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Dielectric Relaxations in Plasma-Polymerized Hydrocarbons and Fluorocarbons

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ABSTRACT

The dielectric behavior of plasma-polymerized ethylene (PPE), ethylene/acetylene (PPEA), ethane/vinyl chloride (PPEVC) and tetrafluoroethylene (PPTFE) was studied over a frequency range of 10^2 to 10^5 Hz between -150 and 100°C. After exposure to the atmosphere, each of the polymers exhibited a pronounced loss peak. This relaxation process was designated as the γ_p process, and was attributed to the local mode motion of several molecular segments. The average activation energy for all four polymers was found to be 13.8 kcal/mole. It was proposed that oxidation introduces carbonyl groups into the nonpolar polymer chain. The added polar carbonyl groups then act as tracers to render the molecular motions observable by dielectric measurements. The presence of these carbonyl groups was confirmed by concomitant IR spectroscopic determinations. Comparison of the experimental data with the Kirkwood-Froelich theory was found to be satisfactory.

INTRODUCTION

The synthesis of polymers in a low-pressure electrical discharge is often referred to as plasma polymerization. By using this technique, highly cross-linked, pinhole-free polymer films have been formed from a large number of organic and organometallic vapors. Because of their good dielectric properties, plasma-polymerized films have been found to be useful as thin film insulators and capacitors [1-5]. Knowledge of the dielectric behavior of these materials is important not only for these applications, but also because it offers an insight into the molecular structure of the polymer. Previous workers have reported on the dielectric data for plasma-polymerized styrene [6, 7], acrylonitrile [4] and hexamethyldisiloxane [8]. In this work, we have investigated the dielectric relaxations in several plasma-polymerized hydrocarbons and one fluorocarbon. An attempt is made to identify quantitatively the origin of these relaxations in relation to the structure of the plasma-polymerized materials.

EXPERIMENTAL

Details of the plasma polymerization reactor have been presented previously [9]. Essentially it consists of an evacuable bell jar containing two parallel disk electrodes. The glow discharge is sustained by an International Plasma Corporation Model 3001 Radiofrequency Generator operating at 13.56 MHz delivering up to 150 W power. Aluminum foil and NaCl crystals were used as substrates for subsequent dielectric and IR measurements, respectively. Gaseous monomers (CP grade) were purchased from the Matheson Gas Co.

The dielectric instrument consists of a Model 716C capacitance bridge, Model 1232-A tuned amplifier and null detector, and a Model 1310-B oscillator, all manufactured by the General Radio Company. A Balsbaugh LD3 three terminal parallel plate capacitor was used as the dielectric cell. Samples were prepared by cutting two disks from the polymer-coated aluminum foil substrate, and placing the disks in the dielectric cell so that the uncoated sides were in contact with the capacitor plates. The cell assembly was placed in a Statham Model SD30 Temperature Chamber, which can provide constant temperatures between -180 and 200°C.

Infrared spectra of the polymer were obtained by depositing a film on a NaCl crystal. The spectra were recorded with a Perkin-Elmer Model 137 Spectrophotometer.

RESULTS AND DISCUSSION

In Fig. 1 are shown the dielectric loss curves at 10^2 , 10^3 , 10^4 , and 10^5 Hz for plasma-polymerized ethylene (PPE). It can be seen in Fig. 1(a) that for the freshly polymerized PPE, there is only a very broad and weak loss maximum near -20°C for the 1 kHz curve. The rise in $\tan \delta$ above 50°C is most likely due to dc conductivity effects [10]. After the same film has been exposed to the atmosphere for 190 hr and then kept in a 90°C air oven for 1 hr, the -30°C loss peak now shows an increase in intensity by nearly an order of magnitude (Fig. 1b). It is known that plasma-polymerized films contain considerable free-radical concentration [11-14], and that PPE also has a large concentration of unsaturated double bonds [10, 13, 14]. Thus the exposure to air must have

