A partial reduction of this vacancy ferrite, by treatment at 600° C in an oven swept by a mixture of hydrogen and nitrogen (1% H_2), saturated in water vapour (passed through a saturator, maintained at 50° C; $P_{H_2O} = 9.1$ torr) and equipped with a quenching system, produces an oxide, the composition of which (7.46 wt % Fe(II); 52.5 wt % Fe(III); 13.5 wt % Ba) is very close to that of the oxide $Ba_3Fe(II)_4Fe(III)_{28}O_{49}$ (of composition 7.49 wt % Fe(II); 52.42 wt % Fe(III); 13.81 wt % Ba). The specific saturation magnetization measured at a temperature of 4 K on this sample ($\sigma_S = 66.0$ emu g^{-1}) agrees with a type MYS_N structure ($\sigma_{S(calc.)} = 67.4$ emu g^{-1}). On the other hand, the specific saturation magnetization measured at room temperature ($\sigma_S = 49.6$ emu g^{-1}) is lower than that reported by Brady [1].

Consequently, although the existence of the ferrite $Ba_3Fe(II)_4Fe(III)_{28}O_{49}$ with a MYS_N structure seems plausible it is not proved that such a phase is present in the materials considered by Brady.

Acknowledgements

Specific saturation magnetization values were determined from the variation of specific magnetization with applied magnetic field in the "Service National des Champs Intenses", Grenoble, France and we are especially grateful to Professor R. Pauthenet for the provision of this service.

References

1. L. J. BRADY, *J. Mater. Sci.* 8 (1973) 993.
2. B. DURAND and J. M. PÂRIS, *Ann. Chim. Fr.*

Received 14 April
and accepted 12 May 1980.

B. DURAND
J. M. PÂRIS
Laboratoire de Chimie Minérale III,
Université Claude Bernard,
Lyon I,
69622 Villeurbanne Cedex,
France

Deformation and relaxation studies of polycarbonate using the split Hopkinson pressure bar method

Polymers are nowadays employed frequently as construction materials in applications where they are subjected to rapid mechanical deformations. Because polymers are viscoelastic materials they respond appreciably differently when deformed at high rates of strain than when under static conditions. Therefore it is a matter of importance to be able to characterize the dynamical mechanical behaviour of polymers also at high rates of loading.

There is strong evidence that the macroscopic behaviour of polymers during rapid non-linear deformation conditions is intimately related to changes of both static and dynamic microstructure. The dynamic microstructure, which is expressed by molecular relaxations, has been a topic of comprehensive studies [1–4]. It has been shown that the molecular relaxations of polymers contribute strongly to many of the important engineering properties of these materials; for example, ductile–brittle transition [5], yield stress [6, 7], fatigue [8, 9] and impact strength [10, 11]. There are, however, a multitude of open questions which must be solved before the general laws which govern the macroscopic deformation–molecular response relationships of polymers can be formulated. Experimental studies using different measurement methods are therefore important.

In this note, we report that the split Hopkinson pressure bar (HPB) method which has been used in deformation studies of metals [12–14], polymers [15] and composites [16] may also give information about the relaxation behaviour of polymers during compression loading conditions.

The split Hopkinson pressure bar is commonly used in the form reported by Hauser [12], in which a cylindrical test sample is sandwiched between two long steel bars (an elastic input bar and an elastic output bar). The loading is initiated by impacting the input bar with the striker bar, producing a stress pulse whose duration is determined by the length of the striker bar. We have

0022–2461/81/010275–05$02.50/0

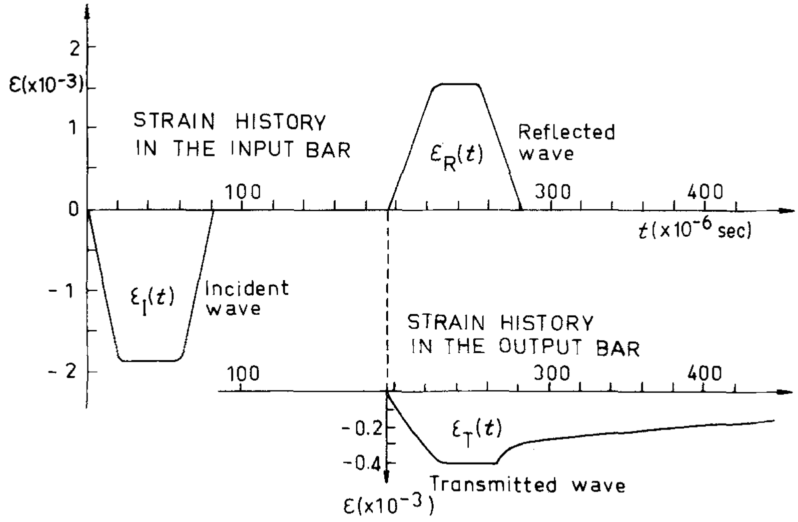

Figure 1 Strain–time pulses from split Hopkinson pressure bar test on PC at 298 K.

used in our experiments a self constructed apparatus where the velocity of the striker and thus the stress amplitude is regulated by air pressure. The applied loading and deformation of the specimen were determined from the displacements and forces at the two faces of the pressure bars by means of analysis of strain gauge data.

