

# Physical ageing of polypropylene in glassy state

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Physical ageing behaviour of a semicrystalline polymer, polypropylene, has been studied at a pressure-temperature state ( $P = 2.5$  kbar,  $T = 15^\circ\text{C}$ ) for which the amorphous region is in the glassy state. Polypropylene contains 57% crystallinity and its glass transition temperature at atmospheric condition is  $-20^\circ\text{C}$ . The ageing behaviour was monitored by measuring the Young's modulus ( $E$ ) from the stress-strain curves as a function of ageing time up to 200 h. The Young's modulus of the rapidly pressure quenched samples increased at 0.4% per ageing hour of the initial value for up to 30 h and tapered off thereafter. The glassy polypropylene also exhibited a memory behaviour when it was given a pressure perturbation.

## 1. Introduction

Physical ageing of polymeric glasses with regard to high pressure has been studied by many investigators in recent years [1-4]. Memory effect of the glasses has also been revealed when they were given temperature and/or pressure perturbations [5-7]. However, physical ageing of semicrystalline polymers, when the amorphous region is brought to the glassy state, has not yet attracted much attention. A study has been made to determine physical ageing characteristics and the memory behaviour of polypropylene (PP) at  $P = 2.5$  kbar and  $T = 15^\circ\text{C}$ , where the amorphous region of the polymer is in glassy state. The Young's modulus ( $E$ ) was used as the parameter to monitor the physical ageing. Others have also used  $E$  for the same purpose [8]. PP was chosen for this study because it possesses a distinct glass transition temperature ( $T_g = -20^\circ\text{C}$  at atmosphere pressure) [9, 10], and the dependence of  $T_g$  on pressure has been established [11]. PP samples exhibited the ageing behaviour similar in its general characteristics to many amorphous polymers although they possess very different structure and morphology. PP also showed the memory effect when pressure perturbation was given.

## 2. Experimental details

A commercially extruded rod of PP was machined in a form of right circular cylinders (1.27 cm diameter and 2.54 cm in length) for compressive tests. The density of the material is  $0.90\text{ g cm}^{-3}$ . The crystallinity was estimated to be 57% from a DSC and X-ray diffractometer scans. The glass transition pressure ( $P_g$ ) at room temperature has been reported to be 2.05 kbar [11]. The compressive stress-strain tests were carried out in a thick-walled high pressure testing chamber which is capable of maintaining pressure to 7 kbar and temperature from  $-100^\circ\text{C}$  to  $+100^\circ\text{C}$ . Details of the testing apparatus and testing procedures can be found elsewhere [12]. The pressure transmitting fluid used in this study was Dow Corning 200 silicone oil of 5 cs viscosity. No absorption of fluid or swelling of the

specimens were observed under our experimental conditions. Testing temperature was controlled within the range of  $\pm 1^\circ\text{C}$ . Pressure was increased at a rate of  $0.25\text{ kbar min}^{-1}$  and decreased at  $0.5\text{ kbar min}^{-1}$ . The strain rate was kept constant at  $0.4\text{ cm min}^{-1}$ .

The experimental procedure was as follows: Temperature of a PP sample was first lowered to  $15^\circ\text{C}$  from room temperature at atmospheric pressure. Then pressure was increased to 2.5 kbar at  $15^\circ\text{C}$  (control state) as shown in Fig. 1. The rubbery phase of the sample transformed to the glassy phase at 1.52 kbar. The sample was allowed to age at 2.5 kbar and  $15^\circ\text{C}$  and was given a compressive load to obtain the stress-strain response after a specified time, as 5 h. Once a sample was tested in compression, the sample was discarded in order to remove any ambiguity on the effect of the loading history on the ageing. A new sample was given the same  $P, T$  history and was then aged for a longer time and tested in compression. The selected ageing times were 0.5, 1, 10, 20, 50, 100 and 200 h. A series of PP sample were given a pressure perturbation only from the control state by increasing pressure from 2.5 kbar to 3.5 kbar without delay maintaining  $T = 15^\circ\text{C}$  as shown in Fig. 2. The samples were kept at the perturbed state for 10 h before they were returned to the control state. Each sample was then tested in compression for its stress-strain response at different ageing times.

## 3. Results

Typical compressive stress-strain curves obtained at the control state ( $P = 2.5$  kbar,  $T = 15^\circ\text{C}$ ) for various ageing times namely, 0.5, 50 and 200 h are shown in Fig. 3. At least three tests were conducted for each ageing time. The entire stress-strain curves shifted upwards, exhibiting increased modulus, the yield strength, and the elastic energy and the total energy stored, as an increasing function of ageing time. The Young's modulus,  $E$ , was determined from the initial slope through the origin of the curves. An average value of  $E$  was calculated and plotted in Fig. 4.

