

Dielectric Relaxations of Water Molecules Occluded in Polymeric Media: Some Hydrophobic Polymer Systems

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ABSTRACT: The contributions of water occluded in polymeric media to dielectric relaxation were examined in detail on hydrophobic polymer specimens exposed to 18.7 torr humidity (78.6% relative humidity) at 25°C. The polymers examined were polyethylenes, oxidized polyethylenes, polystyrene, poly(styrene-*co*-acrylonitrile), poly(methyl methacrylate), and poly(vinyl acetate). In these polymers, except for the polyethylenes, the dielectric water relaxation peak usually appeared in a temperature range around 200 K (at 1 kHz) with an activation energy of about 40 to 50 kJ mol⁻¹. The magnitude of dielectric dispersion due to water was calculated by the Onsager equation, assuming that occluded water molecules can rotate freely. The calculated values are about twice as large as the observed values for each system. This implies that the motion of water molecules is subject to certain hindrances from the polymeric media. In polyethylenes, especially in oxidized polyethylenes, the behavior of water molecules was markedly different from that in other polymers. Low- and medium-density polyethylenes absorbed virtually no water, while high-density polyethylene and oxidized polyethylenes absorbed a little. These polyethylenes exhibited two loss peaks at about 230 and 270 K with the activation energies of about 120 and 316 kJ mol⁻¹, respectively.

KEY WORDS Dielectric Water Relaxation / Water Absorptivity / Magnitude of Dielectric Dispersion / Dielectric Loss Peak / Polyethylene / Polystyrene / Poly(styrene-*co*-acrylonitrile) / Poly(methyl methacrylate) / Poly(vinyl acetate) /

Many authors have studied the influence of water on dielectric and mechanical relaxations in hygroscopic polymers including natural and biological polymers^{1,2} such as cellulose, proteins, and nucleic acids, and also in some textile fibers including nylon.³⁻⁷ In these polymers the major role of water appears to be the formation of hydrogen bonding between water molecules and polar groups in the polymers.

Many studies have also been carried out on hydrophobic and nearly nonpolar polymers such as polyethylene,⁸ poly(ethylene terephthalate),⁹ poly(alkyl methacrylate),¹⁰⁻¹² polybenzoxazole,¹³ and polystyrene and styrene containing copolymers.^{14,15} Particularly, Gall and McCrum¹⁰ in-

vestigated the dynamic mechanical relaxation in poly(methyl methacrylate) caused by water occluded in the polymer, and have designated it as the "water relaxation."

Generally, almost all polymers containing polar groups in the main chain or in the side groups, exhibit a secondary relaxation below their glass-transition temperature, T_g .¹⁶ Such a relaxation is often attributed to small-scale local motions such as torsional oscillation of the main chain or rotation of the polar side groups. However, in dielectric measurements on such polymers one often finds a small loss peak in the vicinity of the 200 K region, which eventually disappears after the polymer has been thoroughly dried. Accordingly, there arises the question as to what extent such secondary dielectric relaxations are due not to the intrinsic properties of

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the polymer under examination, but to the motion of water molecules occluded in the polymer. In this paper, we attempt to clarify the "dielectric water relaxation" process exhibited by several hydrophobic polymers such as polyethylenes, polystyrene, poly(styrene-co-acrylonitrile) random copolymers, poly(vinyl acetate), and poly(methyl methacrylate). We examined the mobility of water molecules and the magnitude of dielectric water relaxation as a function of water content in the polymer matrix. For this purpose we prepared wet and dry specimens under fixed conditions, and measured the complex dielectric constant of the specimens as a function of water content.

EXPERIMENTAL

Materials

High-Density Polyethylene (HDPE). A high-density PE (Hizex 1200 J from Mitsui Petrochemical Industries) was dissolved in boiling xylene and precipitated by cooling to remove additives. The precipitate was washed with xylene and acetone, and then dried *in vacuo* for three days. The molecular weight was about 1.2×10^5 as determined from the intrinsic viscosity $[\eta]$ in decalin at 130°C .¹⁷ The density was 0.956 g cm^{-3} .

Medium-Density Polyethylene (MDPE). The MDPE sample employed was UBEC 2020 from Ube Industries, an extremely low dielectric-loss PE, specially made for submarine cable use.¹⁸ The reported density was 0.931 g cm^{-3} and the degree of short chain branching was 9 ($-\text{CH}_3$) groups per 1000 ($-\text{CH}_2-$) units.¹⁸

Low-Density Polyethylene (LDPE). The LDPE sample employed was an UBE Z-194N LDPE from Ube Industries. The density was 0.925 g cm^{-3} and $[\eta]$ in 130°C decalin was $112 \text{ cm}^3 \text{ g}^{-1}$. These LDPE and MDPE samples were purified in the same way as the HDPE sample.

Oxidized Polyethylenes (OX..PE). Purified MDPE and HDPE samples were oxidized by irradiation with ultraviolet light. At first each sample was compression molded into a film of 0.2 mm thick, and then irradiated with a UV-light at 70°C for 4 h. The irradiated film was melted and remolded so as to distribute carbonyl groups uniformly throughout the PE matrix. The content of the carbonyl groups was determined to be 1/150 ($-\text{CH}_2-$) units for OXMDPE and 1/175 for

OXHDPE, by comparing the intensity of ($-\text{C}=\text{O}$) stretching relative to that of ($-\text{CH}_2-$) bending and/or wagging of the polymer with that of cyclopentadecanone.

Polystyrene (PS). A narrow-distribution polystyrene was purchased from Pressure Chemical Co. and used without further purification. The catalogue molecular weight was 3.9×10^5 and the M_w/M_n was 1.06.

Poly(styrene-co-acrylonitrile) Random Copolymers (SAN). Three copolymers, designated as SAN-I, SAN-II, and SAN-III, were prepared by suspension polymerization with benzoyl peroxide initiator at 90°C for 16 to 20 hours. The acrylonitrile content was 26.9, 30.6, and 36.9 wt%, respectively. The molecular weights of SAN-I and SAN-II were 2.0×10^5 and 2.2×10^5 , respectively, as estimated by gel-permeation chromatography with tetrahydrofuran (THF) carrier using PS elution standards. The value of SAN-III could not be determined by GPC, since the polymer was insoluble in THF. However, the $[\eta]$ value in DMF at 30°C was $172 \text{ cm}^3 \text{ g}^{-1}$, which was about the same as those of SAN-I and SAN-II.

