Polymer 44 (2003) 2817–2822

polymer

www.elsevier.com/locate/polymer

Hysteretic heating of modified poly(methylmethacrylate)

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Received 31 January 2003; received in revised form 2 February 2003; accepted 3 February 2003

Abstract

The hysteretic thermal response of two polymers, polymethyl-methacrylate (PMMA_REF) and a tougher modified PMMA + *N*-methyl glutarimide (PMMA_MOD) has been investigated under compressive cyclic loading at high stress levels. The modification increases the ability of PMMA_REF to undergo plastic deformation. This work characterizes the thermomechanical response of both polymers at high cyclic stress levels (of the order of σ_y), that were not previously investigated. The comparison clarifies the contribution of increased chain mobility on the hysteretic heating phenomenon, with emphasis on the nature of a significant exothermal peak that was previously observed in commercial polycarbonate (PC). In this work, both PMMA_REF and PMMA_MOD were subjected to compressive cyclic loading, and the temperature was continuously monitored until specimen failure. The experimental results show that, despite the higher toughness PMMA_MOD, the two polymers fail in a very similar fashion, both in terms of temperature rise and bulging failure mode, without the initial thermal peak that was observed in commercial PC. It thus seems that the unique thermomechanical response of PC is neither related to its plastic flow properties, nor to its ability to undergo high cyclic stresses. It is suggested that a cyclic stress induced/related exothermal phase transition might be responsible for the thermal peak in this material.

Keywords: Hysteretic heating; Polymethylmethacrylate; Cyclic loading

1. Introduction

Polymers that are subjected to cyclic loading are well known to develop self (hysteretic)-heating as the loading progresses. The reason for that is the viscous nature, whether elastic or plastic, of the material [1,2]. Typically, the stresses and strain are not in phase, thus creating a hysteresis loop over a closed cycle. A part of the mechanical energy enclosed in the loop is stored into the modified microstructure while the remaining part is released as heat [3,4]. This thermomechanical coupling has been well characterized for the case of metals, e.g. by Taylor and Quinney [5]. Since then, several models have been developed to describe the phenomenon in various constitutive models, as described in Ref. [6]. Considering polymers, it has long been recognized that cyclic loading may cause a conventional type of fatigue failure, provided the frequency of cycling is sufficiently low to minimize temperature changes in the polymer. However, when the frequency exceeds a few hertz, noticeable heating may develop, thus causing a significant softening of the material until final failure of the specimen [2]. The phenomenon has been recently modeled by Molinari and Germain [7]. The above-mentioned concerns the case where the cyclically applied stresses are relatively low, i.e. significantly below the yield stress of the material. However, there are relatively few references in the literature on the subject of hysteretic heating. Surprisingly, almost no information is available for the case of high cyclic stresses that are of the order of the yield stress of the material. The commonly observed and reported pattern, for low overall stresses, is that of an initial rapid temperature rise, followed by a well defined plateau and a rapid temperature rise again to be followed by final failure [2].

Recently, Rittel [8] investigated the cyclic properties of commercial polycarbonate (PC) and poly(methylmethacrylate) (PMMA) that were both subjected to relatively high stresses. In these experiments, the ratio of the maximum applied stress to yield stress was of the order of unity for PC, whereas it did not exceed 0.45 for PMMA, due to what was considered to be premature failure of the

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doi:10.1016/S0032-3861(03)00109-5

specimens. PMMA developed the well-known pattern described above, with the observation that as the applied stress range increased, the duration of the plateau decreased. By contrast, when the maximum cyclic stress exceeded $0.8\sigma_y$, PC developed a sharp and significant initial thermal peak, followed by a decrease of temperature, plateau and temperature rise again until final failure. Several attempts were made to understand the origin of this peak, including annealing treatments, and repeated loading sequences. However, no clear picture emerged as to the underlying physical reason for the thermal peak.

