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Effect of Absorbed Chemicals on the Internal Motions in Poly(tetrafluoroethylene)

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ABSTRACT: Dynamic mechanical measurements were made on samples of poly(tetrafluoroethylene) that had been saturated with various halocarbons. The peaks in loss modulus associated with the amorphous γ-relaxation near −90 °C and the crystalline β-relaxation near room temperature were unchanged by the presence of these additives. An additional loss peak appeared at a temperature that was generally near −30 °C, and the modulus was reduced at all higher temperatures. The α-relaxation, which appears as a peak in the loss compliance at 134 °C, is shifted to 45–70 °C in the swollen samples.

Poly(tetrafluoroethylene) (PTFE) is well-known for its resistance to a wide variety of chemicals.[1-3] However, it can absorb limited amounts of certain compounds. In an earlier study,[4] it was found that the sorption of compounds containing hydrogen was very low and did not depend on the solubility parameter. The sorption of compounds without hydrogen depended on the solubility parameter in the manner expected for a partially crystalline polymer having a solubility parameter of 6.2. The gain in weight at saturation was 1.4% for chloroform, 2.0% for carbon tetrachloride, and up to 11% for perfluorocarbons. It was also reported that one fluorinated additive, FC-75, had a plasticizing effect on PTFE. These effects are easily overlooked in a world dominated by aqueous fluids and hydrocarbons. The purpose of the present study is to explore the effect of absorbed chemicals on the internal motions in PTFE.

Experimental Section

Samples of PTFE sheeting $^1/_{32}$ in. thick were immersed in various chemicals either at room temperature or at the boiling point until the weight no longer increased. The weight gains are shown in Table I. The dynamic mechanical properties were determined by means of a Du Pont dynamic mechanical analyzer (DMA)[5] that had been interfaced with a Hewlett-Packard calculator.[6] Data from initial experiments on the effects of chloroform and carbon tetrachloride on the modulus, E', and the loss modulus, E'', are shown in Figures 1 and 2. The γ- and β-relaxations are clearly seen, but the well-known[7] α-relaxation is not. This is because the experimental setup became inappropriate when the modulus became very small. The operation of the DMA depends on the resonant frequency of the instrument coupled to the sample. The modulus is proportional to the difference between the squares of the coupled frequency and the resonant frequency of the instrument alone,[6] about 2.4 Hz. As the modulus decreases with increasing temperature, this difference in frequency and the associated damping may become unreadable. This problem may be overcome by decreasing the length of the sample to increase the resonant frequency. This length was shortened from $^1/_2$ to $^1/_4$ in. for a new control and samples saturated with the dimer of hexafluoropropylene (HFP) and Freon 113, CCl_2FCClF_2. Plots of E' and E'' for these samples are shown in Figures 3 and 4.

γ- and β-Relaxations

The properties of the viscoelastic relaxations in PTFE have been discussed in detail by McCrum.[7] The lowest temperature softening process is the γ-relaxation near −90 °C. It is attributed to the motion of short-chain segments in the amorphous regions. As seen in Figures 2 and 4, the γ-relaxation is not affected by the presence of the sorbates. This probably means that the motion is entirely intramolecular. It is true that in these compositions most short segments will not be adjacent to a sorbate molecule. Nevertheless, some change in the shape of the loss peak would have been expected if intermolecular factors were involved.

The β-relaxation near 30 °C occurs in the crystalline regions,[7] and it is thought to be related to the first-order crystalline transitions at 19 and 30 °C. In the saturated samples, it remains near 30 °C, and the height of the peak in the loss modulus, E'', is unchanged. This was expected since this is a crystalline phenomenon, and the guest molecules are expected to reside in the amorphous regions. This conclusion is supported by the fact that the properties of the crystals as measured by differential scanning calorimetry and X-ray diffraction are unchanged.

β′-Relaxation

The designation β′ has been assigned to loss phenomena located between the γ- and β-relaxations. Such a relaxation has occasionally been discussed in the literature. Becker[8] reported a mechanical loss peak at −30 °C and 10 Hz, and Krum and Muller[9] reported a dielectric loss peak at −13 °C and 10^3 Hz. Ohzawa and Wada[10] concluded that this relaxation occurs in the amorphous regions and is the primary glass transition for PTFE, although it has frequently been obscured by the more prominent β-relaxation. Some support for an amorphous assignment was found in the work of McCall et al.[11] Araki[12] studied the region of the β′-relaxation by stress relaxation, thermal expansion, and dielectric measurements. He reported evidence for two amorphous relaxations around −40 and −15 °C. In recent work by Lau, Suzuki, and Wunderlich,[13] it was concluded that the glass transition in PTFE is spread over a broad range of temperature in this region. Vega and English,[14] working with fluorine-19 NMR, found evidence for a high-frequency motion beginning at −40 °C in the amorphous regions which increases in amplitude rather than frequency with increasing temperature. This is very different from the behavior of a conventional glass transition.