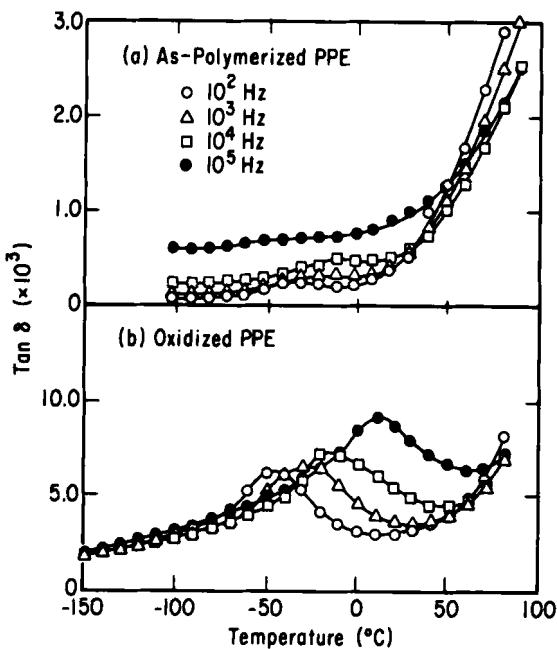


FIG. 1. Dielectric loss tangent as a function of temperature for plasma-polymerized ethylene at four frequencies. (a) As-polymerized; (b) exposure to atmosphere at ambient conditions for 190 hr and followed by heat treatment at 90°C for 1 hr.

caused a great deal of oxidative reactions to take place, resulting in the formation of polar groups in the polymer which give rise to increased dielectric loss.

For the sake of comparison, the dielectric data for two additional plasma-polymerized hydrocarbons were investigated. In Fig. 2 are shown the loss tangent curves for plasma-polymerized ethylene/acetylene (PPEA). It has been shown previously [14] that the polymerization of ethylene/acetylene mixtures results in increased unsaturation in the polymer structure. Thus only a 68-hr exposure to air at ambient temperature was sufficient in producing a noticeable increase in the intensity of the -30°C loss peak (1 kHz).

We have demonstrated in a recent publication [15] that ethane can be polymerized in the plasma into a film which contains very little unsaturation. Its rate of polymer deposition was found to be an order of magnitude slower than that of ethylene. However, the introduction

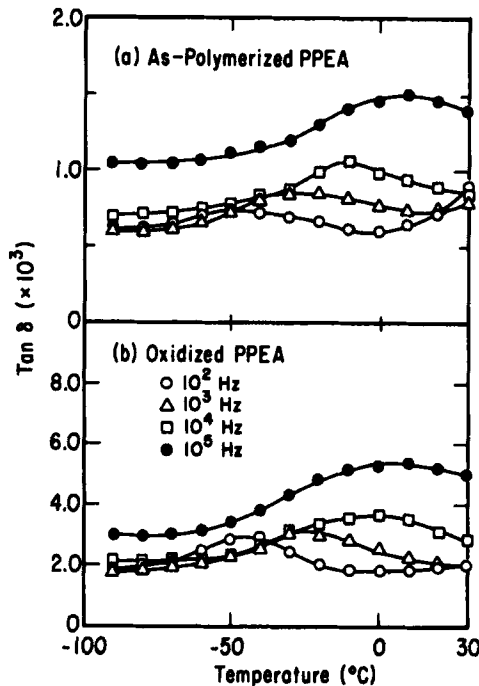


FIG. 2. Dielectric loss tangent as a function of temperature for plasma-polymerized ethylene/acetylene at four frequencies. (a) As-polymerized; (b) exposed to atmosphere at ambient conditions for 68 hr.

of a small amount ($\sim 5\%$) of halogenated hydrocarbon, such as vinyl chloride, caused a dramatic increase in its deposition rate while incorporating a negligible amount of the latter. In other words, the added halogenated hydrocarbons serve as polymerization catalysts. In Fig. 3 are shown the dielectric loss data for the plasma-polymerized ethane/vinyl chloride (PEVC). Elemental analysis shows that the polymer contains only 0.43% chlorine by weight. Since PEVC contains very little unsaturation, 35 days of exposure to air were required to produce the substantial increase in intensity of the -30°C peak (1 kHz) shown in Fig. 3(b).

