

# Deformation in Glassy Polymers

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## SYNOPSIS

On the basis of known nonlinearity of intermolecular force fields, we discuss the interpretation of PVT (pressure, volume, and temperature) behavior, pressure–temperature superposition for polymers, and the relationship between yield stress and tensile modulus. For PVT behavior of polymers, our theoretical results coincide with the experimental data, and their response to pressure is universal. The maximum theoretical yield strain,  $\epsilon_y$ , for glassy polymers is 1.08, and this value is beyond the elastic limit for glassy polymers. The previously established empirical relationship between yield stress,  $\sigma_y$ , and tensile modulus,  $E$ :  $\sigma_y = 0.028 E$ , which again, is universal for glassy polymers, is predicted also by our phenomenological model. The theoretically predicted values of yield stress for glassy polymers range from 24 MPa to 84 MPa, coinciding with published experimental results. We discuss how the phenomenological model is helpful in the understanding of nonlinear viscoelasticity of glassy polymers © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The nonlinear viscoelastic behavior of glassy polymers is an important topic in materials science. It is difficult to obtain satisfactory quantitative predictions of values of yield stress. However, a universal empirical relationship between yield stress and tensile modulus has been found for glassy polymers.<sup>1–4</sup> Recently, Striuk<sup>3</sup> has discussed the relationship between yield stress and tensile modulus for amorphous glassy polymers, introducing a new idea connected with the nonlinear intermolecular force field. It turns out that the small-strain moduli and the yield stress can be predicted, while a qualitative explanation was obtained for some hitherto unexplained experimental facts. The implication is that behavior close to yield basically differs from that at small strains. Thus, flow at the yield point is not simply an acceleration of small-strain creep.<sup>3</sup> Indeed, a new idea is needed to understand the behavior of compression and yielding of glassy polymers.

In this article, we first use the known nonlinearity of the intermolecular force to derive a reasonable

phenomenological model. This allows us to discuss the equation of state for polymers. We then discuss the response of polymers to pressure and the yielding behavior of glassy polymers.

## BACKGROUND THEORY

The intermolecular forces between two individual particles is modeled by a Mie potential function:<sup>3</sup>

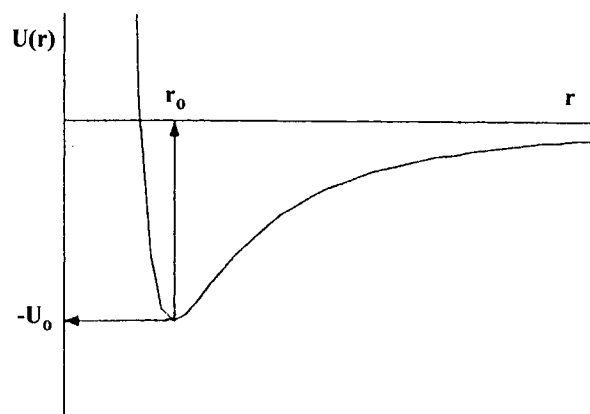
$$U(r) = U_o/(\alpha - \beta)(\alpha(r_o/r)^\beta - \beta(r_o/r)^\alpha), \quad (1)$$

where  $U(r)$  is the interaction energy,  $r$  is the distance between the centers of gravity, and  $U_o$ ,  $r_o$ ,  $\alpha$ , and  $\beta$  are constants. This form of interaction energy diagram is shown in Figure 1. The  $r_o$  constant is the distance at which the energy is at a minimum. This equation can also be written in the following form:<sup>5</sup>

$$U(V) = -A/V^m + R/V^n, \quad (2)$$

where  $A$ ,  $R$ ,  $n$ , and  $m$  are constants,  $V$  is the molar volume, and  $m$  and  $n$  are the exponents for the attraction and repulsion terms, respectively.

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**Figure 1** Interaction energy,  $U(r)$ , as a function of the distance,  $r$ , between the molecules.