Poly(methyl methacrylate) (PMMA). The PMMA sample was polymerized in toluene at -40°C with butyllithium initiator. The molecular weight was 5.4×10^5 as determined from $[\eta]$ in benzene at 30°C .^{17,19} The isotacticity, X_{ii} , was determined to be 76% by high-resolution NMR.

Poly(vinyl acetate) (PVAC). The PVAC sample was polymerized in methanol with an azobisisobutyronitrile initiator. The polymer was purified by repeated dissolution and precipitation with acetone and petroleum ether. The precipitate was dried in a vacuum oven at 40°C for three days. The molecular weight was determined to be 2.4×10^5 from $[\eta]$ in acetone at 30°C .¹⁷

Methods

Film Preparation. All films except that of PMMA were prepared by compression molding. The molding temperature was 140, 150, 180, and 180°C for PE's, PVAC, PS, and SAN's, respectively. Films of PMMA were prepared by solvent casting from a benzene solution. Films of about 0.3 mm thick were cut into disks of 5 cm diameter, and coated with evaporated-gold electrodes for dielectric measurements. The gold electrode was usually 50 to 60 nm thick, as estimated from the weight increase of the

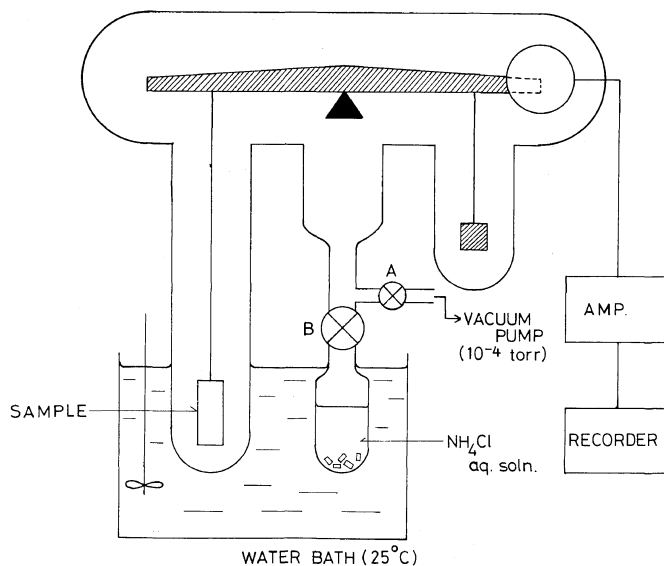


Figure 1. Schematic diagram of a Cahn Electrobalance system for measuring water sorption behavior of polymers.

film, and the surface resistivity was less than $10\ \Omega$. The electrode surfaces were observed by a Hitachi scanning electron microscope (Model S-301).²⁰

Dielectric Measurements on Wet and Dry Samples. All films with evaporated-gold electrodes were kept over a saturated ammonium chloride solution in a container at 25°C from one to four days. The solution provided an atmosphere of 18.7 torr and the relative humidity, RH, of $78.57 \pm 0.40\%$. Each film was weighed at every 10 hours to follow the process of water absorption. The film was then weighed precisely by an analytical balance and placed in a three-terminal cell for dielectric measurement. As described below, this procedure was effective only for PVAC, SAN, and PMMA, which absorbed fairly large amounts of water. Rates and maximum amounts of water uptake by other nonpolar polymers such as PE and PS were determined by a Cahn electrobalance. The wet film in the cell was dried at about 10^{-2} torr for 5 minutes to remove any water which might be deposited on the film surface. Then the cell was filled with helium and rapidly cooled to 80 K in a liquid nitrogen bath. A series of dielectric measurements on the wet film was started, with the temperature being raised successively, at a rate of about $0.4\ \text{K}\ \text{min}^{-1}$. After these measurements, the film was dried *in situ* for one to four days by connecting the cell to

a vacuum line (about 10^{-4} torr). The dried film was then subjected to a series of dielectric measurements as before. After this, the film was again weighed to determine a weight decrease. For the dielectric measurements we used a capacitance bridge (General Radio 1615-A) and an automatic capacitance bridge (Yokogawa-Hewlett-Packard) over a frequency range from 100 Hz to 100 kHz.

Absorption of Water by Polymers. The amount of water absorbed was measured with an analytical balance (Mettler B6GD) as described above or with a Cahn electrobalance. The latter was used for PE and PS, which absorbed only a very small amount of water. The sensitivity of the electrobalance was about 0.005 mg per one gram of polymer. The electrobalance was also used to study the kinetics of water sorption and desorption. Figure 1 shows a schematic view of such a setup. The assembly was placed in an air-conditioned room. A film of 100 to 800 mg was suspended from the arm of the balance, and dried thoroughly by evacuation through the stopcock A for one or two days. The stopcock A was then closed and a vapor of 18.7 torr (78.6% RH) was introduced through the stopcock B. The weight change in the film was recorded on a pen-recorder. When equilibrium was reached, the stopcock B was closed and the cell was reduced to a vapor pressure of 10^{-4} torr so as to observe the

desorption process.

RESULTS

Absorption and Desorption of Water

Absorption and Desorption Rates. Examples of

absorption and desorption curves are shown in Figure 2 for PS, SAN-II, and a few PE samples. No appreciable absorption of water is seen for either MDPE or LDPE films. For all samples except PS and SAN, the water absorption and desorption appear to reach equilibria within one day. For PS

