 for the PMMA. While the PMMA specimen displayed the above-mentioned ‘classic’ behavior, the PC specimens developed an immediate sharp, thermal peak at stresses exceeding  $0.8 \sigma_y$ , trailed by a lower temperature plateau. Following the thermal plateau, both materials exhibited a final, rapid, temperature rise, leading to failure. For the PMMA specimens, it was evident that the duration of the temperature plateau was inversely proportional to the cyclic stress magnitude applied to the specimen. Different attempts were made to unravel the physical mechanism generating the thermal peak, including annealing treatments and repeated loading. However, no definite conclusion was reached as to the microstructural factors underlying these observations. Three possible factors were considered as possible causes for the thermal peak phenomenon. Firstly, it was noted that a higher cyclic stress magnitude could be applied to PC (for which

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the peak was observed), when compared to PMMA specimens, which exhibited early failure, thus precluding a direct comparison. Another possible cause could be the superior ability of PC to undergo plastic deformation, as compared to the PMMA. Finally, an exothermic process with a sharp completion (or endothermic process with a sharp initiation) may also be symptomatic of a phase transition. However, stress induced phase transitions have not been reported for this material.

Considering the heat transfer process in these experiments, the solution of the coupled heat equation, with appropriate heat transfer boundary conditions, yields a temperature rise, but certainly no temperature drop such as to create a thermal peak. The measured thermal evolution, successfully modeled by Rittel and Rabin [9], was achieved by solving the transient heat equation for such experiments. Using the (rate of) measured mechanical energy dissipated in each cycle as the input (rate of) energy, these calculations were able to reproduce the experimental results quite well, predominantly the thermal peak observed in PC. However, modeling remained purely phenomenological.

In a subsequent work, Rittel et al. [10] tested the potential role of molecular chain mobility in the material, and that of the cyclic stress magnitude on the thermomechanical reaction of the above-mentioned materials, with respect to PC. High stress cyclic loading was applied to specimens of modified PMMA, to which glutarimide units were added, as in Tézé and et al. [11]. This modification increases the plastic deformability of the material, as well as its fracture resistance [12]. Although the modified PMMA (PMMA\_MOD) could withstand higher levels of cyclic stress, a thermal peak was not observed in the material, and it displayed a self-heating and failure pattern similar to that of regular PMMA. The results seemed to support the suggestion that the thermal peak in PC results from some sort of phase transition, rather than the high stress magnitude or the plastic deformation that the specimens undergo.

The purpose of the present work was to further verify the conclusions obtained by Rittel, et al. [10], as to the nature of the thermomechanical properties of the materials discussed, with emphasis on the role of chain mobility. This paper reports the result of high stress magnitude cyclic loading of two different types of amorphous semi-aromatic polyamides (SAPAs), with respect to the three aforementioned characteristics that may govern the thermal response of the material.

## 2. Materials and experiments

Since, the chain dynamics, plastic, damage and fracture behavior of these polymers are quite well documented in the recent literature [13–16], two types of amorphous SAPAs, namely II and 1.8T, were selected for the present study. The II material is a commercial polymer supplied by EMS Co. and the 1.8T material was kindly provided by ARKEMA France. The chemical structure of the investigated polymers is shown in Fig. 1. The relevant mechanical properties are listed in Table 1. Both materials were checked to be strictly amorphous by means of differential scanning calorimetry and X-ray

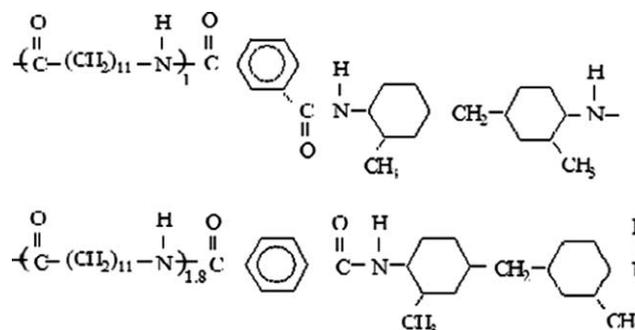


Fig. 1. Chemical formulae of the SAPAs II and 1.8T.

