

Effects of Absorbed Water on Physical Properties of Polyesters

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Synopsis

In previous articles, we reported the change in physical properties of hydrophobic polymers caused by absorption of a very small amount of water. This article describes the changes in physical properties of three polyesters owing to absorption of water. The tested polymers were poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and polyethylene 2,6-naphthalate (PEN). PBT has more flexible main chains than that of PET, and PEN has more rigid main chains. The dielectric measurements revealed that water absorption results in shortening the relaxation time for PET, while the relaxation time for moist PBT becomes longer. The larger amount of absorbed water yields the higher density of PET and the lower density of PBT. The water absorption of the polyesters also yields increments in dielectric constants and relaxation strength. Distribution of relaxation time of the polyesters is narrowed by absorption of water.

INTRODUCTION

Physical properties of hydrophobic polyesters were considerably affected by absorption of a small amount of water.¹⁻³ To obtain the absolute values of physical constants and compare the experimental results obtained under different conditions, it is necessary to elucidate the relationship between physical properties and the amount of water absorbed in the polymers.

This study was undertaken to determine the effects of absorbed water in polyesters on the relaxation time of the torsional vibration of main chains (i.e., local mode relaxation of the polymers). Dielectric constant and increment, relaxation time and distribution in local mode relaxation of the polymers are greatly affected by a small amount of water. Accordingly, the amount of absorbed water in the polymers should be regarded as an important factor when we compare the experimental results obtained at different institutions and examine reproducibility of the results.

Properties of such polyesters as electric insulation material vary with absorbed water. Therefore, relationships between physical properties of the polyesters and amount of absorbed water should be considered when designing electric insulation materials.

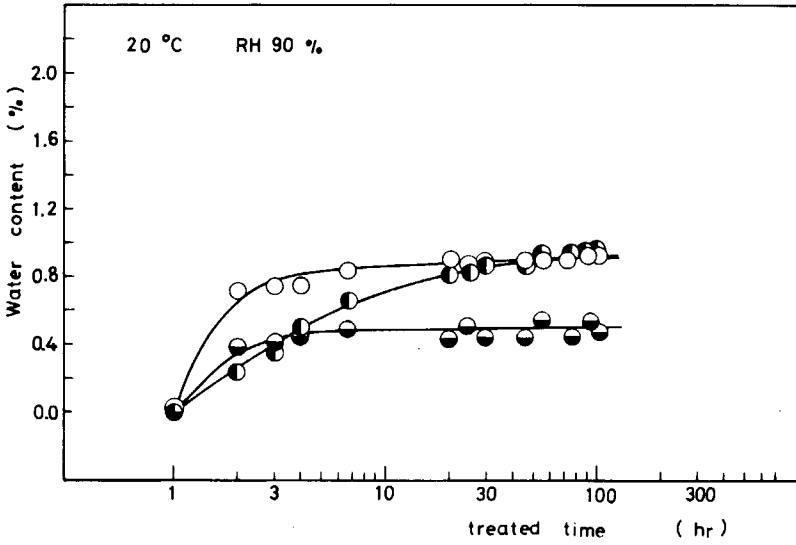


Fig. 1. Change of absorbed water content against treating time at 90% relative humidity at 20°C for (○) PET, (◐) PBT, and (●) PEN.

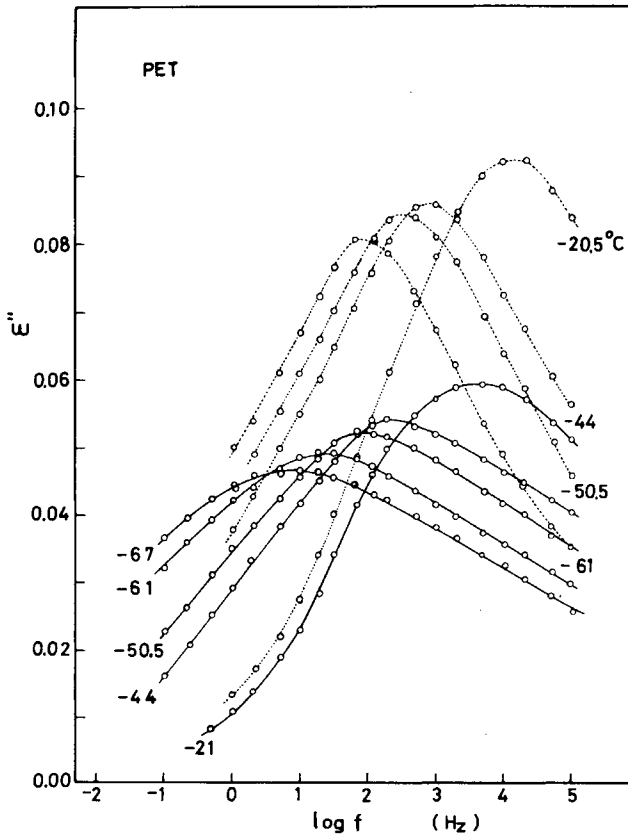


Fig. 2. Frequency dependence of dielectric loss ϵ'' at various temperatures. (···) wet sample, (—) dry sample of PET.