The apparatus was equipped with a temperature chamber. High temperature ($T >$ room temperature) were regulated by means of heat resistances and low temperatures with a VARIAN V-4557 temperature controller. The construction of the test machine will be given in detail elsewhere [17].

The temperature rise during impacts was measured by a digital thermometer using a thermocouple embedded in the specimen. The thermocouple consisted of NiCr-alloy and Ni wires with diameters of 0.25 mm. The final size of the joining bead was approximately 0.5 mm. A hole with approximately the same size as the bead was drilled radially into the specimen to its centre. The bead of the thermocouple was then forced into the hole, so that an intimate contact between the thermocouple and the polymer was obtained.

In this note the impact compressive behaviour of polycarbonate (PC) has been studied. A commercial grade PC (Makrolon 3100 from Bayer AG) was obtained in the form of a rod nominally 30 mm in diameter. The rod was turned into cylindrical samples of 12 mm diameter and 6 mm length. The end faces were flat and parallel to within 0.01 mm. The ends of each specimen were lubricated before testing with Molykote 33 grease (or with Molykote 321 R spray in the case of the measurements below 203 K).

During the HPB experiments three separate strain pulses were recorded: the incident loading pulse and the reflected pulse from the input bar and the transmitted pulse from the output bar.

Fig. 1 shows an example of strain–time pulses which were obtained from a test of PC at 298 K.

From the three strain–time histories the stress, strain, strain rate and energy loss of the specimen can be calculated by assuming that the theory of one dimensional elastic wave propagation holds [15].

Fig. 2 shows the calculated compressive stress–strain curves for PC at different temperatures.

Table I gives strain rates, yield strengths, total and plastic strains which were calculated from the data of Fig. 2.

Fig. 2 shows that the deformation mechanism of PC is ductile at all measurement temperatures. This is in agreement with earlier results which showed that during instrumented Charpy impact measurements the transition from ductile to brittle fracture occurs only at 143 K [18].

In most cases the stress–strain curves of PC samples showed clear upper and lower yield points. Fig. 2 shows that the measurements at 353 and 383 K were exceptional in this respect. Several adjustment measurements showed that this anomaly is real. Its origin is not yet clear

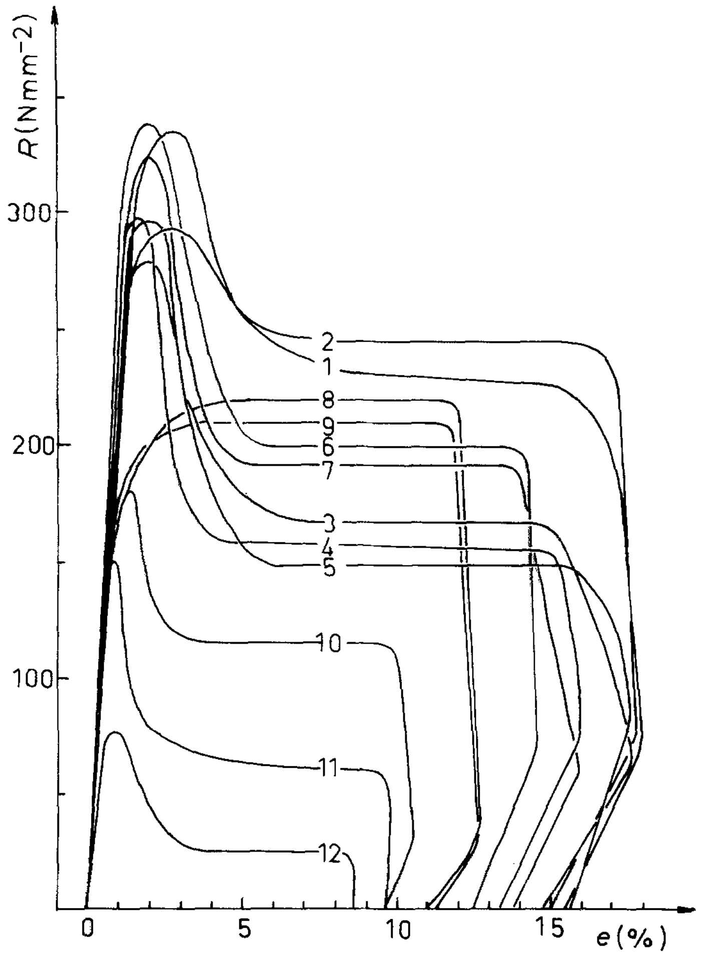

Figure 2 Stress–strain curves for PC in compression at various temperatures. The numbers of the curves refer to Table I.