diffraction. The two polymers were dehydrated at 50 °C for 24 h prior to testing, and then annealed at room temperature for at least 48 h. All the tests were carried out under load control on an MTS 810-25T servo-hydraulic machine. Preliminary testing, to determine the mechanical properties, consisted of compressive and tensile experiments at various strain rates. The recorded data was converted into true stress–strain curves, assuming material incompressibility and correcting for machine compliance. A second set of tensile tests was performed using an extensometer attached to the specimens' gage.

For the cyclic compression tests, cylindrical specimens (10 mm diameter, 11 mm length) were machined from 12 mm thick cast plates. In order to measure the temperature at the center of the specimens (the point with the highest temperature), a K-type thermocouple was inserted into a 0.3 mm diameter hole, drilled into the specimen, at mid-length, perpendicular to its axis (Fig. 2). The thermocouple was sealed in using a PMMA solution, produced by dissolving polymer chips in chloroform, and left for curing for 24 h at room temperature.

Cyclic testing was carried out under load control, with the minimal load kept at approximately 10% of the magnitude of the maximal load, in order to ensure continuous contact with the specimen throughout the test. All the cyclic tests were performed at a frequency of 15 Hz (unless otherwise noted). The specimen temperature was continuously monitored throughout the test at a frequency of 1 Hz.

Table 1  
Physical characteristics of the investigated materials

Type of SAPA	$T_g^a$ (°C)	$T_\alpha$ (1 Hz) <sup>b</sup> (°C)	$\sigma_y$ at 25 °C <sup>c</sup> (MPa)	$K_{Ic}$ at 20 °C <sup>d</sup> (MPa m <sup>1/2</sup> )
II	151	161	110	2.3
1.8T	124	137	95	3.0

<sup>a</sup> Glass transition temperature, as determined by differential scanning calorimetry at a heating rate of 10 °C min<sup>-1</sup>.  $T_g$  taken at the point in which the heat capacity change from glass to rubber. From Refs. [13,14].

<sup>b</sup> Temperature of the main mechanical relaxation  $\alpha$ , as determined by dynamic mechanical analysis at the frequency 1 Hz.  $T_\alpha$  taken at the maximum of the loss modulus  $E''$  peak. From Refs. [13,14].

<sup>c</sup> Nominal yield stress, as measured on compressive stress–strain curves recorded at a strain rate of  $2 \times 10^{-3}$  s<sup>-1</sup>. From Ref. [14].

<sup>d</sup> Critical stress intensity factor, as deduced from three point-bending experiments in mode I on notched samples. From Ref. [16].

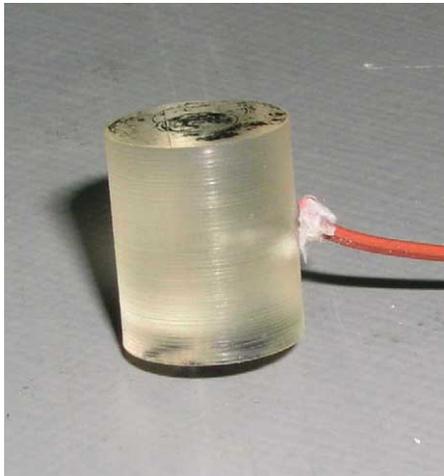


Fig. 2. Cylindrical specimen with embedded thermocouple.