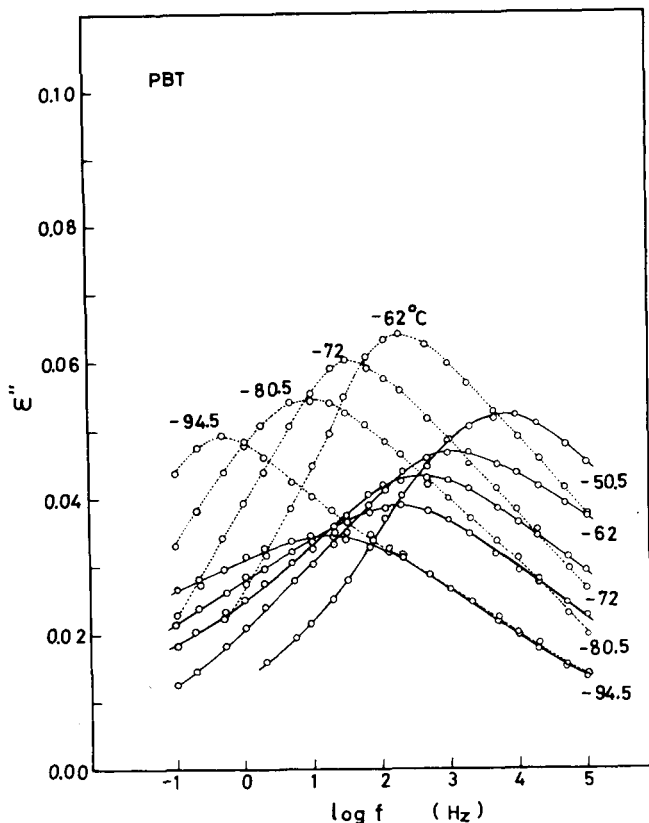


Fig. 3. Frequency dependence of dielectric loss ϵ'' at various temperatures. (···) wet sample, (—) dry sample of PBT.

EXPERIMENTAL

Sample Preparation

In this study three polyesters are used, namely, poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and polyethylene 2,6-naphthalate (PEN). The main chain of PEN is more rigid than that of PET because it contains the naphthalene ring instead of the phenylene ring. The main chain of PBT is more flexible than that of PET, since PBT contains two additional methylene units in the main chain.

The film sample of PET was supplied by Teijin Co., Ltd. The film was amorphous, unoriented, and 50 μm thick. Biaxially drawn PEN film (100 μm) was supplied by Teijin Co., Ltd. The amorphous and unoriented PEN sample was prepared by melting and subsequent quenching in ice water. A film sample of PBT (60 μm) supplied by Mitsubishi Kasei Co., Ltd. was used without further treatment.

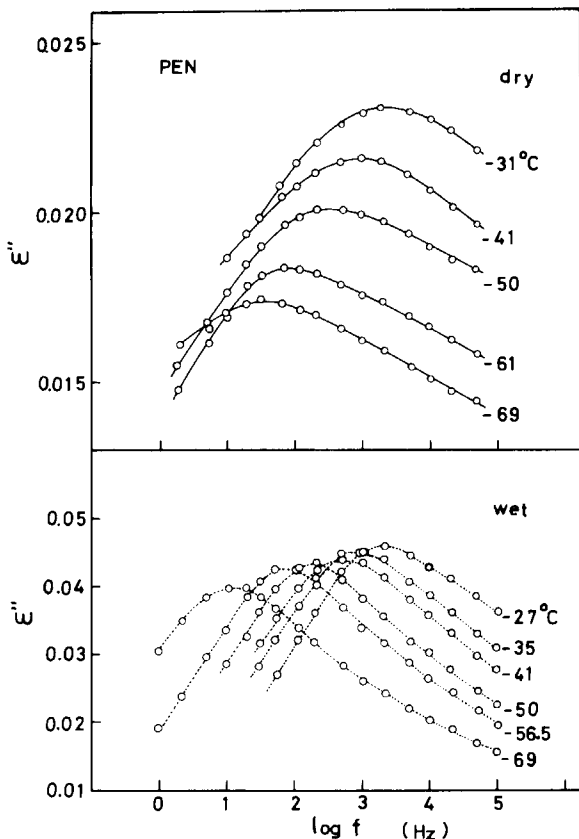


Fig. 4. Frequency dependence of dielectric loss ϵ'' at various temperatures. (···) wet sample, (—) dry sample of PEN.

Humidity Conditions

The dry samples of the polyesters were prepared by drying in a vacuum desiccator for two weeks until the weight remained constant. The wet samples were prepared at 20°C in a closed vessel which had relative humidity maintained at 90% and contained saturated aqueous solution of zinc sulfate for 24 hr.

