Fluoroelastomers—dependence of relaxation phenomena on composition*

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The dynamic-mechanical properties of some fluoroelastomers were determined as a function of composition at low frequency (≈1 Hz), by means of a free oscillation torsion pendulum, between −180°C and the softening point. Vinylidenefluoride (VDF)–hexafluoropropene (HFP) copolymers of molar composition 0–39% HFP and terpolymers of VDF and HFP with up to 30 mol% tetrafluoroethylene (TFE) and a constant VDF to HFP molar ratio of 3.4 were considered. Two relaxation processes typical of the amorphous phase were found. The first, located at about −87°C, is related to local motions and the transition temperature was found to be independent of composition for copolymers, while it depends on TFE molar content for terpolymers. The second is related to the glass transition and the transition temperature depends on the composition. However, for semicrystalline copolymers the double glass transition phenomenon was observed. When crystallinity goes to zero at about 20 mol% HFP, only one transition is observed. It was also found that ordered structures can take place for terpolymers when TFE molar concentration exceeds 20%. The crystal disorder transition of pure PVDF (75°C) is observed also for low HFP concentrations but the transition temperature is strongly reduced. Analogies between the VDF–HFP and E–P systems are also discussed.

(Keywords: vinylidene fluoride copolymers; vinylidene fluoride terpolymers; fluoroelastomers; dynamic-mechanical properties; tetrafluoroethylene sequences; secondary relaxation; double glass transition; crystal disorder transition)

INTRODUCTION

The most important class of fluorinated elastomers, which display outstanding end use properties, is represented by copolymers of vinylidene fluoride (VDF) and hexafluoroprene (HFP) and by terpolymers where the third monomer is tetrafluoroethylene (TFE). In the course of a comprehensive investigation for this class of high performance materials, the following topics have been investigated:

(1) influence of fluorine content and HFP/VDF ratio on the structure and end use properties[1] for terpolymers;
(2) influence of VDF content on the crystallinity of copolymers[2];
(3) influence of composition on the glass transition temperature (T_g) of copolymers and terpolymers[3];
(4) sequence distribution by ^{19}F nuclear magnetic resonance (n.m.r.) spectra of copolymers and terpolymers and the influence of composition on the crosslinking mechanism[4].

Since no data are known in the literature about the relaxation behaviour of the VDF–HFP system, the aim of this work is to determine the influence of composition on the dynamic-mechanical spectra of copolymers. Some work on the influence of increasing TFE content for terpolymers with a constant VDF/HFP ratio of ≈3.4 is also reported.

EXPERIMENTAL

Materials

Seventeen samples with VDF/HFP molar ratio ranging from 100/0 to 60/40 were prepared by emulsion copolymerization[3]. Due to the impossibility of homopolymerizing HFP by the usual free radical conditions[5], the composition range is limited to copolymers with HFP content <50 mol%. Six terpolymers with constant VDF/HFP constant molar ratio of 3.4 and TFE content up to 29.3 mol% were prepared by the same polymerization process.

All the samples were prepared by semicontinuous emulsion polymerization in a 5 l stainless steel stirred reactor at 70–100°C and 10–20 atm (0.1–0.2 MPa) in 3.5 l demineralized water using ammonium persulphate as initiator and continuously feeding a gaseous monomer mixture having the same composition as the desired polymer. The initial gas composition in the reactor was adjusted to yield the desired polymer composition. The reactor conditions were varied to obtain appropriate molecular weights (viscosity numbers were in the range 80–120 ml g^{-1} in dimethylformamide at 30°C) for all the polymer compositions.

Polymers were coagulated by pouring the latexes into an equal volume of a stirred 6 g l^{-1} aluminium sulphate solution, washed with demineralized water and dried at 70°C for 16 h. Sample composition was determined from ^{19}F n.m.r. spectra, recorded at 188.4 MHz on a Varian XL 200 spectrometer, according to the assignments of chemical shifts in the literature[1,4,6,7].

