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# Structure and Ductility of Glassy Polymers

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## Summary

A structural model of the ductile-brittle transition of amorphous polymers has been proposed. According to this model the total free volume consists of two parts: the intermolecular free volume and the volume of spherical holes of diameter about 1 nm. Only the intermolecular free volume is considered to be responsible for the degree of ductility of a material.

## Introduction

The free volume is the primary physical parameter affecting the molecular mobility of polymer melt. The most convenient measure of the free volume is a fractional expansion free volume

$$f_e = \frac{V_T - V_o}{V_o} \qquad (1)$$

where $V_T$ is the observed volume at temperature T and $V_o$ is the volume occupied by the molecules at 0 K in close-packed crystalline state.

The fractional expansion free volume at the glass transition temperature $T_g$ seems to be a universal constant for all polymers from 0.11 to 0.13 (BONDI 1964). The considerably increased ability of molecular rearrangements of ductile polymer glasses of e.g. PC, PETP or PA relative to PS, PMMA or PVC does not correspond with the constant value of their fractional free volume. It seems more reasonable to consider the free volume distribution as the prime candidate for treating the interrelation of volume and physical properties.

Our experimental results (BOUDA 1976) indicate that the density of PMMA and PA6 during cyclic loading below the $T_g$ slowly decreases. At the same time, the decrease of heat capacity of PMMA in the temperature range from 350 to 400 K, the decrease of mechanical losses at 93 K /1 Hz/ and an increase in shear modulus G´ in the range from 100 to 250 K, where no crazes had formed, seemed to indicate a non-uniform local volume contraction during cyclic loading. This fatigue process inhibits the molecular mobility and embrittles the glass. We suppose that this process is a reactivated spontaneous process of ductile-brittle transition in the glass transition region.

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## The model

The model is based on the existence of the energy of tension in intermolecular bonds which gradually rises when the polymer is cooled near above the glass transition temperature (BOUDA 1977) . This suggestion results from the fact that the thermal dilatations along the chain and between the individual chains differ substantially from each other. An amorphous solid subjected to tension is metastable and bubbles or cracks form spontaneously in it (FISHER 1948). To a first approximation, the spherical holes are supposed to form during the cooling in this temperature region.

The local energy of tension is in equilibrium with the surface energy of the hole S.γ /S is the area of the internal surface of the hole and γ is the energy of surface tension/ because the former relaxes through the growth of the latter. Also the distribution of the energy of tension is the same as the distribution of the surface energy of the holes. When we consider a system with a large number of holes, the fraction of holes of internal surface $S_o$ can be obtained from the distribution formula of energy for Boltzmann statistics

$$\frac{n_o}{n} = \exp\left(-\frac{S_o\gamma}{kT}\right) \tag{2}$$

with k the Boltzmann constant, T the absolute temperature and n the rest of the holes. The fraction $n_o/n$ can also be given the following interpretation: It is the fraction of time in which a single hole is in the activated state of energy $S_o\gamma$. Thus the rate of reversible formation of the holes (FRENKEL 1946)

$$\frac{dn_o}{dt} = \frac{n}{\tau}\exp\left(-\frac{S_o\gamma}{kT}\right) \tag{3}$$

where τ is the relaxation time of holes pulsation. A stable conformation of molecules can be expected at a definite size of the hole, e.g. of internal surface $S_s$ . In this case the proces of the formation of the holes of the internal surface $S_s$ becomes irreversible. The holes cummulate when a polymer is cooled.

At constant pressure the total expansion free volume $V_e$ consists of the volume of stable holes $V_s$ and of the rest of the free volume V:

$$V_e = V_s + V = n_sV_{si} + nV_{mi} \tag{4}$$

where $V_{si}$ is the volume of the individual stable hole and $V_{mi}$ is the medium volume of holes of the rest of the free volume. Now the equation (3) can be rewritten for the real rate of the increase of the volume of stable holes

$$\frac{d(V_e - V)}{dt} = \frac{V}{\tau}\frac{V_{si}}{V_{mi}}\exp\left(-\frac{S_s\gamma}{kT}\right) \tag{5}$$

Neglecting the changes of the expansion free volume $V_e$ in the temperature region of the process, $V_e$ =const., and dividing the equation (5) by the total volume $V_T$ one obtains a real rate of decrease of the rest of fractional free volume $f = V/V_T$:

$$\frac{df}{dt} = - \frac{f}{\tau} \frac{V_{si}}{V_{mi}} \exp\left(- \frac{S_s \gamma}{kT}\right) \qquad (6)$$

According to the free volume theory (DOOLITTLE 1951) $\tau$ is a function of the instantaneous fractional free volume:

$$\frac{\tau}{\tau_e} = \frac{\exp(1/f)}{\exp(1/f_e)} \qquad (7)$$

where $\tau_e$ is the relaxation time of holes pulsation at the temperature $T_e$ of the beginning of the hole formation process. The fractional free volume f equals to the fractional expansion free volume $f_e$ at this temperature. Changing variables from time to temperature via the cooling rate,

$$q' = \frac{d(1/T)}{dt} \qquad (8)$$

equation (6) becomes

$$\frac{df}{d(1/T)} = - \frac{V_{si}}{V_{mi}\tau_e} \frac{f}{q'} \frac{\exp(1/f_e)}{\exp(1/f)} \exp\left(- \frac{S_s \gamma}{kT}\right) \qquad (9)$$

