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SOME PECULIARITIES OF VISCOELASTIC PROPERTIES IN THE SYSTEM POLYMER–POLYMERIC FILLER OF THE SAME CHEMICAL NATURE

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Abstract—The temperature and frequency dependences of complex shear modulus and mechanical losses were studied for epoxide resin filled with the same epoxide resin, i.e. using filler of the same chemical nature. Samples with different amounts of the filler have different physical structures. Experimental results have been discussed on the basis of WLF-method and the free volume concept. It was shown that the viscoelastic properties of the epoxy binder hardened in the presence of the same resin hardened beforehand differ from the properties of the resin hardened without filler. The fractional free volume at the glass temperature was found not to be a universal constant but depends on the physical structure of the system.

INTRODUCTION

It is well known that the temperature dependence of viscoelastic properties of polymers may be described by the Williams–Landel–Ferry (WLF) [1] which contains the fractional free volume f_g at the glass temperature as a universal constant. It has been accepted [2] that the glass temperature of any polymer corresponds to the iso-free volume state with universal value of f_g.

In 1965 one of us [3] suggested that f_g may be dependent on the packing density of macromolecules and of the mode of molecular motion. Later [4] the dependence of f_g on chain molecular parameters was proved for many linear polymers. In another paper [5] the concept of iso-free-volume state was thoroughly considered.

To examine the applicability of this concept, it would be desirable to investigate the constancy of f_g for polymers of various physical structures. So far there have been no such investigation. Our purpose here consists in investigating visco-elastic properties of such a system, obtained by using filled polymer where the same initial polymer was used as a polymeric filler and introduced into the polymer matrix. Such an approach to changing the physical structure of a polymer is similar to the structural change when mineral fillers are incorporated. However, unlike polymers filled with mineral fillers, the effects arising from inner stresses may be excluded, this effect being connected with the difference between thermal expansion coefficients of filler and polymer matrix [6]. Also in this case the temperature dependence of the viscoelastic properties both of matrix and of polymeric filler are very similar, and the analysis of results is facilitated. The main idea of our approach consists of variation of polymeric filler concentration in the matrix of the same chemical nature in order to alter viscoelastic properties [7] and fractional free volume without changing the chemical nature of the system.

EXPERIMENTAL

As polymer matrix and polymeric filler, epoxy resin (a product of condensation of epichlorohydrin and diphenylolpropane) hardened with 10 weight % of polyethyleneamine was used. The average molecular weight of the initial resin was 400, the content of epoxy groups—21%, colour (according to Gardner) 8. The resin was hardened, thus one weight part of polyethylenepolyamine and 10 weight parts of epoxy resin were mixed carefully at room temperature in a vacuum mixer (see Fig. 1). The reaction mixture was poured into teflon forms with cell size 5 × 10 × 50 mm. This mixture was hardened for 24 hr at 20° and 8 hr at 150°. After hardening, samples were tested according to a described method [8]. The same samples were ground to a powder using milling cutter. The powder was then placed into the ball mill and milled at liquid nitrogen temperature to a powder with particle size about 3–10 μm. This powder was used as a filler for the same epoxy resin. The filler was introduced into the reaction mixture and, after 10 min mixing in vacuum mixer, was returned into the forms and hardened as described above. The amounts of filler were 5, 10, 25 and 40 weight %. Another method of sample preparation was also used. The samples of filled resin were prepared containing 5% (weight) of filler obtained by grinding a sample filled beforehand with 5% of filler, and samples with 5% of filler, obtained from the preceding sample. There were thus incorporated in the system either different amount of hardened polymer as a filler, or equal amounts of fillers

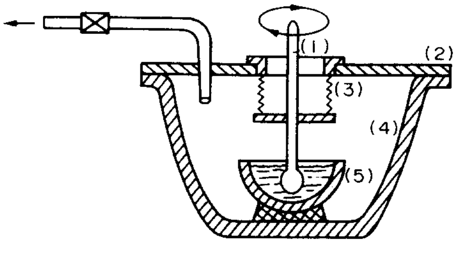

Fig. 1. Vacuum mixer: (1) mixing device; (2) cover; (3) silfon; (4) excicator cap; (5) porcelain mortar.

obtained from successive filled samples. In these cases the structures and properties of fillers were different, reaching with every new filling some limiting properties, these properties being dependent on the structure and properties of the binder, hardened on the filler surface.