The n.m.r. spectra were also used to estimate the presence of ordered structures in high TFE terpolymers;

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Table 1 Composition and relaxation processes for VDF–HFP copolymers

		β Process		α_L Process		α_U Process		α_C Process		
Sample	HFP (mol%)	T_β (from G'') (°C)	Δ_{max}	$T_{\alpha,L}$ (°C)	Δ_{max}	$T_{\alpha,U}$ (°C)	Δ_{max}	T (°C)	Δ_{max}	T_m (°C)
CA	0	−86	0.085	−38	0.240	25	0.160	75	0.320	150
CB	2.5	−88	0.108	−38	0.240	20	0.298	45	0.320	130
CC	5.2	−84	0.127	−35	0.230	13	0.450	–	–	108
CD	10.2	−88	0.153	–	–	0	0.860	–	–	65
CE	12.9	−84	0.160	–	–	−6	1.250	–	–	(53)
CF	15.5	−84	0.184	–	–	−11	1.850	–	–	(40)
CG	17.5	−86	0.200	–	–	−14	2.660	–	–	(30)
CH	17.6	−89.5	0.200	–	–	−15	3.000	–	–	–
CK	19.2	−87.8	0.210	−17	3.50	–	–	–	–	–
CL	20.9	−87.8	0.220	−16	3.50	–	–	–	–	–
CM	24.2	−89.5	0.220	−15	3.60	–	–	–	–	–
CN	26.0	−89.5	0.230	−13	3.60	–	–	–	–	–
CO	27.3	−86	0.230	−10	3.30	–	–	–	–	–
CP	30.3	−84	0.230	−7	3.30	–	–	–	–	–
CQ	34.7	−84	0.230	−5	4.60	–	–	–	–	–
CR	39.0	−81	0.240	−2	3.50	–	–	–	–	–
CS	39.2	−84	0.240	−2	3.20	–	–	–	–	–

Table 2 Composition, structure and relaxation processes for VDF–HFP–TFE terpolymers

				β Process		α Process	
Sample	HFP (mol%)	TFE (mol%)	CF_2 pentads (mol%)	T_β (from G'') (°C)	Δ_{max}	T_α (°C)	Δ_{max}
CL	20.9	–	–	−87.8	0.220	−16	3.50
TA	20.6	4.8	0.1	−89.5	0.220	−13	3.60
TB	19.8	9.6	0.3	−91.2	0.230	−12	3.60
TC	17.6	14.5	0.7	−94.4	0.228	−12	3.60
TD	17.7	19.5	1.6	−99.1	0.235	−10	3.60
TE	16.1	24.8	2.8	−102.1	0.228	−5	3.00
TF	15.1	29.3	4.7	−103.5	0.228	−2	2.60

currently it is possible to determine the concentration of CF_2 pentads[8]. Sample compositions are reported in *Tables 1* and *2* for copolymers and terpolymers, respectively.

Dynamic-mechanical measurements

Specimen dimensions were 65 × 10 × 1 mm. Specimens were obtained by compression moulding at temperatures between 210 and 150°C, after which they were quickly cooled down to room temperature.

Dynamic-mechanical spectra (DMS) were determined by means of a Brabender Torsionautomat free oscillation torsion pendulum. The natural frequency range was between 3 Hz (below T_g) and 0.1 Hz (above T_g). The scanning speed was always 1°C min^{-1}. Measurements of both resonant frequency and mechanical damping were taken at 1°C intervals.

RESULTS

Some dynamic-mechanical spectra, measured in the composition range where major variations are observed, are reported in *Figure 1* for copolymers and *Figure 2* for terpolymers as $\log G'$ *versus* T and $\log \Delta$ *versus* T curves (G' and Δ are the real part of the complex shear modulus and the logarithmic decrement, respectively). Three to four relaxation regions plus the beginning of melting, which can be seen in the present study only for copolymers with high VDF content, are evident and they will be discussed in detail below.

Data on relaxation processes are reported in *Tables 1* and *2*, together with composition data, in terms of the temperature at the maximum and the value of Δ at the maximum. Pentad concentration as a function of TFE content is reported in *Figure 3*.