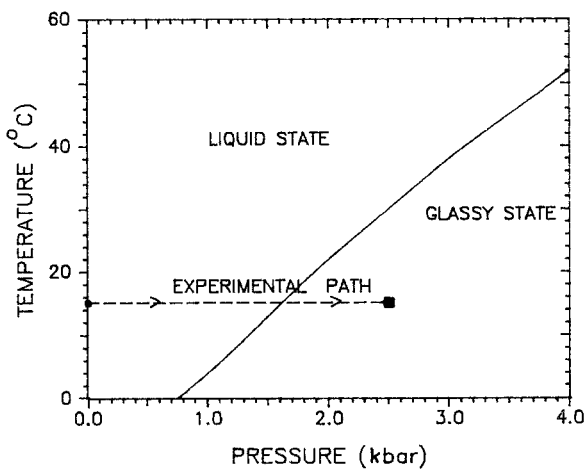


Figure 1 Schematic path profile to reach the experimental state.

Scattering of  $E$  values from the average was within 3 percentile. The full line in Fig. 4 represents the best least square fit, using PLOTIT program. The modulus increases rapidly up to about 50 h of ageing time from  $E_0 = 2.37 \times 10^5$  psi to  $E = 2.68 \times 10^5$  psi at 50 h and thereafter increases rather slowly to  $E = 2.75 \times 10^5$  psi at 200 h.

Fig. 5 shows the increase of the yield strength (2% offset) as a function of the ageing time. The yield strength increases rapidly only up to 20 h going from 9600 psi to 10400 psi and then shows almost no increases thereafter.

The memory effect due to pressure perturbation is shown in Fig. 6. The full line represents the physical ageing of the control sample, manifested in young's modulus ( $E$ ). The dashed line is the variation of  $E$  with ageing time of the perturbed samples at the same control state.  $E$  begins at much higher value (approximately  $3.15 \times 10^5$  psi), decreases rather rapidly with ageing time, and finally joins the control curve at about 30 h later.

#### 4. Discussion

Polypropylene, a semicrystalline polymer, exhibits physical ageing phenomenon when the amorphous phase is rather rapidly transformed into the glassy state. The ageing behaviour is very much similar to many amorphous polymers and elastomeric glasses [4]. It also reveals the memory effect when the samples

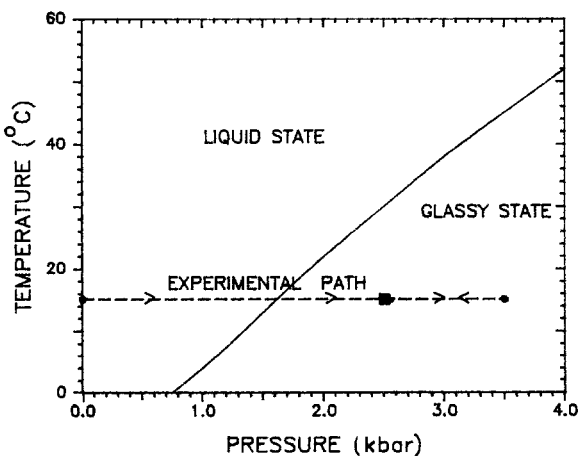


Figure 2 Schematic path profile for memory behaviour.

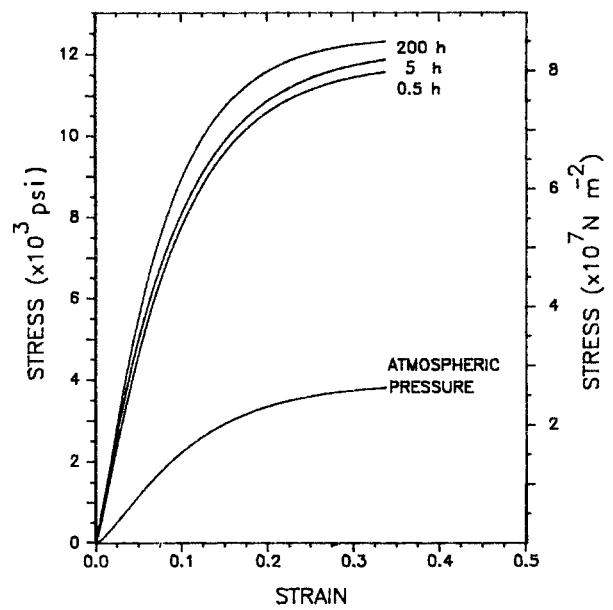


Figure 3 Compressive stress-strain curves at various ageing times at 25 kbar.