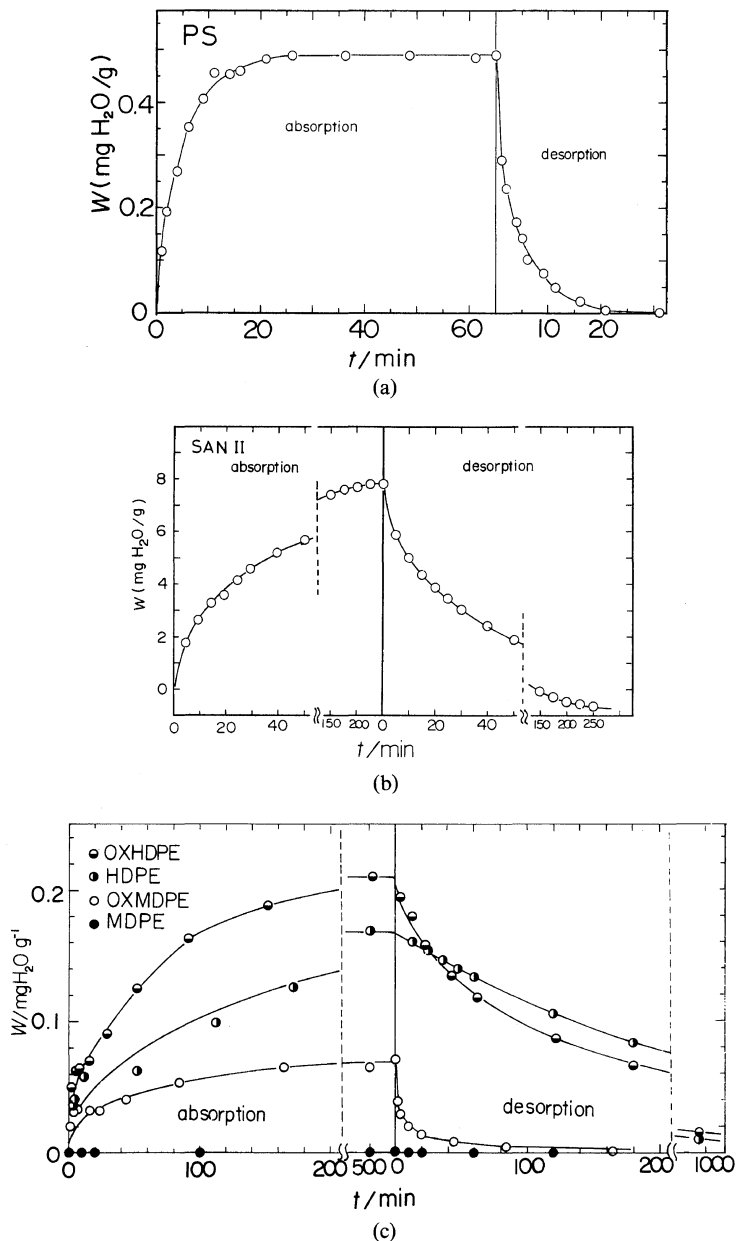


Figure 2. Water absorption and desorption under 18.7 torr humidity (78.6 %RH) at 25°C by (a) polystyrene, (b) SAN-II, and (c) polyethylenes.

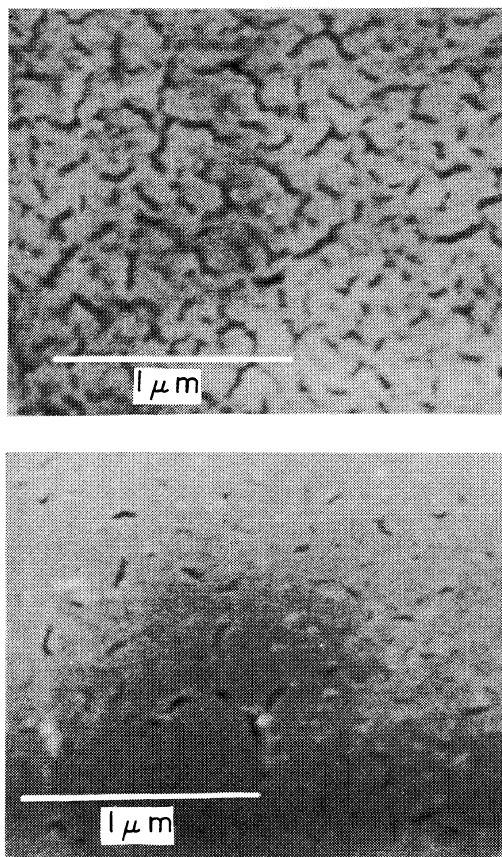


Figure 3. Scanning electron micrographs of PS surfaces coated with evaporated-gold electrodes of about 20 nm (top) and 60 nm (bottom) thick.

and SAN the rates were very rapid. Particularly for PS, almost 50% of the absorbed water was lost by drying within 5 minutes.

One might suspect that the rates as well as the equilibrium amounts of water uptake by the polymer films would be influenced by the evaporated-gold electrodes for dielectric measurements. We examined the sorption behavior of the coated films, and found that the rates as well as the amounts of water were not much different from those of uncoated films. Then we examined the surface of coated films by a scanning electron microscope. Examples of coated PS films used for dielectric measurements are shown in Figure 3, where fairly large cracks can be seen on the surface. Through these cracks, water molecules may easily reach the surface of bulk polymers, and hence the absorption rates may not

be very much retarded.

Amounts of Water Uptake. Equilibrium amounts of water, w_e , absorbed by polymers under a humidity of 18.7 torr at 25°C are listed in Table I. Residual amounts of water, w_r , in specimens after drying the water-saturated specimen (at 10^{-2} torr for five minutes) are also listed in Table I. We see a considerable difference between these values for PS. We thus employed the values of w_r for PS in the later for analyzing the relation between the magnitude of dielectric water relaxation, $\Delta\epsilon$, and the water content.

Dielectric Properties

Poly(vinyl acetate) (PVAC) and Poly(methyl methacrylate) (PMMA). Figures 4 and 5 show the temperature dependence of the dielectric loss factor, ϵ'' , for dry and wet specimens of PVAC and PMMA, respectively. The former shows a clear loss peak due to the dielectric water relaxation (at 1 kHz) in the temperature range around 200 K. The loss curve for the dry PVAC film, prepared by drying at 10^{-4} torr for 40 h, exhibits a small and broad loss peak at about 210 K. This peak, however, did not disappear even after extensive drying for an additional three days. At about 290 K, the value of ϵ'' for the wet specimen began to increase sharply, while that for the dry specimen did not. The increase in ϵ'' is obviously due to the onset of primary relaxation in PVAC, in which the absorbed water might act as a plasticizer to lower the primary loss peak temperature. In fact, wet PVAC specimens are leatherlike, whereas dry specimens are brittle at room temperature. The influence of absorbed water on the T_g and other mechanical properties will be described elsewhere.

