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TEMPERATURE AND MOLECULAR-WEIGHT DEPENDENCE OF THE STRAIN HARDENING BEHAVIOUR OF POLYCARBONATE

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In this study the temperature dependence of the post yield behaviour of two commercial grades of polycarbonate were investigated. The strain hardening modulus is found to decrease substantially with increasing temperature. A decrease in molecular weight only appears to have a small influence on the strain hardening behaviour, whereas it leads to a dramatic decrease in the failure strain of the material.

Introduction

When subjected to a tensile test, a glassy polymer displays an initial elastic region followed by rate depended yielding, due to stress-activated segmental motion. The post-yield behavior of glassy polymers is governed by two phenomena; firstly intrinsic strain softening, that leads to a decrease in the stress level with increasing deformation, and secondly strain hardening, that leads to a subsequent increase of the stress level. This investigation will focuss on the latter.

It seems generally accepted that the strain-hardening response in (glassy) polymers originates from the rubber elastic response of the entanglement network [1-3], the prime indication being the complete recovery of plastic deformation if the polymer is heated above the glass-transition temperature. However, a quantitative agreement between the strain-hardening modulus observed in the post-yield behaviour below T_g, and the rubber-plateau modulus that is observed above T_g, still seems to be lacking [3]. In this study it is attempted to clarify this disagreement by investigating the temperature dependence of the strain hardening modulus of two grades of polycarbonate with different molecular weights.

Experimental

The materials investigated were two commercial grades of polycarbonate, Lexan 101 from General Electric and Macrolon CD2000 from Bayer. The Lexan 101-grade had a weight-average molecular weight M_w of 33500 g/mol, whereas the CD2000 grade had a M_w of approximately 13000 g/mol (estimated from shear viscosity).

The most straightforward way to study the post-yield behaviour experimentally is to apply large homogeneous deformations. However, most polymer systems, and especially polycarbonate, are prone to inhomogeneous deformation (necking). In polymer glasses, this tendency to strain

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localisation is especially influenced by intrinsic-strain softening. A possible way to enable large homogeneous plastic deformations is therefore to eliminate strain softening by mechanical conditioning. For this purpose axis-symmetrical tensile bars were subjected to large strain torsion at room temperature. The torsion was applied manually, by clamping the sample in a universal lathe and turning one side over 720~degrees, with a line on the sample as a reference. Subsequently the sample was returned to its undeformed state by rotating in the opposite direction, again using the line on the sample as a reference. On these pre-conditioned samples tensile tests were performed at a strain rate of 10^{-2} s^{-1} at various temperatures below T_g.

Torsional dynamic mechanical analysis was performed on a Rheometrics RDS II in a plate-plate geometry at a frequency of 1 Hz and temperatures of 170 to 240 °C, well above the glass transition temperature. The samples were compression moulded disks with a thickness of 2 mm and a diameter of 25 mm.

Results

In Figure 1 the results of the tensile experiments are presented in a plot of true stress versus the strain measure (λ^2-λ^{-1}). After this mechanical treatment, the strain softening behaviour has disappeared and the samples deform homogeneously in a standard tensile test. Due to the mechanical treatment the strain softening effect has almost totally disappeared and the bars are observed to deform homogeneously. From Figure 1 it is clear for both materials that the post yield behaviour at all temperatures can be represented by a neo-hookean strain hardening response visualised by a linear relationship between the true stress and (λ^2-λ^{-1}), or :

$$\sigma(T) = \sigma_y(T) + G_R(T)(\lambda^2 - \lambda^{-1}) \tag{1}$$

where σ_y is the yield stress, λ is the draw ratio and G_R represents the strain hardening modulus. According to the Gaussian network approximation the shear modulus of a cross-linked network can be expressed as:

$$G_R = nkT \tag{2}$$

where n is the number of elastically active chains and k is Boltzmann's constant. In this classical rubber-elastic approach an increase of temperature will typically lead to an increase of the strain hardening modulus. However, in contrast to the chemical network that is assumed in the Gaussian network approach, the molecular network in a thermoplastic material is of a physical nature, Viz. entanglements. It is therefore not surprising that the values of the strain-hardening moduli determined from the experimental data in Fig. 1, represented in Table I, clearly *decrease* with increasing temperature. According to Arruda [4] this decrease is related to a decrease of the number of elastically active chains n, which is equivalent to an increase in the number of monomer units between entanglements. In other words, the network relaxes (dis-entangles) with increasing temperature.

