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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

DIELECTRIC PROPERTIES OF POLYMERS BASED ON HEXAFLUOROPROPYLENE

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Abstract

Dielectric measurements have been made at frequencies from 10 Hz to 100 kHz and temperatures from 4 K to at least 300 K on a number of polymers containing units of hexafluoropropylene (HFP). These included copolymers of tetrafluoroethylene (TFE) and HFP, the homopolymer of HFP, elastomeric copolymers of HFP and vinylidene fluoride, and alternating copolymers of methyl vinyl ether with TFE and HFP. The effect of an ether linkage between the CF_3 group and the chain was also considered. Most of these polymers exhibited a main chain local mode relaxation near 228 K and a side group relaxation near 93 K.

Keywords: copolymers of methyl vinyl ether, dielectric properties, elastomeric fluoropolymers, hexafluoropropylene, perfluoro methyl vinyl ether, polyhexafluoropropylene, relaxations, tetrafluoroethylene/hexafluoropropylene copolymers

Introduction

Although they are nonpolar, many fluoropolymers exhibit a dielectrically active low temperature γ-relaxation which is associated with the motion of short chain segments in the amorphous regions [1, 2]. In FEP resin, the copolymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), there is a small loss peak associated with the high temperature α-relaxation, [1, 2] and an additional loss peak at 94 K and 1 kHz which has only been observed in fluoropolymers containing side groups [2, 3].

The γ-relaxation in FEP occurs at a somewhat higher temperature than in other polymers of TFE. This has been attributed to overlap with the β-relaxation, a hypothesis which was supported in studies of the effect of pressure [4].

We have now extended the earlier work to a wider range of polymers containing HFP. These include copolymers of TFE and HFP having various comonomer ratios and the homopolymer, polyhexafluoropropylene (PHFP). The effect of inserting an oxygen between the CF_3 group and the main chain has

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been examined. Other examples are the elastomeric copolymers of HFP with vinylidene fluoride (VF_2) and the terpolymer with TFE. Finally, measurements were made on alternating copolymers of methyl vinyl ether (MVE) with TFE and HFP, respectively.

Experimental

The dielectric measurements were made in the same way as in an earlier report, [2]. Copolymers of TFE with 13 and 18 mol % HFP were supplied by Dr. R. A. Morgan of the DuPont Washington Laboratory at Parkersberg, West Virginia. The sample of PHFP and a copolymer of TFE with 57 mol % HFP were made by the process of Eleuterio [5, 6]. The samples of elastomers and the copolymers of MVE were supplied by Dr. W. W. Schmiegel of DuPont Elastomers.

Copolymers of TFE and HFP

Copolymers of TFE with from 7 to 57 mol% HFP were studied, as well as the homopolymer, PHFP. The thermal properties are summarized in Table 1. The dissipation factors at 1 kHz are plotted against temperature in Fig. 1. The copolymers containing up to 18 mol% HFP are semicrystalline, although the crystallinity as judged by the latent heat at the melting point decreases markedly with increasing levels of HFP. There is also a steady decrease in the melting point as observed by differential scanning calorimetry (DSC).

While the glass transition was not seen in DSC scans of the copolymer containing 7 mol% HFP, it did appear at higher levels as expected in view of the higher amorphous contents. The glass temperature by DSC decreased from