A summary of the polymerization conditions of these hydrocarbons and their dielectric behavior is given in Table 1. In column 6 are shown the dielectric constants (ϵ') of the plasma-polymerized films before and after oxidation. With the exception of PPEA the dielectric constants of the oxidized films are higher than those of the as-polymerized films. It is of interest to note that these values are

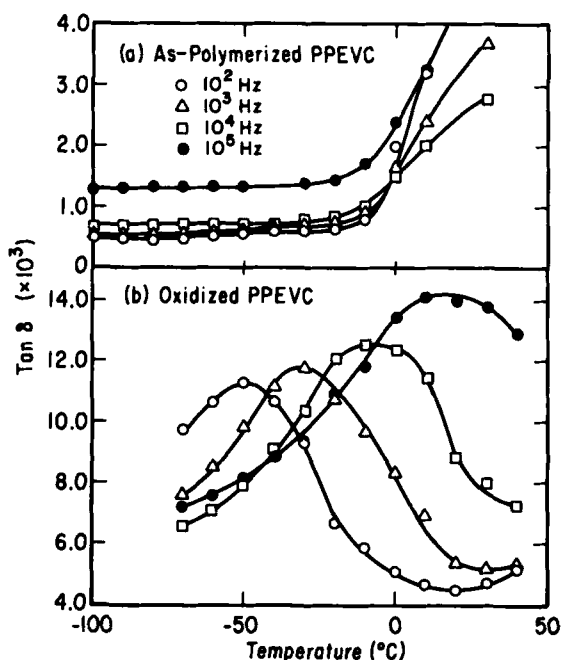


FIG. 3. Dielectric loss tangent as a function of temperature for plasma-polymerized ethane/vinyl chloride at four frequencies. (a) As-polymerized; (b) exposed to atmosphere at ambient conditions for 35 days.

TABLE 1. Polymerization Conditions and Dielectric Data of Plasma Polymerized Films

Polymer	Monomer flow rate (STP cm ³ /min)	Pressure (mmHg)	Power (W)	Dielectric film thickness (μ m)	ϵ'		ΔH (kcal/mole)
					As polymerized	Oxidized	
PPE	80 (Ethylene)	2.0	85	19.7	3.57	4.20	13.8
PPEA	80 (Ethylene) 12 (Acetylene)	1.8	100	15.2	4.48	4.16	14.1
PPEVC	53 (Ethane) 2.5 (Vinyl chloride)	1.8	90	11.7	4.11	5.59	13.5
PPTFE	8.5 (Tetrafluoroethylene)	0.25	80	29.0	-	5.23	12.7

all substantially higher than ϵ' of the conventional polyethylene (~ 2.3). These observations are in agreement with literature data on plasma-polymerized styrene [16] and hexamethyldisiloxane [8].

To verify the existence of polar groups produced by oxidation of the plasma-polymerized hydrocarbons, we show in Fig. 4 the IR spectra for PPE, PPEA, and PPEVC before and after exposure to air. In all three instances, substantial increases can be noted in the absorption of the peaks at 3400 cm^{-1} (OH stretching) and 1700 cm^{-1} ($\text{C}=\text{O}$ stretching) after oxidation. In addition, there is also increased absorption in the 1000 to 1300 cm^{-1} region normally attributed to OH deformation and CO stretching vibrations observed in alcohols and alkyl ketones [17].