In the simplified treatment the process is running when the polymer is cooled from the temperature $T_e$ to the temperature $T_g$. It can be supposed that the parameters $V_{si}/V_{mi}$, $q'$ and $\gamma$ are constants within these limits. An approximative solution can be used if $f \to 0$:

$$\frac{1}{f} = \frac{1}{f_e} + \ln\left\{ 1 - \frac{V_{si}}{V_{mi}\tau_e} \frac{kT_e^2}{qS_s\gamma} \left( \exp - \frac{S_s\gamma}{kT_e} - \exp - \frac{S_s\gamma}{kT_g} \right) \right\} \qquad (10)$$

or

$$\frac{\tau}{\tau_e} = 1 - \frac{V_{si}}{V_{mi}\tau_e} \frac{kT_e^2}{qS_s\gamma} \left( \exp - \frac{S_s\gamma}{kT_e} - \exp - \frac{S_s\gamma}{kT_g} \right) \qquad (11)$$

where $q = dT/dt$, the cooling rate, is negative when the temperature decreases.

The value of the fractional free volume f in equation (10) can be interpreted as an effective intermolecular free volume which "survives" into the glassy state. The calculated value of volume f of some polymers listed in Table 1 are plotted in Fig. 1 as a function of logarithm of cooling rate $q = dT/dt$. The ratio of relaxation times $\tau_e/\tau$ of these polymers computed from equation (11) is plotted in Fig. 2.

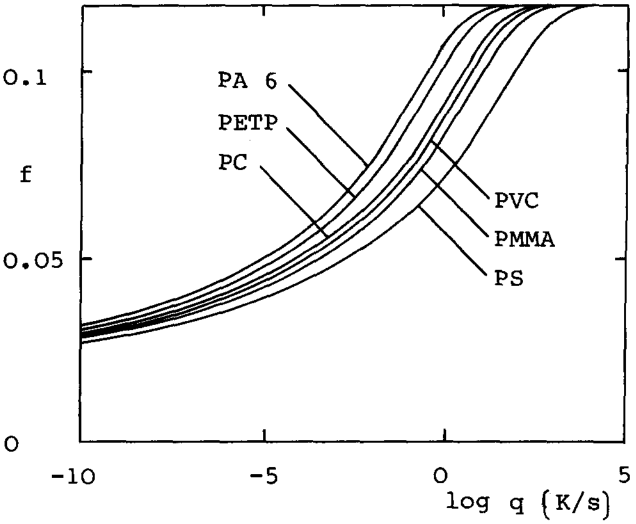

Fig. 1. The effective intermolecular fractional free volume f as a function of logarithm of cooling rate q = dT/dt of some amorphous polymers in a glassy state

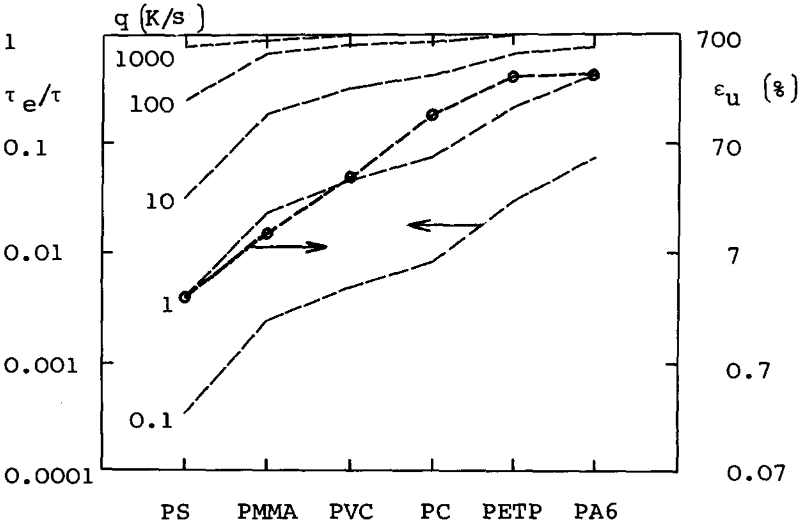

Fig. 2. The ratio of relaxation times $\tau_e/\tau$ in comparison with the experimental values of ultimate elongation $\varepsilon_u$ of some polymers in glassy state. The parameter q is the cooling rate.