We next assume the following: (1) no phase transition occurs during compression; (2) the compression of the volume under external pressure is due to the change in molecular chain segment separation; and (3) the internal pressure,  $P_i$ , determined by the change of the internal energy resulting from the thermal motions of the chain segments, is equal to the external pressure:

$$P = P_i. \quad (3)$$

Here,  $P_i$  is the sum of two terms; the pressure due to internal energy and the thermal pressure:

$$P_i = -(dU/dV)_T + P(V,T). \quad (4)$$

The first term is the pressure along the absolute zero temperature isotherm and is governed by the internal energy, and the second term is the additional pressure generated by thermal motions. At constant temperature,  $P_i$  depends on the value of  $(dU/dV)_T$ . Therefore, it may be considered that  $P_i$  is determined approximately by the change in the internal energy resulting from the change in volume. The effect of thermal motions of the chain segments on  $P_i$  is considered to be the change in the internal energy and the volume at zero pressure with temperature:

$$P_i = -(\delta U/\delta V)_T. \quad (5)$$

Combining eqs. (2) and (5), the following three equations are obtained:

$$P = -mA/V^{m+1} + nR/V^{n+1} \quad (6)$$

$$B = -V(\delta P/\delta V)_T \\ = -m(m+1)A/V^{m+1} + n(n+1)R/V^{n+1} \quad (7)$$

$$(\delta B/\delta P)_T = n + m + 2 \\ - (n+1)(m+1)P/B, \quad (8)$$

where  $B$  is the bulk modulus.

From eqs. (6)–(8), the precise solutions for the relationship between bulk modulus, pressure, and volume can be obtained.<sup>5</sup>

$$B(T,P) = B(T,0)/(n-m)$$

$$\{ (n+1)[V(T,0)/V(T,P)]^{n+1} \\ - (m+1)[V(T,0)/V(T,P)]^{m+1} \} \quad (9)$$

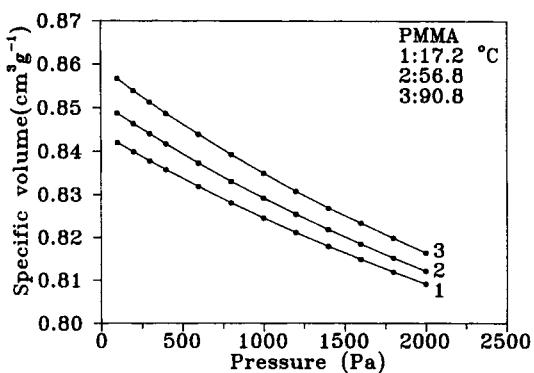
$$P = B(T,0)/(n-m) \{ [V(T,0)/V(T,P)]^{n+1} \\ - [V(T,0)/V(T,P)]^{m+1} \}. \quad (10)$$

The parameters  $n$  and  $m$  are constants<sup>5</sup> for all polymers (including the glassy, crystalline, and liquid states). The values of  $n$  and  $m$  are 6.14 and 1.16, respectively.<sup>5</sup>  $B(T,0)$  and  $V(T,0)$  must be estimated by fitting eq. (10) to experimental data. Thus, eq. (10), which describes the PVT relationships in polymers, is not a predictive relationship on its own. However, we may derive useful conclusions regarding the pressure and temperature superposition of compressed polymers and the relationship between yield stress and tensile modulus for glassy polymers, as is shown in the following section.

## RESULTS AND DISCUSSION

### PVT Behavior of Polymers

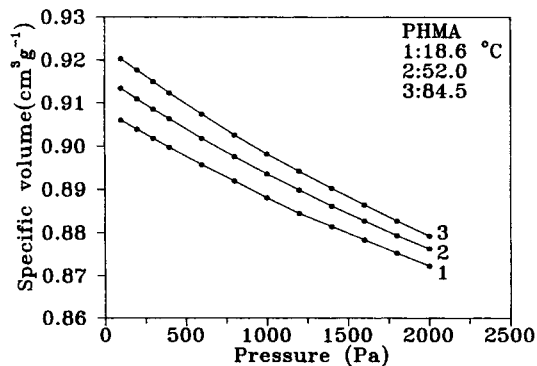
Figures 2, 3, and 4 are the comparison of calculated results using eq. (10) with experimental data<sup>6</sup> for poly(methyl methacrylate) (PMMA), poly(hexamethyl methacrylate) (PHMA), and branched polyethylene (BPE), respectively. In comparing the theoretical results with experimental data, the parameters  $B(T,0)$  and  $V(T,0)$  were obtained by fitting eq. (10) to the experimental data. The quantitative comparison between theoretical results and experimental data was made for each polymer. The results given in Figures 2, 3, and 4 show that eq. (10) accurately describes the isothermal compression behavior of polymers in the glassy state and also in the crystalline state. The average error in the absolute