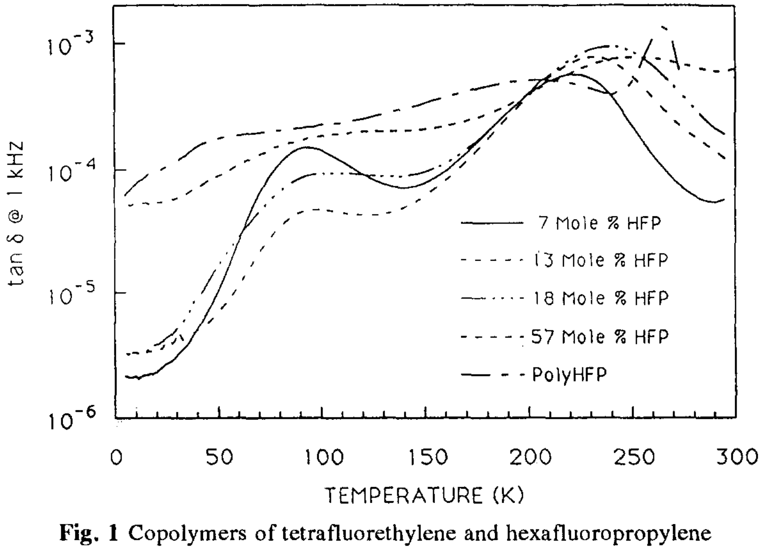

Fig. 1 Copolymers of tetrafluorethylene and hexafluoropropylene

Table 1 Copolymers of TFE and HFP

Mol% HFP	7		13		18		57		100	
DSC data										
T_g/°C	–		61		50		35		128	
T_m/°C	271		203		150		–		–	
ΔH_m/J g^{-1}	21		11		6		–		–	
Dielectric data										
Scan	*T*	f	*T*	*f*	*T*	*f*	*T*	*f*	*T*	*f*
α-Relaxation										
T/°C, at 1 kHz	102		87		70		63		195	
γ-Relaxation										
T/K, at 1 kHz	222	215	233	216	239	233	252	243	209	195
E_a/kcal mol^{-1}	16.3	13.4	16.6	13.7	16.3	13.7	13.2	11.7		
ΔF^*/kcal mol^{-1}										8.4
δ-Relaxation										
T/K, at 1 kHz	94	89	97	92	108	94	99	73	70	
E_a/kcal mol^{-1}	3.67	4.40	3.77	3.88	3.98	3.81	2.38	1.30	2.17	
ΔF^*/kcal mol^{-1}	3.68	3.46	3.84	3.56	4.12	3.67		2.89	2.63	2.39

61°C at 13 mol% HFP to 35°C at 57 mol% HFP but rose again to 128°C for the homopolymer of HFP.

Dielectric measurements were made at frequencies from 10 to 10^5 Hz. Maxima in the dissipation factor were located using both isochronal temperature scans (*T*-scans) and isothermal frequency scans (*f*-scans). The α-relaxation, which is related to the glass transition, followed a pattern parallel to the DSC data decreasing from 102°C at 7 mol% HFP to 63°C at 57 mol% HFP and increasing to 195°C for PHFP for a frequency of 1 kHz.

The temperature of the γ-relaxation which is attributed to the motion of relatively short chain segments in the amorphous regions increased gradually with the level of HFP but was somewhat lower in the homopolymer, PHFP.

The low temperature δ-relaxation is a characteristic of fluoropolymers which have side groups [2, 3]. This relaxation remained near 100 K in the copolymers but decreased to 70 K in PHFP. The effect of composition on the magnitude of the dissipation factor in this temperature region as shown in Fig. 1 is more striking. For the copolymers containing from 7 to 18 mol% HFP, the δ-relaxation has a relatively sharp maximum, and the dissipation factor decreases markedly at lower temperatures. However, for PHFP and the copolymer with 57 mol% HFP, the dissipation factor is higher, particularly at very low temperatures, and the maximum is much less well defined. The relatively sharp maximum is thought to be a characteristic of fluoropolymers in which the side groups are mostly or entirely well separated from each other. The higher, broader loss seems to be associated with sequences of HFP units.

The α–relaxation or glass transition is seen dielectrically in PHFP at 195°C at 1 kHz. As shown in Fig. 1, there is a β-relaxation which does not appear in any other polymer of this family. For a frequency of 1 kHz, the peak appears at 265 K in *T*–scans and 261 K in *f*-scans. The activation energy for this process is about 18 kcal mol^{-1}.

Effect of an ether linkage in the side group

A particularly interesting pair of polymers differs only in the presence of an ether oxygen in the side group. One is the copolymer of TFE with 18 mol% HFP which has already been discussed. The other is a copolymer of TFE with 17.5 mol% perfluoro methyl vinyl ether (PFMVE). These materials are compared in Table 2 and Fig. 2.

One effect of incorporating the ether linkage is to decrease the glass transition by DSC from +50 to –12°C. Similarly, the temperature of the dielectric α-relaxation in *T*-scans at 1 kHz is reduced from 70 to 20°C.

The temperature of the γ-relaxation is also reduced as are its activation energy and the associated maximum value of the dissipation factor. Because of this shift in the γ-relaxation, the low temperature δ-relaxation, which exhibits a maximum in the *T*-scans in Fig. 2 for the copolymer with HFP, only appears as a shoulder for the copolymer with PFMVE. However, it does exhibit maxima in *f*-scans. The δ-relaxation seems to be the same for the two polymers when one considers the temperature at 1 kHz, the activation free energy based on *f*-scans, and the maximum value of the dissipation factor.

