able impurities at low supercooling. Of particular interest to the design engineer is the temperature at which these spherulites melt, particularly if the service temperature of the extrudate is high, such as in hot water tubing etc. It is hoped to observe the growth and behaviour of these spherulites in detail using an optical microscope with hot stage attachment.

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Time–stress supersition in some creep experiments

A. Franceschini and A. Momo
Centro Ricerche FIAT, Orbassano, Italy
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Elastomer-modified thermoplastics have gained acceptance by automotive producers as a result of a combination of good processability, moderate prices and adequate performance. Examples are the adoption of rubber-modified polypropylenes, like Moplen SP 25 and others, in the dashboards and bumpers of some cars, where they exhibit high impact resistance. In this context we are presently engaged in a program aimed at comparing the creep resistance of various polypropylene-based materials, differing in both rubber and filler content and from different producer. We are thus conducting conventional measurements of elongation *versus* time in tensile creep apparatus.

From a practical point of view, it would be highly desirable to be able to hasten the test, for instance by enhancing the stress to which samples are subjected, or temperature, or both. A fundamental prerequisite to any kind of acceleration must be, of course, the previous demonstration that the mechanisms operating in the "accelerated situation" are the same which are active in the "actual situation" (in our case, creep at a low to moderate temperature, and low applied stresses). As for "stress acceleration", a positive clue would be the existence of a master curve for time–stress superposition, analogous to the time–temperature superposition in amorphous linear polymers above the glass transition[1,2].

Recent reports hint at such curves in particular cases[3–6], but we have been unable to find explicit reference which would warrant such a procedure, especially in the case of a crystalline thermoplastic like polypropylene, eventually rubber-modified.

As a consequence, we have empirically probed the existence of master curves in the case of two propylene–ethylene copolymers, tested at different tensile stress levels, and at a constant temperature of 32°C. *Figures* 1 and 2 show the experimental data: the materials are, respectively, a copolymer (Moplen EPT 30R, from Montedison) and an elastomer-modified copolymer (Moplen SP 25).

The data were successfully reduced to single master curves (*Figures* 3 and 4) by shifting along the time axis (a small vertical shift makes the coincidence better, although its physical significance is not yet clear). As reference stresses we chose those corresponding to 40% of the tensile yield stress (13.1 MPa for Moplen EPT 30R; 10.8 MPa for Moplen SP 25). The two master curves are exactly superposable. Both shift factors are collected in *Table* 1.

We tentatively suggest a possible connection be-

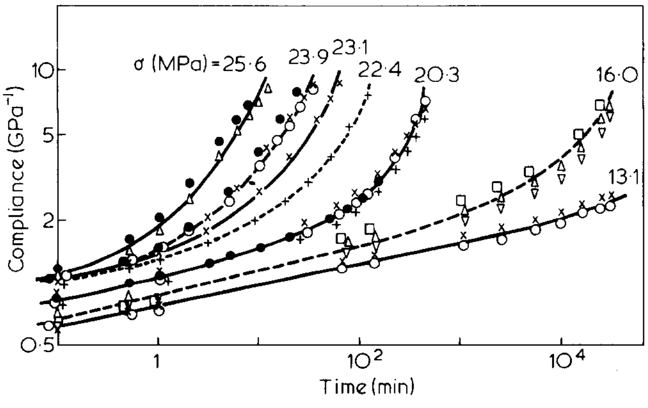

Figure 1 Creep curves for Moplen EPT 30 R at 32°C

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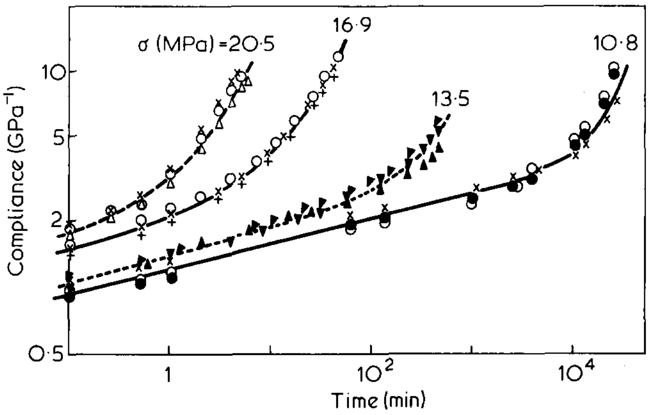