The β maximum

Copolymers. The β maximum, which is generally attributed to local motions for polyvinylidenefluoride (PVDF)[9], is the maximum located at the lowest temperature; it appears as a shoulder of the α maximum for pure PVDF and becomes more and more well defined with increasing HFP content, as shown in *Figure 1b*.

Better resolution between this maximum and the α maximum can be achieved if $\log G''$ is plotted against T; another way of plotting G'' was suggested by Fuoss and Kirkwood for dielectric relaxations[10]: $\log G''$ is plotted as a function of the reciprocal absolute temperature. By this method, after making some assumptions, an estimation of the width and symmetry of the distribution of relaxation times can be obtained.

G'' data measured between −175°C and the temperature at which the left side of the α maximum begins to rise were used and the Fuoss–Kirkwood plot is shown in

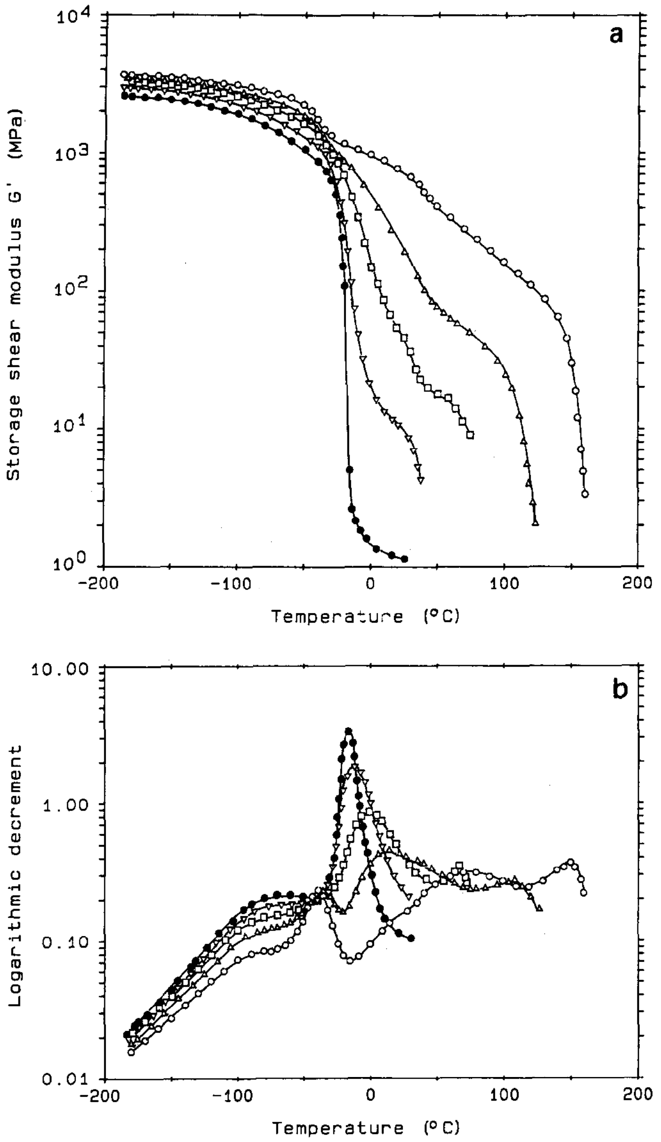

Figure 1 (a) Storage modulus and (b) mechanical damping as a function of temperature for copolymers: ○, 0; △, 5.2; □, 10.2; ▽, 15.5; ●, 20.9 mol% HFP

Figure 4 for some copolymers. It is evident that the distribution of the relaxation times of the β process is skewed to the low temperature side and such an asymmetry seems to become larger with decreasing HFP concentration.

Temperatures at the maximum, obtained from the G'' *versus* $1/T$ plot, and the maximum intensities (Δ values) are plotted in *Figure 5* against HFP content; here two other features of this relaxation process become evident. First, the temperature of the maximum seems to be nearly independent of the HFP content. Second, the intensity increases with HFP content and reaches an almost constant value for compositions >20–25 mol% HFP.