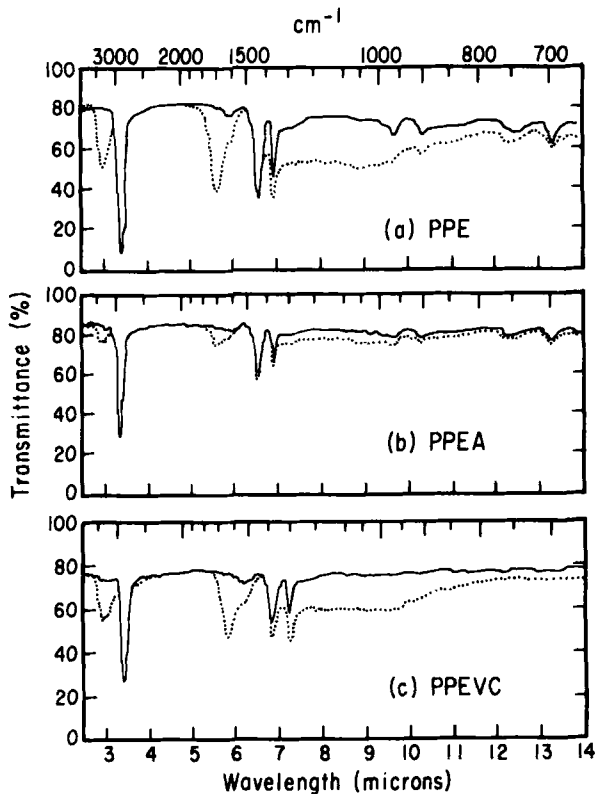


FIG. 4. Infrared spectra of plasma-polymerized (a) ethylene, (b) ethylene/acetylene, and (c) ethane/vinyl chloride. Solid lines: as-polymerized films. Dotted lines: oxidized films (see legends of Figs. 1, 2, and 3 for oxidation conditions).

The preceding data indicate that the increased dielectric losses observed after oxidation could be ascribed to either or both hydroxyl and carbonyl groups. To further examine this question, we determined the dielectric loss curves for plasma-polymerized tetrafluoroethylene (PPTFE) shown in Fig. 5. Because of its extremely rapid rate of oxidation, it is not possible to prepare a PPTFE film without the presence of oxygen-containing groups. It is seen here that the oxidized PPTFE exhibits a very similar dielectric behavior to that of plasma-polymerized hydrocarbons shown in Figs. 1 to 3. Its IR spectrum (Fig. 6), however, shows the presence of only CO groups. Because of its lack of hydrogen atoms, it is not possible for PPTFE to form OH groups upon oxidation. The absence of OH groups from this polymer strongly suggests that the loss peak observed at -30°C (1 kHz) is associated with the CO groups. It is of interest to note that in their work on the dielectric behavior of oxidized low-density polyethylene (LDPE), Mikhailov et al. [18] found a similar increase in dielectric loss with increasing oxidation. These authors attributed their observation to the carbonyl groups attached to the main chain acting as tracers. The well-known γ -relaxation of the non-polar polyethylene [10] at -100°C (1 kHz) was rendered observable by the presence of these polar tracer groups.

We note in Figs. 1, 2, 3, and 5 the similarity in the loss curves of PPE, PPEAC, PPEVC, and PPTFE. We shall designate the

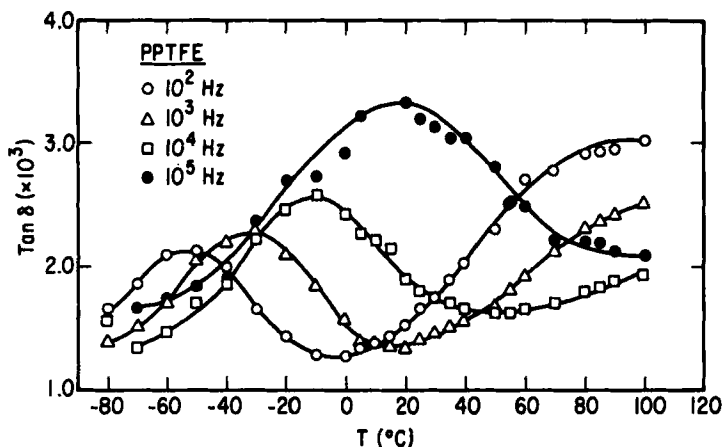


FIG. 5. Dielectric loss tangent as a function of temperature for plasma-polymerized tetrafluoroethylene at four frequencies after exposure to the atmosphere at ambient conditions for 90 hr following polymerization.