In contrast to PVAC, the dielectric water relaxation in PMMA appears only as a small shoulder at about 230 K, in Figure 5. Since the stereoregularity of the PMMA sample is nearly isotactic, the secondary loss peak due to rotation of the side groups overlaps the primary loss peak. The peaks are found at about 310 and 360 K, respectively. The sharp increase in ϵ'' in the range above 250 K is due to these processes, in which the dielectric water relaxation peak is obscure. The insert in Figure 5 shows a difference $\Delta\epsilon''$ in the loss between the wet and dry PMMA specimens. The indicated $\Delta\epsilon''$ curves clearly exhibit water relaxation peaks at about 230 K. The $\Delta\epsilon''$ of these curves increased in a

Table I. Specifications of polymer samples and their water absorptivity

Code	Specifications	Water content mg g^{-1} under 18.7 torr (78.6 %RH) at 25°C ^a			
		w_s	w_r	w_{calc}	w_{lit} (ref)
LDPE	UBE Z-194N	<0.005	—	<0.001 (eq 4)	} Many data (22—26) including w_{calc} (by eq 3) =0.03—0.14 (26)
MDPE	UBEC 2020	<0.005	—		
HDPE	HIZEX 1200J	0.17	0.17		
OXMDPE	1 (C=O)/150 (CH ₂)	~0.05	~0.05		
OXHDPE	1 (C=O)/175 (CH ₂)	0.21	0.21		0.11 (25)
PS	Pressure Chem. PS	0.49	0.23	0.41—1.9 (eq 3)	
	$10^5 M_w = 3.9, M_w/M_n = 1.06$				
SAN-I	$10^5 M_v = 2.0, X_{\text{AN}} = 26.9\%$	5.2	5.0		
SAN-II	$10^5 M_v = 2.2, X_{\text{AN}} = 30.6\%$	7.2	6.1		2—3 (21)
SAN-III	($10^5 M_v = 2.0$) $X_{\text{AN}} = 36.9\%$	8.2	7.6		
PMMA	$10^5 M_v = 5.4, X_{\text{it}} = 76\%$	8.7	7.7	0.54—10.2 (eq 3)	1—4 (21)
PVAC	$10^5 M_v = 2.5$	17.9		0.47—3.5 (eq 3)	25.2 (28), 55 (29)

^a w_s , equilibrium content; w_r , residual amount after 5 min drying at 10^{-2} torr; w_{calc} , calculated by eq 3 or 4 with δ_p employed = 9.4 ± 0.9 , 11.0 ± 1.9 , and 10.0 ± 1.1 for PS, PMMA, and PVAC, respectively. w_{lit} , literature values.

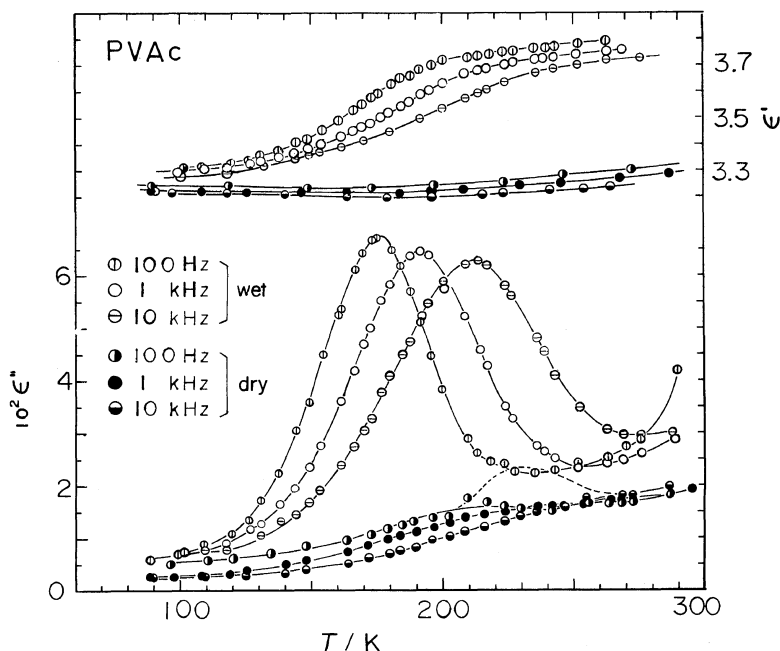


Figure 4. Temperature dependence of dielectric constant, ϵ' , and loss factor, ϵ'' , for wet and dry films of PVAc. The dashed curve represents Ishida's data.³²

range above 260 K. This may be ascribed to the shift of the primary loss peak of the wet PMMA specimen due to the plasticizing effect of the absorbed water.

Polystyrene (PS) and poly(styrene-co-acrylonitrile)s (SAN). Figure 6 shows the temperature dependence of ϵ'' for PS, while Figure 7 shows that for three SAN samples. As seen in the figures,

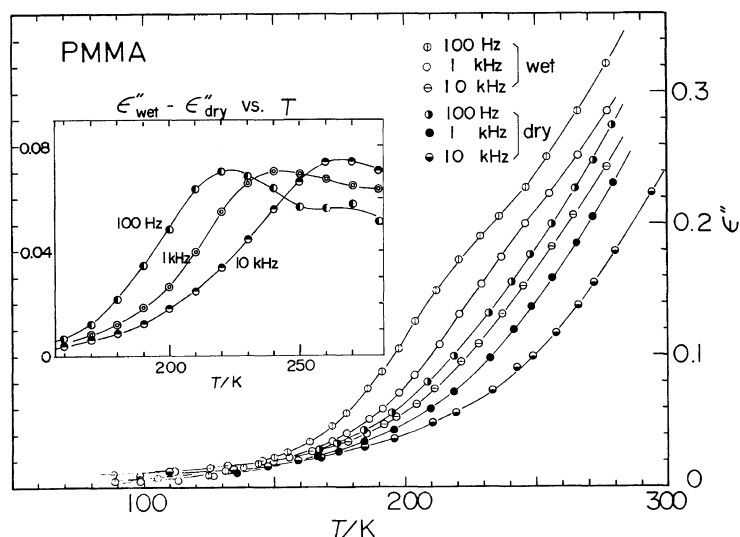


Figure 5. Temperature dependence of dielectric loss factor, ϵ'' , for wet and dry films of PMMA. The insertion shows the contribution of water, $\Delta\epsilon'' = \epsilon''_{\text{wet}} - \epsilon''_{\text{dry}}$.