Dielectric Measurement

The three-terminal method was employed to take accurate electrical measurements.⁴ A tin foil electrode was attached to a sample containing a thin coat of grease and the sample was enclosed in an environmental chamber. The dielectric measurements were carried out with conventional equipment, i.e., the General Radio type 1620-A, frequency range 30–10⁵ Hz and the Ando Denki bridge TR-4, frequency range 10⁻¹–20 Hz at temperature range of -95 to 20°C. In order to prevent absorption and desorption of water on the sample surface, the side surface of the films and the narrow slit between the main electrode and the guard electrode were coated with a thin layer of grease, and the top and bottom surfaces of the film were covered with tin foil.

The dielectric constants, before and after the measurements under variation

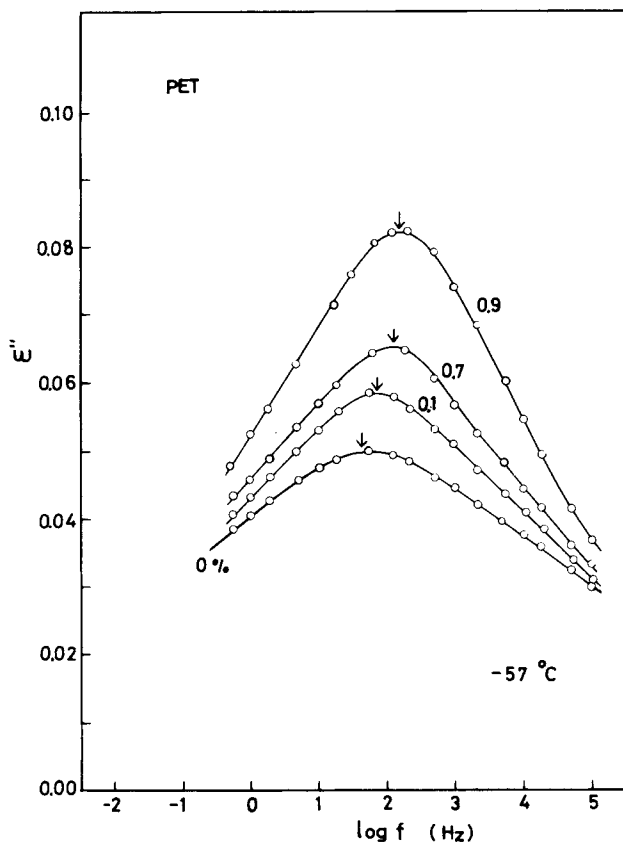


Fig. 5. Frequency of dependence of dielectric loss ϵ'' of PET at -57°C in which different amounts of water are absorbed.

of temperature, were in good agreement. This indicates that the amount of absorbed water in the sample did not change while the measurement was performed. Absorption and desorption of water did not take place during the measurement.

The density of each sample was measured at 23°C using a density gradient tube with *n*-heptane and carbon tetrachloride.

RESULTS AND DISCUSSION

Figure 1 shows the change of absorbed water content in polyesters against treating time at 90% relative humidity at 20°C . Absorbed water contents of PET and PBT become constant after about 10 hr; it took an additional 10 hr for PEN because of its larger thickness. The absorbed water contents after 24 hr of the samples were as follows: PET = 0.88, PBT = 0.48, and PEN = 0.84 wt %.

Figures 2, 3, and 4 show the frequency and dielectric loss ϵ'' at various temperatures for the wet (the dotted line) and dry (the solid line) samples of PET, PBT, and PEN, respectively. As ϵ'' in the dry sample of PEN is very small, the scale of longitudinal axis of the top chart of Figure 4 is extended by five times. As seen in the figures, local mode dispersion lines of wet samples have better

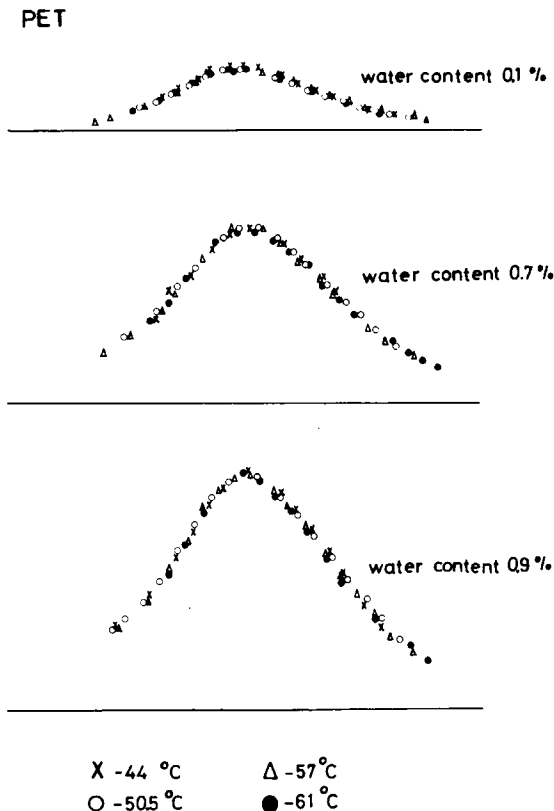


Fig. 6. Superimposed curves of the samples (PET) containing various amounts of absorbed water at (X) -44°C , (Δ) -57°C , (O) -50.5°C , and (\bullet) -61°C .