TABLE I Mechanical data of PC based on HPB measurements

Number of curve	Test temperature (K)	Strain rate ($\times 10^3$ sec^{-1})	Compressive yield strength (N mm^{-2})	Total strain (%)	Plastic strain (%)
1	163	3.0	330	17.8	1.0
2	193	3.0	290	17.7	2.3
3	223	2.9	280	17.3	8.0
4	253	2.7	290	15.8	6.2
5	273	3.0	290	17.5	12.3
6	298	2.6	330	15.2	11.3
7	313	2.6	320	15.9	14.1
8	353	2.1	220	12.7	9.2
9	383	2.1	210	12.6	11.5
10	403	1.8	180	10.6	8.8
11	423	1.6	150	9.8	5.5
12	433	1.5	80	8.7	1.5

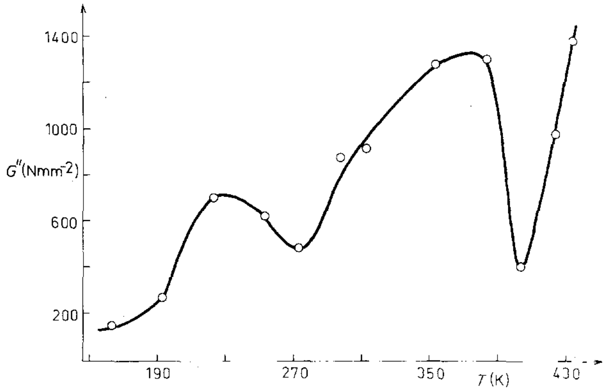

Figure 3 The apparent loss modulus G'' of PC versus temperature.

although the strain rate effect is a possible explanation [19].

Yield strength of PC decreased as a function of increasing temperature (see Table I). The decrease of yield strength was not monotonous which may be a consequence of the effects of different molecular relaxations upon the yield. Because mechanical energy is dissipated to heat during relaxation processes the measurement of temperature rise during deformation seemed to be a reasonable method to study relaxations in PC during compressive deformation.

The strain history in the output bar (Fig. 1) clearly shows the viscoeleastic response of PC to compressive impacts.

The dissipated energy is related to the temperature rise according to the following well known equation

$$\Delta Q = \Delta T m c_p \qquad (1)$$

where ΔQ is the heat energy, ΔT is the temperature rise, m is the mass of the specimen and c_p is the specific heat of the specimen.

In cyclic deformation the energy (ΔW) dissipated per complete cycle is given by the following expression [1]

$$\Delta W = \pi \gamma_0^2 G'' \qquad (2)$$

where γ_0 is the strain amplitude and G'' is the mechanical loss modulus.

Equation 2 can also be written in the form

$$G'' = \frac{\Delta W}{\pi \gamma_0^2}. \qquad (3)$$

When it is assumed that the rise of the strain during a HPB test corresponds to a quarter of a complete dynamic stress–strain cycle and the quantity γ_0 of Equation 3 is substituted by the total compression strain $e_{\max}$ we can write

$$4\Delta Q \approx \Delta W. \qquad (4)$$

Combination of Equations 3 and 4 gives

$$G'' = \frac{4\Delta Q}{\pi e_{\max}^2}. \qquad (5)$$

Equation 5 is a semiquantitative measure of energy loss during compression testing. Because it is still difficult to estimate the absolute exactness of G'' of the HPB test we call it the apparent loss modulus. The rise time of the impact stress pulse can be used to estimate the (single) frequency corresponding to impact [20]. In our case the frequency was of the order of 1 kHz.

Fig. 3 shows the G'' values of PC as a function of temperature as measured from the temperature rise and the strain in HPB experiments.

According to Fig. 3, HPB measurements indicate the existence of three mechanical losses in PC in the temperature range studied.

The low temperature maximum at 220 K evidently corresponds to the $T < T_g$ relaxation [4] which can be resolved into several processes originating from some local motions of the main chain phenyl and/or carbonyl groups [21]. The rapid rise of G'' near 430 K indicates the onset of glass–rubber (T_g) relaxation. The intermediate loss maximum near 370 K is still enigmatic. It has been observed as a shoulder in dynamic mechanical and dielectric measurements [21]. It has been proposed that this process is a precursor of the T_g-process [20] or that it is associated with stresses induced in the moulding or drawing of a specimen [21]. The high intensity of G'' of HPB measurements for the intermediate process supports the hypothesis that it is a precursor of the T_g-process. It is interesting to note that we could show the existence of this intermediate process also by measuring the notched impact strength of PC as a function of temperature [22]. The intensity of the impact strength maximum near 370 K diminished rapidly on annealing (the annealing embrittlement effect) which was also consistent with the hypothesis of the T_g-precursor nature of the intermediate process.