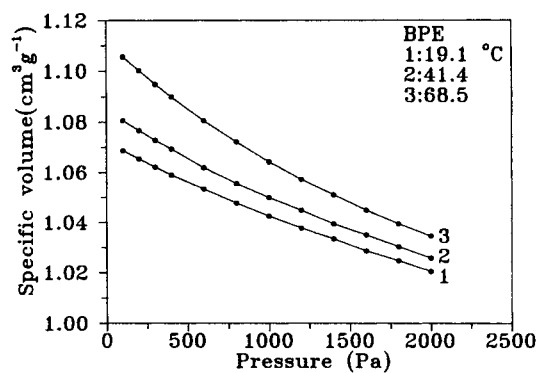
**Figure 2** PVT behavior of PMMA. The solid line is the theoretical results.

values of the specific volume between experimental and theoretically calculated values is about  $\pm 0.0002 \text{ cm}^3 \text{ g}^{-1}$ , which is within experimental error. The error is slightly larger at high temperatures than that in low temperatures. At high temperature, the thermal pressure determined by the thermal motions makes a larger contribution to  $P_i$ . Therefore, when eq. (4) was reduced to eq. (5), this introduced a larger error at high temperature.

Recently, Arends<sup>7</sup> applied the Lennard-Jones potential function, which is the same as eq. (1), to amorphous polymers. He modeled successfully the PVT behavior of glassy polymers. He found when the polymer was in the glassy state, the parameters shown in Lennard-Jones potential function correspond to the volume and internal energy of the polymer at absolute zero of temperature. The results implied that the assumptions in obtaining eqs. (9) and (10) are correct. Thus, it is not surprising that eq. (10) can be used to describe accurately the PVT behavior of polymers.



**Figure 3** PVT behavior of PHMA. The solid line is the theoretical results.

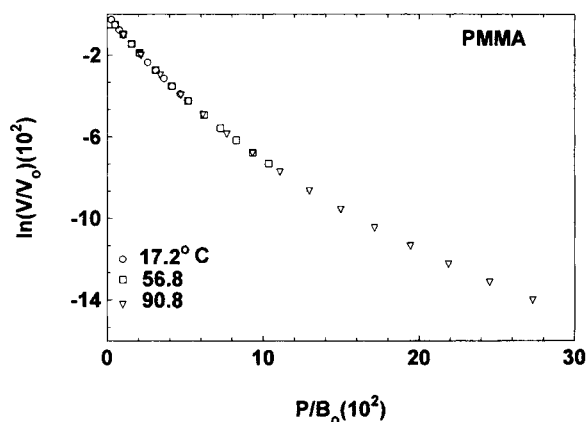


**Figure 4** PVT behavior of BPE. The solid line is the theoretical results.

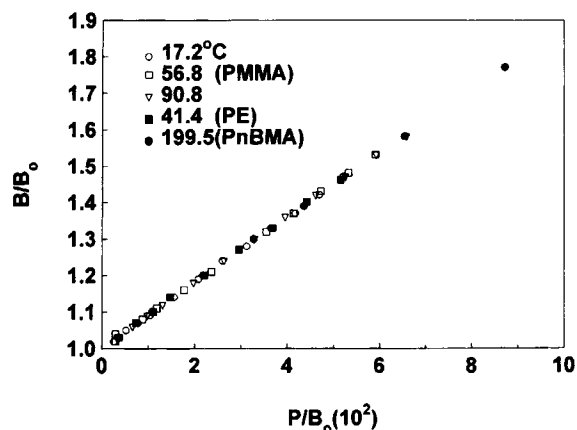
### Pressure and Temperature Superposition Behavior of Compressed Polymers

Sanchez<sup>8</sup> studied the compression response of polymers, solvents, and polymer solutions to hydrostatic pressure. These results satisfied a corresponding state behavior. The response of polymers to pressure is universal, as found experimentally.<sup>8</sup> On the basis of eqs. (9) and (10), the pressure and temperature superposition of polymers can also be investigated.