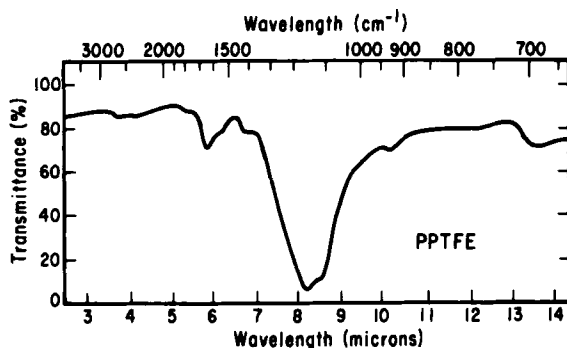


FIG. 6. Infrared spectra of plasma-polymerized tetrafluoroethylene after exposure to atmosphere at ambient conditions for 90 hr following polymerization.

low-temperature loss peak (-30°C at 1 kHz) the γ_p -relaxation.

By plotting the logarithm of the frequency vs the reciprocal of the temperature for the maximum of the loss peak, the activation energy ΔH is readily obtained:

$$\omega/\omega_0 = \exp(-\Delta H/RT) \quad (1)$$

Values of the activation energies thus determined are given in the last column of Table 1. They are nearly the same within experimental error, and have an average of 13.8 ± 1.4 kcal/mole.

The relationship of the CO groups to the γ_p -relaxation can be demonstrated quantitatively by means of the well-known Kirkwood-Froelich equation [19, 20]

$$\Delta\epsilon = \frac{4\pi N g \mu_0^2}{3kT} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \left(\frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \right) \quad (2)$$

where ϵ_0 and ϵ_∞ are the dielectric constants of the polar group, in our instance the carbonyl group, at very low and very high frequencies, N is the number of CO groups, g is the Kirkwood correlation function, μ_0 is the dipole moment, and the quantity $(g\mu_0^2)^{1/2}$ is sometimes known as the effective dipole moment [10].

The relaxation strength, $\Delta\epsilon$, can be experimentally determined from [21]

$$\Delta\epsilon = \left(\frac{2\Delta H}{\pi R}\right) \int_0^{\infty} \epsilon'' d(1/T) \quad (3)$$

In Eq. (3), ΔH is the activation energy. For PPE, $\Delta\epsilon$ was determined from the data in Fig. 1(b) by graphical integration to be 0.812. In order to compare this with the theory of Kirkwood and Froelich, we take $\epsilon_0 = \epsilon_{\infty} = 4.27$ (see Table 1). The value of N is calculated from

the IR data using the Beer-Lambert law, since the extinction coefficient of CO groups is known [22] to be 220 liter/mole-cm. Inserting these values into Eq. (2), we find the effective dipole moment to be 2.4 D, which compares favorably with the literature value of 2.7 D for the carbonyl group [23]. One possible reason for the slightly lower value of μ_0 from our data may be due to our neglect of the contribution from the hydroxyl groups, whose dipole moment is somewhat lower ($\mu_0 = 1.7$ D) [23].

In his study of the dielectric relaxation in conventional polyethylene, Booi [24] has attributed the α -relaxation to the carbonyl groups in the oxidized polymer. According to that work, the dielectric loss constant should be directly proportional to the number of carbonyl groups. Since we are also assigning our γ_p -relaxation to the carbonyl groups, the same linear relation should also hold true. Figure 7 shows the ϵ'' vs N plot for the four plasma-polymerized films in this work. A reasonably good straight line can be drawn through all the experimental points.

The finding that the same straight line is valid for all four polymers is interesting. We recall that in Figs. 1, 2, 3, and 5 the γ_p -loss peaks all occur at comparable temperatures, and that in Fig. 8 and Table 1 these relaxations all have similar activation energies. The implication here is that the observed relaxations in these four polymers can be attributed to the same mode of molecular motion. It is of interest to note that although the loss curves of plasma-polymerized hydrocarbons and fluorocarbon are similar to each other, they bear no apparent resemblance, respectively, to those in conventional polyethylene (PE) and polytetrafluoroethylene (PTFE). It is perhaps not surprising that such differences are found. Plasma-polymerized films, as have been demonstrated previously [9], are totally amorphous and very highly cross-linked. Conventional PE and PTFE, on the other hand, are highly crystalline and uncross-linked. Thus the α -relaxation of PE and the β -relaxation of PTFE are both due to crystalline regions of these polymers and cannot be observed in the plasma-polymerized films. The α -relaxation of PTFE is amorphous in origin, but occurs at temperatures considerably higher than the maximum temperature (100°C) covered in this work.