The swollen samples show a higher loss than a control in this region. In most cases, there is a peak between −50 and −30 °C. The modulus decreases here and remains lower than that of a control at all higher temperatures. The fact that absorbed chemicals strengthen the β′-relaxation confirms its assignment to the amorphous regions.

α-Relaxation

The α-relaxation does not appear as a peak in E'', but it can be seen as a decrease in E' near 120 °C for the PTFE control in Figure 3. This relaxation can be seen more clearly by considering the real and imaginary parts of the complex compliance, D' and D''. These quantities are related to E' and E'' through the following expressions.

$$D' - iD'' = 1/(E' + iE'')$$

$$D' = E'/(E'^2 + E''^2)$$

$$D'' = E''/(E'^2 + E''^2)$$

Table I
Sorption of Chemicals by PTFE

compd	formula	bp, °C	% wt gain of PTFE
perfluorodimethylcyclohexane (PFDMCH)		~102	7.5
HFP dimer	$(CF_3)_2CFCF{=}CFCF_3$ (95%) $(CF_3)_2C{=}CFCF_2CF_3$ (5%)	48	6.8
HFP trimer	$(CF_3)_2C{=}C(CF(CF_3)_2)CF_2CF_3$ $[(CF_3)_2CF]_2C{=}CFCF_3$ $(CF_3)_2CFCF{=}C(C_3F_7)CF_3$	110	6.1
Freon 11	CCl_3F	23.8	4.2
Freon 112	CCl_2FCCl_2F	92.8[a]	4.0
Freon 113	CCl_2FCClF_2	47.6	5.6
Freon E-3	$F(C(CF_3)FCF_2O)_3CHFCF_3$	158	4.0
carbon tetrachloride		76.8	2.0
chloroform		61.2	1.4

[a] mp 29.5 °C.

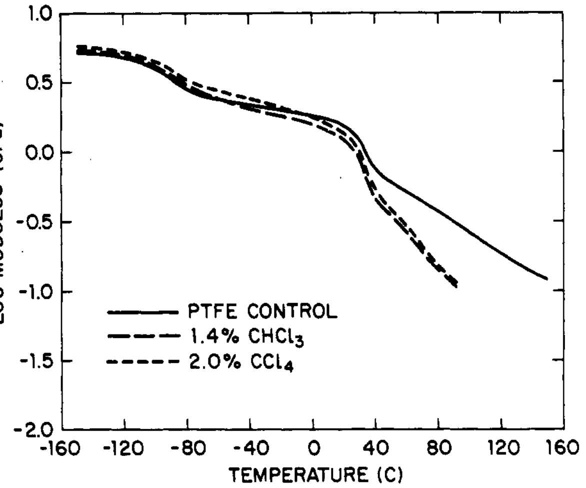

Figure 1. Effect of chloroform and carbon tetrachloride on the modulus of PTFE.

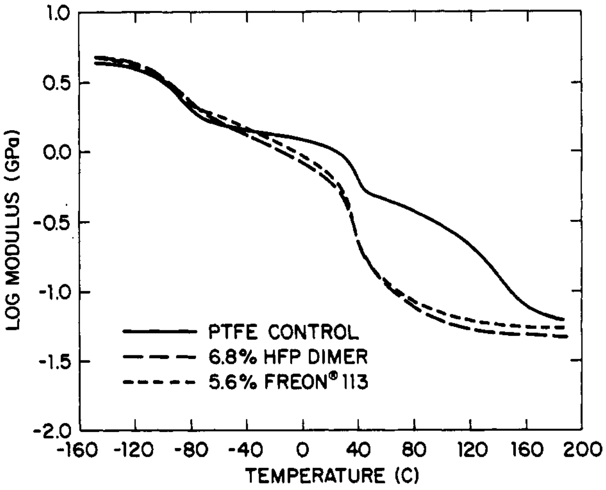

Figure 3. Effect of HFP dimer and Freon 113 on the modulus of PTFE.