### 3. Results

#### 3.1. Monotonic testing

Both materials were subjected to tension and compression tests at different strain rates in order to characterize the strain rate sensitivity and yield stress of the materials. The main results of these tests are summarized in Tables 2 and 3. As expected, both materials are strain-rate sensitive, and both exhibited an increase of approximately 10 MPa per decade of strain rate (Table 3). While both materials yielded at similar strains, II appears to be stronger, yielding at higher stress magnitudes, throughout the strain-rate range tested, as shown in Figs. 3 and 4. These findings are consistent with earlier observations connecting the mechanical behavior to the polymer chemical structure [14]. The slightly higher yield stress of II with respect to 1.8T results essentially from the decrease of the mean length of the lactam unit (Fig. 1), owing to an increase in Young's modulus (Tables 1 and 2). By contrast, replacing the terephthalic ring by an isophthalic ring has almost no effect on the modulus.

The results obtained from the tensile tests are rather similar to those from the compression, although it is more difficult to determine the exact yield stress from this data (Fig. 5). As expected, the brittle character of the samples tends to disappear as the strain rate is decreased. For cyclic testing, the uniaxial stress applied to the specimens will be noted in non-dimensional form, normalized by the appropriate compressive

Table 2  
Tensile test results

Material	$\dot{\epsilon}$ ( $s^{-1}$ )	$\sigma_y$ (MPa)	$E$ (GPa)	UTS (MPa)
II	0.001	<sup>a</sup>	2.14	<sup>a</sup>
	0.01	<sup>a</sup>	2.09	<sup>a</sup>
	0.1	<sup>a</sup>	2.07	<sup>a</sup>
1.8T	0.001	<sup>a</sup>	1.61	<sup>a</sup>
	0.01	<sup>a</sup>	1.64	<sup>a</sup>
	0.1	<sup>a</sup>	1.60	<sup>a</sup>

<sup>a</sup> Specimen failed prior to yield point, possibly as a result of stress concentration related to the knife-edges of the extensometer.

Table 3  
Compression test results

Material	$\dot{\epsilon}$ ( $s^{-1}$ )	$\sigma_y$ (MPa)	$E$ (GPa)	$\sigma_{max}^a$ (MPa)
II	0.001	70	2.78	102
	0.01	80	3.33	108
	0.1	90	3.01	114
1.8T	0.001	60	2.11	84
	0.01	70	2.43	90
	0.1	80	2.88	96

<sup>a</sup> Maximum stress value prior to barrelling.

yield stress, namely  $\sigma_y=90$  and 80 MPa for II and 1.8T, respectively.

#### 3.2. Cyclic testing

Cyclic testing was performed applying a maximum stress magnitude in the range of  $0.64 \sigma_y$ – $0.95 \sigma_y$ . As mentioned earlier, the maximum applied stress level is similar to that applied by Rittel et al. [10], thus significantly greater than those applied by Rittel [8]. Typical temperature evolutions at the center of the specimen, for various stress magnitudes, are shown in Figs. 6 and 7 for materials 1.8T and II respectively. Most of the tests were continued until either a total of 120,000 cycles or until specimen collapse.

As expected, all specimens, from both materials, displayed a rapid initial temperature rise, the extent of which was proportional to the applied stress. Above a certain stress level, of  $0.80 \sigma_y$  for 1.8T and  $0.83 \sigma_y$  for II, the specimens developed an immediate monotonic temperature rise, leading to failure, much like the results recorded by Rittel et al. [10]. However, for slightly lower stress magnitudes, both materials displayed thermal peaks, resembling those developed by PC specimens under similar loading conditions [8]. Although both materials exhibited thermal peaks, their behavior is not