Dynamic mechanical properties were studied using the frequency relaxometer [9] in the range 0.004–0.4 Hz and temperatures 80–140° (i.e. in the region of the glass transition of hardened epoxy resin). Temperature and frequency dependences of complex shear modulus (G*) and mechanical losses (tan δ) were determined experimentally. Using the WLF-method and the Eqn. [9]:

$$\lg a_T = -\frac{C_1^0(T - T_0)}{C_2^0 + T - T_0} \tag{1}$$

the master curves of frequency dependence $\lg G^* = f(\lg \omega a_T)$ were constructed and the temperature dependence of reduction shift factor a_T was estimated. From the generalized curves $\lg G' = f(\lg \omega a_T)$ the relaxation time spectra were calculated using the Ninomiya–Ferry method [10]. Temperature dependence of lg a_T was used to determine the coefficients C_1^0 and C_2^0 of Eqn. (1) from the plot of $(T - T_0)/\lg a_T$ vs $(T - T_0)$. The values of coefficients C_1^0 and C_2^0 at the glass temperature were found [9] as:

$$C_1^g = \frac{C_1^0 C_2^0}{C_2^0 + T_g - T_0} \quad \text{and} \quad C_2^g = C_2^0 + T_g - T_0.$$

Fractional free volume at T_g was calculated as

$$f_g = 1/(2.3\, C_1^g).$$

RESULTS AND DISCUSSION

Figures 2 and 3 show temperature dependence of the real part of complex shear modulus G′ and tan δ for hardened resin with different amounts of filler from the same hardened resin. It is seen that the filler greatly influences the temperature dependence of viscoelastic properties. At relatively small concentration of filler, the temperature dependence of viscoelastic functions are shifted to lower temperatures and the rate of change of modulus with temperature is higher than for pure hardened resin. Increase in filler concentration shifts curves to higher temperatures and properties become comparable to those of pure resin because of increased proportion of epoxy filler in the system. Thus, in spite of the chemical identity of filler and binder, the properties are dependent on the filler concentration. Similar effects were explained earlier [11] by the influence of filler surface on molecular mobility during hardening and on the structure of surface layers. Therefore we can consider the system as consisting of two parts: polymer with properties of pure hardened resin (filler) and hardened resin with properties modified by the effect of filler surface. The values of fractional free volume f_g calculated from visco-elastic characteristics were used for proving the idea about glass transition as a iso-free-volume state. Figure 4 shows the dependence of f_g (curve 1) and glass temperature (curve 2) on filler concentration. T_g was taken at the temperature corresponding to maximum mechanical losses. It is seen that f_g is not constant and differs from the universal value $f_g = 0.025$. At the same time evident correlation exists between f_g and T_g (Fig. 5). Data presented in Fig. 4 confirm the idea that filler surface influences very strongly the processes of network formation and its structure and density, the properties of binder at the filler–binder interface being changed as a result. Thus in composites formed by chemically identical polymer, depending on the method of preparation, there is inconstancy both of fractional free volume and, as shown by study of the temperature dependence of f_g, coefficients of thermal expansion of free volume. These data are not in conformity with the concept of the iso-free-volume state.

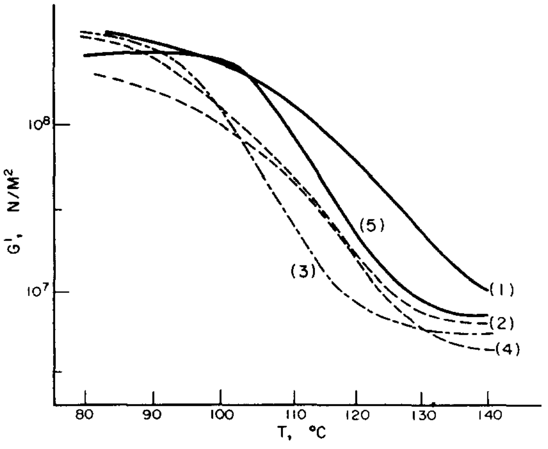

Fig. 2. Temperature dependence of real part of complex shear modulus for epoxy resin filled with the same hardened resin: (1) pure resin; (2) $\psi = 0.05$; (3) $\psi = 0.1$; (4) $\psi = 0.25$; (5) $\psi = 0.4$. Frequency −0.04 Hz.