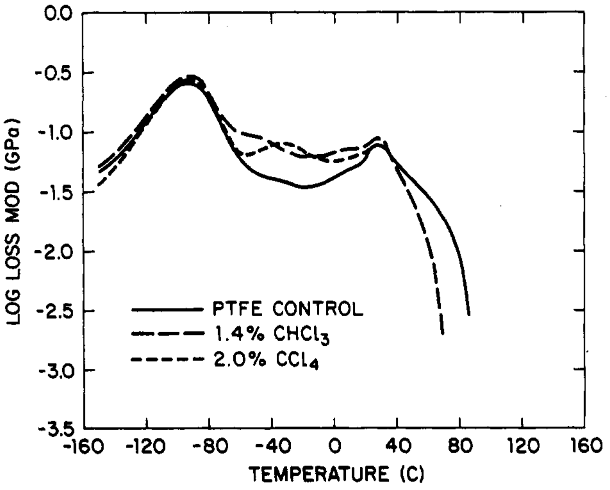

Figure 2. Effect of chloroform and carbon tetrachloride on the loss modulus of PTFE.

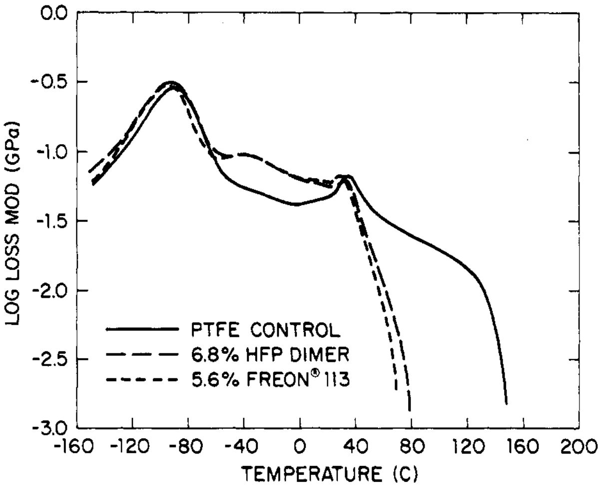

Figure 4. Effect of HFP dimer and Freon 113 on the loss modulus of PTFE.

The loss compliance, D'', is plotted against temperature in Figure 5 for samples swollen with perfluorocarbons and Figure 6 for samples swollen with Freons. The peak that occurred at 134 °C in the control was shifted to 45–70 °C. In some cases, the β-relaxation can be seen as a shoulder near 40 °C on the low-temperature side of the peak. In others, the α- and β-relaxations largely overlap. Although the maximum in E'' for the β-relaxation is unchanged in

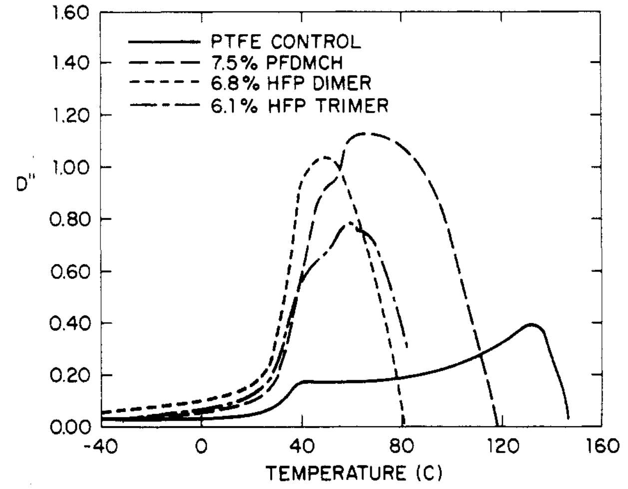

Figure 5. Effect of perfluorocarbons on the loss compliance of PTFE.