On the basis of these preliminary results we conclude that the HPB method is a valuable tool in relaxation studies of polymers. Therefore studies of different construction plastics using this method are in progress in our laboratory.

References

1. N. G. McCRUM, B. READ and G. WILLIAMS, "Anelastic and Dielectric Effects in Polymeric Solids" (John Wiley and Sons, New York, 1967).
2. W. P. SLICHTER, *J. Polymer Sci.* **C14** (1966) 33.
3. R. F. BOYER, *Rubber Chem. Technol.* **36** (1963) 1303.
4. P. TÖRMÄLÄ, *J. Macromol. Sci. – Rev. Macromol. Chem.* **C17** (1979) 297.
5. W. RETTIG, *Eur. Polymer J.* **6** (1970) 853.
6. J.-C. BAUWENS, *J. Polymer Sci.* **C33** (1971) 123.
7. A. HILTNER and E. BAER, *Polymer* **15** (1974) 805.
8. R. W. HERTBERG, J. A. MANSON and M. D. SKIBO, *ibid.* **19** (1978) 359.
9. S. SIKKA, *Mater. Sci. Eng.* **41** (1979) 265.
10. P. I. VINCENT, *Polymer* **15** (1974) 111.
11. M. KISBENYI, M. W. BIRCH, J. M. HODGKINSON and J. G. WILLIAMS, *ibid.* **20** (1979) 1289.
12. F. E. HAUSER, *Exp. Mech.* **6** (1966) 395.
13. C. K. H. DHARAN and F. E. HAUSER, *ibid.* **10** (1970) 370.
14. W. N. SHARPE, Jr and K. G. HOGE, *ibid.* **12** (1972) 570.
15. S. C. CHOU, K. D. ROBERTSON and J. H. RAINEY, *ibid.* **13** (1973) 422.
16. L. J. GRIFFITHS and D. J. MARTIN, *J. Phys. D: Appl. Phys.* **7** (1974) 2329.
17. E. PÄÄKKÖNEN and P. TÖRMÄLÄ, Tampere University Report Series.
18. B. HARTMANN and G. F. LEE, *J. Appl. Polymer Sci.* **23** (1979) 3639.
19. K. W. CHASE and W. GOLDSMITH, *Exp. Mech.* **14** (1974) 10.
20. E. SACHER, *J. Macromol. Sci. – Phys. B* **11** (1975) 403.
21. D. C. WATTS and E. P. PERRY, *Polymer* **19** (1978) 248.
22. E. PÄÄKKÖNEN, P. KEMPPAINEN and P. TÖRMÄLÄ, Proceedings of the Scandinavian Symposium on Materials Science, University of Luleå, Sweden, August 1980.

*Received 17 April
and accepted 12 May 1980.*

PERTTI TÖRMÄLÄ
ESKO PÄÄKKÖNEN
PIRKKO KEMPPAINEN
*Institute of Materials Science,
Tampere University of Technology,
POB 527,
SF-33101 Tampere 10,
Finland*

Cyclic plastic behaviour of metastable Fe–30 wt % Ni alloy at 293 and 373 K

Until recently the fatigue behaviour of metastable austenite alloys has been reported by only a few investigators [1–3]. The cyclic hardening/softening behaviour is not well established as these alloys transform to martensite during cyclic deformation and it seems necessary to separate the hardening due to the martensite formation from the hardening/softening behaviour due to the multiplication and rearrangement of dislocations. In this note an attempt to separate these phenomena of a metastable austentic steel consisting of 0.005 wt % C, 0.003 wt % Si, 0.002 wt % Mn, 0.003 wt % P, 0.004 wt % S and 30.1 wt % Ni at 293 and 373 K is reported. Fatigue tests were carried out in fully reversed bending using a Schenck type fatigue machine of 450 cpm frequency. A temperature increase in the specimen was not detected under the experimental conditions used when the plastic strain amplitude did not exceed 3.5×10^{-3}.

The variations of plastic strain amplitude were measured dynamically by the mechanical method shown in Fig. 1. The total strain amplitude (Equation 1) can be calculated from the relative displacement a of the specimen measured by a differential transformer. Equation 2 gives the plastic strain amplitude.

$$\epsilon_t = \frac{2e}{l}\tan\theta \left(\theta = \frac{a}{2r}\right) \qquad (1)$$