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Extrapolating deformation behaviour of rubber to high rates and high pressures

C. M. Roland*

An important and oft-utilised viscoelastic property of polymers is their conformance to the time–temperature superposition principle. However, it is well established that in the glass transition zone, where both the local segmental and global chain modes contribute to the response, polymers are thermorheologically complex. Extrapolations of mechanical and other properties through the glass transition zone thus entail large errors. An alternative procedure that accounts for the pressure and volume dependences is based on the empirical fact that both local segmental and global relaxation times of polymers are a function of the product variable, TV^{γ}, where T is temperature, V is specific volume, and γ is a material constant. The utility of this scaling property is described.

Keywords: Time–temperature superpositioning, Thermodynamic scaling, Pressure

Introduction

The low frequency motions of high molecular weight ('entangled') rubbery polymers directly govern processing and forming operations and also underlie many properties of the cured elastomer. Invariably theoretical models of the dynamics of entangled chains are based on the idea of reptation (longitudinal 'snakelike' diffusion),[1,2] which has intuitive appeal and yields many results in reasonable agreement with experiments.[3,4] One failing of reptation models is in accounting for the effect of temperature or pressure on the rheology and processing of polymer melts. At short times chain segments move freely within a 'tube' of the entanglement, with these short range motions described by the Rouse model.[5] Rouse motion terminates when the entanglement constraints begin to exert an effect. The reptation model has two species dependent parameters, the local friction coefficient, ς, which is identical to the Rouse friction factor, and a parameter characterising the degree of entanglement. This means that the temperature dependence of the chain dynamics is governed entirely by ς. Since ς is the same as the local friction coefficient for the segmental motion, the prediction of reptation models is that the T dependence of the entire viscoelastic response from the glass transition to terminal flow is constant. This serves as the basis for the well known time–temperature superposition principle, by which master curves of dynamic and transient mechanical properties are constructed. These master curves typically provide information about the response at times ranging from small fractions of a second through decades, even though the actual data are only measured over very narrow range (typically 3 or 4 decades).[5]

Although time–temperature superpositioning is common and can yield useful predictions, when the data extend into the glass transition (or softening) zone, polymers exhibit thermorheological complexity; that is, the actual behaviour departs significantly from the superposed master curves. Specifically, the global chain dynamics vary more weakly with temperature than do the local segmental modes. First discovered in polystyrene by Plazek,[6] the breakdown of the time–temperature superposition principle is observed in all polymers for which it has been rigorously tested. However, such a test requires that data be measured over a range of times or frequencies that encompasses both the chain motions and the local segmental modes. This requirement is most easily met by measurements in the glass transition zone (viscoelastic softening regime). The breakdown of time–temperature superpositioning has been demonstrated in poly(vinyl acetate),[7] polypropylene glycol,[8] poly(phenylmethylsiloxane),[9] polybutadiene,[10,11] polyisobutylene,[12] atactic polypropylene,[13] poly(alkyl glycidyl ether)[14] and atactic polypropylene.[15] The differing temperature response near T_g and the similar behaviour well above T_g are illustrated in Fig. 1 for amorphous polypropylene.[15] Note that well above the glass transition, the characteristic time constants for the global and local segmental dynamics become proportional to each other, so that reliable master curves can be obtained for high temperature or long time data.

The effect of temperature on the viscoelastic response is mirrored inversely by the effect of hydrostatic pressure. While more thermal energy enhances the dynamics, the greater molecular crowding resulting from the application of pressure slows both the local and global motions. For polymers the effects of temperature and density on the dynamics are roughly equal; that is, when temperature is changed the consequent variation in the

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Naval Research Laboratory, Code 6120, Washington, DC 20375-5342, USA

