The Abnormality in the Mechanical Behavior of Polyvinyl Acetate-Carbon Tetrachloride Gel

By Kazuyoshi OGINO

(Received February 23, 1959)

It is well known that many polymeric substances are typically visco-elastic: their stress under constant strain decreases continuously with time; i. e. stress relaxation is observed. In this case, it is usual that the stress deteriorates with time, and this is expected from the following consideration: when a specimen is held under a constant strain, the relative position or the configuration of the molecules changes with time so as to attain a more unstrained position, and thus the stress which corresponds to this strain decreases with time. This is the stress relaxation in "normal" condition.

On the other hand, Tobolsky et al. found[1] that some abnormalities in the stress relaxation under constant elongation appear at about 100°C when natural and several synthetic polymers are heated in the air. Further, they thought that the structural or chemical changes are reflected in the visco-elastic behavior of these substances. This phenomenon is known as the chemorheological process.

Many examples of abnormalities in the mechanical properties of polymeric substances have been interpreted as the result of the scission of the network chain or the cross-linking reaction by oxygen in the air[*,2].

The author found that the mechanical behavior of swollen polyvinyl acetate gels, which were cross-linked slightly with diallyl adipate and swollen in several organic solvents, shows abnormality when carbon-tetrachloride was used as a solvent; i. e. their stress *increases* continuously with time when the temperature was raised above 50°C. When one chooses polyvinyl acetate, polymethyl acrylate, polymethyl methacrylate or polystyrene as the polymeric substance, and chloroform, benzene, toluene, carbon tetrachloride or methanol as the solvent, the combination of polyvinyl acetate and carbon tetrachloride is the only system which causes an increase in stress under constant strain. The purpose of this paper is to report this abnormality, and to make a possible interpretation for this phenomenon.

Experimental

Materials.—Commercial monomeric vinyl acetate was shaken several times with aqueous alkaline solution, and with distilled water. This process was repeated three times. The monomer was then distilled under reduced pressure.

Diallyl adipate was synthesized by esterification of allyl alcohol with adipic acid, and was purified by fractional distillation under reduced pressure**.

Carbon tetrachloride was purified by washing with aqueous alkaline solution and by distillation.

Vinyl acetate monomer mixed with cross-linking agent was polymerized thermally in bulk in a sealed glass tube under the presence of benzoyl peroxide as initiator (about 0.5 wt. %). This had been purified by recrystallization. At the beginning of polymerization, the temperature was kept at about 50°C until the contents were solidified, and was then held at 100°C for 12 hr.

The polymer rod was cut into several pieces, about 1 cm. in length, and was brought to the swelling equilibrium in carbon tetrachloride.

Apparatus. — The apparatus used in this

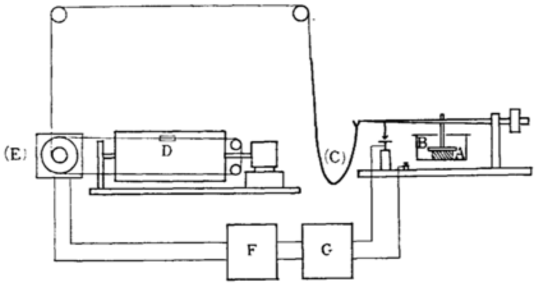


Fig. 1. The apparatus for the measurement of stress relaxation.
A: Specimen. B: Solvent. C: Chain.
D: Rotating drum & pencil.
E: Balancing motor. F: Relay.
G: Amplifying circuit.

---

[1] A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.*, **13**, 3 (1945).

[*] The effect of oxygen upon the stress relaxation or creep was studied by the measurement which is known as the intermittent and continuous method.

[2] R. D. Andrews, E. E. Hanson and A. V. Tobolsky, *J. Appl. Phys.*, **17**, 352 (1946).

[**] This cross-linking agent is the same as was used in the previous work; K. Ogino, This Bulletin, **31**, 577 (1958).

experiment is the same as the one used in the previous work[3], and is shown in Fig. 1.

The temperature of the sample was controlled by circulation of water from a water bath, and was read directly by a thermometer immersed in the solvent. The temperature was so high (about 50°C) that in some cases the fluctuation was observed to some extent, but this did not exceed 1°C.