The following three factors could be deemed to cause the thermal peak. The first is the higher cyclic stresses applied to PC, for which the thermal peak was indeed observed, that were not reached in PMMA. The second factor could be related to the superior ability of PC to undergo plastic deformation, as compared with PMMA. Finally, the nature of the thermal peak, indicative of an exothermal process with a sharp completion, suggests some kind of phase transition. The reason for that is that the solution of the coupled heat equation, with appropriate boundary conditions for conduction and convections, yields a temperature *rise*, with an eventual stabilization, but no temperature *drop*. Rittel and Rabin [9] successfully modeled the observed evolution of the temperature, by solving the transient heat equation for these experiments. Here, the input (rate of) energy was the measured mechanical (rate of) energy in each cycle. These calculations replicated quite accurately the evolution of the temperature in the specimens, including the thermal peak observed in PC.

The purpose of the present work was to test the potential role of the chain mobility, and that of the maximum cyclic stress level on the thermomechanical response of these materials, by comparison with PC.

The idea was to consider a modified PMMA to which glutarimide units were added, in the spirit of Tézé et al. [10]. These units increase the plastic deformability of the material and its fracture resistance as well [11]. In this paper, we report our results on the cyclic loading of modified PMMA, the related thermal phenomena and discuss the relative role of the three above mentioned factors.

2. Materials and experimental

Two types of materials were examined, subsequently designed as ‘PMMA_REF’ and ‘PMMA_MOD’, to indicate reference and modified PMMA, respectively.

Some physical properties of the samples, as previously determined by Tézé et al. [10], are given in Table 1. PMMA_REF was kindly supplied by Atofina France. PMMA_MOD is a random copolymer of methyl methacrylate and *N*-methyl glutarimide (24:76 mol%), produced some years ago by Röhm and Haas under the trade name Kamax T 260. T_α, which is the mechanical expression of the glass transition temperature, was taken at the maximum of the E'' loss peak in viscoelastic experiments performed at the frequency 1 Hz.

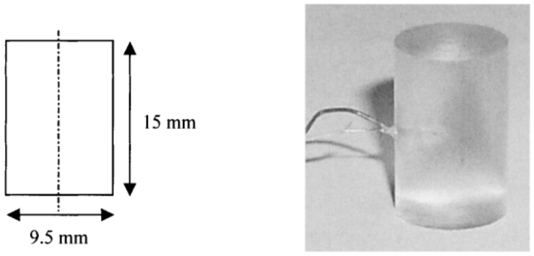
Table 1
Physical characteristics of the samples

	M_n (g mol^{-1})	M_w (g mol^{-1})	T_α (°C)	Young’s modulus at 50 °C (GPa)
PMMA_REF	66,000	119,000	117	2.5
PMMA_MOD	49,000	106,000	158	3.0

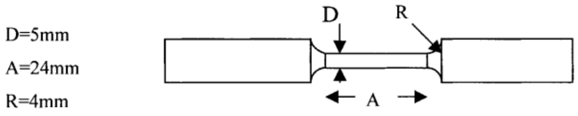
The materials were cast into 12 mm-thick plates. Cylindrical specimens were manufactured from longitudinal strips machined from the plates for compression testing. Tensile specimens were manufactured with a gage length of 24 mm and a diameter of 5 mm. Mechanical testing was carried out under load control on an MTS 810-25T servo-hydraulic machine. A preliminary series of quasi-static tension and compression tests was carried out at various strain rates, to identify the yield stress of the materials and its rate sensitivity.

Cylindrical specimens (9.5 mm diameter, 15 mm height) were instrumented by introducing a small K type thermocouple at mid-height into the center of the cylinder. A small (0.3 mm) diameter hole was drilled, the thermocouple was inserted and the hole was then sealed with a liquid PMMA mixture obtained by dissolution of polymeric chips into chloroform. The specimens were then left for curing for 24 h in room air at ambient temperature (Fig. 1).

Compression quasi-static data was converted into engineering and true stress–strain curves, assuming material incompressibility after correcting for the machine stiffness. Tensile testing was carried out using an extensometer attached to the specimen’s gage (Fig. 1).



(a) Compression cylinder



(b) Tensile specimen

Fig. 1. Experimental specimens. (a) Compression cylinder, sketch and actual specimen with the embedded thermocouple. (b) Tensile specimen.