Figure 2 Creep curves for Moplen SP 25 at 32°C

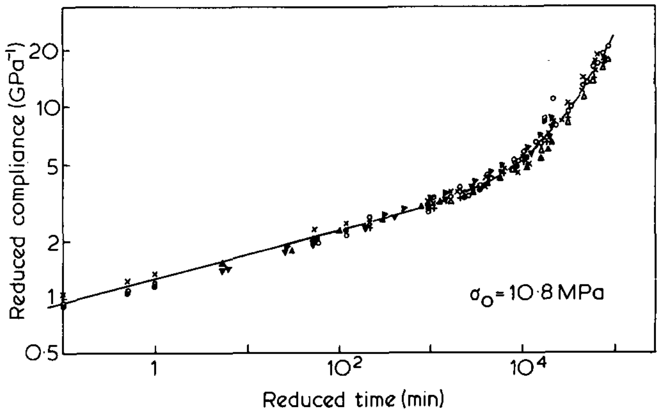

Figure 3 Master curve for creep of Moplen EPT 30 R at 32°C

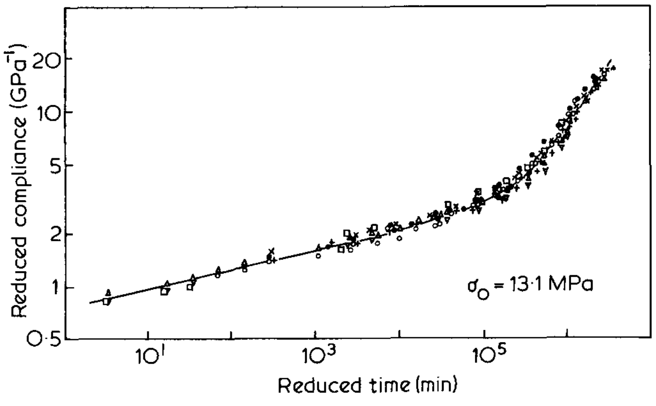

Figure 4 Master curve for creep of Moplen SP 25 at 32°C

tween this superposition and the Zhurkov equation for "polymer life"[7]:

$$\tau = \tau^* e^{E-\gamma\sigma/RT} \tag{1}$$

where τ is time to fracture under a constant tensile stress σ and at temperature T; E is the energy of bond dissociation; R the gas constant; and τ^* and γ are two material constants.

τ in equation (1) is simply the end-point of a creep curve of the kind shown in *Figures* 1 and 2, pursued up to the rupture of the sample. Assuming that all such creep curves may be reduced to a single master curve, related to an arbitrary reference stress σ_R, we make now the hypothesis that such a master curve holds until the end point: the abscissa of this point, which is common to all experimental curves, is the "reduced time to fracture". For a generic creep test, such reduced time to fracture will be $a_\sigma\tau$ (a_σ is the time shift factor); for the reference test it will be τ_R (a_σ in this case is 1 by definition). By comparison we obtain:

Table 1 Shift factors at 32°C

Material	Stress (MPa)	Number of runs	a_σ[1]	k[2]
	13.1	2	1	1.00
	16.0	3	32	1.22
Moplen[3]	20.3	4	2640	1.68
EPT 30 R	22.4	1	9450	1.75
	23.1	1	43 200	2.00
	23.9	3	75 200	2.06
	25.6	2	256 000	2.26
	10.8	3	1	1.00
Moplen[3]	13.5	3	63	1.35
SP 25	16.9	3	2190	1.55
	20.5	3	18 600	1.78

[1] Shift factor along the log time axis;
[2] shift factor along the log compliance axis;
[3] annealed 2 h at 140°C, then slowly cooled

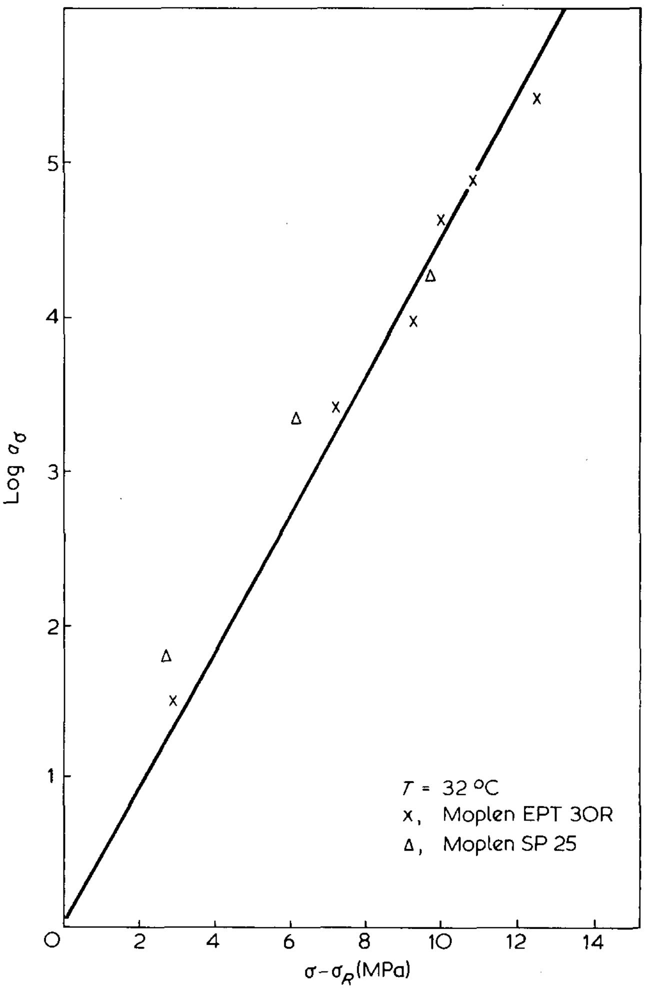

Figure 5 Shift factor a_σ as a function of stress

$$a_\sigma \tau = \tau_R \qquad (2)$$

and, by recalling equation (1), applied both to stress σ and σ_0, we obtain:

$$a_\sigma = e^{\gamma(\sigma - \sigma_R)/RT} \qquad (3)$$

Starting from the Zhurkov equation we thus arrive at an exponential dependence of a_σ on $(\sigma - \sigma_R)$; to test its validity we have reported the data of *Table* 1 as a semilog graph (see *Figure* 5). The plots follow the predicted linear correlation fairly well.

One might therefore argue that the suggestion of a master curve extending up to the fracture is at least approximately valid: the present limits of our apparatus have not yet allowed its experimental verification (the samples reach the basement of the test chamber before breaking).

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