Following Sanchez's definition,<sup>8</sup> we have studied pressure and temperature superposition behavior for PMMA, BPE, and poly(*n*-butyl methacrylate) (PnBMA), using a reduced pressure  $P/B(T,0)$ . The results at several temperatures are shown in Figures 5 and 6. A comparison of theory with experimental results was also made for polydimethylsiloxane, as shown in Figure 7. The experimental data were obtained from the literature.<sup>8</sup> In this case, a reference pressure of zero was used. Note that all data for



**Figure 5** Theoretical reduced isothermal volume for PMMA vs. reduced pressure using a reference pressure of zero.



**Figure 6** Theoretical reduced isothermal modulus for PMMA, BPE, and PnBMA vs. reduced pressure using a reference pressure of zero.

different temperatures fall very precisely onto a single nonlinear curve. The theoretical bulk modulus clearly satisfies pressure–temperature superposition. This is not a surprise, because isothermal compression is a function of  $P/B(T,0)$  only.<sup>8</sup> These results, including the Sanchez results,<sup>8</sup> provide future guidance for theoretical models that can describe pressure–temperature superposition behavior. The theoretical results show that the response of polymers to pressure is universal.

Clearly, the change of volume with pressure and the pressure–temperature superposition of polymers can be described by eqs. (9) and (10), which were obtained on the basis of the idea of nonlinearity of the intermolecular force fields. It may also be used to help understand the nonlinear viscoelasticity of glassy polymers.

### Yield Stress Prediction for Glassy Polymers

We next pose the question: can the model be used for the calculation of the yield stress, and for the study of the relationship between stress and strain for glassy polymers?

Consider the ideal tensile test. Under multiaxiality of stress, the local load is represented by only three normal stresses, the so-called principal stresses,  $\sigma_{xx}$ ,  $\sigma_{yy}$ , and  $\sigma_{zz}$ .

$$F = \sigma_{xx} + \sigma_{yy} + \sigma_{zz} \quad (11)$$

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma \quad (12)$$

$$l_x = l_y = l_z = 1$$

$$l_{x0} = l_{y0} = l_{z0} \quad (13)$$

$$V \sim l^3$$

$$V_0 \sim l_0^3. \quad (14)$$

It can also be assumed that

$$\sigma_{xy} = \sigma_{yz} = \sigma_{zx} = 0. \quad (15)$$

Now consider compression and tension processes. Under ideal state conditions, they are opposite tests. Thus, it is possible to define the relationship between pressure,  $P$ , and tensile stress,  $F$ , as follows.

$$F \sim -P \quad (16)$$

$$E \sim B, \quad (17)$$

where  $E$  is the tensile modulus.

According to eqs. (10) to (14), the relationship between stress,  $\sigma$ , and strain,  $\epsilon = l/l_0$ , in the uniaxial tension test is given by:

$$\sigma = E(\epsilon^{-6.48} - \epsilon^{-21.42})/14.94. \quad (18)$$

Letting  $d\sigma/d\epsilon = 0$ , results in the following relations

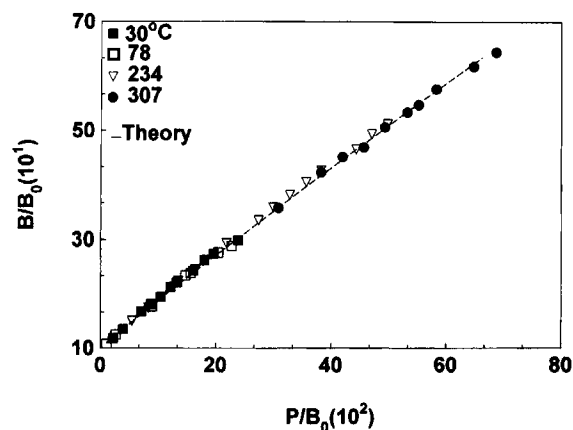
$$\sigma_y(\text{yield stress}) = 0.028E \quad (19)$$