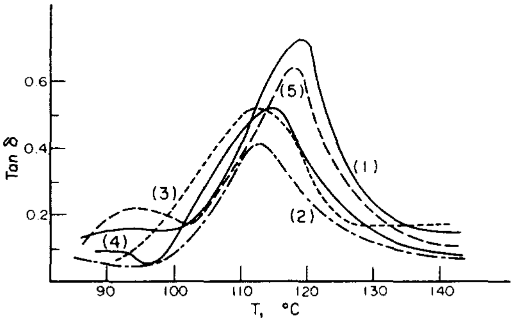

Fig. 3. Temperature dependence of mechanical losses: (1) pure resin; (2) $\psi = 0.05$; (3) $\psi = 0.10$; (4) $\psi = 0.25$; (5) $\psi = 0.4$; Frequency 0·04 Hz.

Now we discuss the visco-elastic properties of composites obtained with successive incorporation as

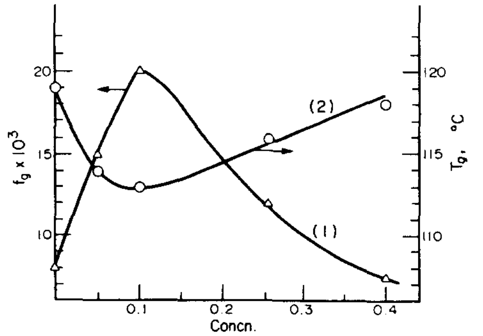

Fig. 4. Concentration dependence f_g and temperature of maximum of mechanical losses T_g for filled resin.

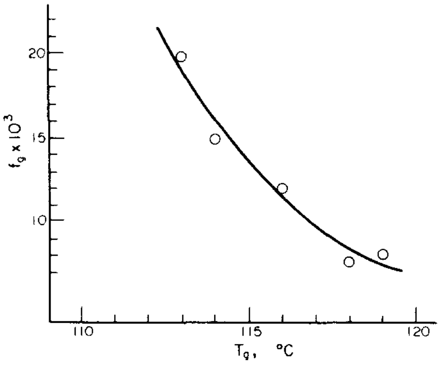

Fig. 5. Dependence f_g on T_g.

filler polymer previously filled. The idea of such a consecutive type of filling consists of obtaining polymer materials where filler properties are similar to the properties of surface layers of binder. That means we try artificially to increase the proportion of polymer with properties changed under the influence of filler to reach the state of "pure surface layer". The properties of the last sample should be very close to the properties of surface layers of polymer onto polymeric filler surface. Having investigated such composite materials, we can obtain better information about the influence of filler on the structure of surface layers of polymer.

Figures 6 and 7 present the temperature dependence G′ and tan δ for samples obtained by the consecutive method. Curve 1 refers to pure hardened resin, curve 2 to resin filled with 5% filler from sample 1, curve 3 to sample with 5% filler from sample 2, etc. It is seen that, when the properties of filler approach the properties of the resin hardened in the presence of filler, all the curves are shifted to lower temperatures, the shift being decreased with number of filling, as can be seen from f_g, calculated for the samples under consideration:

Number of filling:	0	1	2	3	4
$f_g \cdot 10^3$	8	15	19	20	20

To find out the changes in molecular mobility in such consecutively filled specimens, their relaxation spectra were calculated (Fig. 8). It is seen that in filled specimens there are some shifts of the spectra compared to that for the initial hardened resin, this shift being most pronounced in the region of high relaxation times. At the same time in the region of small relaxation time, some broadening of the spectrum was observed. The shift to the higher relaxation times shows that the mobility of large structural elements (segments) becomes less. The spectral broadening in the region of low relaxation times may be explained by the higher defectiveness of the network structure formed in the presence of polymeric filler. In such a way, we can try to describe viscoelastic properties of polymers changed under the influence of the surface for the case when contribution of bulk characteristics is continuously diminished.

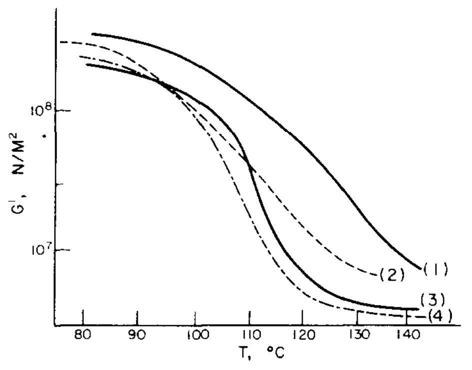

Fig. 6. Temperature dependence of real part of complex shear modulus for specimens filled according to consecutive method: (1) pure resin; (2) 1st filling, $\psi = 0.05$; (3) 2nd filling, $\psi = 0.05$; (4) 3rd filling, $\psi = 0.05$. Frequency 0.04 Hz.