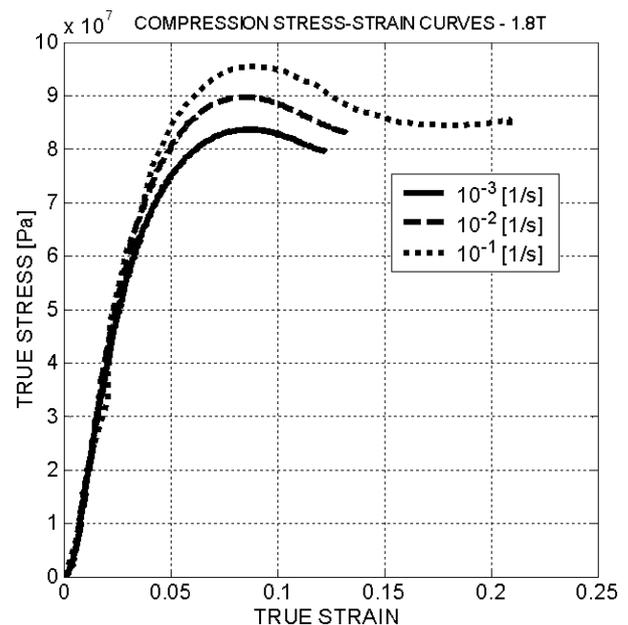


Fig. 3. Compressive true stress–strain curves of 1.8T at different strain rates.

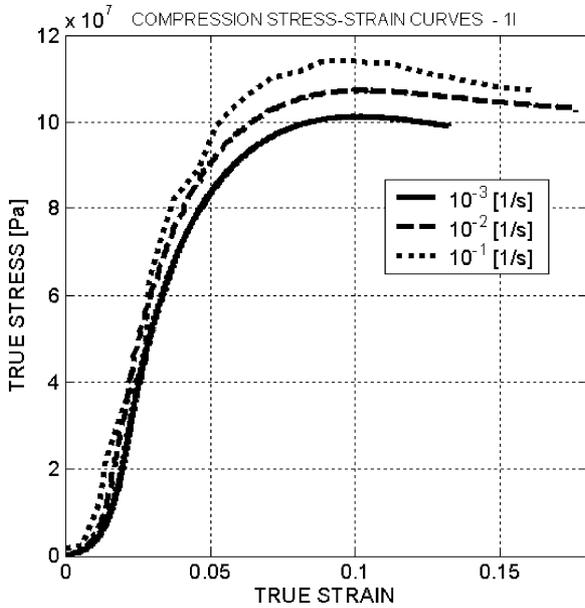


Fig. 4. Compressive true stress–strain curves of II at different strain rates.

identical, and it is still different from that of PC. For 1.8T the thermal peak remained independent of the maximum stress magnitude applied in terms of both maximum temperature and cycle duration. By contrast the peak temperatures in II were directly proportional to the stress applied. In 1.8T the peak value was always noted to be 51 °C, whereas it varied between 40 and 50 °C for the II specimens. The peak subsided for II and 1.8T after 6000 and 10,000 cycles or more, respectively.

All of the specimens that reached final failure, whether right off the start or after a large number of cycles, did so rapidly, in

a relatively small number of cycles, providing no early signs prior to failure. The failure mechanism seems to be similar in both materials; the specimens exhibited a shear plane, at approximately 45°, passing through the center of the specimen, which seems to have undergone (or approached) the glass transition (Fig. 8). In these experiments, the specimens were not thermally insulated. As the cylinders were in contact with steel plates, heat could be dissipated by conduction, yielding the characteristic failure pattern in which most of the damage occurs at the center of the specimen, while some heat was convectively transferred to the surroundings. Additional evidence of the heat transfer process could be noted from the fact that the cylinders’ ends remained round. Strictly speaking, the deformation process neither be viewed as adiabatic nor as isothermal. However, the low thermal conductivity of the material limits its ability to dissipate heat for the continuous heat generation process, so that the core temperature increases until final failure. The exact heat transfer problem of such tests has been addressed in detail by Rittel and Rabin [9].

Some specimens displayed a loss of transparency, irrespective of whether final failure was reached (Figs. 8 (right) and 9). This phenomenon is probably related to crazing (a cavitation process) [14] or to a transition in the molecular structure of the material.