*Corresponding author, email mike.roland@nrl.navy.mil

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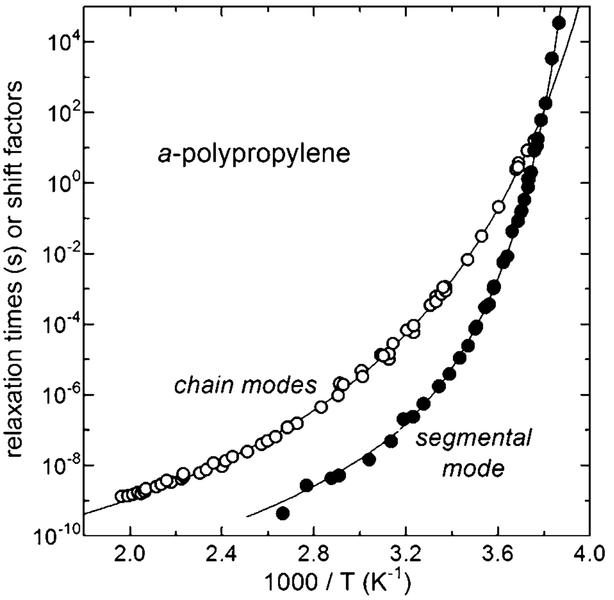
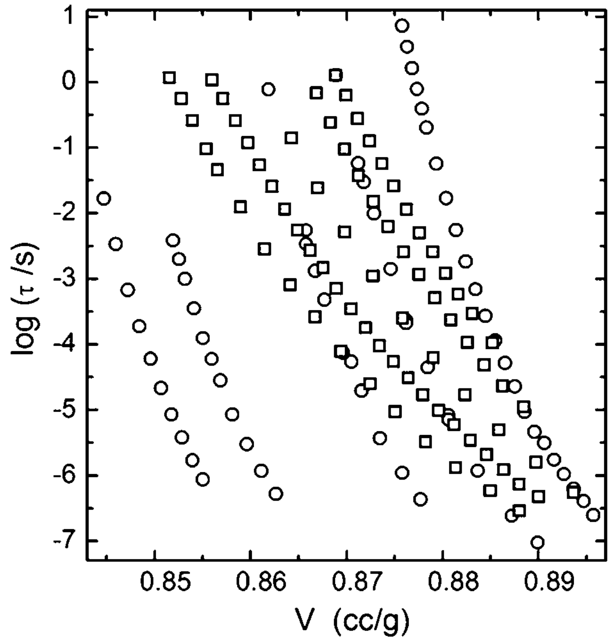


1 Local segmental relaxation times (filled symbols) and time–temperature shift factors for global chain motions (open symbols) for amorphous polypropylene. Data were obtained by combining dynamic and transient mechanical, dielectric relaxation and NMR measurements.[15] Temperature dependence is steeper for local modes at low temperature, with curves becoming parallel at higher *T*



2 Local segmental relaxation times for siloxane polymer.[19] Data were measured versus pressure at various fixed temperatures in range from 4 to 30°C (squares) and versus temperature at various fixed pressures in range from 0·1 to 250 MPa (circles). Latter are steeper because changing *T* changes both thermal energy and volume

dynamics is due about equally to changes in thermal energy and to changes in local packing.[16,17] Unfortunately, rheological data on polymers under elevated pressure are sparse. It is much easier to carry out dielectric relaxation measurements at high pressure.[18] In this paper, the author describes how dielectric relaxation times for any condition of temperature and pressure can be determined from measurements at any other condition of *T* and *P* (including ambient pressure), by exploiting a recently discovered scaling law,[18] applicable to the dynamics of polymers over the entire range of their equilibrium viscoelastic response. While this scaling law cannot be used to obtain relaxation times beyond their measured range, it enables the thermodynamic conditions (e.g. pressure or volume) associated with any given value of the relaxation time to be predicted from experiments at ambient pressure.

