

## COMPARISON OF THE VISCOELASTIC PENETRATION AND TENSILE BEHAVIOUR OF POLY(METHYL ACRYLATE) AND POLY(ETHYL ACRYLATE)

Jaroslav HROUZ, Michal ILAVSKÝ, Ivan HAVLÍČEK and Karel DUŠEK

*Institute of Macromolecular Chemistry,  
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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The viscoelastic penetration and tensile behaviour of poly(methyl acrylate) and poly(ethyl acrylate) in the main transition region have been investigated. It was found that the time-temperature superposition could be carried out in the case of the penetration viscoelastic behaviour; the temperature dependence of the penetration and tensile shift factors was the same. The superimposed curves of the penetration and Young modulus allowed us to calculate the dependence of the Poisson ratio and thus to characterize the change in sample volume with deformation. It was demonstrated that the penetration method of determination of the viscoelastic behaviour is equivalent to the tensile method.

In our preceding paper<sup>1</sup> we described an apparatus for measurement of the penetration modulus under stress relaxation conditions and discussed the possibilities of using this method, *e.g.* in the determination of the penetration modulus of materials for which no samples of defined shape could be prepared. The results of measurements of poly(*n*-alkyl acrylate) networks in the rubberlike region were used to determine conditions under which the penetration modulus is independent of the indentation depth, sample thickness, radius of the indentation sphere and friction of the sample against its support or against the indentation sphere. It was shown that with all the above conditions observed, the penetration modulus  $A$  corresponds to the modulus in simple compression or elongation. So far, however, all the measurements, both those performed with our apparatus and with an apparatus developed earlier<sup>2,3</sup> (operating in the creep régime) have been carried out in the rubberlike region, in which the time dependences of penetration characteristics are not pronounced. A strong time dependence of the mechanical behaviour is characteristic particularly in the main transition region, where the modulus of elasticity usually decreases by four orders of magnitude within 5–10 time decades. Since no direct measurement of deformation functions is feasible in such a long time interval, the time-temperature superposition principle is usually employed<sup>4</sup>.

This paper deals with a comparison of the viscoelastic penetration and tensile behaviour of crosslinked poly(methyl acrylate) and poly(ethyl acrylate) in the main transition region. The main attention is concentrated on the possibility of using the time-temperature superposition method in the treatment of penetration data and the procedure for determination of the time and temperature dependence of the Poisson ratio  $\mu$  characterizing the change in sample volume with deformation on the basis of the penetration and tensile moduli.

## EXPERIMENTAL

**Sample preparation.** The poly(methyl acrylate) sample (PMA) was prepared by the crosslinking copolymerization of the monomer with a small amount ( $0.1 \cdot 10^{-4} \text{ mol cm}^{-3}$ ) of 3,6,9-trioxadecamethylene diacrylate as the crosslinking agent; the sample of poly(ethyl acrylate) (PEA) was also prepared by radical polymerization without any crosslinking agent. The polymerization proceeded at 333 K for 24 h between teflon plates; the initiator was N,N'-azobis(isobutyronitrile) at the concentration  $3 \cdot 10^{-3} \text{ mol/l}$ .

**Measurement of deformation characteristics.** The tensile relaxation measurement was carried out on samples  $60 \times 10 \times 3 \text{ mm}^3$  using an Instron apparatus in the time range 10–1000 s. The PMA sample was measured between 271 and 334.5 K, that of PEA between 249 and 313 K. The time dependence of force in the glassy state and in the transition region was recorded with a load cell having the  $10^3 \text{ N}$  (CTM) range at deformations  $\epsilon = (l - l_0)/l_0 = 0.01$  ( $l$  and  $l_0$  are the deformed and initial sample lengths, respectively). The load cell with the 20 N (B) range was used in the rubberlike region, and the samples were deformed to  $\epsilon \approx 0.05$ . The Young modulus  $E(t)$ , was determined from  $E(t) = F(t)/(S_0\epsilon)$  where  $F(t)$  is force and  $S_0$  is the initial cross-section of the sample.