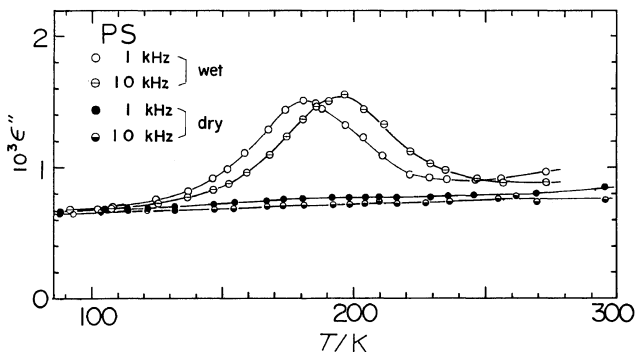


Figure 6. Temperature dependence of dielectric loss factor, ϵ'' , for wet and dry films of PS.

the wet films of these polymers clearly exhibit a loss peak due to the water relaxation, which is absent in the corresponding dry films. These loss peaks appear and disappear by changing the ambient humidity. The loss peak temperature, T_{max} , at 1 kHz for PS and SANs increases slightly with increasing acrylonitrile content, x_{AN} , (by weight fraction) as:

$$T_{\text{max}} = 71.7x_{\text{AN}} + 181 \quad (\text{in K})$$

The value of ϵ'' for dry SAN films increases with increasing temperature. This increase may be due partly to the onset of motions associated with the primary relaxation processes at the glass transitions of these polymers. When dry SAN samples were

allowed to absorb moisture by standing in open atmosphere for a few days, the samples exhibited a peak in mechanical loss tangent δ at 110 Hz at about 190 K. The $\tan \delta$ peak was located close to the dielectric water relaxation peak, and presumably the two peaks appeared by the same mechanism. Details of the mechanical water relaxation in this polymer are not yet clear.

Polyethylene (PE) and Oxidized Polyethylene (OX..PE) Samples. Figures 8, 9, and 10 show, respectively, the temperature dependence of ϵ'' for the dry and wet films of LDPE, for those of unoxidized and oxidized MDPEs, and for those of unoxidized and oxidized HDPEs. The wet films of

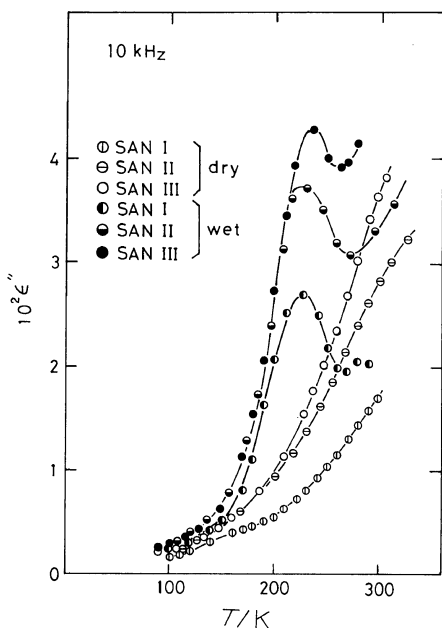


Figure 7. Temperature dependence of dielectric loss factor, ϵ'' , for wet and dry films of SAN-I, SAN-II, and SAN-III.

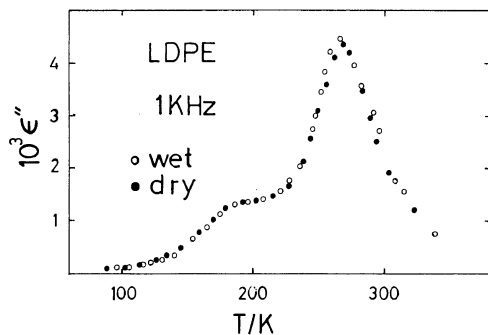


Figure 8. Temperature dependence of dielectric loss factor, ϵ'' , for wet and dry films of LDPE.

HDPE and OXHDPE were prepared by keeping the samples in an atmosphere of 78.6% relative humidity for 24 h. Measurements on dry films were carried out after treatment in the dielectric cell at 10^{-4} torr for 40 h at room temperature, or, in some cases, for 70 h at 70°C . However, the MDPE film was treated in a moist atmosphere for 70 h, and the wet MDPE film was dried in the dielectric cell at 10^{-4} torr for 70 h at 70°C . An unoxidized LDPE film was also treated in the same manner as was the

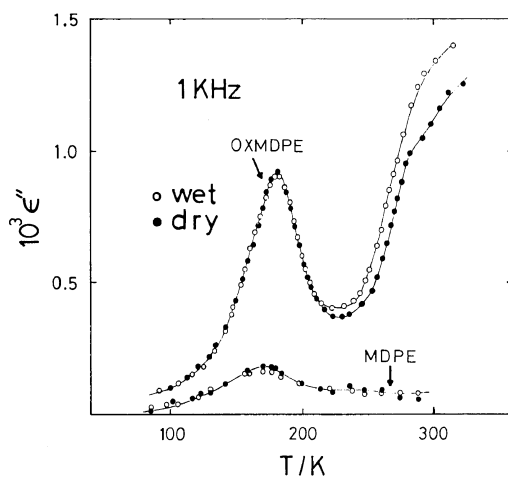


Figure 9. Temperature dependence of dielectric loss factor, ϵ'' , for wet and dry films of unoxidized and oxidized MDPEs.

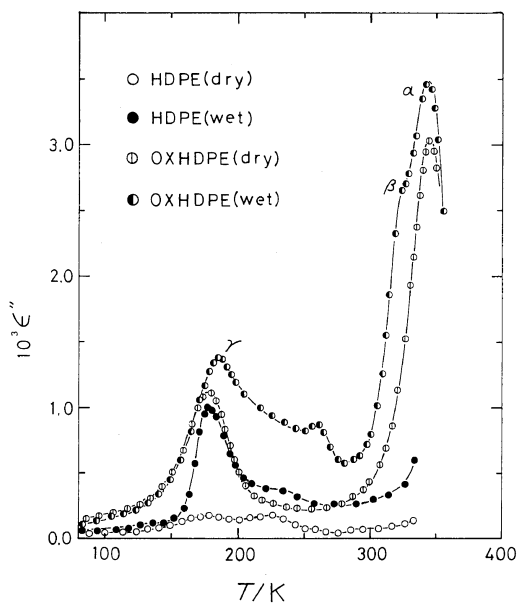


Figure 10. Temperature dependence of dielectric loss factor, ϵ'' , for wet and dry films of unoxidized and oxidized HDPEs.