Cyclic testing was carried under load control out at a frequency of 15 Hz. The temperature was continuously recorded throughout the test.

3. Results

3.1. Quasi-static testing

Typical results obtained from compression and tension testing at a nominal strain rate of $\dot{\varepsilon} = 5 \times 10^{-4}\ \mathrm{s}^{-1}$, are shown in Fig. 2. In this figure, the initial part of the true stress–strain curves of the two materials is shown for both tensile and compressive tests. These figures show that each materials exhibit relatively symmetric initial tensile and compressive mechanical properties. A slight difference in strength levels between compressive and tensile data is also evident. The compressive flow curve is higher than the tensile one, as an indication of the hydrostatic pressure sensitivity of the polymeric materials.

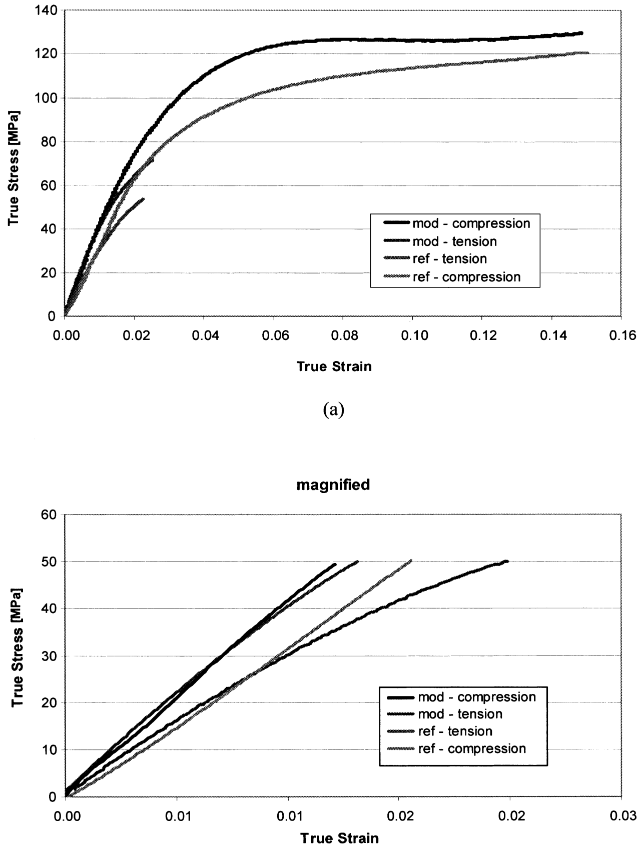
However, PMMA_MOD appears to possess a higher strength as noted from its plastic flow curve and apparent elastic modulus. The mechanical properties are summarized in Table 2. It should be noted that the macroscopic yield stress (elastic limit) was determined as the point beyond which a linear stress-strain relationship is no longer observed (typically $\varepsilon = 0.001$–0.002, see Table 2), and not as the peak stress, $\sigma_{\max}$, as done for instance by Tézé et al. [10]. This definition is adopted for its simplicity, while an extended discussion of the limits of linear viscoelasticity can be found, e.g. in Bodner and Ishai [12]. It should be emphasized, as mentioned previously, that the tensile data was obtained by extensometric technique whereas compressive data was reduced from load–displacement recordings (accounting for the machine stiffness). The latter is thus necessarily slightly less accurate than the former. Yet, it provides valuable information in the present case where cyclic compression is applied.

Table 2
Mechanical properties of PMMA_REF and PMMA_MOD. The numbers next to the yield stress indicate the corresponding strain. The numbers in parentheses indicate the corresponding strain. The experiments were carried out at $\dot{\varepsilon} = 3.5 \times 10^{-4}\ \mathrm{s}^{-1}$

	E (GPa)	σ_y (MPa)	$\sigma_{\max}$ (MPa)
Tension PMMA_REF	3.10	39 (0.014)	53.0
Tension PMMA_MOD	4.03	49 (0.013)	71.0
Compression PMMA_REF	–	57 (0.0120)	76
Compression PMMA_MOD	–	65 (0.017)	117