TABLE 1

Medium values of the energy of surface tension $\gamma$ , glass transition temperature $T_g$ and ultimate elongation $\varepsilon_u$ at about 300 K of some amorphous polymers in a glassy state (KREVELEN 1976, DOMININGHAUS 1976)

| Polymer | $\gamma$ ($J/m^2$) | $T_g$ (K) | $\varepsilon_u$ (%) |
|---|---|---|---|
| Polystyrene (PS) | 0.034 | 371 | 2.5 |
| Poly /methylmethacrylate/ (PMMA) | 0.039 | 379 | 10 |
| Poly /vinylchloride/ (PVC) | 0.039 | 355 | 30 |
| Polycarbonate of bisphenol A (PC) | 0.045 | 420 | 125 |
| Poly /ethyleneterephtalate/ (PETP) | 0.042 | 342 | 275 |
| Polyamide 6 (PA 6) | 0.043 | 330 | 300 |

## Discussion

In order to check the validity of the model some published experimental data were used. For the fractional expansion free volume $f_e$ in equ. (10) the value 0.12 is substituted for all polymers (BONDI 1964) . For the temperature $T_e$ temperature ($T_g$ + 200 K) is substituted. This temperature range roughly corresponds with the rubbery behaviour of polymers (KREVELEN 1976).

A linear correlation between the ratio $\tau_e/\tau$ and the ultimate elongation as a measure of ductility is supposed. Both parameters are plotted in Fig.2 for all the individual polymers. The vertical position of $\tau_e/\tau$ -lines depends strongly on the ratio $V_{si}/V_{mi}/\tau_e$ in equation 11. The value of $10^7 s^{-1}$ shifts the $\tau_e/\tau$-line for medium cooling rate (1 K/s) to co-incidence with the line of experimental stated ultimate elongations. The ratio $V_{oi}/V_{mi}/\tau_e$ can be interpreted as a frequency of molecular rearrangements corresponding to the hole pulsation. The value $10^7$ $s^{-1}$ seems to be reasonable in this context. Also the area of internal surface of the hole $S_s$ is estimated from the diagram in Fig.2. The change of $S_h$ influences the slope of $\tau_e/\tau$-lines. The same slope of the $\tau_e/\tau$-line for medium cooling rate 1 K/s and the line of experimental stated ultimate elongation has been achieved for $S_s = 3.27 \times 10^{-18}$ $m^2$ /universal for all the polymers/. This area corresponds to the spherical hole of diameter 1.02 nm or to the volume of 0.56 $nm^3$. This volume is comparable with the size of molecules and seems to be quite plausible.

It can be seen in Fig. 1 that for very slow cooling rates the effective fractional intermolecular free volume f approaches the value 0.025. This value represents the time-independent part of the free volume and corresponds to the free volume $f_g$ in the WLF equation (FERRY 1970). For mediunm cooling rates the volume f depends strongly on materials parameters, namely on the energy of surface tension $\gamma$ and on the glass transition temperature $T_g$. The brittle polymers have distinctly less value of the volume f than ductile materials such as PC, PETP and PA 6.

The relative small differences of f results in widely different relaxation times $\tau$ caculated from equation(11) (Fig.2) .

The ratio $\tau_e/\tau$ is directly proportional to the considerably increased ductility of PC, PETP or PA 6 relative to vinyl polymers such as PS or PMMA. The diagram also conforms to the obvious observed dependence of ductility on the cooling rate in the glass transition region. From the model follows that for extremly high cooling rates the ductility of polymers in the glassy state should approach the ductility of polymers in the rubbery state.

The model is an interpretation of our experimental results of the non-uniform local volume contraction during cyclic loading. According to the model, the decrease of the intermoleculare free volume is reactivated by cyclic loading in the glassy state, but instead of the formation of spherical holes the crack or craze formation is supposed.

The surroundings of the growing holes may be, to a certain extent, bi-axilly oriented and hardened. In this case, the structure of polymer glass should contain solider hollow spherical regions of diameter about 2 or 3 nm. These regions are sometimes observed in amorphous polymers by electron microscopy, but can not be detected by X-ray diffraction (MARICHIN 1977) because of the same average density of such a region in comparison with density of the matrix.

## References

BONDI, A.: J.Polym.Sci.,A2, 3159 (1964)

BOUDA, V., ZILVAR, V., STAVERMAN, A.J.: J.Polym.Sci., Polym. Phys.Ed. 14, 2313 (1976)

BOUDA, V.: IUPAC Symp. MACRO-Dublin 1977, Proceedings, Pap. IV-20

DOMININGHAUS, H.: Die Kunststoffe und ihre Eigenschaften, Düsseldorf, VDI Verlag 1976

DOOLITTLE, A.K.: J.Appl.Phys. 22, 471 (1951)

FERRY, J.D.: Viscoelastic Properties of Polymers, 2nd ed., New York, London, Sydney, Toronto, Wiley 1970

FISHER, J.C.: J.Appl.Physics 19, 1062 (1948)

FRENKEL, J.: Kinetic Theory of Liquids, Oxford, The Clarendon Press (1946)

MARICHIN, V.A., MJASNIKOVA, L.P.: Nadmolekuljarnaja struktura polimerov, Leningrad, Chimija (1977)

VAN KREVELEN, D.W.: Properties of Polymers, Amsterdam, Oxford, New York, Elsevier (1976)

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