symmetry than the lines of dry samples and ϵ'' increases when the polyesters absorb water. This is not caused by the dipole of absorbed water but by change of mobility of the polymer chains, and consequently ϵ'' values of the polymer themselves are changed by water absorption.^{3,5} The frequency for the maximum dielectric loss f_{\max} was shifted by absorption of water. Behavior of f_{\max} of each sample is different. The f_{\max} of PET is shifted to the higher frequency with absorption of water (Fig. 2). As average relaxation time is the reciprocal of f_{\max} , absorption of water makes the relaxation time of PET shorter. In the case of PBT and PEN (Figs. 3 and 4) the $f_{s_{\max}}$ are shifted to lower frequency, i.e., the relaxation time becomes longer with increase of absorbed water.

The frequency dependences of dielectric loss ϵ'' of PET samples in which different amounts of water are absorbed at -57°C are shown (Fig. 5). As mentioned above, the f_{\max} of PET is shifted to higher frequency with increase of absorbed water. The ϵ'' values, which are obtained by subtraction of the ϵ'' values of dry samples from the ϵ'' values of wet samples, were plotted against different frequencies at various temperatures. The resultant curves are superimposable when the curves are shifted along the horizontal axis. The superimposed curves of the samples containing various amounts of absorbed water are shown in Figure 6. The figure reveals that although the height of the superimposed curves increase with an increase of water content in the sample, the width at a half the

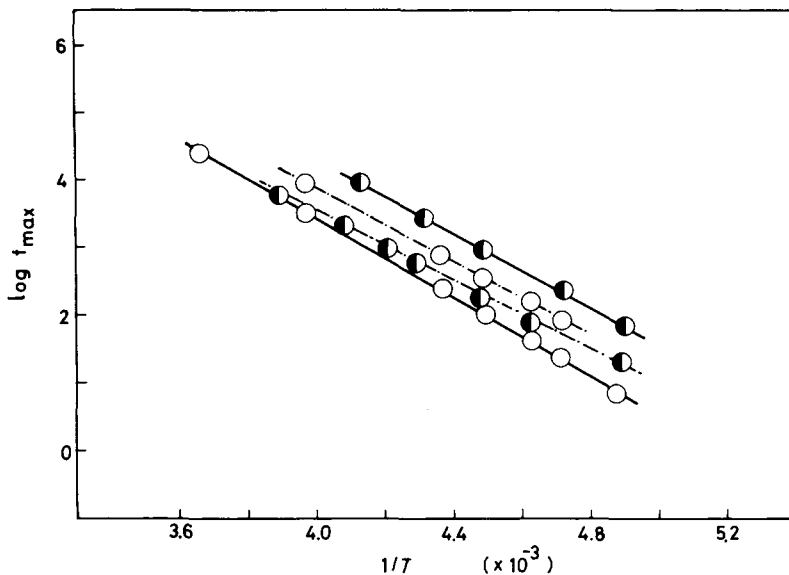


Fig. 7. Change of f_{max} against the reciprocal of absolute temperature. (—) Dry, (---) wet, (○) PET, (●) PEN.

height of every superposed curve is the same. Though the physical meaning of the superimposed curve is not clear at present, the fact that the shape of the curve is not changed by absorbed water content seems to suggest that the distribution of relaxation time is not affected by absorbed water content. This may be related to the state of absorbed water.

Figures 7 and 8 show the $f_{s_{max}}$ of the polyesters against the reciprocal of the absolute temperature. The activation energies are calculated from the slope

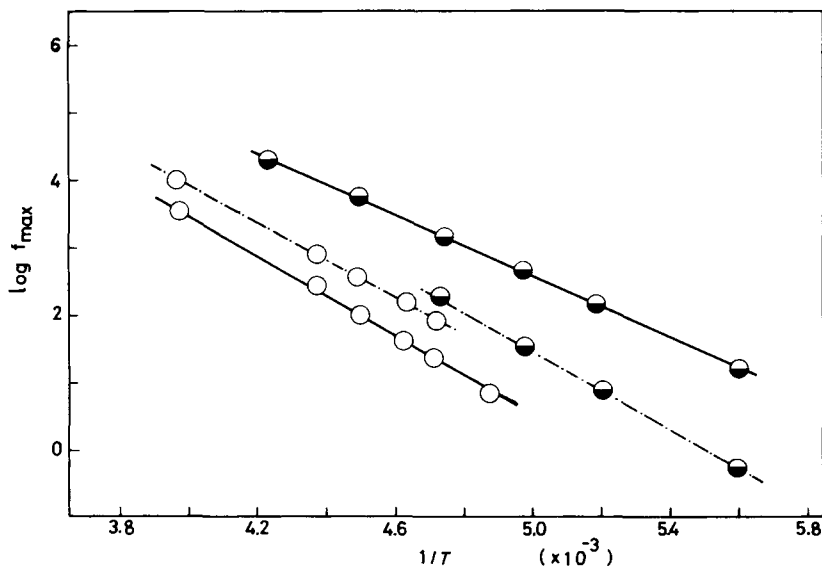


Fig. 8. Change of f_{max} against the reciprocal of absolute temperature. (—) Dry, (---) wet, (○) PET, (●) PBT.