Temperature (°C)	G_R [MPa], Lexan 101	G_R [MPa], CD2000
25	23.7	23
50	21.3	20.6
75	18.7	17
100	15	13.5

Table I: Temperature dependence of the strain hardening modulus of Lexan 101 and Macrolon CD2000

In the polymer rheology field, it is well established that relaxation of the entanglement network results from reptation [5]. With this process in mind, it seems instructive to compare the temperature dependence of the strain hardening modulus, shown in Table I, to that of the dynamic shear modulus G_D measured (1Hz) in the melt (Figure 2).

In the case of both materials, the temperature dependence of the strain-hardening modulus appears to correlate well with the relaxation behaviour of the entanglement network in the melt. This observation supports the view that strain hardening originates from a rubber-elastic response of the entanglement network, which becomes operable when segmental motion is allowed.

At low temperatures, the strain hardening modulus is only slightly influenced by a reduction in molecular weight. This could be expected, since the molecular weight between entanglements is not influenced by chain length. However, as the number of entanglement per chain decreases, the relaxation of the network will occur faster, which leads to the differences that are observed between the two grades at higher temperatures (Fig.2). A more dramatic effect of a decrease in molecular weight is its strong influence on the strain to break, as can be observed in Fig.1.

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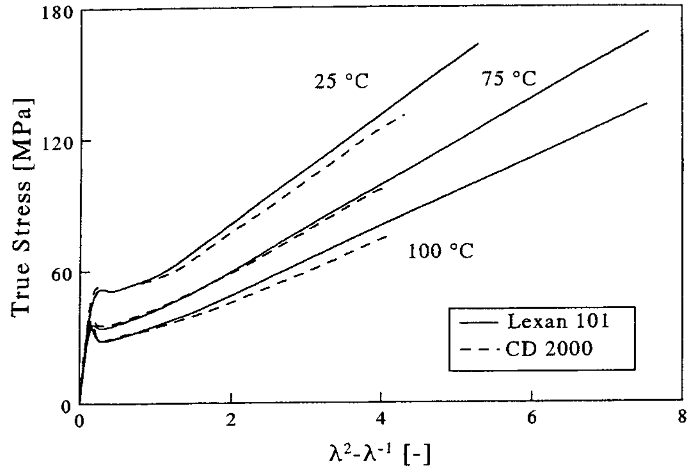

Figure 1. True stress-strain curves of mechanically pre-conditioned samples of Lexan 101 (solid line) and Macrolon CD2000 (dashed line) at various temperatures

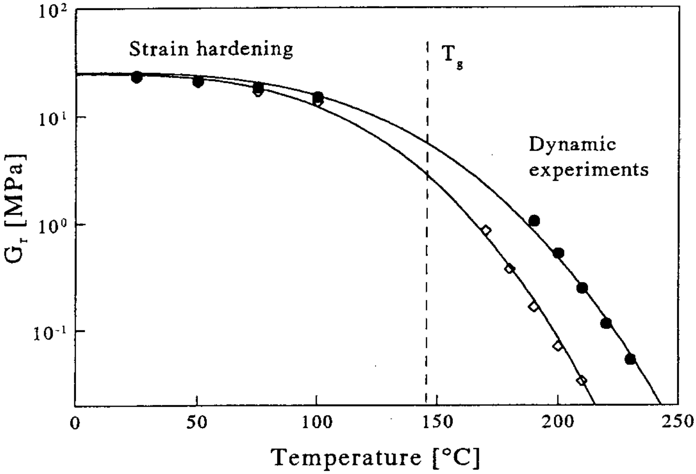

Figure 2 Strain hardening modulus and dynamic shear modulus vs. temperature for Lexan 101 (solid symbols) and CD2000 (open symbols)