MDPE film. As shown in Figures 8 and 9, hardly any influence of water on ϵ'' could be detected in the unoxidized LDPE and MDPE films. Furthermore, we prepared a wet MDPE film by submerging it directly into warm water at 40°C for 70 h, and examined its dielectric behavior. However, no

Table II. Magnitude of dielectric dispersion, $\Delta\epsilon$, apparent activation energy, E_a , and loss peak temperature, T_{\max} , at 1 kHz for dielectric water relaxations in various polymers

	$10^3 \Delta\epsilon_{\text{obs}}$	$10^3 \Delta\epsilon_{\text{calc}}$	$E_a/\text{kJ mol}^{-1}$	T_{\max}/K
HDPE	6.5	7.9	121	177
OXHDPE	5.3	9.5	120 ± 50	209
PS	5.1	11.5	46	181
SAN-I	100	250	42	200
SAN-II	134	280	41	203
SAN-III	160	370	43	207
PMMA	250	330	51	242
PVAC	320	770	38	192

influence on ϵ'' could be found either even after this treatment.

As shown in Figures 8, 9, and 10, the most significant contribution of water molecules to the dielectric behavior of PEs is seen for HDPE samples. The loss peak commonly found in dry PE samples at about 180 K is due to the γ -relaxation process which is intrinsic in PE but not in water.¹⁶ A wet HDPE film, on the other hand, shows a significant increase in the height of the loss peak at 180 K.

In Figures 9 and 10, we notice that a slight modification of PE chains by, *e.g.*, oxidation drastically changes the dielectric behavior of both dry and wet films. The γ -relaxation peak is significantly enhanced by oxidation in the dry films of MDPE and HDPE. These wet films exhibit a somewhat larger γ -peak and also a new peak in the region from 230 to 260 K region. Another peak found at 350 K in a dry OXHDPE film also increases significantly in a wet OXHDPE film. The contribution of water to ϵ'' toward HDPE and OXHDPE was very much different from that for other LDPE and MDPE as well as for other polymers such as PS, PVAC, and PMMA.

Magnitudes of Dielectric Dispersion for the Water Relaxation Processes. From the dielectric loss data given above, we calculated $\Delta\epsilon_{\text{obs}}$, the magnitude of dielectric dispersion or the strength of dielectric relaxation due to water molecules, using the equation¹⁶:

$$\Delta\epsilon_{\text{obs}} = (2E_a/\pi R) \int_0^\infty \Delta\epsilon'' d(1/T) \quad (1)$$

where $\Delta\epsilon'' = \epsilon''_{\text{wet}} - \epsilon''_{\text{dry}}$ at a fixed frequency, and E_a and R are the apparent activation energies and

the gas constant, respectively. The results are listed in Table II. For comparison, we calculated the values of $\Delta\epsilon_{\text{calc}}$ from the amounts of water occluded in the films, w_t , using Onsager's equation,¹⁶ and assuming the free rotation of water molecules in the polymer:

$$\Delta\epsilon_{\text{calc}} = \frac{4\pi N\mu^2 3\epsilon_0(\epsilon_\infty + 2)^2}{27kT (2\epsilon_0 + \epsilon_\infty)} \quad (2)$$

where N is the number of dipoles (in this case, water molecules) with the moment μ in unit volume, k is the Boltzmann constant, and ϵ_0 and ϵ_∞ are the dielectric constants at the low and high frequency sides of a particular relaxation process, respectively. Since the difference, $\epsilon_0 - \epsilon_\infty$, is small for the dielectric water relaxation, we assumed that the values of ϵ_0 and ϵ_∞ were equal to the dielectric constant, ϵ' , of the wet polymer at the loss peak

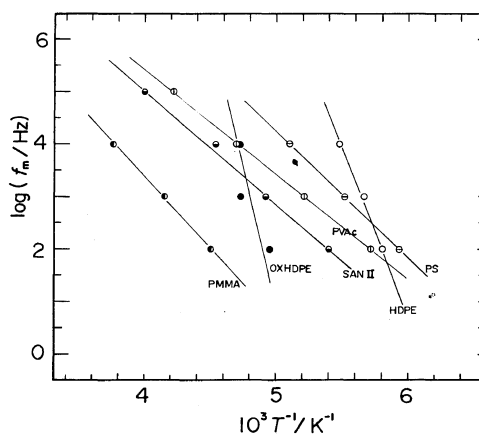


Figure 11. Plots of \log (frequency f) versus reciprocal loss peak temperature, $1/T_{\max}$, for dielectric water relaxation in various polymers.

temperature. The values of $\Delta\epsilon_{\text{calc}}$ are also listed in Table II.

Apparent Activation Energies. Figure 11 shows plots of $\log(\text{frequency } f)$ versus reciprocal absolute temperature, $1/T_{\text{max}}$, at the loss peaks of the dielectric water relaxations examined here. These plots are often called activation plots. Apparent activation energies, E_a , determined from the slopes of the activation plots are also listed in Table II. The values of E_a are about 45 kJ mol^{-1} for most of the polymers examined except HDPE and OXHDPE. The values for the PE samples are unusually large, compared with those for ordinary secondary relaxation processes found in various polymers.¹⁶