The penetration relaxation measurement was carried out with an apparatus described earlier<sup>1</sup> on samples 6 mm thick within the time range 10–1000 s and at temperatures ranging from 263 to 333.5 K for the PMA sample, and from 248 to 298 for the PEA sample. The samples were thermostated in a specially developed thermostating brass cylinder, thermally insulated by means of foamed rubber with a reinforced ground base, with the thermostated liquid circulating inside. The indentation sphere, 0.3 cm in diameter, was connected with an inductive force transducer (100 N range) by means of a glass tube (to prevent heat losses), and the sample was immersed in silicone oil, in order to secure heat transfer, and also for lubricating contact surfaces. The indentation at the elastic response 0.02 N (*cf.*<sup>1</sup>) was taken as zero deformation. The indentation depth in the glassy state and in the transition region was 0.04 cm, that in the rubberlike state was 0.05 cm, which allowed us to observe conditions under which the penetration modulus was independent of the ratio of sample thickness to the radius of the indentation sphere<sup>1</sup>. Correction for the deformation of the apparatus (especially for the load cells used) was taken into account in all the measurements; such correction is important in measurements of polymers in the glassy state, *e.g.* with the Instron apparatus the correction amounts up to 1/3 of the deformation. The penetration modulus  $A(t)$  was determined using the relation<sup>1</sup>

$$A(t) = 3F(t)/(16d^{3/2}R^{1/2}), \quad (I)$$

in which  $d$  is the indentation depth and  $R$  is the radius of the indentation sphere.

## RESULTS AND DISCUSSION

*Time-Temperature Superposition*

An example of the recorded time dependence of the reduced penetration modulus  $A_p(t) = A(t) T_0/T$ , where the reference temperature  $T_0 = 298 \text{ K}$  and  $T$  is the temperature of measurement corresponding to the dependence of  $A(t)$ , is shown in Fig. 1 for PMA; a similar dependence was obtained for PEA. It can be seen from Fig. 1 that the time-temperature superposition of the penetration modulus  $A(t)$  is feasible.

Also in the case of the Young reduced modulus  $E_p(t) = E(t)$ ,  $T_0/T$  it was possible to superimpose experimental dependences; the resulting superimposed curves both of the penetration ( $A_p(t)$ ) and of the Young ( $E_p(t)$ ) modulus of PMA and PEA are given in Fig. 2. The dependences of the shift factors of  $\log a_T$  on temperature determined both from the penetration and from the Young modulus for the two polymers are given in Fig. 3.

The shift of superimposed curves of the reduced penetration modulus of  $\log A_p(t)$  towards shorter times  $\log t/a_T$ , compared with the reduced Young modulus  $\log E_p(t)$ , or the decrease in  $A_p(t)$ , compared with  $E_p(t)$  at constant time, (Fig. 2) is rather related to the shear character of the penetration modulus and will be discussed later. The shift of curves  $A_p(t)$  and  $E_p(t)$  of PEA compared with the respective curves of PMA towards shorter times  $t/a_T$  by some three orders of magnitude corresponds to a decrease in the glass transition temperature<sup>5</sup> of PEA ( $T_g = 249$  K) compared with PMA ( $T_g = 281$  K) and is due to the longer flexible chain of PEA. The monomeric frictional coefficients  $\log \xi_0$  (cf.<sup>4</sup>) of PMA and PEA were calculated from the positions of curves  $\log E_p(t)$ , where the dependence  $\log E_p(t) - \log t/a_T$  has the slope  $-1/2$ , according to<sup>6</sup>

$$\begin{aligned} \log \xi_0 = & 2 \log E_p(t) - 2 \log 3 - 2 \log (a_0 N_0 / 2\pi M_0) - \\ & - \log (kT/6) - 2 \log \Gamma(1/2) + \log (t/a_T), \end{aligned} \quad (2)$$