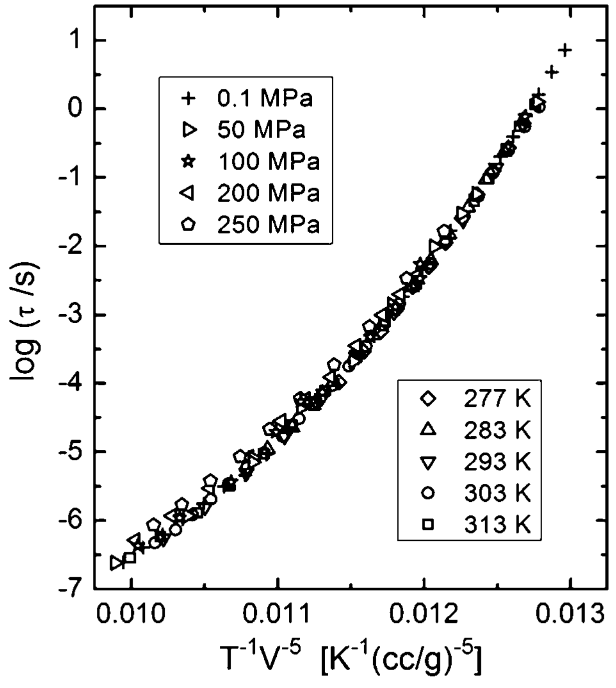
Thermodynamic scaling

The author illustrates this scaling by using local segmental relaxation times measured dielectrically as a function of temperature and pressure for polymethyltolylsiloxane (PMTS).[19] The data are plotted versus specific volume in Fig. 2 and it is obvious that the local segmental dynamics are not defined by volume or density. However, in Fig. 3 the same data collapse to a single curve when plotted versus the product of temperature times specific volume with the latter raised to a power; i.e.

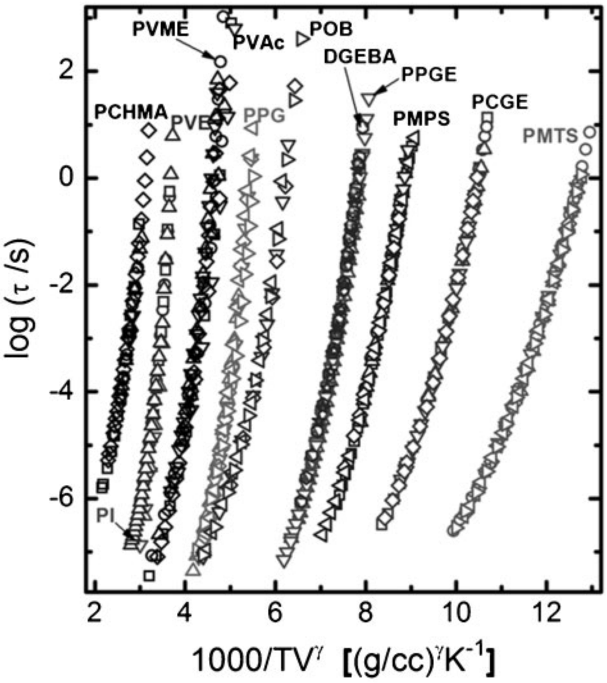
$$\tau = f(TV^{\gamma}) \tag{1}$$

In this equation f represents some unknown function and γ is a material constant (independent of T, V and P). The scaling exponent, $\gamma = 5 \pm 0{\cdot}05$ for PMTS, is determined empirically as the value yielding superposition of the relaxation times.

In Fig. 4 relaxation times for 11 polymers are plotted versus TV^{γ}. The data superpose well, with values of γ falling in the range from 1·9 for 1,4-polyisoprene to 5·6 for polymethylphenysiloxane.[20] Generally, γ is smaller for polymers than for molecular liquids,[18] consistent with the fact that the motions of polymers are less



