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Effect of Cooling Rate on the Viscoelastic Properties in the Plastic Zone of Solid Polymers

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ABSTRACT

PMMA and PC samples were subjected to several cooling rates from the glass transition temperature .

Stress-relaxation data , obtained with these samples under strains larger than the yield strain, were not influenced by the cooling rate previously experienced by the material . This shows that after yielding the effect of previous aging is quickly erased; similar indications , drawn from calorimetric measurements , were already available in (11-12) .

INTRODUCTION

The aging and/or annealing effect on many properties of solid polymers , especially at small strains, have been extensively studied by many authors ; in particular Struik (1) reports a remarkable amount of results and reviews most of the material available in the literature .

Aging and annealing or more in general the thermal history undergone by the material certainly (1b) have a significant effect, although smaller than at small strains, also on the properties at large strains . For instance changes of yield stress (1 b, 2, 3) and embrittlement in tensile and impact tests have been observed (4- 9) . Furthermore material densification (1, 3, 13, 14) and enthalpy relaxation (which parallels the enthalpy absorbed at the glass transition temperature) on aging or annealing have been measured (3, 8-12) .

On the other hand there are indications that the enthalpy relaxed may be regained by the material by means of tensile drawing (11-12) .

This work is oriented towards ascertaining the role of aging in the behavior after material yielding . The results

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obtained by means of some compression tests up to very large deformations, performed on both polycarbonate and polymethylmetacrylate samples, which had been subjected to different thermal histories, are here presented .

EXPERIMENTAL

The materials studied were bisphenol A polycarbonate (Lexan®) and polymethylmetacrylate (Plexiglas®) , which were supplied in the form of rods . Cylindrical samples with L = D = 1 cm for PMMA and L = D = 0.9 cm for polycarbonate were prepared by machining .

All the samples of each material were annealed together for 0.5 hr at about 10°C above their glass transition temperature and were then quenched in ice-water . They were heated separately up to about their glass transition temperature

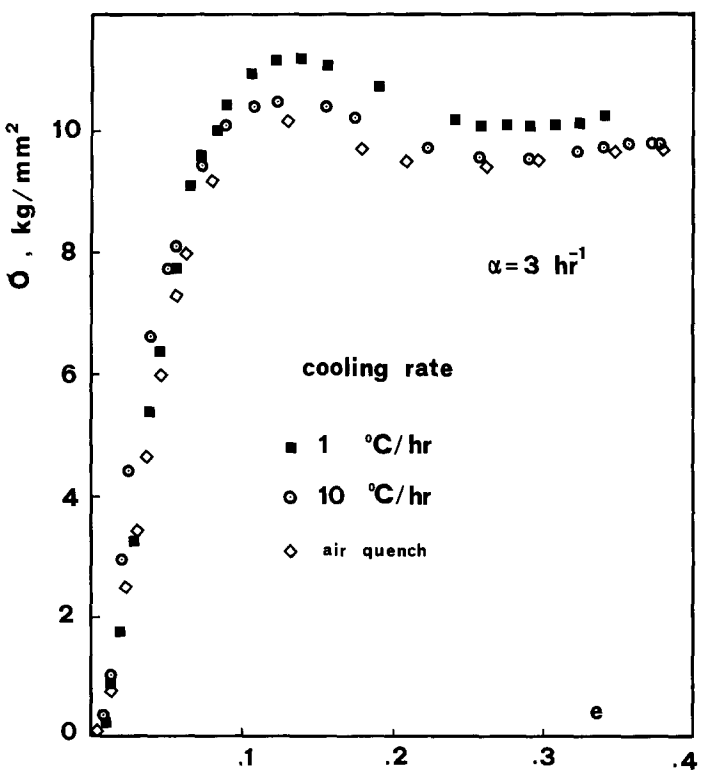

Fig. 1 Compression stress-strain behavior of PMMA samples subjected to different cooling rates . α is initial deformation rate .

(i.e. the PC samples to 150°C and the PMMA ones to 100°C) and were subjected separately to different cooling rates, that is air quenching, 60°C/hr, 1°C/hr for the PC samples and air quenching, 10°C/hr and 1°C/hr for the PMMA ones .

Stress relaxation measurements after constant velocity compression ramps were performed at room temperature by means of an Instron testing machine Mod. 1115 .

RESULTS AND DISCUSSION

The stress σ obtained during the loading ramps previous to relaxation tests is reported in figs. 1 and 2 versus the strain $e \equiv \Delta l/l_o$, where l_o is the initial sample height and Δl the sample height decrease during compression . Both the materials examined showed the same features . In particular, analogously

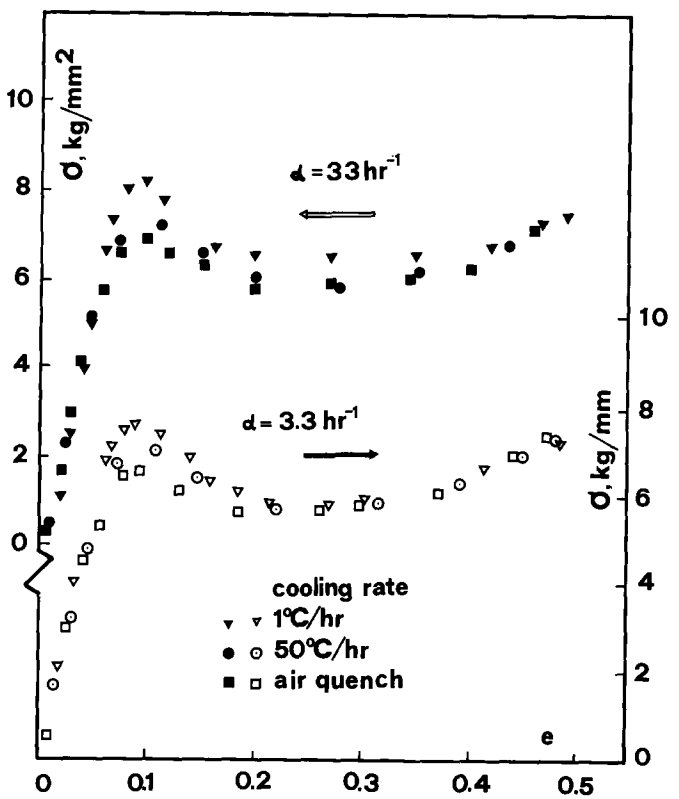

Fig. 2 Compression stress-strain behavior of PC samples subjected to different cooling rates . α is initial deformation rate .