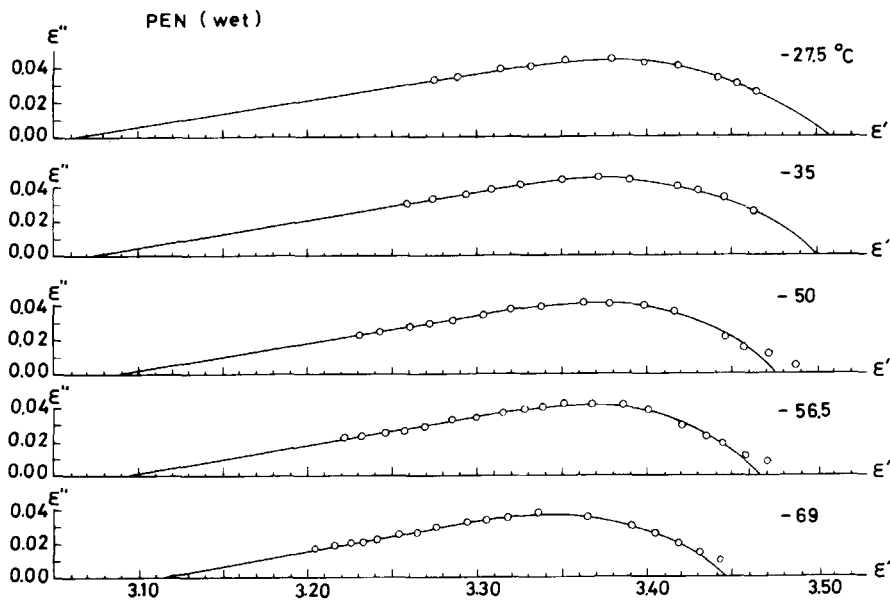


Fig. 9. Locus in complex plane of the skewed arc function for wet PEN.

of the lines and are about 12 kcal/mole for dry and wet samples. The values do not depend on amounts of absorbed water or on chemical composition of the main chain of the polyesters. Therefore, water in polyesters is not absorbed chemically, but physically.⁵

The complex plane plots for the local mode relaxation process of PEN at various temperatures are given in Figure 9. Figure 10 shows the relaxation process of PBT under dry and moist conditions. These typically polymeric dispersion lines are circular arcs at low frequencies and linear at high frequencies. The limiting low- and high-frequency dielectric constants ϵ_0 and ϵ_∞ , respectively, can be developed as the high- and low-frequency intercepts with the horizontal

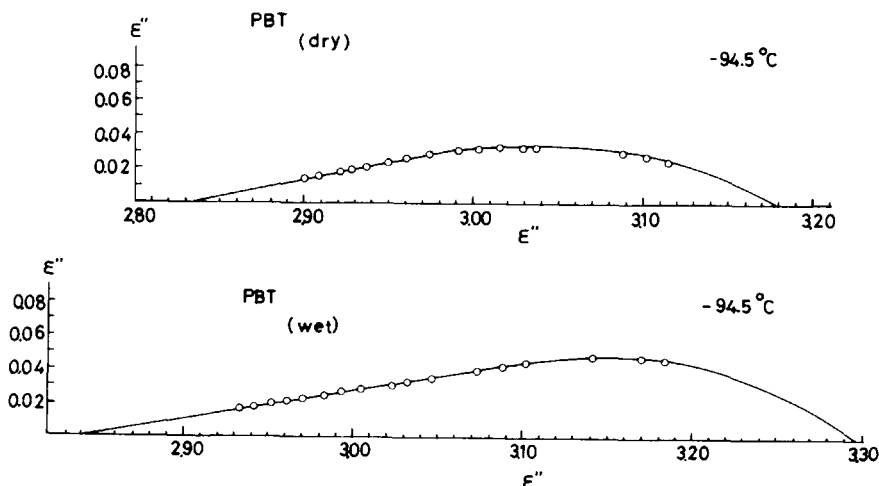


Fig. 10. Locus in complex plane of the skewed arc function for dry (top) and wet (bottom) PBT at -94.5°C .