Terpolymers. Figure 2b shows that the β maximum of terpolymers at constant VDF/HFP ratio becomes more resolved with increasing TFE content as the β transition moves towards lower temperatures, while the α process moves in the opposite direction.

For homogeneity of data treatment, T_β was determined from the plot of $\log G''$ *versus* $1/T$ (*Figure 6*), as for copolymers. This plot shows not only that T_β is shifted towards lower temperatures but also that the β maximum broadens by skewing to the low temperature side with increasing TFE content. Since the intensity of the β maximum remains practically unchanged with increasing TFE molar concentration (*Figure 7b*), this suggests that the introduction of TFE units increases the relaxation strength of the β process. This can also be appreciated from the trend of the $\log G'$ *versus* T curves (*Figure 2a*). However, calculations to measure quantitatively the relaxation strength from G' data were not possible because the degree of overlapping of the α and β processes varies with composition, being a maximum for the parent copolymer.

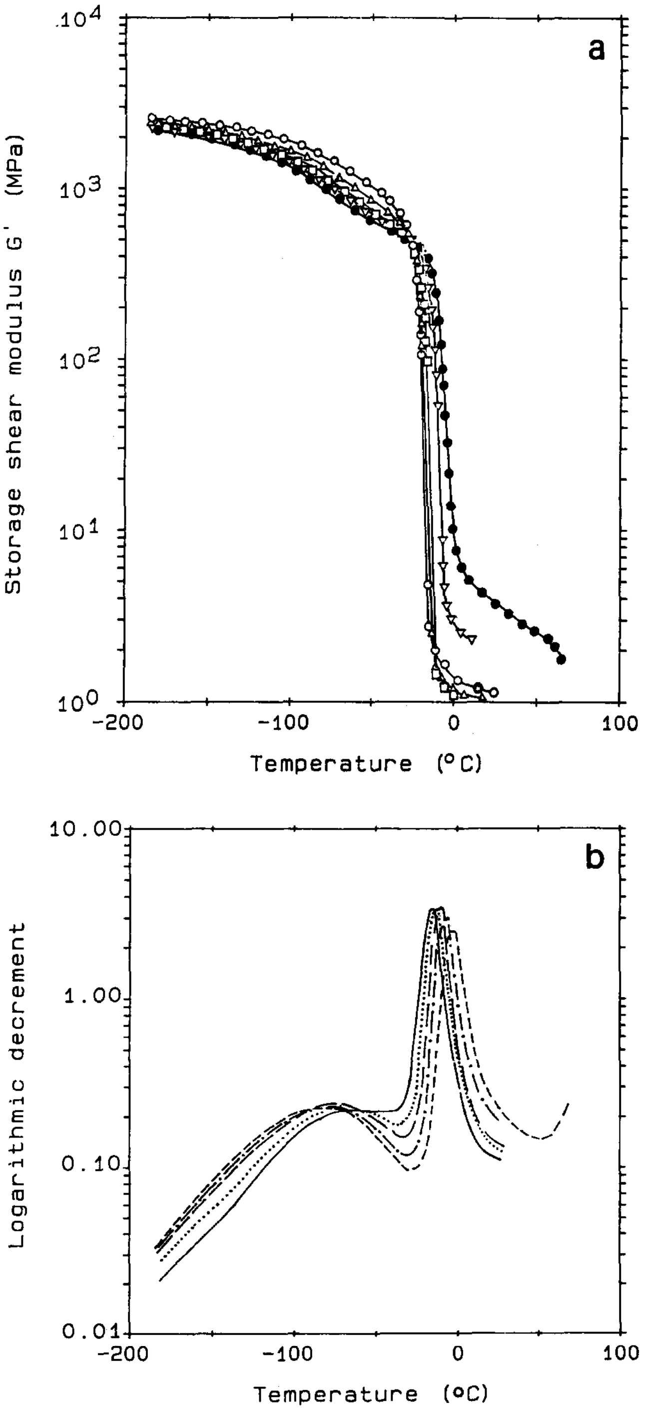

Figure 2 (a) Storage modulus and (b) mechanical damping as a function of temperature for terpolymers with constant VDF/HFP ratio, and increasing TFE content: ○, ——, 0; △, ····, 9.6; □, — — —, 19.5; ▽, —·—, 24.8; ●, – – –, 29.3 mol% TFE