to what was observed in tensile tests (1b, 2, 3) samples subjected to smaller cooling rates showed a larger yield stress . Furthermore both in figs 1 and 2, where two values of the strain rate α are considered, the curves approach each other after yielding .

Let us briefly discuss the meaning of these observations . Certainly the material relaxation time (or the spectrum of relaxation times) decreases as the stress increases and only when it is sufficiently small, may yielding take place . The changes induced in the material by large strains may thus (15) be considered the inverse of aging and in fact a larger yield stress is observed with samples more efficiently aged by means of a smaller cooling rate . Also, the fact that, after yielding, the stress-strain curves of figs 1 and 2 approach each other suggests that the differences induced in the samples by previous (aging) treatments are quickly erased .

Similar indications were in fact drawn in (11-12) from the observation that tensile drawing of ABS resins produced an enthalpy change matching the entalpy relaxation due to the thermal history undergone by the sample .

More detailed indications may be obtained from the stress-relaxation data reported in figs 3 and 4 as σ / σ_o (where σ_o

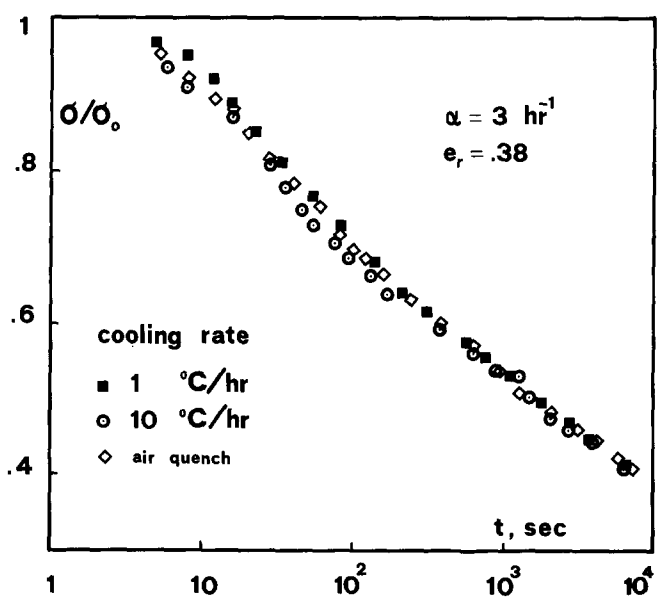

Fig. 3 Compression stress-relaxation behavior of PMMA samples subjected to different cooling rates . e_r is relaxation strain .

is the stress at the end of the loading ramp) versus time t . For each material all the tests were performed at the same strain e_r (larger than the yield strain) on the samples whose loading was already considered in figs 1 and 2 .

The data of figs 3 and 4 show that the cooling rate does not affect the relaxation behavior after yielding . In other words, in this zone, the relaxation time does not seem to depend upon the relaxation time of the material prior to the test, which conversely is certainly influenced by the previous thermal history and/or aging : the increase of small strain relaxation time is completely reversed by the yielding process .

On the other hand the data of fig. 4 show that, as already observed in other cases (16) , the material viscoelastic behavior in the plastic zone (after yielding) depends on the strain rate adopted in the loading ramp .

Both the effects mentioned above may be summarized as follows . Whatever is the aging history experienced previously

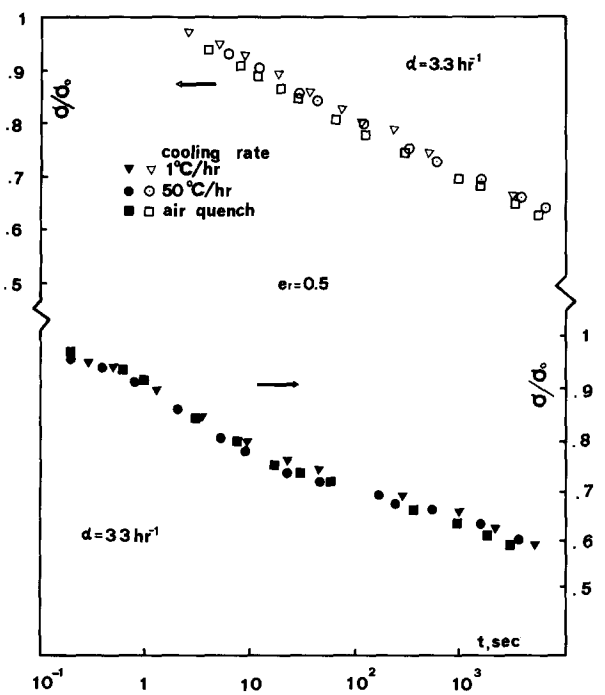

Fig. 4 Compression stress-relaxation behavior of PC samples subjected to different cooling rates . e_r is relaxation strain .

by the material, in order to have yielding, the molecular mobility has to increase to a level which depends only on the strain rate α ; during this process the effect of previous aging is completely erased .

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