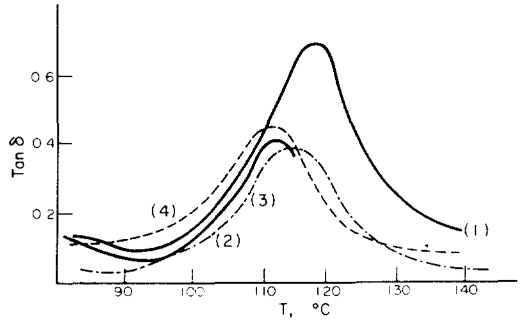

Fig. 7. Temperature dependence of mechanical losses for the specimens referred to in Fig. 6.

It was also of interest to discover if there are different properties for the surface layers of the same resin hardened in the presence of quartz filler (filler with high surface free energy). For this purpose, we have compared the viscoelastic properties and fractional free volume for filled specimens of different compositions. Sample 1 was obtained by hardening the epoxy resin in the presence of 11 vol % of quartz powder, sample 2 contained 14% of epoxy filler, sample 3 25% of filler which was obtained from resin hardened in the presence of 44% quartz filler. Thus this latter sample contained a mixed filler from 44% of quartz and 56% of epoxy resin hardened in the presence of quartz. Therefore sample 3 contained 11% of quartz filler and 14% of epoxy filler with properties of surface layers of polymer formed in the presence of filler. Comparison (Fig. 9) shows that the spectrum for sample 3 differs essentially from those for samples

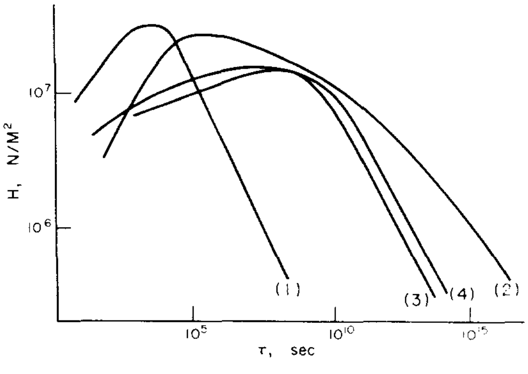

Fig. 8. Relaxation time spectra for specimens referred to in Fig. 6.

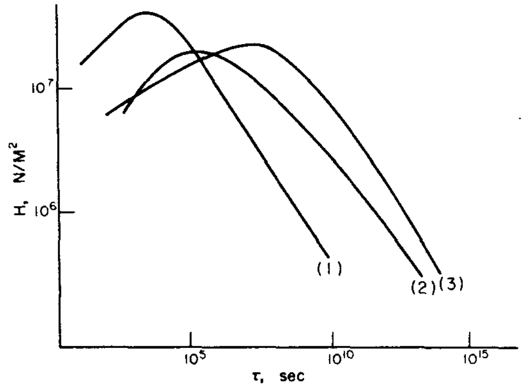

Fig. 9. Relaxation time spectra for epoxy composition (see the text).

1 and 2. Here, for sample 3 $f_g = 0.028$, for sample 2 $f_g = 0.008$ and for sample 1 $f_g = 0.026$, whereas for pure resin $f_g = 0.008$. This comparison shows the specimens are very different as for spectral composition of relaxators and value of f_g. This means that pure physical factors influencing formation of polymer network in surface layers and their structure lead to changes in molecular mobility and fractional free volume which cannot be described in the framework of the iso-free-volume state concept, which is at best only a very rough approximation. What is of great importance is that such a picture was discovered for a polymeric system which is heterogeneous but chemically identical.

CONCLUSION

The experimental results lead to a conclusion about inapplicability of the iso-free-volume-state concept for describing glass transition phenomena and visco-elastic properties. We believe that the free volume theory describes these processes only phenomenologically but not quantitatively. The free volume theory when applied to processes near the glass transition point does not take into account that the glass transition is connected not only with the appearance of the free volume but with chain flexibility and intermolecular interaction between chains, these factors being responsible for deviation vs polymer behaviour near T_g from that predicted by the free volume theory.

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