

Changes in Physical Properties of Polycarbonate by Absorbed Water

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Synopsis

In this paper, we report the changes in physical properties of polycarbonate caused by absorbed water and supply basic data for the application of this effect. Absorbed water increases monotonously with increase in relative humidity. Along with the increase in absorbed water, the relaxation time of the β process increases, the glass transition temperature rises, the area of the endothermic peak at the glass transition temperature increases, and the dynamic Young's modulus decreases. We conclude that the absorbed water fills holes but does not function as a crosslinking agent.

INTRODUCTION

It is generally known that the physical properties of hydrophilic polymers such as nylon and cellulose are very much affected by absorbed water, and many experiments concerning the effect of water on such hydrophilic polymers have been reported.

On the other hand, polycarbonate, a hydrophobic polymer, absorbs only 0.15 wt-% water at 50% relative humidity at 20°C. It was reported that even such a small amount of water in polycarbonate has a considerable effect on the physical properties of the bulk polymer¹; however, only a few papers have reported the changes in physical properties.

It is, in fact, necessary in order to make a condenser and work with the plastics to know the changes in dielectric constant and glass transition temperature when water is absorbed. Our experiments were carried out for two purposes: one, to investigate, the relationship between the physical properties and the absorbed water content; and the other, to consider the state of the absorbed water in the polymer. The results obtained from these experiments are valuable as basic data for polymer application.

EXPERIMENTAL

Sample Preparation. An original film sample supplied by Idemitsu Kosan Co., Ltd., was used throughout this study. A film 213 μm thick, consisting of an amorphous and unoriented bisphenol A polycarbonate, hereafter referred to as PC, was dried well in an air bath at 130°C for 100 hr and desiccated with phosphorus pentoxide at 24.5°C for a month to obtain a dry sample. This sample was used as standard; its infrared absorption at 3620 cm^{-1} , caused by absorbed water,² was almost zero. Other samples were of the same thickness to eliminate a thickness correction.

Humidity Setting. Desired contents of water were obtained at 24.5°C in closed vessels containing saturated aqueous solutions of zinc chloride, calcium

chloride, magnesium nitrate, potassium nitrate, ammonium sulfate, or barium chloride.

Measurement of Absorbed Water Content. The absorbed water content was measured using a microbalance.

Glass Transition Temperature. Data of the glass transition temperature (T_g) were obtained using a differential scanning calorimeter (Perkin-Elmer DSC, Type II) at a heating rate of 20°C/min. A hermetically sealed sample pan was used to minimize evaporation of the absorbed water. The temperature and area of the endothermic peak at T_g were calibrated with indium.

Dielectric Measurement. The three-terminal method using an electrode arrangement was adopted for making accurate electrical measurements. A tin foil electrode was attached to a sample with a thin layer of silicon grease and the sample was enclosed in an environmental chamber. The complex dielectric constant of the sample was measured in a frequency range of 10⁰–10⁵ Hz and a temperature range of –80°C to room temperature. Under the above conditions, a β process associated with the local mode motion was observed.³

Measurement of Dynamic Young's Modulus. The dynamic Young's modulus was obtained at 24.5°C, using a Toyo Baldwin viscoelastometer, Model DDV-I, at 138 Hz, by blowing air having a specified relative humidity into the meter.

RESULTS AND DISCUSSION

Figure 1 shows the change of absorbed water at various relative humidities (R.H.) at 24.5°C with time and indicates that the absorbed water content becomes constant after about 100 hr. The result agrees with that obtained by Allen et al.⁴ The change of water content with increasing R.H. at 100 hr is shown in Figure 2(a). The weight per cent of absorbed water in the polymer increases monotonously with increase in R.H., in agreement with the results of Sekita et al.⁵