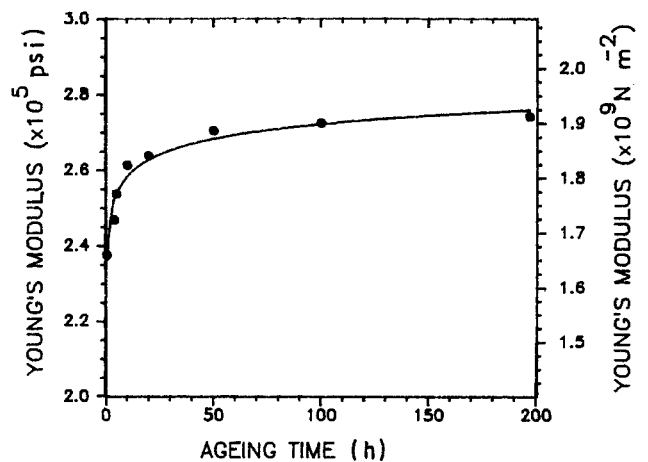


Figure 4 Effect of physical ageing on Young's modulus.

were perturbed and the memory behaviour is also very much like the amorphous polymers and elastomeric glasses [7]. These behaviours are originated in the amorphous glassy region as there cannot be any change in crystallinity at these states of pressure and temperature. The ageing phenomenon must originate from the molecular level even though the hierarchical

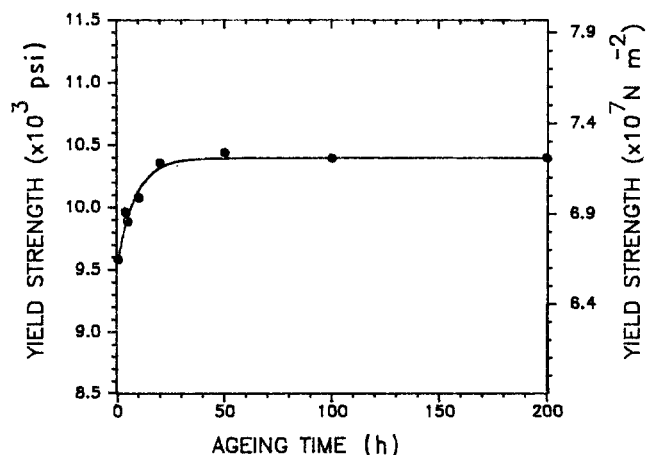


Figure 5 Effect of physical ageing on yield strength.

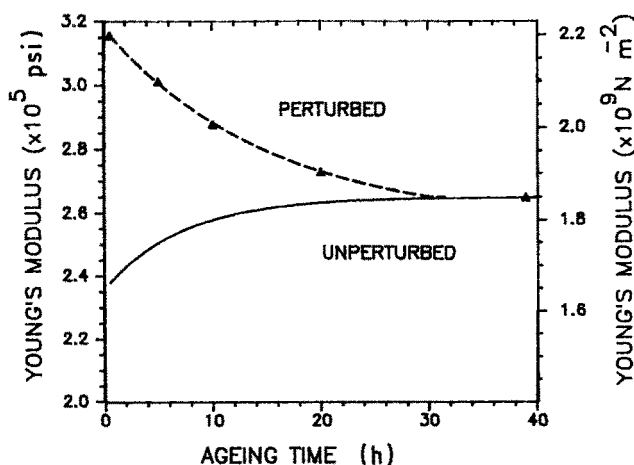


Figure 6 Memory behaviour of samples by pressure perturbation.

structure of a semicrystalline polymer like PP is very complex.

It has been shown that the Young's modulus is proportional to  $\delta = (V(t) - V_{\infty})/V_{\infty}$  where  $V_{\infty}$  is the equilibrium volume, provided that the compressive material response is linear elastic [4], as  $1/E = A(P, T)(1/\delta - 1/\delta_{\infty})$ . Many semicrystalline polymers can be expected to undergo physical ageing. In view of the evidence shown in this paper, one must reassess experimental data produced in the past at low temperatures (below  $T_g$ ), such as dynamic mechanical studies or at high pressures (above  $P_g$ ), such as stress-strain behaviour, without regard to physical ageing

and memory effects. Any low temperature and high pressure studies or applications must take into consideration all temperature, pressure and ageing history since the effects of physical ageing on mechanical properties are very significant.

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