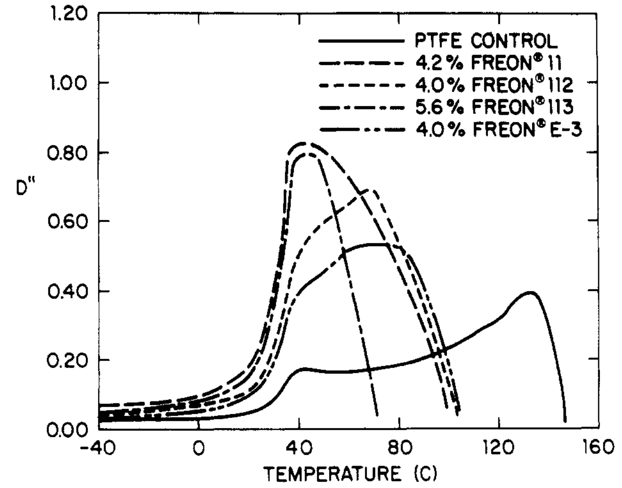

Figure 6. Effect of Freons on the loss compliance of PTFE.

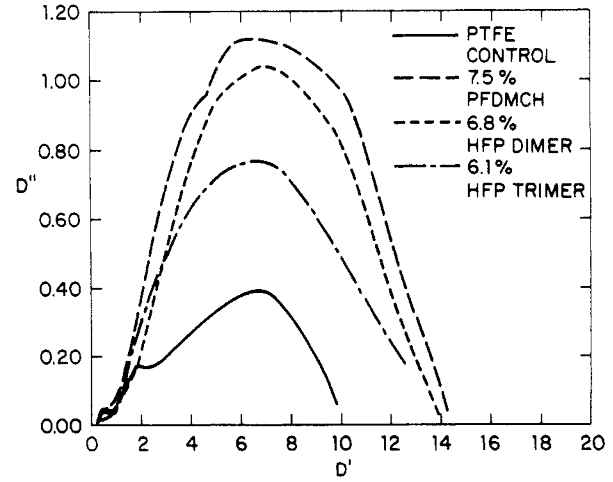

Figure 7. Complex plane plot for the compliance of PTFE saturated with perfluorocarbons.

the swollen samples, the maximum in D'' is increased, because E' is decreased.

Complex plane plots, D'' vs. D', are shown in Figures 7 and 8. It is seen that the absorbed chemicals not only lower the temperature of the α-relaxation but also increase the relaxed compliance, the value of D' for which D'' would extrapolate to zero on the high-temperature side of the peak. That quantity is increased from about 10 GPa^{-1} in the control to 11–12 GPa^{-1} in the Freon-swollen samples and about 14 GPa^{-1} in the samples swollen with perfluorocarbons. The γ- and β-relaxations are also seen in these plots at low values of D'.

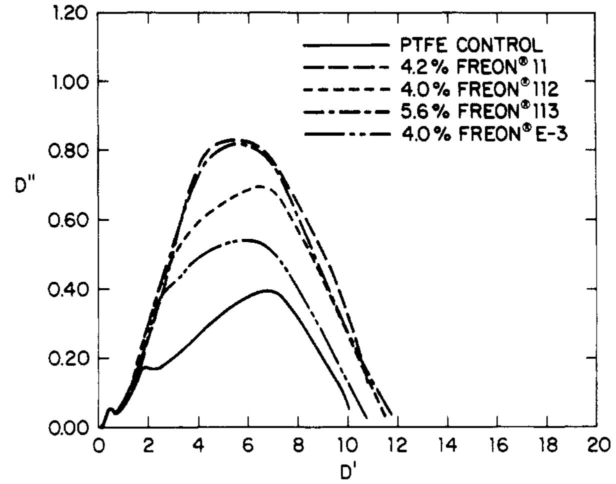

Figure 8. Complex plane plot for the compliance of PTFE saturated with Freons.

Conclusions

Studies of the effect of absorbed chemicals can increase our understanding of relaxation in polymers. In the case of PTFE, the assignments of the α-relaxation to the amorphous regions and the β-relaxation to the crystalline regions were confirmed. The β'-relaxation which had occasionally been reported in the past[8-12] was strengthened and seen with increased clarity. It has long been recognized[7] that the γ-relaxation is due to the motion of short-chain segments in the amorphous regions. The absence of any effect by absorbed chemicals shows that this is a purely intramolecular phenomenon.

Registry No. PTFE, 9002-84-0; PFDMCH, 26637-68-3; HFP dimer, 13429-24-8; HFP trimer, 6792-31-0; CCl_3F, 75-69-4; CCl_2FCCl_2F, 76-12-0; CCl_2FCClF_2, 76-13-1; $F(C(CF_3)FCF_2O)_3CHFCF_3$, 3330-16-3; CCl_4, 56-23-5; $CHCl_3$, 67-66-3.

References and Notes

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