Results and Discussion

Fig. 2 shows the relation between stress and time at about 50°C under 20% strain. It is clear from this figure that the stress in these gels decreases slightly in the first step and then increases. The degree of this increase in stress becomes larger as the degree of swelling diminishes.

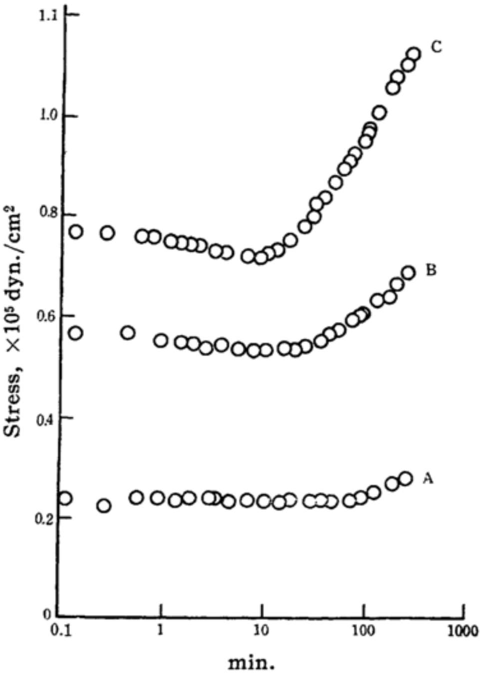


Fig. 2. The relation between stress and time under 20% strain (vertical compression) in CCl_4.
A: Volume fraction 0.24 at 48°C.
B: Volume fraction 0.33 at 49°C.
C: Volume fraction 0.42 at 49°C.

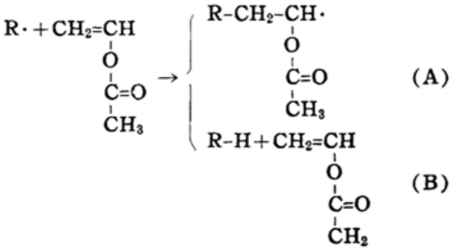
Oxygen from the air can not be considered to be the cause of this abnormality, because this occurs only in the system of polyvinyl acetate and carbon tetrachloride, and does not occur in any other polymer-solvent combinations. It is difficulty to find any reason for the effect of atmospheric oxygen being found in this system alone. The structural difference between vinyl acetate and methyl acrylate is only in the position of the carbonyl group. There must consequently be some special meaning for the vinyl acetate system. This can be interpreted as follows.

It is well known that in the solution polymerization, especially when carbon tetrachloride, carbon tetrabromide, chloroform, sulfur dichloride or mercaptane is chosen as solvent, the chain transfer with solvent molecules occurs very easily and each polymer molecule contains fragments of the solvent[4]. Such a compound is known as telomer, and the reaction is called telomerization. Fig. 3 shows the mechanism of the chain transfer with carbon tetrachloride as an example.

On the other hand, the chain transfer with monomeric vinyl acetate takes place in the scheme as shown in Fig. 4.

$$\begin{aligned}&\mathrm{Mn\cdot + CCl_4 \rightarrow MnCl + \cdot CCl_3}\\&\mathrm{\cdot CCl_3 + M \rightarrow M\cdot CCl_3\cdot \rightarrow MnCCl_3\cdot}\\&\mathrm{MnCCl_3\cdot + CCl_4 \rightarrow \underset{(Telomer)}{Cl\cdot Mn\cdot CCl_3} + \cdot CCl_3}\end{aligned}$$

Fig. 3. The chain transfer with carbon tetrachloride.



$$\mathrm{R\cdot + CH_2{=}CH(O{-}C{=}O{-}CH_3) \rightarrow \begin{cases} \mathrm{R{-}CH_2{-}CH(O{-}C{=}O{-}CH_3)\cdot} & \text{(A)} \\ \mathrm{R{-}H + CH_2{=}CH(O{-}C{=}O{-}\dot{C}H_2)} & \text{(B)} \end{cases}}$$

Fig. 4. The chain transfer with vinyl acetate.

In this case, it is noticeable that the radical of type B is produced. This is considered to be the cause of the existence of vinyl groups which are connected to the end of the branching along the long chain molecule of polyvinyl acetate[5]. In the case of the other monomers, such as methyl acrylate, methyl methacrylate or styrene, radicals of this type rarely exist. The existence of this radical, and consequently the possibility of the existence of vinyl groups at the end of each branching in polymer is the characteristic feature of vinyl acetate.