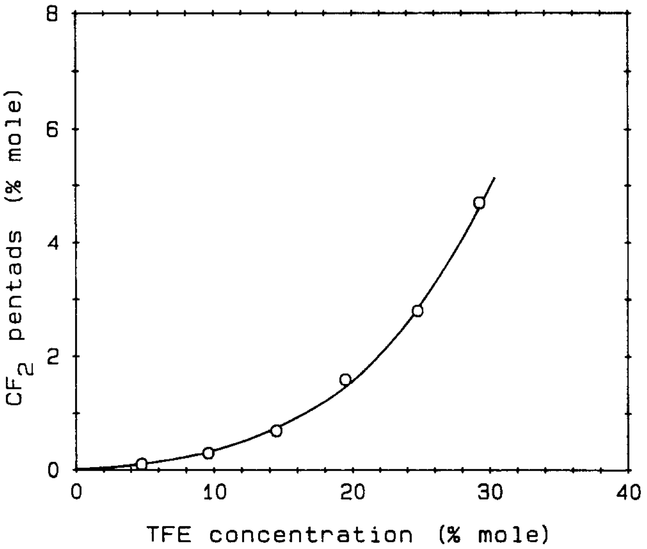

Figure 3 CF$_2$ pentads as a function of TFE content for terpolymers

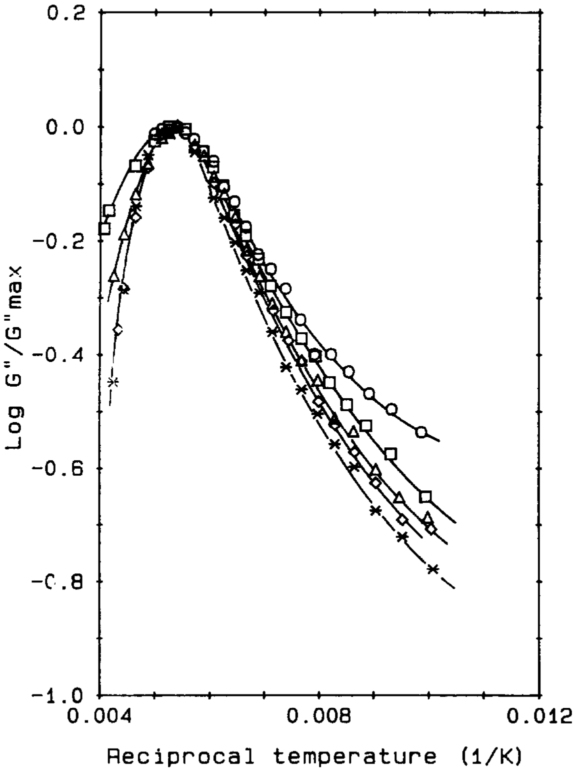

Figure 4 The Fuoss–Kirkwood plot for the β maximum of copolymers: ○, 0; □, 10.2; △, 19.2; ◇, 30.3; ∗, 39.2 mol% HFP

The concentration dependence of T_β is unusual, as shown in *Figure 7a*, where T_β is plotted against TFE molar content. An inflection point is observed at about 18 mol% TFE, after which T_β seems to tend towards a lower limiting value. It is very interesting to observe that if T_β is plotted against pentad concentration the inflection point disappears, as shown in *Figure 8*.

The limiting temperature must, of course, be that of the γ relaxation of the pure polytetrafluoroethylene, which is estimated from the plot to be -105°C. Taking into account that G'' maxima occur at lower temperatures than Δ maxima, the value obtained can be considered to be in good agreement with that reported in literature (-97°C at 1 Hz[11]).