#### 4. Discussion

The present study was carried out to elucidate the contribution of chain mobility on the hysteretic behavior of glassy polymers. One should keep in mind that the reported behavior of the selected materials, II and 1.8T, is much more similar to that of polycarbonate than to that of

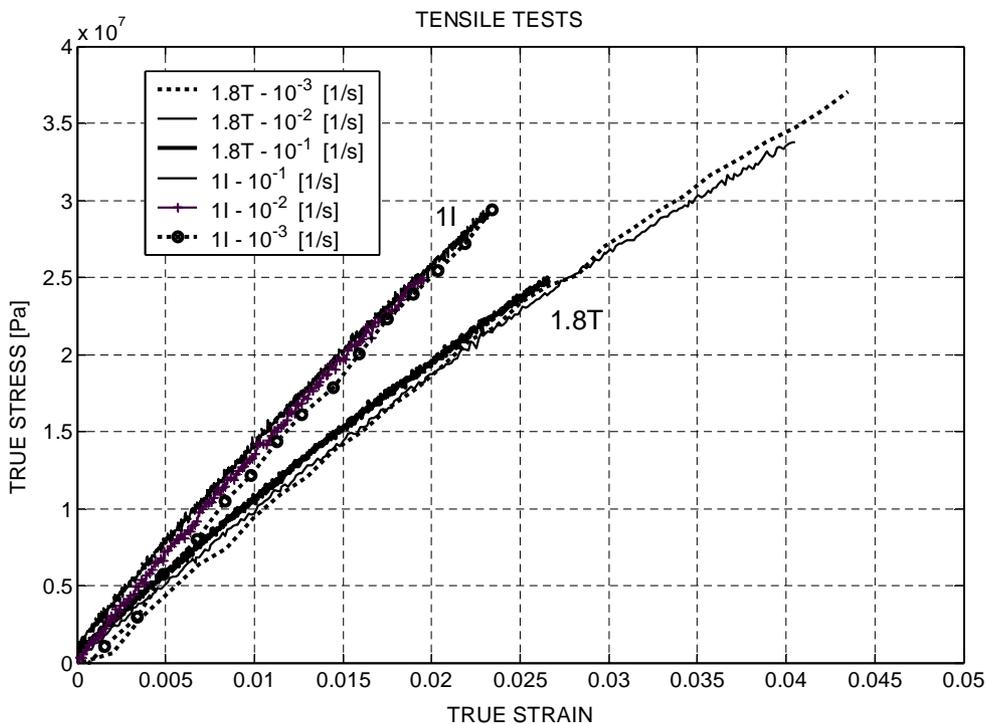


Fig. 5. Tensile true stress–strain curves of the two materials at different strain rates.