Hence, the polymer which has a structure like that shown schematically in Fig.

---

[3] K. Ogino, This Bulletin, **31**, 580 (1958).

[4] P. J. Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937); J. W. Breitenbach and H. Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

[5] O. L. Wheeler, E. Iarin and R. N. Crozier, *J. Polymer Sci.*, **9**, 159 (1952).

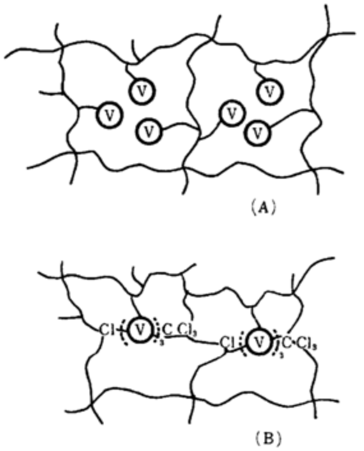


Fig. 5. The schematic diagram to show the internal structure of polyvinyl acetate. (V=Vinyl group)

5A will be produced when vinyl acetate is polymerized thermally in bulk in a sealed tube under the presence of benzoyl peroxide as an initiator. Therefore, when this polymer is brought to the swelling equilibrium with carbon tetrachloride, and is maintained at about 50°C, telomer will be formed between carbon tetrachloride and vinyl groups present at the end of each branching. This feature is shown in Fig. 5B. If this reaction occurs, the effective molecular weight between junction points decreases, and so the stress will increase. In order that this reaction, telomerization, may take place, it is necessary that radicals exist in this system. This postulation seems to be satisfied because the initiator which was added initially into the monomer will still remain undecomposed in the polymer, and further, it is demonstrated, for example, by Ingram6), that radicals which are created in the course of polymerization will remain unchanged.

To confirm this postulation, the mechanical property of polyvinyl acetate, which was swollen at room temperature in carbon tetrachloride with 5% bromine added, was investigated. By this treatment, vinyl groups may be saturated and radicals may be consumed by bromine; i. e. it may be considered that the cause which provokes telomerization will be removed. This result is shown in Fig. 6. It is clear that after the treatment with bromine solution the " normal " relaxation

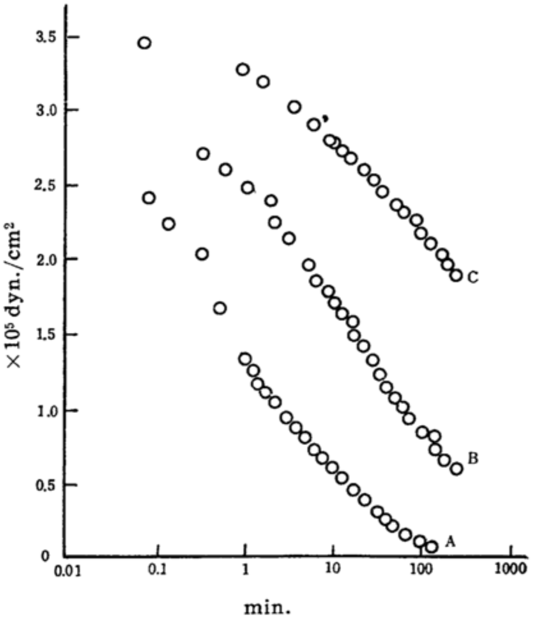


Fig. 6. The relation between stress and time under 20% strain after the treatment by bromine solution in carbon tetrachloride.

of stress is observed. The volume fraction of polymer in bromine solution is larger than that in carbon tetrachloride. This may be due to the polar effect of substituted bromine atoms.

If it may be assumed that the abnormality observed in the system polyvinyl acetate-carbon tetrachloride gel arises from telomerization between vinyl groups and solvent, it is expected that when chloroform is used as a solvent a similar abnormality will be observed. But, as shown in Fig. 7, this was not observed. This may be due to the fact that chloroform is a good solvent for polyvinyl acetate and the degree of swelling becomes very great, so the chain molecules will be fairly far apart from each other in this solvent compared with the case in carbon tetrachloride***.

Tobolsky et al. showed that the splitting or reforming reaction of cross-linkages by oxygen occurs between chain molecules7), and that if the number of splits per cubic centimeter is a linear function of time, the decay of stress follows the Maxwellian

---

6) D. J. E. Ingram et al., *Trans. Faraday Soc.*, 54, 409 (1958).