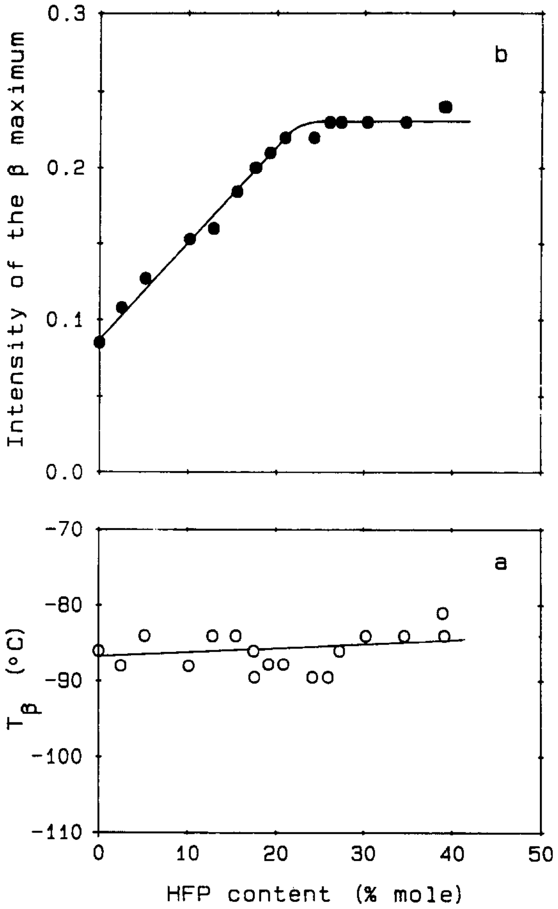

Figure 5 (a) β Relaxation temperature and (b) its intensity for copolymers as a function of composition

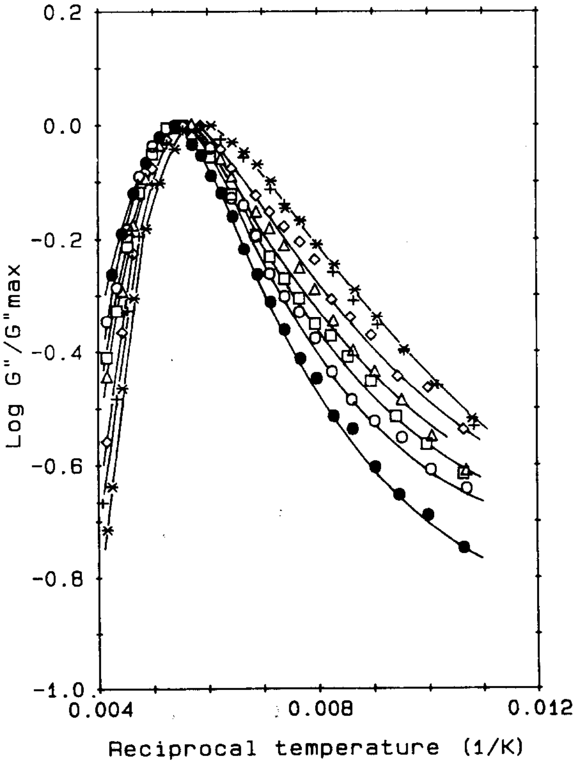

Figure 6 Fuoss–Kirkwood plot for the β maximum of terpolymers: ●, 0; ○, 4.8; □, 9.6; △, 14.5; ◇, 19.5; +, 24.8; ∗, 29.3 mol% TFE