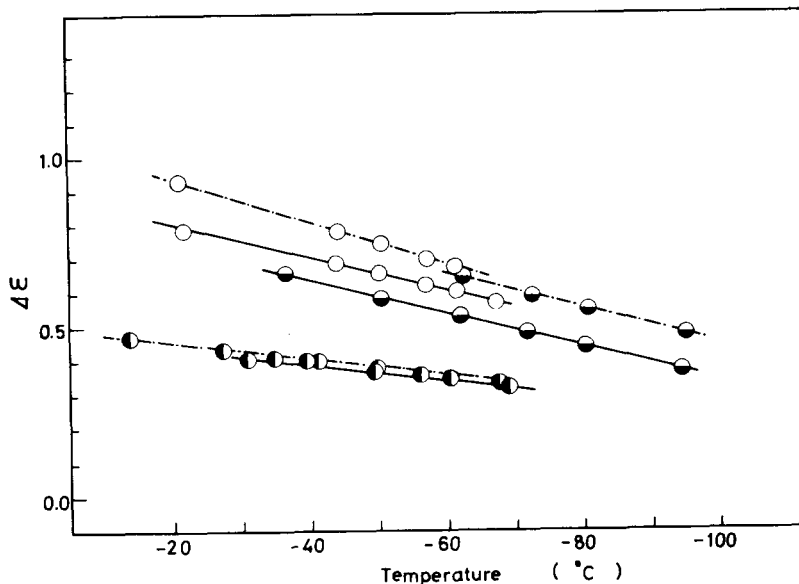


Fig. 11. Temperature dependence of dielectric increments. (—) Dry, (---) wet, (○) PET, (◐) PBT, (●) PEN.

axis by externalization of the lines. Using such ϵ_0 and ϵ_∞ dielectric increments $\Delta\epsilon (= \epsilon_0 - \epsilon_\infty)$ were obtained. The temperature dependence of $\Delta\epsilon$ of the polyesters are shown in Figure 11. Dielectric increments $\Delta\epsilon$ value of PET, PBT, and PEN increase with an increase in absorbed water content and decrease with decreasing temperature.

Figure 12 presents dielectric constant ϵ' at 1 kHz at various temperatures. Dielectric constants of the wet samples are larger than those of the dry samples, and ϵ' increases linearly with increasing temperature. This fact implies that the

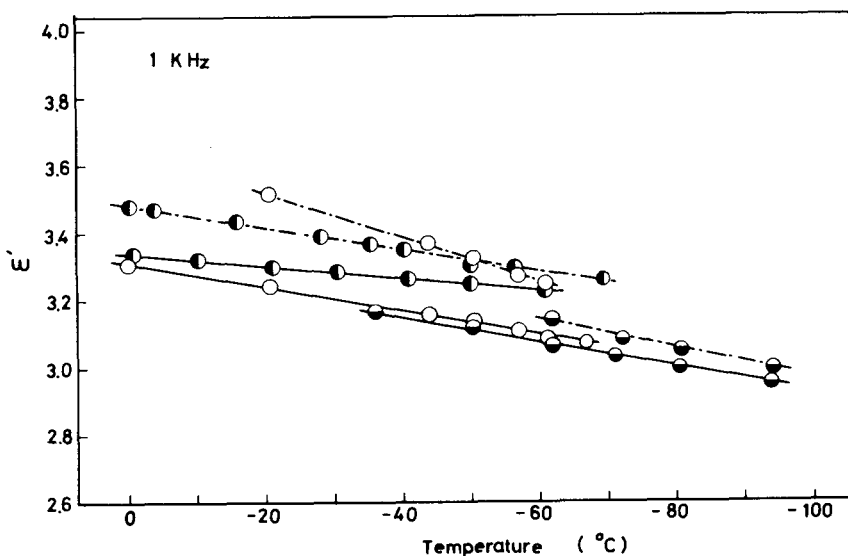
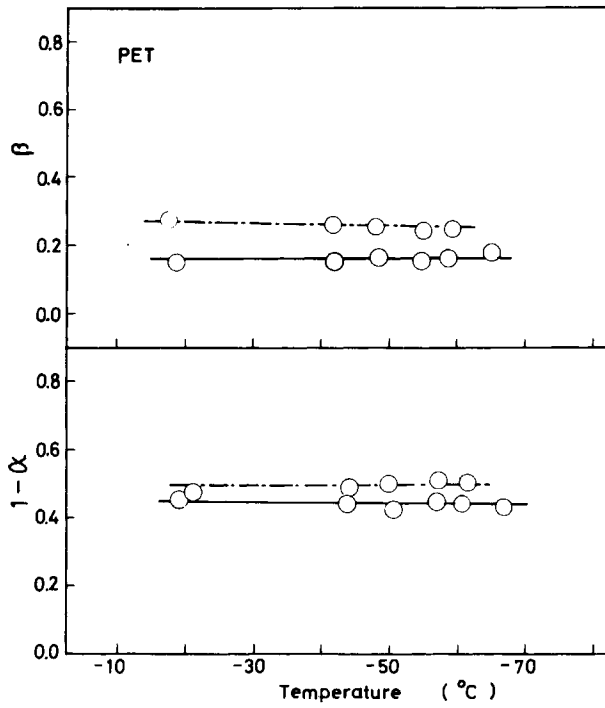
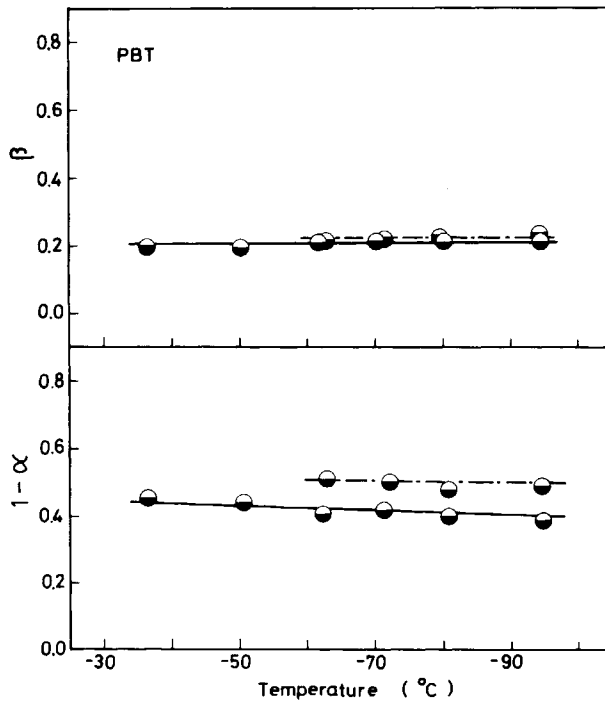