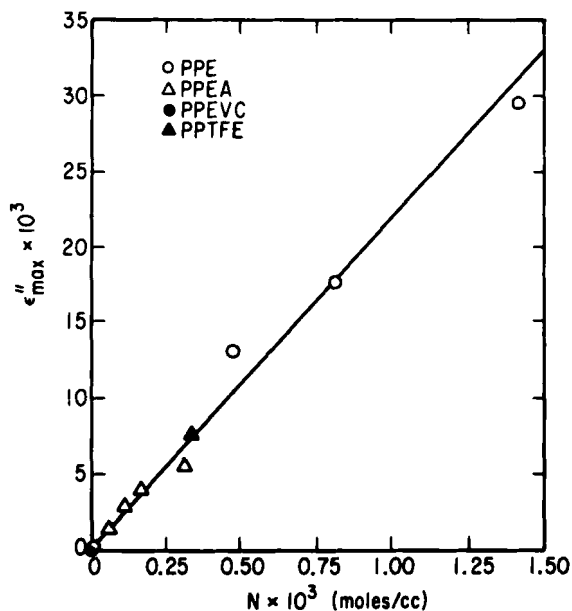


FIG. 7. Plot of dielectric loss constant of plasma-polymerized material as a function of carbonyl group concentration.

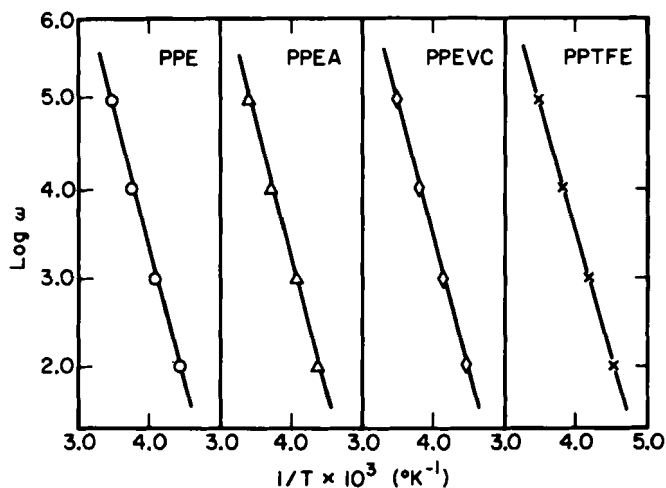


FIG. 8. Activation energy plots (Eq. 1) for plasma polymerization of ethylene, ethylene/acetylene, ethane/vinyl chloride, and tetrafluoroethylene.

In conventional PE the γ -relaxation is located near -100°C at the measurement frequency of 1 kHz. The mechanism for this relaxation is believed to be local mode motions involving several molecular segments [10]. Schatzki [25] has proposed this motion to be a crankshaft motion. He found an activation energy of 11.4 to 14.9 kcal/mole for this relaxation, which is in good agreement with his theoretical estimate of 13 kcal/mole. However, there is now some doubt regarding the validity of this mechanism because of the discovery of some new data that are inconsistent with the model [25]. More recently the γ -relaxation has been found to consist of two components [26, 27]: one is crystalline in origin (γ_c) and the other amorphous (γ_a). Kakizaki and Hideshima [27] reported the activation energies of these two relaxations to be 23 and 13 kcal/mole, respectively. In conventional PTFE the γ -relaxation [28] is located near -90°C at 1 kHz with an activation energy of 18 kcal/mole, very similar to that of PE. Its molecular mechanism is believed to also be a local mode motion of short chain segments [10].