The dielectric constant ϵ' at 1 kHz and 20°C increase with R.H., as shown in

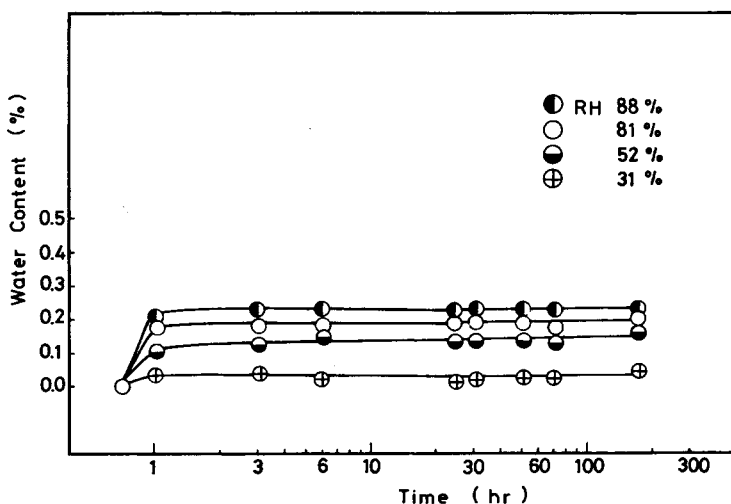


Fig. 1. Changes in absorbed water content at various relative humidity values at 24.5°C with time.

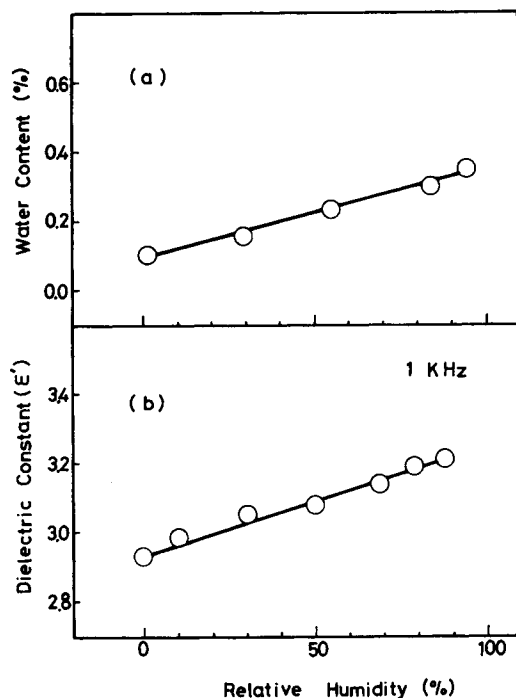


Fig. 2. (a) Change in water content with relative humidity for 100 hr. (b) Change in dielectric constant with relative humidity.

Figure 2(b). It can be said that the increase of the dielectric constant goes parallel to the increase of the absorbed water.⁶

The dielectric constant ϵ' and loss ϵ'' change as the polymer absorbs water. This is not caused by the dipole of the water, but by the change in mobility of the polymer chains, and consequently ϵ' and ϵ'' of the polymer themselves are changed by absorbing water.

Let us consider the change in molecular motion due to water absorption. Figure 3 shows the relationship between the frequency for the maximum dielectric loss f_{\max} and the reciprocal of the absolute temperature. The apparent activation energies are calculated from the slope of the R.H. and are about 13 kcal/mole above 30% R.H. These values indicate that water in PC is not absorbed chemically, but physically.⁶

The reciprocal of f_{\max} is the most probable relaxation time τ , and so it is regarded as a measure for the rate of molecular motion. Figure 3 shows that f_{\max} shifts to the lower frequency at a fixed temperature with increase in R.H. Figure 4 shows the relationship between the relaxation time and R.H. It indicates that the relaxation time becomes longer with increasing R.H. and increases at a low rate for 50% or higher R.H.

The change in T_g with increase in R.H. is shown in Figure 5. It is seen that T_g rises with increase of absorbed water. As described in our previous papers,^{8,9} the β relaxation process is closely related to T_g through the segmental molecular motion. Therefore, it is reasonable to assume that the change in T_g goes parallel with that in the β relaxation with R.H.

From the experimental T_g and β relaxation results, it can be considered that the absorbed water acts not as plasticizer but as antiplasticizer.