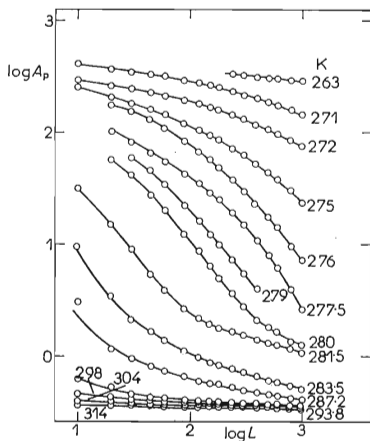


FIG. 1  
The Dependence of the Reduced Penetration Modulus  $A_p$  (MPa) on Time  $t$  (s) for Poly(methyl Acrylate)

where  $a = (\overline{r_0^2})^{1/2}/Z$ ,  $\overline{r_0^2}$  is the mean square chain end distance in the molecule,  $Z$  is the degree of polymerization,  $N_0$  is the Avogadro number,  $\rho$  is density,  $M_0$  is the weight of the monomeric unit,  $k$  is the Boltzmann constant and  $\Gamma$  is the gamma function. The  $\log \xi_0$  values (calculated assuming that  $a = 6.8 \cdot 10^{-8}$  cm) at 298 K are given in Table I. Virtually the same values were obtained also from the dependence of  $\log A_p(t)$  on  $\log t/a_T$  with the slope  $-1/2$  by using Eq. (2) and  $A_p(t) \approx E_p(t)/3$  (Table I), which means that the penetration modulus corresponds to the shear modulus (this holds for  $\mu = 1/2$  and will be discussed later). The magnitude of  $\log \xi_0$  of PMA is in good agreement with a value published earlier<sup>7</sup>. The decrease in  $\log \xi_0$  of PEA by some three orders of magnitude compared with  $\log \xi_0$  of PMA approximately corresponds to a difference found earlier for  $\log \xi_0$  values of poly(methyl methacrylate) and poly(ethyl methacrylate) at 373 K (*cf.*<sup>4</sup>).

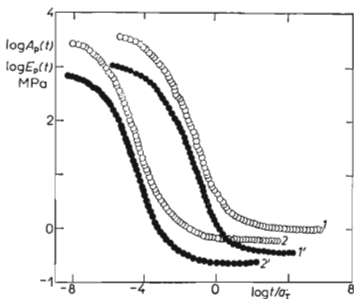


FIG. 2

The Dependence of Superimposed Curves of the Reduced Penetration Modulus  $A_p$  (MPa) and of the Tensile Modulus  $E_p$  (MPa) on Time  $t/a_T$  (s) for the Reference Temperature 298 K

1 PMA,  $E_p(t)$ ; 1' PMA,  $A_p(t)$ ; 2 PEA,  $E_p(t)$ ; 2' PEA,  $A_p(t)$ .

FIG. 3

The Dependence of the Shift Factor  $\log a_T$  on Temperature  $T$

1 PMA; 2 PEA; ●, ○ tensile measurements; ●, ○ penetration measurements; ■, □ dynamic measurements (*cf.*<sup>8</sup>); - - - - WLF curve with constants  $C_1$ ,  $C_2$  given in Table I.

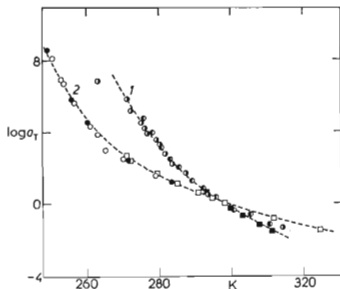


Fig. 3 shows a good agreement between the temperature dependences of the penetration and tensile shift factors  $\log a_T$  of both polymers together with the shift factors determined earlier from dynamic experiments on the same samples<sup>8</sup>. The dependences of  $\log a_T-T$  determined in both cases satisfy the Williams-Landel-Ferry equation (cf.<sup>4</sup>) with parameters  $C_1$ ,  $C_2$  given in Table I: parameters  $C_1$ ,  $C_2$  were obtained

TABLE I

The Viscoelastic Characteristics of Poly(methyl Acrylate) and Poly(ethyl Acrylate) Related to 298 K

$c$  Concentration of the crosslinking agent (3,6,9-trioxaundecamethylene diacrylate), the other symbols are defined in the text;  $f_g$  related to the corresponding glass transition temperatures (PMA 281 K, PEA 249 K).