It appears plausible that the γ_p -relaxation which we have found in plasma-polymerized hydrocarbons and in PPTFE can be attributed to similar local motions. The location of the loss maxima has been shifted upwards by nearly 70°C because of the very high degree of cross-linking in plasma-polymerized materials. Its activation energy is of a comparable order of magnitude as those in conventional PE. Experimentally, the γ -relaxation has been found to shift upscale in temperature for conventional PE samples cross-linked by high-energy radiation [29]. Similar interpretations for the secondary relaxations in plasma-polymerized hexamethyldisiloxane and styrene have been given by Kolotyarkin et al. [8] and Ieda et al. [7], respectively.

In the papers by Kolotyarkin and Ieda and their co-workers, changes in the dielectric properties of the plasma-polymerized films upon exposure to the atmosphere were attributed to the sorbed water. To check the validity of such a hypothesis in our plasma-polymerized ethylene, we subjected our sample to heat treatment at 90°C for 1 hr to remove the sorbed water, but found no change in the dielectric behavior. Another PPE sample was then prepared in the reactor. After the discharge had been terminated, pure dried oxygen was bled through the reactor for 43 hr. One more sample was prepared under identical conditions, but upon the completion of polymer deposition the film was immediately removed from the reactor and immersed in water that had been degassed by refluxing for 4 hr. The water-polymer system was kept in vacuo for 43 hr. The dielectric loss curves for these two treated films are shown in Fig. 9. It is apparent that only in the oxygen-treated PPE can the γ_p -relaxation

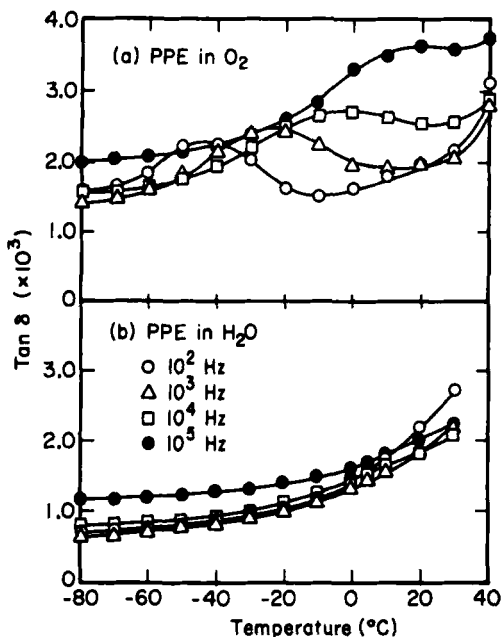


FIG. 9. Dielectric loss tangent as a function of temperature for plasma-polymerized ethylene at four frequencies. (a) After exposure to dried oxygen for 43 hr; (b) after exposure to degassed water for 43 hr.

be observed. Exposure to oxygen-free water produced no apparent effects. Thus in PPE it can be concluded that the observed relaxation is due to the local mode motion rendered observable by the introduction of carbonyl groups as tracers through oxidation. The presence of sorbed water had no significant effect on its dielectric behavior.

Finally, we note in Fig. 5 the onset of a second loss peak, which we shall call the β_p -peak, at elevated temperatures for PPTFE.

At 100 Hz the loss tangent appears to have a maximum around 100°C. In conventional PTFE there is a double β -relaxation process located around 10 and 90°C, and an α -relaxation around 150°C at 1 kHz. The former is presumably crystalline in origin [28] and cannot be responsible for a β_p -peak. Though the α -process has been attributed to the amorphous region [28], it occurs at a temperature substantially higher than our β_p -relaxation. We hypothesize that the β_p -relaxation is due to the motion of the tertiary carbon

structures such as the cross-link sites. This is the type of molecular motion observed in the β -relaxation of branched PE [30] and in conventional copolymers of ethylene with vinyl monomers [31, 32]. The temperature of the β -relaxation increases from -20°C to more than 100°C with increasing comonomer content. Since our plasma-polymerized films are very highly cross-linked, the β process could be shifted to such a temperature. In principle, such relaxation processes should also occur in our plasma-polymerized hydrocarbons PPE, PPEA, and PPEVC. However, because of the interference of dc conductivity effects, their presence is difficult to ascertain.

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