*** Tobolsky et al. found that the effect of oxygen upon the mechanical property was not observed in swollen polymer, and thought that this might be due to the greater distance of chain molecules in the swollen state than in the dry state1).

7) A. V. Tobolsky, D. Metz and R. B. Mesrobian, *J. Am. Chem. Soc.*, 72, 1942 (1950).

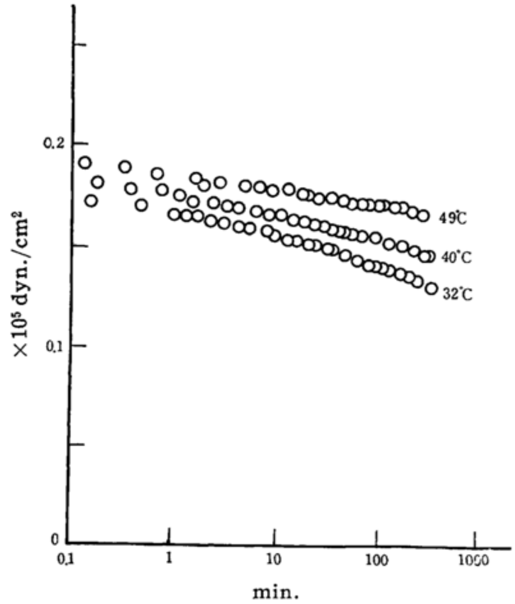


Fig. 7. The relation between stress and time in chloroform. (The volume fraction: 0.020)

decay law[8], or

$$f(t) = f(0)\exp(-kt)$$

where $f(0)$ is the stress at time zero, $f(t)$ the stress at time t, and k the rate constant.

Now, for the system polyvinyl acetate-carbon tetrachloride gel, if a is the number of vinyl groups at time zero between junction points, and x of this group are consumed at time t by telomerization, the following equation can be postulated because the rate of telomerization, dx/dt, will be primarily dependant upon the distance between chain molecules[1], and as the reaction proceeds, the chance of two vinyl groups meeting with each other will increase by the presence of newly formed cross-linkage. Thus, the rate of reaction will be proportional to the number of vinyl groups which have been cross-linked; i.e.

$$dx/dt = kx$$

therefore,

$$\ln(x/a) = kt$$

The stress at time t can be considered to be proportional to the number of cross-linkages, x, which are formed between junction points, and so,

$$\ln\{f(t)/f(0)\} = kt$$

Thus, if one plots the results of Fig. 2 as $\ln(f/f_0)$ against t, the curves of Fig. 8 are obtained. The slope in each curve is identical with the rate constant, k, if the term of stress relaxation is neglected.

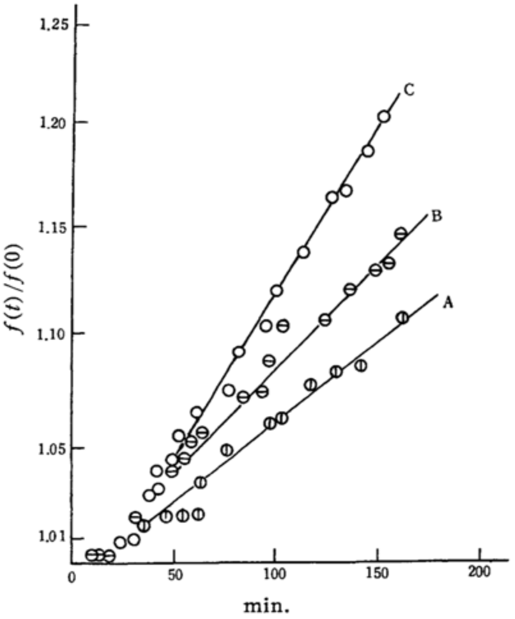


Fig. 8. The plot of $\ln\{f(t)/f(0)\}$ against t at about 50°C.

The abnormality in the mechanical behavior of polyvinyl acetate-carbon tetrachloride gel was interpreted here by telomerization between vinyl groups and solvent.

The author wishes to express his indebtedness to Professor H. Akamatu and Assistant Professor T. Nakagawa for their interest and support, and to Dr. N. Inamoto for his helpful advice and criticism concerning this experiment.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

---

[8] M. D. Stern and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 93 (1946).