3 Segmental relaxation times for PMTS from Fig. 2 as a function of scaling variable TV^{γ} with $\gamma = 5{\cdot}0$



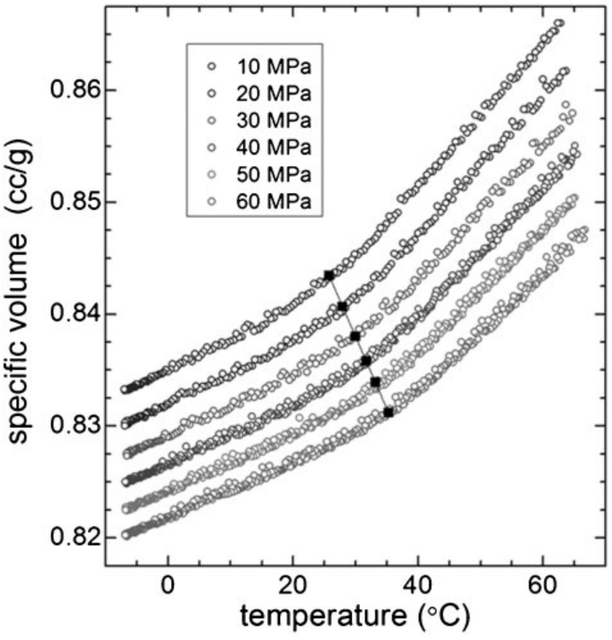
4 Scaled local segmental relaxation times for polycyclohexylmethacrylate (γ=2·5); 1,4-polyisoprene (=3·0); polyvinylethylene (=1·9); polyvinylmethylether (=2·55); polyvinylacetate (=2·6); polypropylene glycol (=2·5); polyoxybutylene (=2·8); diglycidylether of bisphenol A (=2·8); polyphenylglycidyether-co-formaldehyde (=3·5); polymethylphenylsiloxane (=5·6); poly[(o-cresyl glycidyl ether)-co-formaldehyde] (=3·3); and PMTS (=5·0)[18] and references therein]. Each symbol for a given material represents a different condition of *T* and *P*

sensitive to volume changes.[16,17] The weaker influence of volume for polymers is ironic, given their central role in the historical development of free volume models.[5] The smaller γ and weaker V dependence reflect the insensitivity of the chain backbone bonds to pressure, as seen in the small changes in chain end to end distance with pressure[21] and in the small contribution of chain configurational changes to the compressibility of polymers.[22]

Recent molecular dynamics simulations have shown that the magnitude of γ is a measure of the effective steepness of the intermolecular repulsive potential.[23,24] Larger γ, or a steeper repulsive potential, implies greater influence of 'jamming' on the dynamics. Thus, macroscopic measurements on polymers may reveal quantitative information about the forces between the chain molecules, an obvious requisite for developing a first principles model of polymer dynamics.

Scaling exponent from PVT data

If dynamic measurements are carried out at ambient pressure, in principle τ becomes known at all pressures via equation (1), providing the equation of state (V as a function of T and P) and the value of γ are known. Of course, if γ is obtained by superpositioning of relaxation times, then the high pressure viscoelastic data are already available. However, the scaling exponent can be determined directly from PVT data that extend through the glass transition, obviating the need for high pressure relaxation measurements. The relaxation times can then be calculated with high accuracy for elevated pressures (or isochoric conditions) from the experimental τ for ambient pressure.



5 Specific volume of polyvinylacetate measured as a function of temperature at indicated pressures.[28] Solid symbols denote glass transition determined from intersection of rubbery and glassy phase data

Typically the glass transition temperature is determined as the pressure dependent temperature at which the heat capacity or thermal expansion coefficient exhibits a step change. The measured T_g is rate dependent and for the usual experimental conditions corresponds to values of τ in the range from 0·1 to 1000 s. With increasing pressure T_g increases; however, the value of τ at the glass transition remains constant.[18,25] Since $\tau(T_g)$ is constant, if follows from the scaling relation (equation (1)) that $T_g V_g^{\gamma}$ is also constant. Thus, by carrying out PVT experiment through the glass transition, both T_g and V_g are obtained and the scaling exponent calculated from

$$\gamma = -\left.\frac{\partial \log T_g}{\partial \log V_g}\right|_P \tag{2}$$

It can also be shown that the exponent is given by[26,27]

$$\gamma = -\frac{1}{T\alpha_\tau(T)} \tag{3}$$

where α_τ is the thermal expansion coefficient for constant value of the relaxation time, i.e.

$$\alpha_\tau = V^{-1}\left.\frac{\partial V}{\partial T}\right|_\tau = V_g^{-1}\left.\frac{\partial V_g}{\partial T_g}\right|_P \tag{4}$$

Figure 5 shows PVT data for polyvinylacetate measured through the glass transition at various pressures. From these data, the scaling exponent, γ=2·21±0·14, can be obtained using either equations (2) or (3).[28]

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