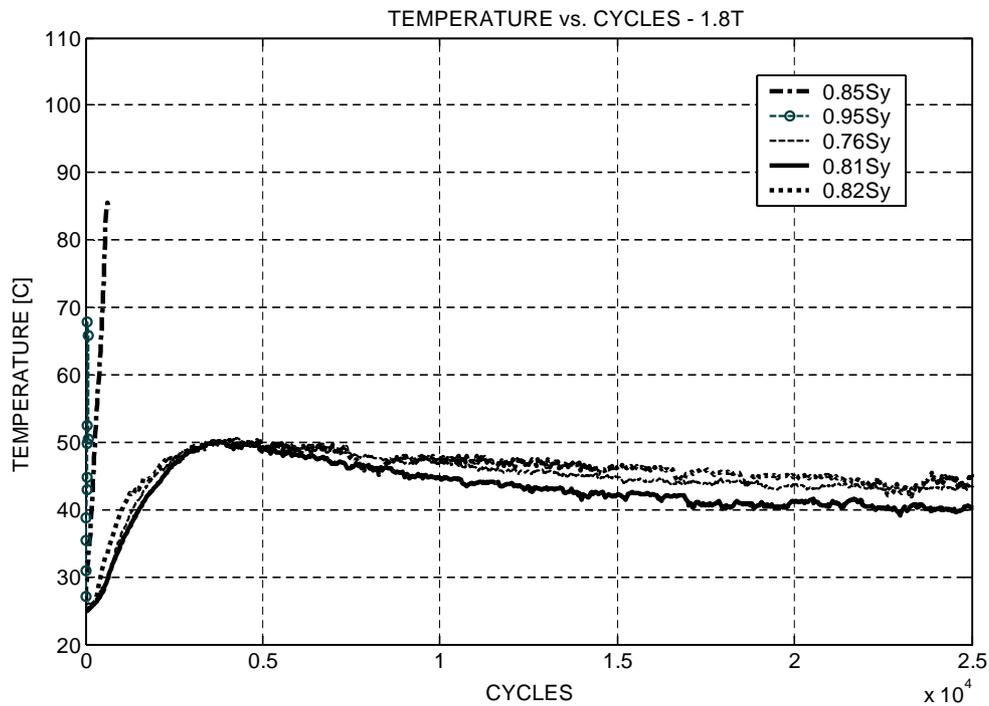


Fig. 6. Temperature vs. number of cycles for cyclic testing of 1.8T ( $f=15$  Hz).

poly(methylmethacrylate), and even PMMA\_MOD. Like PC, they exhibit, at low temperature, a strong secondary relaxation  $\beta$  [13], which is expected to strongly affect both their plastic behavior [14] and deformation micro-mechanisms [15]. The main known differences between 1I and 1.8T concerns the degree of cooperativity of the  $\beta$  motions (lower for 1I), the ability to form crazes in tensile tests (larger for 1I) and the

resistance to impact (lower for 1I). However, there still remains a need to shed more light on polymer fatigue failure and hysteretic heating mechanisms. The two materials exhibited a well-defined thermal peak under cyclic loading. Furthermore, the failure mechanism, via a shear plane, resembles that of PC, rather than barreling or bulging as is apparent in unmodified PMMA specimens (Fig. 9). This evidence interconnects

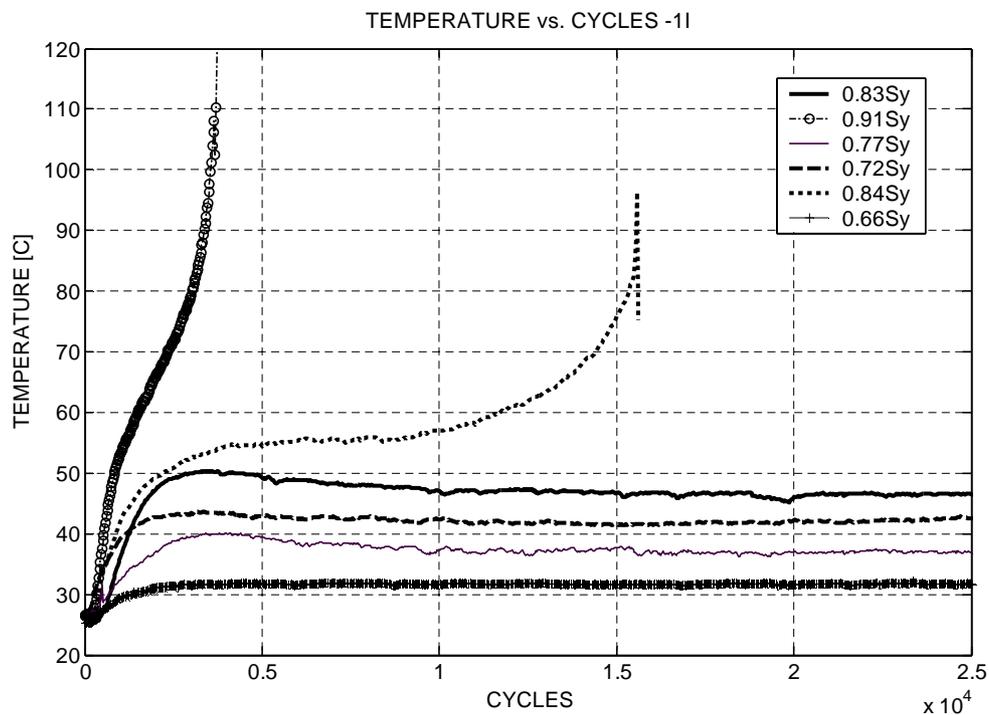


Fig. 7. Temperature vs. number of cycles for cyclic testing of 1I ( $f=15$  Hz).