$$\epsilon_y(\text{yield strain}) = l/l_0 = 1.08 \quad (20)$$

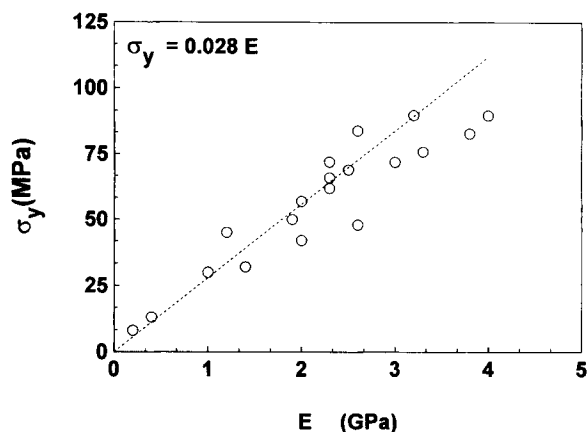
or

$$(l - l_0)/l_0 = 0.08, \quad (21)$$

where  $l_0$  is the initial length of the specimen under zero tension,  $l$  the length under uniaxial tension.



**Figure 7** Comparison of the theoretical value with experimental results for polydimethylsiloxanes. The experimental data were obtained from the literature.<sup>8</sup>



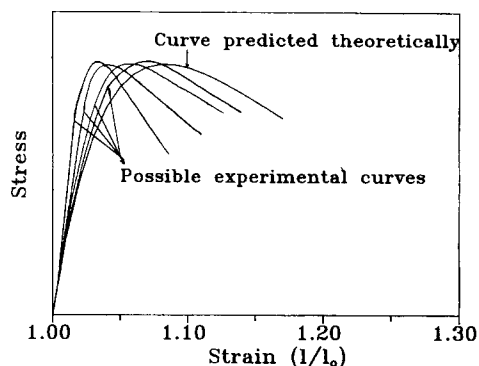
**Figure 8** Theoretical (dashed line) and experimental tensile modulus vs. tensile yield stress. The experimental data are from the literature.<sup>2</sup>

Thus, a relationship can be obtained that can describe the stress and strain yield behavior for glassy polymers. However, eq. (18) does not provide a universal relationship between stress and strain as such, as distinct from yield values. Obviously,  $\epsilon_y$  is the limiting yield strain or maximum yield strain for glassy polymers.

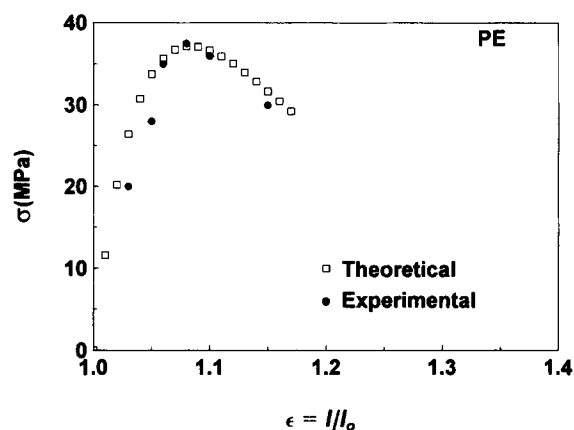
Yield and tensile strengths for polymers are very comparable and usually fall in the range 10 ~ 80 MPa.<sup>9</sup> The typical values of tensile moduli are 1 ~ 3 GPa.<sup>9</sup> We can estimate approximately the yield stress using eq. (19). The range of the yield stress for glassy polymers so estimated is from 28 to 84 MPa. The values of yield stress for glassy polymers coincide with experimental results.<sup>9</sup>

Figure 8 is a comparison of theory with experimental yield strength data. These experimental data are from the literature,<sup>2</sup> which include both crystalline and glassy polymers.