A striking effect of the ether linkage is the addition of a new relaxation to which we assign the letter ε at 28 K. Its activation energy is only about 1

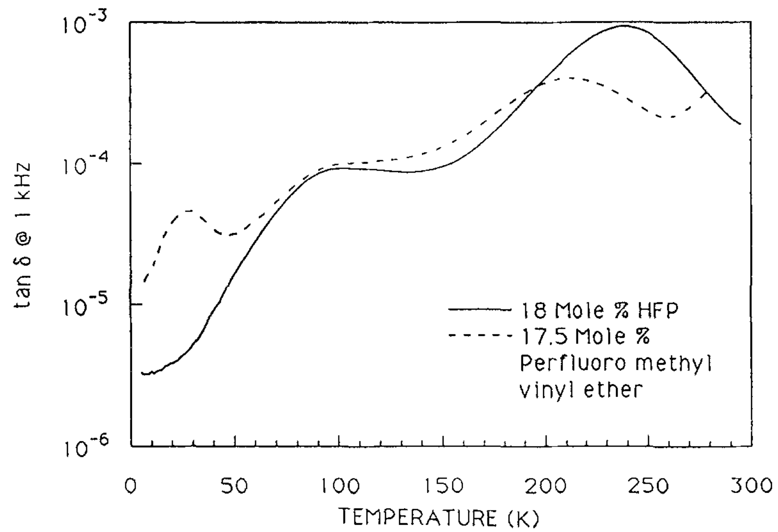

Fig. 2 The effect of an ether linkage in the side group

Table 2 Effect of an ether linkage

Comonomer with TFE	CF_2=CF–CF_3		CF_2=CF–O–CF_3	
Mol%	18		17.5	
T_g/°C, by DSC	50		–12	
Dielectric data				
Scan	*T*	*f*	*T*	*f*
α-Relaxation				
T/°C, at 1 kHz	70		20	
γ-Relaxation				
T/K, at 1 kHz	239	233	213	204
E_a/kcal mol^{-1}	16.3	13.7	14.6	
δ-Relaxation				
T/K, at 1 kHz	108	94		94
E_a/kcal mol^{-1}	3.98	3.81		4.27
ΔF^*/kcal mol^{-1}	4.12	3.67		3.67
ε-Relaxation				
T/K, at 1 kHz			28	28
E_a/kcal mol^{-1}				1.04
ΔF^*/kcal mol^{-1}				1.03

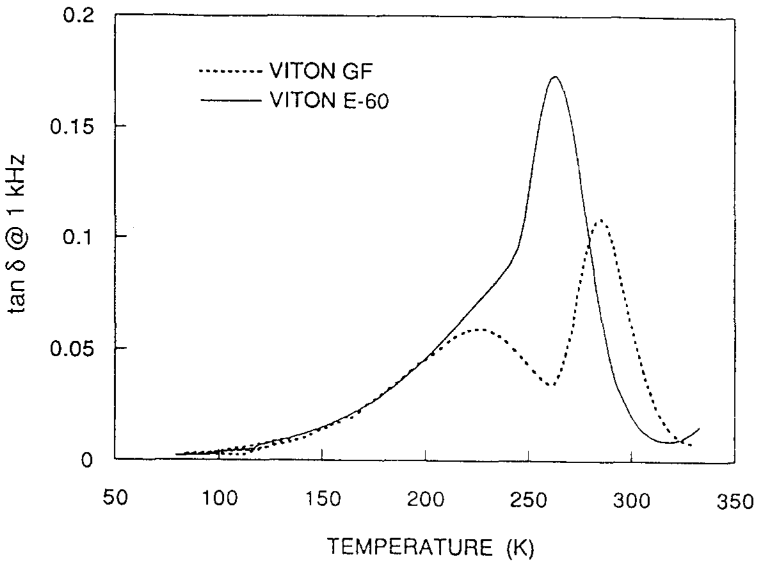

Fig. 3 Viton® Fluoroelastomers

kcal mol^{-1}. This indicates that the OCF_8 side group can undergo a more localized, facile motion than a simple CF_3 group. The fact that the relaxation is dielectrically active means that a dipolar reorientation must be involved.

Viton® Fluoroelastomers

An important class of fluorinated elastomers are the Viton® resins which are copolymers of HFP and vinylidene fluoride (VF_2). Two materials were studied, Viton® E-60 which is binary copolymer (HFP/VF_2) and Viton® GF, a terpolymer with TFE (HFP/VF_2/TFE).

The dissipation factors at 1 kHz are plotted against temperature in Fig. 3. At this frequency, the maximum for the α-relaxation or glass transition occurs at –7 °C (266 K) for the binary copolymer and +13 °C (286 K) for the terpolymer. The peak height is much larger for the former.