DISCUSSION

Solubility of Water in Polymers

Although a considerable amount of data on the equilibrium amount of water absorbed or the solubility of water in polymers can be found in the literature,²¹ reliable data are rather few and available only on several polyethylenes,²²⁻²⁶ PS,²⁷ and PVAC.^{28,29} These data are also listed in Table I. According to Klute,²⁶ the volume fraction, ϕ_w , of water absorbed by a polymer may be related to the Hildebrand solubility parameter of water, δ_w , and to that of the polymer, δ_p ,¹⁷ as follows,

$$-\ln \phi_w = 1 + 18(\delta_w - \delta_p)^2/RT. \quad (3)$$

We employed this equation to estimate ϕ_w and computed the water solubility, w_s , for the present systems from,

$$w_s \cong (\rho_w/\rho_p)\phi_w$$

where ρ_w and ρ_p are the densities of water and the polymer, respectively. As shown in Table I, the calculated values of w_s widely scatter, since the reported values of δ_p ¹⁷ scatter. Klute calculated the solubility of water in polyethylene from eq 3 under the assumption that water molecules are absorbed only in the amorphous region of the PE sample,²⁶ and showed that the solubility varies from 0.14 to 0.03 mg g^{-1} , depending on the value of δ_p employed and the degree of crystallinity of the particular sample. On the other hand, McCall *et al.*²⁵ measured the solubility of water in linear and branched polyethylenes and found that the solubility was less than 0.05 mg g^{-1} polymer. They concluded that the fairly large solubility values

reported in previous papers²²⁻²⁴ might be due to certain polar groups produced in polyethylenes by undesirable side reactions such as oxidation and also to polar residues of catalyst fragments. In this connection, we computed the water solubility, w_s , in pure polyethylene from Schatzberg's water sorption data for pure paraffins.³⁰ Schatzberg found that w_s (at 25°C) in *n*-alkanes from C_7 to C_{16} decreases with increasing molecular weight, M , as,

$$\log w_s = -1.76 \times 10^{-3} M + 2.08 \quad (4)$$

where w_s is given in parts per million (ppm) by weight. This equation suggests that the water solubility in pure polyethylenes is at most of the order of one ppm. As shown in Figure 2, the MDPE sample absorbed practically no water, whereas the HDPE sample absorbed 170 ppm. This may be attributed to the difference in the content of polar atoms attached directly to the chains or of the catalyst fragments, as pointed out by McCall *et al.*²⁵

Table I shows that the water solubility, w_s , in SAN increases with increasing acrylonitrile content, x_{AN} , and can be approximately represented by,

$$10^3 w_s = 0.49 + 13.5x_{\text{AN}} + 20(x_{\text{AN}})^2 \quad (5)$$

where w_s and x_{AN} are given in weight fraction. The second term of this equation indicates that a 1% increase in the content of polar groups produces an increase in water solubility of about 0.1 mg per 1 g polymer. This value is of the same order of magnitude as the water content in oxidized polyethylenes. We examined the relation between the water solubility and the dipole moment μ of the polar groups of a given polymer multiplied by the number N of such groups in a unit volume. Although the water solubility certainly increases with increasing $N\mu$, no quantitative relationship was found.

Magnitude of Dielectric Dispersion

If water molecules can move freely in the polymer matrix, the contribution of water molecules to the magnitude of dielectric dispersion, $\Delta\epsilon$, should be given by eq 2. Figure 12 shows plots of $\Delta\epsilon_{\text{calc}}$ versus $\Delta\epsilon_{\text{obs}}$ constructed from the data in Table II. Apparently the latter values are about one half the former, particularly in polar polymers. Several authors^{3,9,31} calculated that the water relaxation originates from a coupled motion of water molecules with the polar groups of the polymer. In

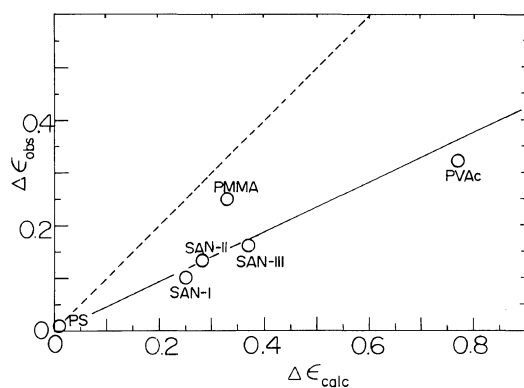


Figure 12. Plots of observed *versus* calculated magnitudes of dielectric dispersion, $\Delta\epsilon_{\text{obs}}$ *versus* $\Delta\epsilon_{\text{calc}}$, due to the water relaxation for various polymers.

other words, the motion of water molecules activates the motions of the polar groups and *vice versa*, giving rise to an additional contribution to the dielectric water relaxation. If this is the case, the value of $\Delta\epsilon_{\text{obs}}$ should be larger than that of $\Delta\epsilon_{\text{calc}}$ estimated from eq 2, unless each of the water molecules is tightly bound by a polar group in such a way that their dipole moments cancel each other out. Our present data suggest that either such coupled motions do not take place or occur to a limited degree.

Since the values of $\Delta\epsilon_{\text{obs}}$ are smaller than the values of $\Delta\epsilon_{\text{calc}}$ calculated by eq 2 for the free rotation of water molecules, the motion of water molecules must be subject to hindrances, which may be of two types. One is the hindrance that restricts the range of angle of oscillation of water molecules, and the other is the hindrance due to the difference in the free energies of water molecules oriented in different directions.

With the former, the system should exhibit an additional loss, since as the temperature is raised, the water molecules would eventually become fully activated and overcome the hindering energy barrier. At room temperature, the water molecules are moving rather freely through the polymer and therefore are fully activated. However, below room temperature, the loss peak due to the water relaxation appears only at about 200 K for all the polymers except oxidized polyethylenes. Therefore the fact that $\Delta\epsilon_{\text{obs}}$ is smaller than $\Delta\epsilon_{\text{calc}}$ can presumably be ascribed to the latter hindrance. If this is the case we may apply a two-site model. If a

molecule has preferred orientations in a few discrete directions, those orientational states may be called "sites." If there are two sites for each water molecule, the magnitude of dispersion is given by,³⁵

$$\Delta\epsilon = [(4\pi N\mu^2)/(3kT)][(\epsilon' + 2)/3]^2 [4K/(1 + K)^2] \quad (6)$$

where K is the Gibbs factor, $\exp(-\Delta G/kT)$, with ΔG being the difference in free energy between the two sites. Although we have no definite evidence for the existence of these water molecules sites in polymers, we find from eq 6 that the order of ΔG for the present systems is about 3 kJ mol^{-1} .