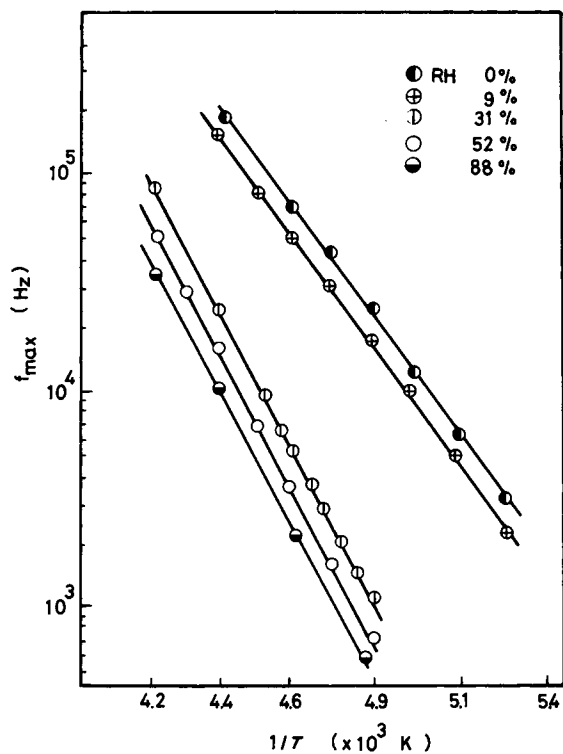


Fig. 3 Relationship between frequency for maximum dielectric loss f_{\max} and reciprocal temperature.

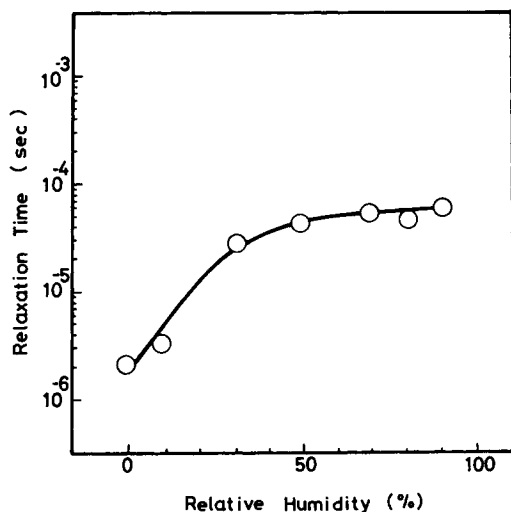


Fig. 4 Relationship between relaxation time and relative humidity.

Generally, an abnormal endothermic peak at T_g is observed by heat treatment below T_g .¹⁰ As the samples used in this study were dried below T_g , an endothermic peak at T_g was observed. Figure 6 shows the variation of the endothermic peak area with increase in absorbed water content. The area of the peak increases with increase in R.H. Wunderlich has explained the thermal behavior

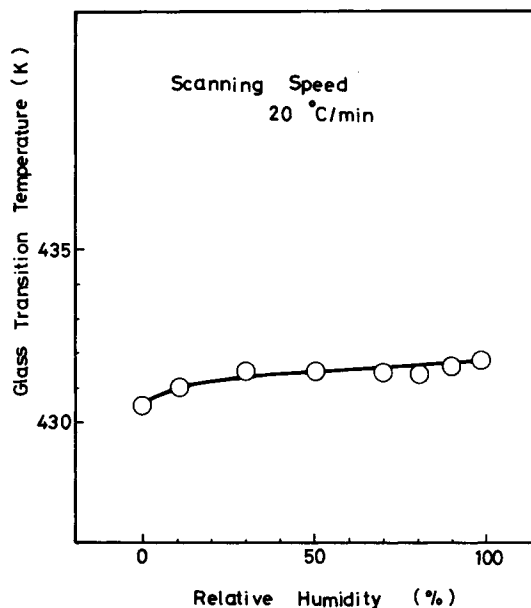


Fig. 5 Change in glass transition temperature with relative humidity.

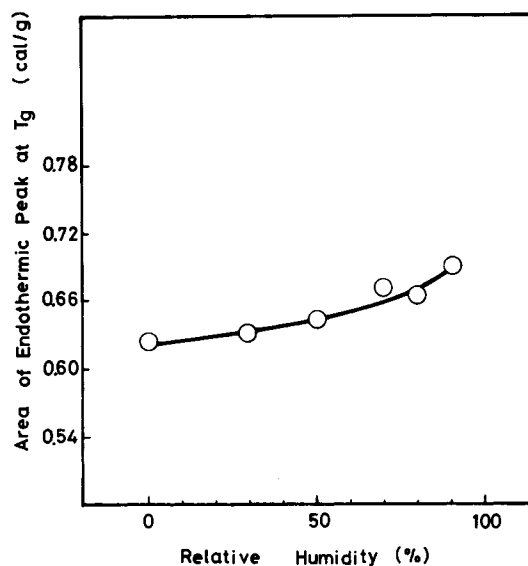


Fig. 6 Change in endothermic peak area at the glass transition temperature with relative humidity.

at T_g using HiraiEyring's hole theory.¹¹ That is to say, the thermal behavior is explained by the relation between the process of freezing holes on cooling and that on going to equilibrium in the number of holes during heating. On slow cooling, the number of frozen holes is small. If the sample is heated rapidly, the relaxation time of the molecular motion does not follow the heating rate and so, temporarily, the number of holes becomes less than that at equilibrium. An endothermic peak, caused by hole formation, is then observed in the DSC curve.