Fig. 8. Failed specimens with shear planes are visible at 45°.

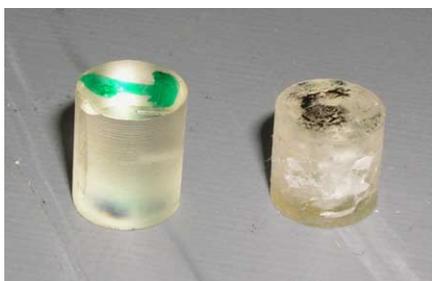


Fig. 9. Two specimens, one of which exhibits loss of transparency (right).

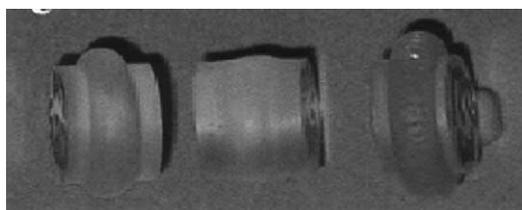


Fig. 10. Unmodified PMMA specimens that have reached failure: barreling is visible at mid-height (reproduced from Ref. [8]).

the failure mechanism with the molecular structure of the material, specifically molecular mobility and reorganization (Fig. 10).

However, the behavior of the two SAPAs was quite different, and still different from both PMMA and PC. The thermal peak in PC lasted approximately 10,000 cycles, similarly to the 1.8T specimens and nearly twice the duration of the II specimens. The PC thermal peak, on the other hand, is much 'sharper', suggesting an energetic threshold phenomenon activation at the peak. It is suggested that the phenomenon may be connected to the transition between micro-deformation mechanisms in the polymers, specifically the transition from shear deformation zones (SDZ) to chain disentanglement crazing (CDC) [14].

Thermo-mechanical differences between the materials produce additional distinctions in their behavior. The peak produced by 1.8T specimens was independent of stress magnitude, suggesting an activation energy threshold, in some 'go-no-go' process. By contrast, the thermal peak of II was stress dependant, displaying higher peak temperatures for higher stress magnitudes, much like PC. This observation suggests a proportional reaction above the activation energy threshold.

The differences in behavior between the different materials may be explained by the reaction of the material to the

SDZ to CDC transition, which acts as the trigger. As the micro-deformation mechanism shifts, the stress-strain rate of the material can change, due to plastic deformations, thereby reducing the hysteretic loop and causing the temperature drop, as the heat dissipation is independent of the deformation mechanism, producing a thermal peak. Another difference may be the ratio between the amount of heat, which is generated in the material and the amount of heat dissipated (which is nearly identical for both materials). If 1.8T generates more heat it could explain why the peak spans over a larger number of cycles.

## 5. Conclusions

Characterization of the hysteretic thermal behavior of the SAPAs II and 1.8T provides further milestones in the understanding of this phenomenon. As ductile materials, likely to deform by shear banding, their behavior resembles polycarbonate much more than polymethylmethacrylate, whose tendency to craze is much larger. Slight differences between II and 1.8T plastic deformation characteristics may also explain their individual thermal response. The appearance of a shear plane, during failure, mimicking PC rather than bulging as normally appears in PMMA, further supports the relation between the molecular structure and the mechanical behavior. It has been shown in this work, that a strong correlation exists between the molecular structure of a polymer and the thermomechanical behavior that characterizes its response to cyclic loading. The central role of chain mobility is thus postulated to be responsible for the observed thermal response of the investigated polymers.

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