As is known, the change of stress with strain depends on thermal history, strain rate, temperature,

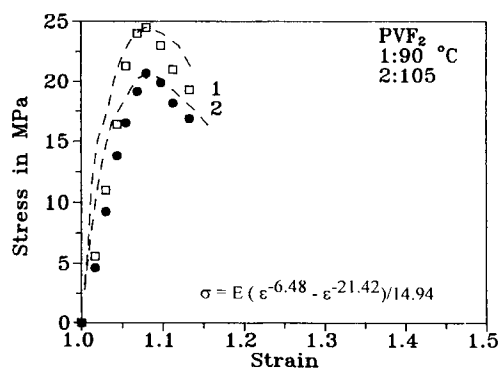


**Figure 9** Schematic experimental stress-strain curves and curve predicted theoretically.



**Figure 10** Comparison of theoretical results with experimental data for the polyethylene (PE). The experimental data are from the literature.<sup>10</sup>

and so on.<sup>1</sup> However, these effects of temperature and thermal history may be absorbed into the tensile modulus,  $E$ . For many glassy polymers, the value of yield strain is lower than the  $\epsilon_y$  value predicted by eq. (20).<sup>1,4</sup> In particular, many stress-strain curves from glassy polymers under uniaxial tension lag behind the curve predicted by eq. (18) (see Fig. 9). However, some stress-strain curves from polymers under uniaxial tension can be described approximately by eq. 18, but it is not universal. Two special examples of polymers in the crystalline state are polyethylene (PE) and poly(vinylidene fluoride) (PVF<sub>2</sub>).<sup>10,11</sup> The comparisons of theory with experimental data are shown in Figures 10 and 11. The tensile modulus,  $E$ , used in eq. (18) was estimated based on the peak value of the experimental stress-strain curve shown in the literature for PE<sup>10</sup> and PVF<sub>2</sub>,<sup>11</sup> respectively, and eq. (19). Especially at, or in the vicinity of, the yield point, the experimental



**Figure 11** Comparison of theoretical values (dash line) with experimental results for poly(vinylidene fluoride) (PVF<sub>2</sub>). The experimental data are from the literature.<sup>11</sup>

values can be well described by eq. (19). This implies that flow at or in the vicinity of the yield point is not simply an accelerated form of the creep at very low strains.

From the above results, it can be seen that the yield stress can be predicted by a model in which time, or any aging effect, is completely absent. For yield stress, the prediction was found to be quantitative, i.e., the relationship between yield stress and tensile modulus is universal for all glassy polymers.

Why is the relationship between stress and strain not universal for glassy polymers? A molecular chain stretched by a force  $\sigma < \sigma_y$  may break at some particular time. The additional energy required for molecular chain rupture is delivered by the random thermal vibrations.<sup>3</sup> Because of the effect of strain rate, at each instant, the molecular chains reach the fracture condition only locally. At  $\sigma \ll \sigma_y$ , some molecular chains may reach the critical fracture condition. So, the yield strain value will be lower than the  $\epsilon_y$  predicted by eq. (20). Thus, different strain rates may result in different stress-strain curves. So, eq. (20) serves only as an interesting observation as regards the yield strain for glassy polymers. It can not be utilized to predict  $\epsilon_y$  reliably for any particular glassy polymer of interest.

At  $\sigma_y$ , the activation energy is rather low,<sup>3,12</sup> and yielding can be described simply and accurately by eq. (19), and also universally.<sup>2-4</sup>

## CONCLUSIONS

PVT behavior, the pressure and temperature superposition behavior of compressed polymers, and a relationship between yield stress and tensile modulus for glassy polymers can be derived on the basis of the nonlinear force field between the molecules.

The maximum theoretical yield strain for glassy polymers has been found to be:

$$\epsilon_y = l/l_0 = 1.08 \text{ (or } (l - l_0)/l_0 = 0.08 \text{)}.$$

The relationship between yield stress and tensile modulus is universal:

$$\sigma_y = 0.028E.$$

The theoretically predicted values of yield stress for glassy polymers (also including polymers in the crystalline state) are from 24 to 84 GPa. They coincide with experimental data.

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