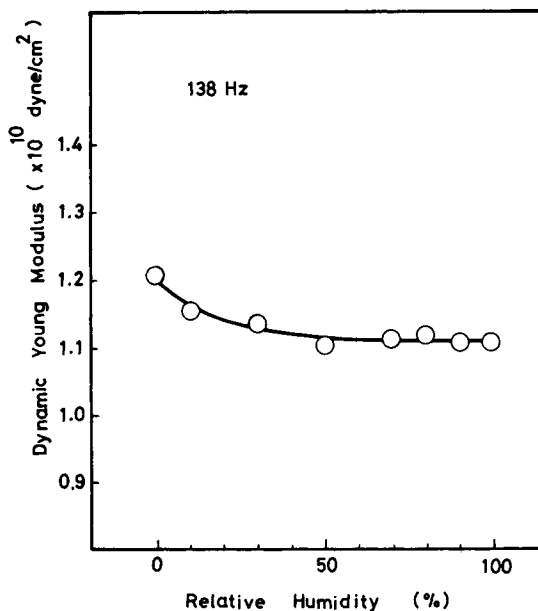


Fig. 7 Change in dynamic Young's modulus with relative humidity.

The changes of the area at T_g and the relaxation time in our case indicate that the larger the peak area at T_g or the larger the amount of absorbed water, the smaller is the number of holes in the sample. That is to say, the water in PC may be absorbed by filling up the holes. According to the free volume theory,¹² T_g and the molecular motion are dominated by fractional free volume in polymers. Hence, the increase in relaxation time and T_g can be explained by a decrease in the fractional free volume in polymers caused by filling up of the holes.

Figure 7 shows the change in Young's modulus E' of elasticity at 138 Hz with change in R.H. It is seen that E' decreases with increase in water content. From this result, we conclude that the absorbed water may not act as a crosslinking agent for the polymer chains, as is observed occasionally in other polymers.

CONCLUSIONS

From the experimental result, we conclude that the absorbed water increases monotonously with increase in relative humidity. The changes in T_g , f_{\max} , and elastic modulus E' suggest that the absorbed water may fill up holes but does not function as a crosslinking agent.

References

1. S. Tahara and Y. Koshino, *Polycarbonate*, Kobunshi-Kankokai Co., Tokyo, Japan, 1966, p. 44.
2. L. H. Little, *Infrared Spectra of Absorbed Species*, Academic Press, London, 1966, p. 239.
3. Y. Ishida and S. Matsuoka, *J. Polym. Sci. C*, **14**, 247 (1966).
4. G. Allen, J. McAlinsh, and G. M. Jeffs, *Polymer*, **12**, 85 (1971).
5. Y. Sekita and A. Kaneko, *Rep. Progr. Polym. Phys. Jpn.*, **14**, 315 (1973).
6. Polymer Society of Japan, Ed., *Mizu to Kobunshi (Water and Polymers)*, Saiwai-shobo Co., Tokyo, Japan, 1972, p. 39.

7. Y. Wada, *Kobunshi no Kotaikozo (Polymer Structure of Solid State)*, Baifukan Co., Tokyo, Japan, 1971, p. 366.
8. E. Ito and T. Hatakeyama, *J. Polym. Sci. Phys. Ed.*, **12**, 1477 (1974).
9. E. Ito and T. Hatakeyama, *J. Polym. Sci. Phys. Ed.*, **13**, 2313 (1975).
10. Y. Mitsuishi and Y. Kuroda, *Sen-i-Gakkaishi (J. Soc. Fiber Sci. Technol. Jpn.)*, **24**, 11 (1968); T. Hatakeyama and H. Kanetsuna, *Kobunshi Kagaku (Chem. High Polym. Jpn.)*, **27**, 375 (1970).
11. B. Wunderlich and D. M. Bodily, *J. Polym. Sci. C*, **6**, 137 (1964).
12. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959); M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

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