Fig. 12. Temperature dependence of dielectric constant ϵ' at 1 kHz. Symbols as in Fig. 11.



(a)



(b)

Fig. 13. (a) Temperature dependence of β and $1-\alpha$ in PET (the parameter in the Havriliak-Negami equation). (b) Temperature dependence of β and $1-\alpha$ in PBT (the parameter in the Havriliak-Negami equation). (c) Temperature dependence of β and $1-\alpha$ in PEN (the parameter in the Havriliak-Negami equation). (—) Dry, (---) wet.

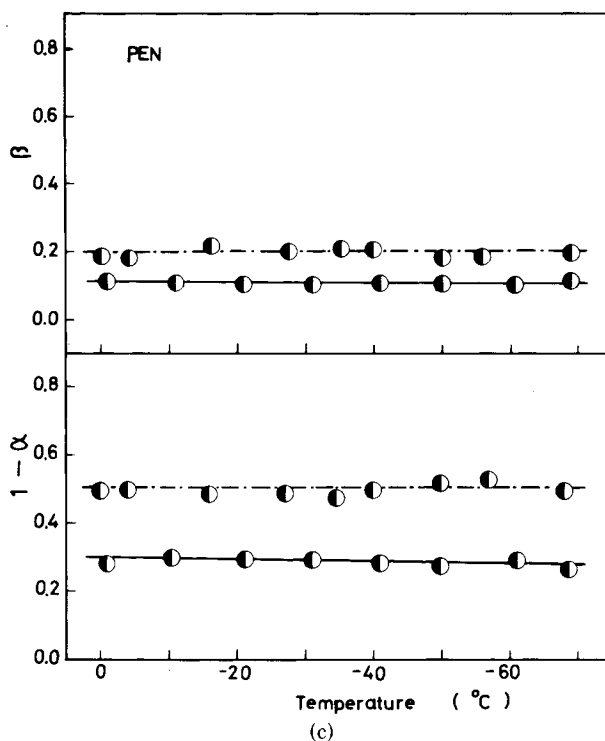


Fig. 13. (Continued from previous page.)

number of the dipole contributing orientation increases with increasing temperature.⁵

The dispersion curves of the tested polyesters given in Figures 9 and 10 cannot be fitted with a circular arc, nor with a skewed semicircle, because the dispersion is polymeric. In this article we consider the above-mentioned experimental results using an empirical equation proposed by Havriliak and Negami.⁶ It is a general representation for the three known dispersions, namely, Debye, circular arc, and skewed semicircle dispersions, as follows:

$$(\epsilon^* - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty) = \{[1 + (i\omega\tau)^{1-\alpha}]\}^{-\beta}$$

where ϵ^* , ϵ_0 , and ϵ_∞ are the complex dielectric constant, the limiting low- and high-frequency dielectric constant, respectively; ω is the circular frequency; τ is a relaxation time; and β and $1 - \alpha$ are constants in the range zero to unity.

Figures 13(a), 13(b), and 13(c) show the parameters, β and $1 - \alpha$, in the Havriliak–Negami equation at a temperature range between 0 and -70°C . As seen in the figures, the parameters $1 - \alpha$ and β do not depend on the change in temperature.

The parameter $(1 - \alpha)$ represents the width of dispersion (the width of dispersion of a relaxation time); the width increases as $(1 - \alpha)$ varies from unity to zero. The $(1 - \alpha)$ parameters of wet PET, PBT, and PEN are almost the same, and $(1 - \alpha)$ of dry PET and PBT are the same, and that of dry PEN is smaller. In other words, the distributions of relaxation times of the three wet polyesters are almost the same, and that of dry PET and PBT are also the same, while the width of the dispersion of dry PEN is broader than those of PET and PBT.