3.2. Strain-rate sensitivity

A series of compression tests was carried out at various nominal strain rates to characterize the strain-rate sensitivity of the two polymers. True stress–strain curves are shown in Figs. 3 and 4 for reference and modified PMMA, respectively. It is first noted that both materials are strain-rate sensitive, as expected. Both exhibit an increase of about 10 MPa per decade of strain rate, as summarized in Table 3. However, an interesting point is that, whereas PMMA_MOD appears to be stronger than the PMMA_REF at the lowest strain rate ($\dot{\varepsilon} = 5 \times 10^{-4}\ \mathrm{s}^{-1}$), as the strain-rate increases, both materials exhibit very similar yield strength levels. In other words, PMMA_MOD is less sensitive to strain rate than PMMA_REF. In a molecular analysis [13], this means



(a)

(b)

Fig. 2. Tensile and compressive true stress–strain curves of the two investigated polymers at $\dot{\varepsilon} = 3.5 \times 10^{-4}\ \mathrm{s}^{-1}$. (a) Global curves. (b) Magnified initial part.

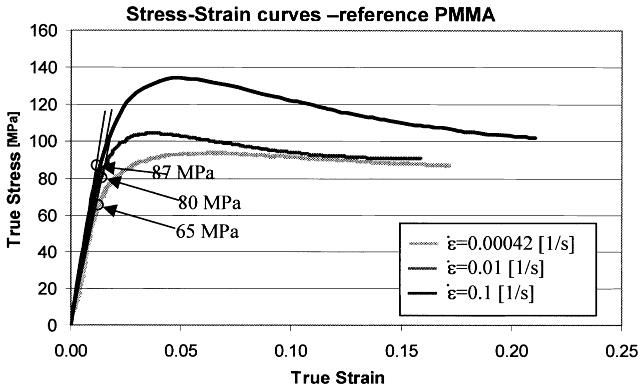


Fig. 3. Compressive true stress–strain curves of PMMA_REF, at various strain rates.

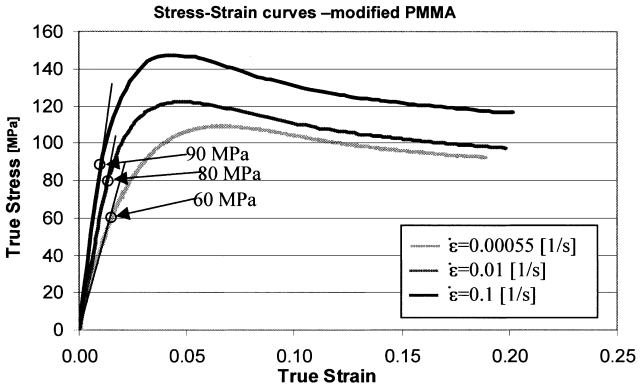


Fig. 4. Compressive true stress–strain curves of PMMA_MOD, at various strain rates.

that the activation volume is larger for PMMA_MOD than for PMMA_REF, as an account for the larger domains sampled by the molecular motions at given temperature. This finding is consistent with Tézé et al.'s observations [10]. At this stage, all the subsequent cyclic tests were related to a reference yield stress $\sigma_y = 90$ MPa that was deemed representative of the compressive cyclic yield stress of both materials.

3.3. Cyclic testing

On the basis of a reference yield stress of $\sigma_y = 90$ MPa, all cyclic tests were performed in the range of $0.45\sigma_y - 1.05\sigma_y$ as the maximum stress level, according to the material. As mentioned previously, the maximum stress levels applied in this study are quite superior to those applied by Rittel [8]. A minimum compressive of 5 MPa was applied to make sure that contact with the specimen was maintained throughout the test. When the specimen started to collapse, the test was interrupted to avoid damage to the loading platens. The evolution of the specimen temperature, for various ranges of stress, is shown in Fig. 5a. As expected, the temperature increases with the cyclic loading, and it reaches higher levels over a smaller number of cycles when higher stresses are applied. When the maximum applied stress is of the order of $0.45\sigma_y$ for PMMA_REF, and $0.61\sigma_y$ for PMMA_MOD, the temperature increases in a classical manner to reach a plateau of about 40 °C. However, when the stress level comes closer to σ_y, the thermal behavior is quite different and the temperature exceeds rapidly 100 °C without a plateau stage. It can be noted that the maximum temperatures that were reached are quite close to the glass transition temperature of PMMA_REF and slightly lower than that of PMMA_MOD (Table 1). A comparison of the behavior of the two polymers for the first 2500 cycles is shown in Fig. 5b. This figure clearly shows that the PMMA_MOD requires higher stress levels when compared with the PMMA REF in order to reach similar temperatures. The difference in stress levels is of about 20% and can be summarized as follows:

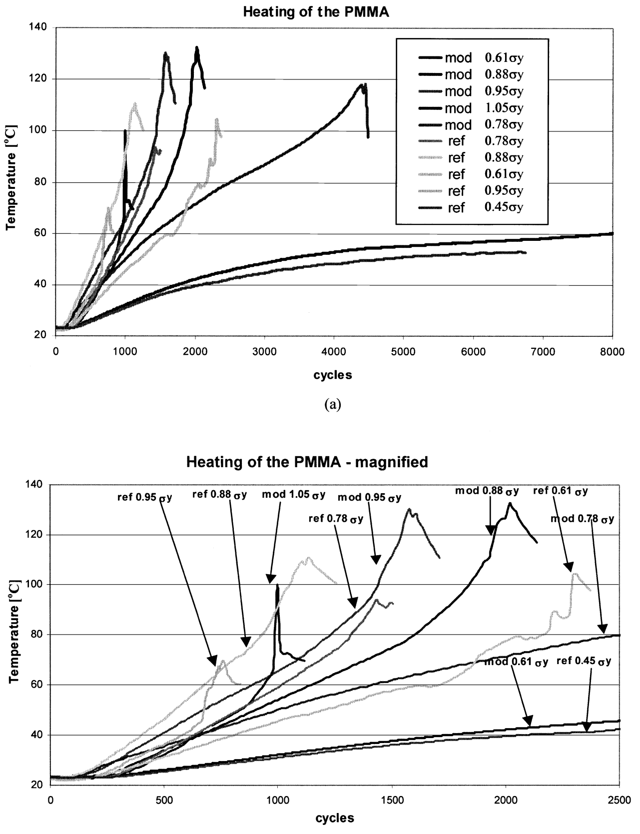
$$\mathrm{mod}(0.61\sigma_y) \approx \mathrm{ref}(0.45\sigma_y),$$

$$\mathrm{mod}(0.95\sigma_y) \approx \mathrm{ref}(0.78\sigma_y), \quad \mathrm{mod}(1.05\sigma_y) \approx \mathrm{ref}(0.80\sigma_y)$$

However, aside from endurance considerations, both the two materials are observed to behave and fail in an identical fashion. No thermal peak of the kind observed in PC were observed in all the experiments, this invalidating the possible relationship with overall chain mobility.

Table 3
Strain rate sensitivity of the yield stress of the investigated PMMA_REF and PMMA_MOD. The results apply to compression tests

Nominal strain rate (s^{-1})	σ_y PMMA_REF (MPa)	σ_y PMMA_MOD (MPa)
10^{-4}	65	60
10^{-3}	72	70
10^{-2}	80	80
10^{-1}	87	90



(a)

(b)

Fig. 5. Evolution of the specimen's temperature as a function of the number of cycles at various normalized stress levels. (a) Global curves. (b) Magnified initial part.

The failure mode of the specimens, for both polymers, is characteristic of that previously observed in commercial PMMA specimens by Rittel [8]. As shown in Fig. 6, failure is localized and consists of a torus-like bulging at the specimen's mid-height. Failure results from localized heat

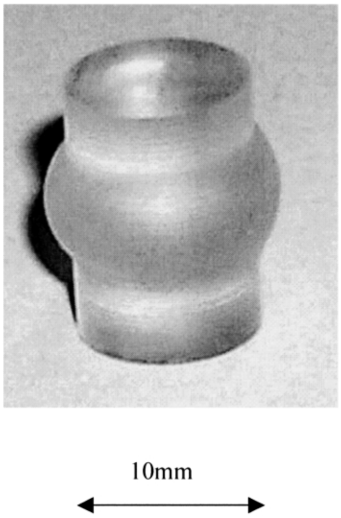


Fig. 6. Failed specimen. Note the localized bulging.

accumulation and inability to dissipate heat to the surroundings and to the rest of the specimen, so that the upper and the lower sections remain cylindrical without change. At mid-height, the sample literally melts and flows due to the pressure. The heat transfer problem has been addressed in detail for this specimen geometry by Rittel and Rabin [9]. Final failure appears suddenly within a short number of cycles and it is not gradual along the test.