Comparison with Literature Data

Poly(vinyl acetate) (PVAC). Ishida *et al.*³² assigned the peak at 220 K at 10 kHz in the dielectric loss curve of PVAC to the motion of the side groups accompanied by the local distortion of the main chains, and called it the β process. In Figure 4, their data for the β relaxation region³² are shown by a dashed curve. The curve clearly shows a peak, in contrast to that of dry PVAC obtained in the present study. For the moment, it is not certain whether the β peak reported by Ishida *et al.* is due entirely to the water relaxation. In fact, a very small but broad peak in dry PVAC in this temperature range did not disappear even after extensive drying of the specimen. However, the magnitude of dispersion for the β process seems too small to be assigned only to the motion of the side groups which have fairly large dipole moments. The loss peak temperature, T_{max} , shifted to a lower temperature with increasing water content. This result might indicate an interaction between water molecules and the polar side groups of PVAC.

Poly(methyl methacrylate) (PMMA). Gall and McCrum¹⁰ measured the dynamic mechanical loss due to water relaxation in stereoregular PMMA. The loss peak temperature that they found for an isotactic PMMA treated in the atmosphere of 50% RH is in agreement with that estimated from our dielectric water relaxation in the wet PMMA sample.

Polystyrene and poly(styrene-co-acrylonitrile). The relaxation process at 200 K in PS was termed the γ process.³¹ This process has been studied by many authors by dielectric, nuclear magnetic resonance (NMR), and ultrasonic methods, and is concluded^{14,15,31} that the γ process involves two

processes which overlap at about 200 K. One process is due to the rotational motion of phenyl groups, and the other to impurities such as water. Since the rotation of phenyl groups does not accompany a change in dipole moment, the associated process can hardly be detected by the dielectric method. As shown in Figure 6, a dry PS specimen shows a flat loss curve in the region about 200 K, revealing no γ loss peak. Therefore, the dielectric γ relaxation in PS should not be due to the intrinsic properties of PS but to water molecules. As shown in Figure 2, PS absorbs water rather rapidly. This fact makes it difficult to remove water thoroughly from PS films and thus to analyze dielectric relaxation data on this polymer.

Dielectric measurements on random copolymers of styrene and acrylonitrile were carried out by Cook *et al.*³³ and Sazhin *et al.*¹⁴ Cook reported that a loss peak at about 200 K, which they designated as the β process, is due to the local motion of acrylonitrile groups. Based on this idea, they proposed a method for estimating x_{AN} from the magnitude of dispersion $\Delta\epsilon$ of the β process.³³ On the other hand, Sazhin ascribed the β process to the motion of water molecules rather than to that of acrylonitrile groups.¹⁴ As shown in Figure 7, Sazhin's conclusion appears to be more plausible. Although Cook *et al.*³³ did not specifically mention how the drying was effected, their specimens might contain moisture. If so, Cook's conclusion is not acceptable. Since the magnitude of dispersion, $\Delta\epsilon$, of the β process is related to water content, which in turn is related to x_{AN} as given by eq 5, the $\Delta\epsilon$ associated with the water relaxation should have the same relation with x_{AN} .

Polyethylenes. As shown in Figures 2, 8, 9, and 10, LDPE and MDPE films hardly absorb water, while HDPE film absorbs water to some extent. These results suggest that the water absorptivity of PE depends neither on the degree of crystallinity nor on the degree of branching. In these figures, we also notice that the dielectric water relaxation behavior changes very much with a slight modification of the polymer. This fact implies that the solubility and the mobility of water molecules in the polyethylene matrix are primarily influenced by the affinity between water molecules and foreign atoms either bonded to the chains or present as impurities. Recently, Nakagawa *et al.*⁸ reported on the same MDPE (UBEC 2020) as used here, stating that

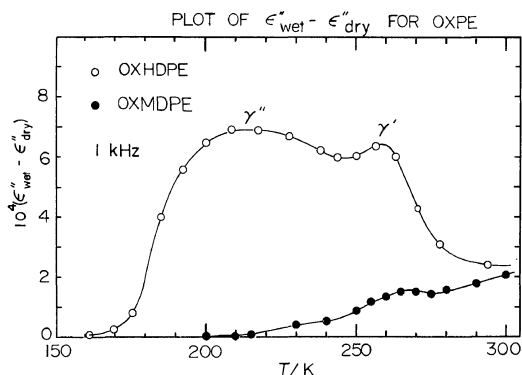


Figure 13. Plots of the contribution of dielectric water relaxation, $\epsilon''_{\text{wet}} - \epsilon''_{\text{dry}}$, versus temperature for OXHDPE and OXMDPE films.

when treated by immersion in hot water of 90 to 100°C for about one hour, the film showed a new loss peak at around 230 K (at 30 kHz). They assigned the new peak to clustered water molecules dispersed in the PE matrix and the other peak at 180 K to free water molecules. As mentioned before, we treated our MDPE film by directly immersing it in water at 40°C for 70 h. However, since the film did not absorb enough water by such mild treatment, the loss peaks they reported were not observed.

The loss curve for the wet OXHDPE film is rather complicated. Recently, Ashcraft and Boyd³⁴ carried out dielectric measurements on oxidized and chlorinated PE. The loss curve for the dry OXHDPE shown in Figure 10 closely resembles their results. As can be seen in this figure, the influence of water on the loss curve for OXHDPE is different from that for HDPE. Figure 13 shows plots of the difference, $\epsilon''_{\text{wet}} - \epsilon''_{\text{dry}}$, versus temperature for the OXHDPE film. The curve may be resolved into a broad loss peak designated as γ'' and a sharp loss peak, γ' . Apparent activation energies for the γ'' and γ' processes are about 120 and 315 kJ mol⁻¹, respectively. These values are much larger than that for the original γ process ($\cong 50$ to 65 kJ mol⁻¹).^{16,34} Therefore, these water relaxation processes might be quite independent of the intrinsic γ process. Also they might be quite different from the processes found in other polymers, if inferred from the large difference in E_a between PE and other polymers (*cf.*, Figure 11). Highly nonpolar media such as PE containing no impurities virtually absorb no water.

Even if they do, the absorbed water may not be able to exist as free and isolated molecules but may form clusters of various sizes. On the other hand, nonpolar media with certain polar impurities such as HDPE and oxidized PE can uptake water. The absorbed water molecules are presumably bound to the impurities, and form clusters as well. However, the clusters are not necessarily bound to the impurities. The clusters formed may contribute to the dielectric relaxation to an extent nearly the same as that by the free molecules, but may have a larger activation energy of the relaxation.

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