Sample	$c \cdot 10^4$ mol cm <sup>-3</sup>	$C_1$	$C_2$ K	$f_g$	$\alpha_f \cdot 10^4$ K <sup>-1</sup>	$\log \xi_0^a$ dyn cm s <sup>-1</sup>	$\log \xi_0^b$ dyn cm s <sup>-1</sup>
PMA	0.1	9.09 <sup>c</sup>	64.54 <sup>c</sup>	0.035	7.4	0.31 <sup>d</sup>	0.33 <sup>d</sup>
PEA	0	6.03	84.0	0.037	8.5	-3.26	-3.34

<sup>a</sup> Determined from the Young modulus  $E_p(t)$ . <sup>b</sup> Determined from the penetration modulus  $A_p(t)$ .  
<sup>c</sup> Values determined by Ferry<sup>4</sup>:  $C_1 = 12.2$ ,  $C_2 = 67.0$ . <sup>d</sup> 0.32 was found by Ferry<sup>7</sup>.

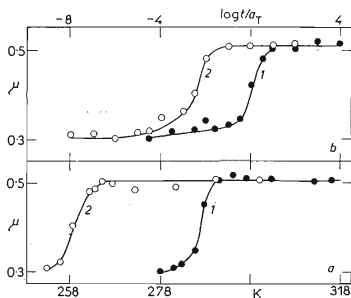


FIG. 4

The Dependence of the Poisson Ratio  $\mu$  on Temperature  $T$  and on Time  $t/a_T$ (s) Calculated Using Eq. (3)

1 PMA, 2 PEA.

by plotting experimental dependences by the least squares method. The magnitude of parameters  $C_1$ ,  $C_2$  of PMA agrees well with the values determined by Ferry from dynamic measurements (*cf.*<sup>4,7</sup>, Table I). The fractional free volumes at the corresponding  $T_g$ ,  $f_g$ , and the free volume temperature expansion coefficients,  $\alpha_r$ , calculated from  $C_1$ ,  $C_2$  after correction for temperature (*cf.*<sup>4</sup>) are given in Table I. Both values,  $f_g$  and  $\alpha_r$  of PMA and PEA are close to the universal values (*cf.*<sup>4</sup>). Hence, the results given in Figs 2 and 3 show that in the case of the viscoelastic penetration behaviour the superposition time-temperature method can be applied with the same success as in the case of the viscoelastic tensile behaviour.

#### *Change of the Volume with Deformation. The Poisson Ratio*

From the penetration of a hard sphere into a planar sample characterized by the Young modulus  $E$  and by the Poisson ratio  $\mu(\mu = (1 - \ln V/\varepsilon)/2$ , where  $V$  is the sample volume) one can determine the penetration modulus  $A$  (Eq. (1)), for which the equation<sup>9</sup>

$$A = E/4(1 - \mu^2) \quad (3)$$

is valid. Eq. (3) shows the shear character of the penetration modulus  $A$ ; for an ideal elastic body ( $\mu = 1/2$ ),  $A = E/3 = G$  (shear modulus).

The temperature dependence of the Poisson ratio  $\mu(t')$  was determined from the temperature dependences of the penetration modulus  $A(t')$  and of the Young modulus  $E(t')$  at the time  $t' = 600$  s using Eq. (3) (Fig. 4a). The time dependences of the reduced penetration modulus  $A_p(t)$  and of the reduced Young modulus  $E_p(t)$  were used in the determination of the time dependences of the  $\mu(t)$  ratios of both polymers at the reference temperature  $T_0 = 298$  K (Fig. 4b). It can be seen in Fig. 4a, b that the overall character of both the temperature and time dependence of  $\mu$  is approximately the same for both polymers. While in the glassy zone of both polymers,  $\mu \approx 0.3$ ; in the transition region,  $\mu$  increases, reaching  $\mu \sim 0.5$  in the rubberlike state. A similar dependence is typical of amorphous polymer systems<sup>10</sup>; while in the glassy region the volume increases with deformation, in the rubberlike state the volume remains unchanged. Owing to the longer side chain, the transition from  $\mu$  0.3 to 0.5 for PEA is shifted to lower temperatures or to shorter times compared with PMA, similarly to  $A_p$  or  $E_p$  (*cf.* Figs 2 and 4). Due to the large scatter of  $\mu$  ( $\pm 10\%$ ) caused by the inaccuracy of the primary data of moduli  $A$  and  $E$ , the dependences of  $\mu$  determined by us may be regarded as a qualitative illustration of the behaviour of systems with respect to the change in volume with deformation.

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