4. Discussion

Two material polymers have been investigated from a thermomechanical point of view. The polymers differ in that additional chain mobility has been conferred to the modified PMMA by suitable additions of glutarimide. This addition adds more ‘plastic’ behavior to the original polymer. Mechanical testing results show that while this addition does not modify the elastic behavior of the material up to the elastic limit, it indeed improves the strength and flow characteristics of the material. As a result, PMMA_MOD exhibits superior mechanical characteristics. When the thermomechanical response of the material is considered, it appears that both materials react identically from a qualitative point of view. This means that the temperature rises faster and reaches higher levels when the cyclic applied stresses increase. For PMMA_REF, the glass transition temperature was reached. PMMA_MOD reached a maximum temperature of about 130 °C which is equivalent to $0.94T_\alpha$ (K). It thus seems that at a lower relative temperature, the material retains a higher stiffness, which reduces the heat generation rate. Consequently, it was observed that the endurance of the PMMA_MOD is superior to that of the base material, PMMA_REF. This means that the modified material can withstand higher cyclic stresses than the base material when the same temperature rise is observed.

However, *both* materials fail in an identical localized bulging failure mode. PMMA_MOD *did not* exhibit an initial thermal peak as was the case in PC. In the present experiments, both materials were cycled at identically high relative stresses. Thus, one can rule out the possibility that an initial thermal peak is solely related to the relative stress level, as in Ref. [8]. On can also rule out the influence of additional chain mobility on the overall heat generation, since the modification brought to PMMA_MOD did not significantly affect its thermomechanical response and failure mode.

Therefore, it appears that the specific behavior of PC is related to the material in itself, through a possible phase transition, that would be responsible for the initial exothermal peak. The fraction of energy that is stored through microstructural changes during the dynamic deformation of polymers has been characterized by Rittel [14]. Salamatina et al. [15] investigated the stored energy of cold work of various polymers. In both works, it is found that the stored energy of cold work is quite high, thus indicating what Salamatina et al. [15] call the *non-isostructural character* of the deformation process. It is likely that the stored energy of cold work can fluctuate as a result of the cyclic loading process, which in turn indicates microstructural fluctuations. However, we are not aware of such a phase transition in this material that would also be necessarily related or induced by cyclic stressing of the material, as opposed to monotonic loading. This suggestion seems nevertheless plausible when one considers the fact that a thermal peak is observed as opposed to a smooth temperature rise related to uniform heat generation process, in which there is no abrupt change of enthalpy.

The present results bring new results on the thermomechanical response of polymers that are subjected to high cyclic stresses, thus complementing the existing available information on this topic. They also show that additional work should be carried out on PC in order to determine whether this material undergoes a cyclic stress related phase transition.

5. Conclusions

- The addition of glutarimide to PMMA leaves the elastic and yield properties unaffected, but increases the toughness of the material.
- From a thermomechanical standpoint, the modification of PMMA increases its endurance in terms of cyclic loading. PMMA_MOD can withstand higher cyclic stress levels than the base material, when identical self heating levels are compared.
- Both materials exhibit identical failure modes when subjected to cyclic loading at identical high stress levels, of the order of the yield stress.
- The increased toughness and ability to sustain plastic deformation of PMMA_MOD does not give rise to a

specific new hysteretic heating pattern, of the kind previously observed in PC.

- The present experiments show that the previously observed thermal behavior of PC is neither related to its flow properties nor to the high level of cyclic stresses.
- The present results indicate a potential (exothermal) phase transition in PC that would be related both to the level (cyclic) nature of the loading process.

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