Table 3 Viton® Fluoroelastomers

Viton®	E–60		GF	
Comonomers	HFP/VF_2		HFP/VF_2 /TFE	
T_g /°C, by DSC	–18		–8	
Dielectric data				
Scan	T	f	T	f
α-Relaxation				
T/°C, at 1 kHz	–7		+13	
β-Relaxation				
T/K, at 1 kHz		223	225	205
E_a /kcal mol^{-1}	13.4	11.9		9.6
ΔF^*/kcal mol^{-1}	10.4			8.1

The secondary β-relaxation appears as a maximum at 225 K in the temperature scan for the terpolymer, but only as a shoulder for HFP/VF_2. This is probably the result of overlap between the two relaxations. Both polymers exhibit maxima for the β-relaxation in *f*-scans, at 223 K for HFP/VF_2 and 205 K for HFP/VF_2/TFE. Below 200 K, the data are almost identical for the two materials. Unlike most polymers containing HFP units, there is no evidence for an additional relaxation near 100 K. The δ-relaxations in other polymers and copolymers of HFP are very weak and might be obscured by the much stronger, higher temperature relaxations in the Vitons®.

Alternating copolymers of methyl vinyl ether with TFE and HFP

These polymers can be viewed as ETFE, the largely alternating copolymer of ethylene and TFE [2, 7], with side groups. That is, the ethylene has a methoxy substituent, and, in the case of HFP/MVE, the TFE units have a CF_3 side group. Whereas, ETFE is a semicrystalline polymer, TFE/MVE and HFP/MVE are amorphous. Their dielectric properties are presented in Table 4 and Fig. 4. For HFP/MVE, separate runs were done for the lower and higher temperature regions and the data are slightly different in the overlap region.

The glass temperatures, as determined by DSC, were –4°C for TFE/MVE and 22.5°C for HFP/MVE. The dissipation factors at 1 kHz exhibited well-defined maxima for the α-relaxation at 284 K (11°C) for TFE/MVE and 312 K (39°C) for HFP/MVE.

The most prominent secondary relaxations appeared as maxima only in *f*-scans. The next lower temperature relaxation below the α-relaxation, which we will designate the β-relaxation, was seen at 159 K for TFE/MVE and 290 K for HFP/MVE. In the case of HFP/MVE, the α- and β-relaxations are very close together. Extrapolations on an Arrhenius plot indicate that they would merge at a frequency and temperature of about 30 kHz and 330 K.

For HFP/MVE, there is an additional relaxation at 117 K. While we designate this the γ-relaxation, it appears to be similar to the δ-relaxations in other polymers containing HFP units. This assignment is supported by the fact that it is not seen in TFE/MVE. This process has a negative activation entropy, a rare feature among relaxations in polymers.

Finally, both TFE/MVE and HFP/MVE exhibit another relaxation at 9 K and 13 K, respectively, in *T*-scans and 7 K in *f*-scans. This probably reflects the reorientation of methoxy side groups and is analogous to the relaxation at 28 K in TFE/PFMVE which was attributed to a similar motion of OCF_3 side groups.