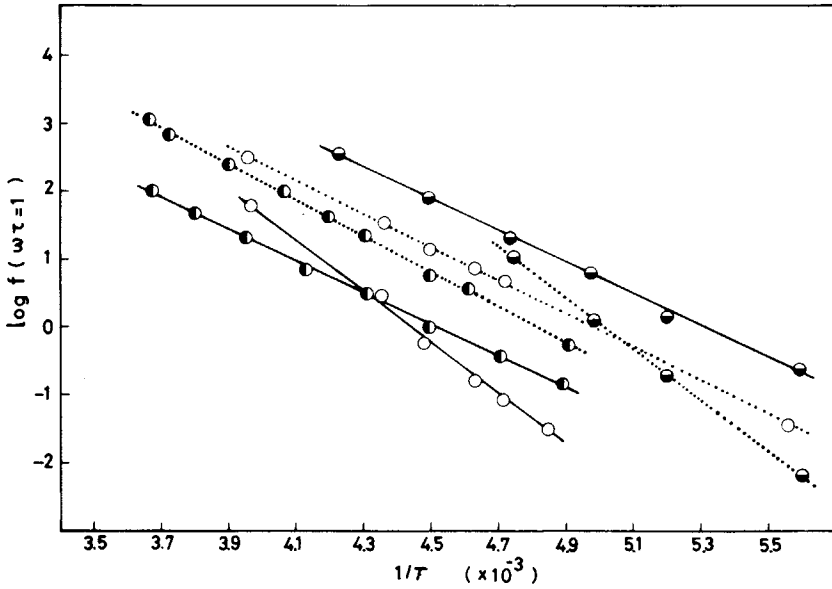


Fig. 14. Temperature dependence of the frequencies of PET, PBT, and PEN at $\omega\tau = 1$. Symbols as in Fig. 11.

The parameter β stands for skewness of the dispersion; the skewness increases as β varies from unity to zero. The β parameters of wet PBT and PEN are the same, and β of wet PET is larger. Hence, the shape of the dispersion of wet PET is close to a circular arc. The β s for dry samples is in a sequence of PBT > PET > PEN. Since methylene groups in the main chain of the molecule contribute to flexibility of the chain, flexibilities of the polymer molecules should be in the preceding sequence. Figures 13(a)–13(c) reveal that increments in flexibility of the molecule results in enhancement of β . The relationship between flexibility of chain molecules and β should be studied further.

Figure 14 shows the temperature dependence of the frequencies for PET, PBT, and PEN at $\omega\tau = 1$ using the Havriliak–Negami method. The frequencies at $\omega\tau = 1$ are lower than $f_{s\max}$ shown in Figures 7 and 8. In PET and PBT, the effect of water absorption on $f(\omega\tau = 1)$ and f_{\max} are the same and the tendency behavior of $f(\omega\tau = 1)$ and f_{\max} to water absorption is also the same. The f of PEN at $\omega\tau = 1$ is shifted to a higher frequency with absorption of water; the f_{\max} is shifted to lower frequency.

The relationship between the change of frequency at $\omega\tau = 1$ and change of the density (Table I) caused by absorption of water is considered below. While the densities of PET and PEN increase with increase of absorbed water, the density

TABLE I
Change in Density with Absorption of Water

	Wet	Dry
PET	1.338	1.337
PEN	1.332	1.330
PBT	1.287	1.289

of PBT decreases. The frequencies at $\omega\tau = 1$ of PET and PEN are shifted to higher regions with absorption of water, and that of PBT is reversely shifted to a lower region. The main chain of PBT is the most hydrophobic of the three substrates because of its methylene groups. Water may be absorbed strongly at the polar group ($-\text{C}=\text{O}$ group) in the main chain of PBT, increasing volume of the polyester. Therefore, the main chain of PBT containing water is assumed to be difficult to move, and consequently, its relaxation time becomes longer, and repulsion of absorbed water and the hydrophobic groups leads to decreasing density. In PET and PEN, water dissolves in the polymer chains filling intermolecular voids and acts as a lubricant. The main chains of PET and PEN contain the same repeating unit ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) as a water-soluble polymer, polyethylene oxide. Therefore, water absorption causes the density to increase and the f_s at $\omega\tau = 1$ is shifted to higher frequency with increase in absorbed water.

Intensive study to clarify the state and function of the absorbed water in the hydrophobic polyesters is in progress. This will be reported shortly.

CONCLUSION

Density and dielectric measurements of PET, PBT, and PEN, revealed that the dielectric constant, loss and increment, and the density of the polymers were considerably affected by absorption of water. The dielectric constant, loss, and increment increase with an increase in absorbed water. Relaxation times of the wet samples obtained from the frequencies at $\omega\tau = 1$ depend on the type of polyester. The f_s at $\omega\tau = 1$ of the polyesters (PET and PEN) containing hydrophobic group is shifted to a higher frequency by the absorption of water, while the f at $\omega\tau = 1$ of the polyester (PBT) containing more hydrophobic groups is shifted to a lower frequency. Densities of PET and PEN increase with absorption of water, while on the other hand, that of PBT decreases under wet conditions.

On the basis of the above results, we conclude that the physical properties of the hydrophobic polymers are affected considerably by a very small amount of absorbed water. Elucidation of the relationship between the physical properties and the amount of absorbed water is significant for designing industrial materials from hydrophobic polyesters.

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