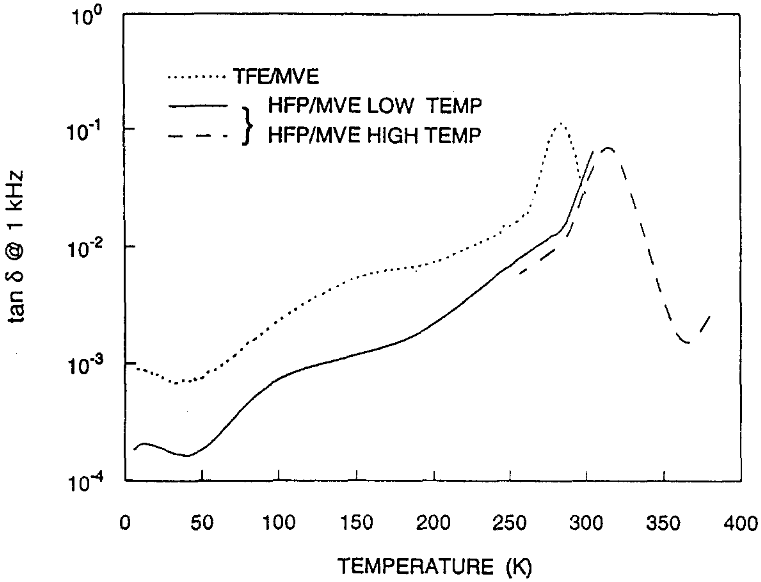

Fig. 4 Copolymers with methyl vinyl ether

Table 4 Alternating copolymers of methyl vinyl ether

Composition	TFE/MVE		HFP/MVE	
T_g /°C, by DSC	–4		22.5**	
Dielectric data				
Scan	T	f	T	f
α-Relaxation				
T/K, at 1 kHz	284	284	312	314*
β-Relaxation				
T/K, at 1 kHz		159		290*
E_a /kcal mol^{-1}		6.2		16.4
ΔF^*/kcal mol^{-1}		6.3		12.4
γ-Relaxation				
T/K, at 1 kHz				117
E_a /kcal mol^{-1}				2.77
ΔF^*/kcal mol^{-1}				4.81
ΔH^*/kcal mol^{-1}				2.57
ΔS^*/cal deg^{-1} mol^{-1}				–17.3
δ-Relaxation				
T/K, at 1 kHz	9	7	13	7

* For HFP/MVE the α- and β-relaxations merge about 330 K and 3×10^4 Hz

** The DSC scan for this material exhibited two step transitions, a small one at –13°C and a large one at +22.5°C

Discussion

The common feature among the polymers discussed here is the presence of HFP units in the polymer chains. It is to be expected that any similarities in their internal motions will be those which are relatively localized. Glass transitions or α-relaxations reflect the motions of longer chain segments and are thus sensitive to variations in the overall structure of the polymer.

Local mode relaxations are analogous to the γ-relaxation which was observed at 194 K in PTFE [2]. They are attributed to motions of fairly short segments, i.e. four or more chain atoms. In semicrystalline polymers, they are a property of the amorphous regions. The properties of these relaxations are summarized in Table 5. The data for the TFE/HFP copolymers, TFE/PFMVE, and the Viton® fluoroelastomers all fall in fairly narrow ranges. For T-scans, the temperature at 1 kHz is 228±15 K, and the activation energy is 15.1± 1.5 kcal mol^{-1}. For f-scans, the temperature is 217±16 K, and the activation energy is 12.3±1.6 kcal mol^{-1}. The alternating copolymers of methyl vinyl ether with TFE and HFP did not exhibit relaxations in these ranges.

Table 5 Local mode relaxations

Polymer	*T*-scans		*f*-scans	
	T/K @ 1 kHz	E_a/kcal mol^{-1}	*T*/K @ 1 kHz	E_a/kcal mol^{-1}
TFE/HFP				
93/7	222	16.3	215	13.4
87/13	233	16.6	216	13.7
82/18	239	16.3	233	13.7
43/57	252	13.2	243	11.7
0/100	209		195	
TFE/PFMVE	213	14.6	204	
Viton® E–60		13.4	223	11.9
Viton® GF	225		205	9.6
Average	228	15.1	217	12.3
σ	15	1.5	16	1.6

Table 6 Side group relaxations

Polymer	*T*-scans			*f*-scans		
	T/K @ 1 kHz	E_a/ kcal mol^{-1}	ΔF^*/ kcal mol–1	*T*/K @ 1 kHz	E_a/ kcal mol^{-1}	ΔF^*/ kcal mol^{-1}
TFE/HFP						
93/7	94	3.7	3.7	89	4.4	3.5
87/13	97	3.8	3.8	92	3.9	3.6
82/18	108	4.0	3.8	94	3.8	3.7
43/57	99	2.4		73	1.3	2.9
0/100	70	2.2	2.6		2.4	
TFE/PFMVE				4	4.3	3.7
HFP/MVE				117	2.8	4.8
Average	94	3.2	3.5	93	3.3	3.7
σ	14	0.85	0.6	14	1.1	0.6

At still lower temperatures, a weak relaxation associated with fluorinated side groups has been observed. Perfluoroalkoxy groups, as well as CF_3 groups, derived from HFP belong to this class [2]. These relaxations are summarized in Table 6. They are observed in the TFE/HFP copolymers, TFE/PFMVE, and the alternating HFP/MVE copolymer. As expected, the TFE/MVE copolymer does not exhibit this relaxation. As discussed earlier, the failure to observe this relaxation in the fluoroelastomers is attributed to the effect of much stronger relaxations at higher temperatures.

In some cases, the side group relaxation appears only as a shoulder in *T*-scans but is resolved as a maximum in *f*-scans. In those scans, the temperature at 1 kHz is 93±14 K, and the activation energy is 3.3±1.1 kcal mol^{-1}. The activation free energy defined by the following equation [8] is 3.7±0.6 kcal mol^{-1}.

$$\Delta F^{*} = RT[\ln(k/2\pi h) + \ln(T/f)]$$

When, as in this case, the activation free energy is independent of temperature, it follows that the activation entropy is close to zero. This is a characteristic of a noncooperative relaxation in which the moving segments act independently of each other [8].

* * *

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