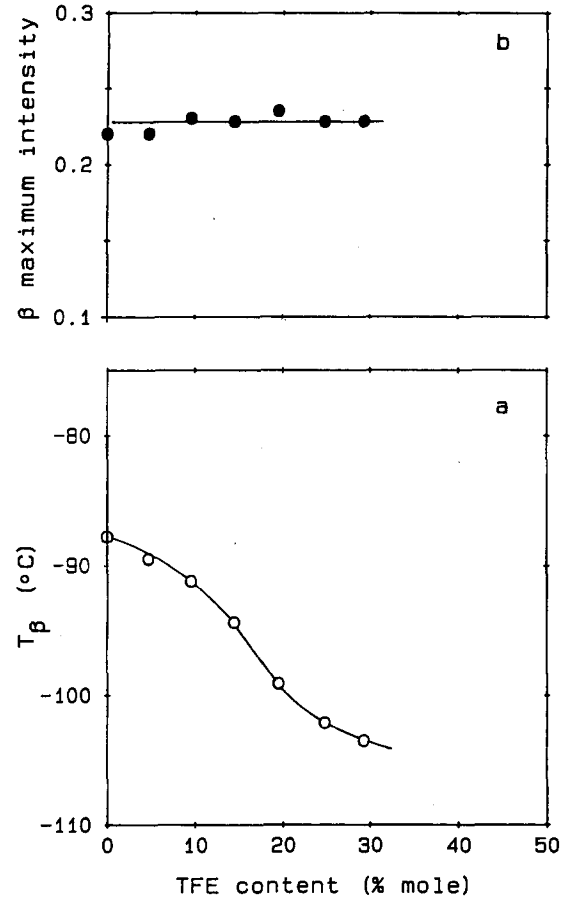

Figure 7 (a) β Relaxation temperature and (b) its intensity for terpolymers as a function of TFE content

The α maximum

Copolymers. The trend of the α maximum, which is related to the glass transition temperature for pure PVDF[9,12,13], shows a very peculiar trend when the composition is changed. It is well known that PVDF shows a double glass transition; such a feature is also typical of some other crystalline polymers, as shown by Boyer[11,13,14]. In his nomenclature the two maxima will be denoted by α_L (lower) and α_U (upper) in the following. The first maximum occurs at about −38°C and the second, which appears as a shoulder of the α_c maximum in the log Δ *versus* T plot, at about 25°C.

Transition temperatures and their intensities are plotted as a function of the HFP molar content in *Figure 9a,b*, respectively. The temperature of the lowest peak (α_L) increases first up to 5 mol% HFP and its intensity remains almost constant. For higher concentrations, up to 19%, the temperature of the α_L maximum can no longer be measured because it is covered by the growing α_U maximum. Log G'' against T plots did not give a better resolution. However, $T_{\alpha,L}$ can be measured by differential scanning calorimetry (d.s.c.); d.s.c. data obtained in a previous work[3] are also reported in *Figure 9*.

The systematic differences between T_α and T_g are due to the different time scales typical of the two different experimental techniques. The α_U maximum shifts towards lower temperatures for HFP concentrations <19% (*Figure 9a*), and its intensity increases steadily up to a limiting value (see *Table 1* and *Figure 9b*). When the HFP content is >19% only one maximum is observed; its intensity, within experimental error (which is large for high damping), remains constant. T_α seems to tend towards an asymptotic value of about ≈0°C for 50 mol% HFP.

Other information can be gained from modulus data in this transition region. It is well known that a semi-empirical relationship can be stated for semi-crystalline polymers between crystallinity and the value of the elastic modulus above T_g[16,17]. Modulus data are

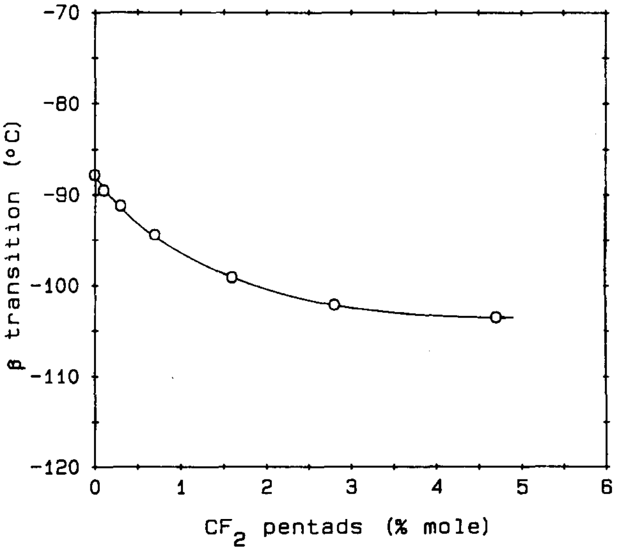

Figure 8 T_β as a function of CF_2 pentad concentration

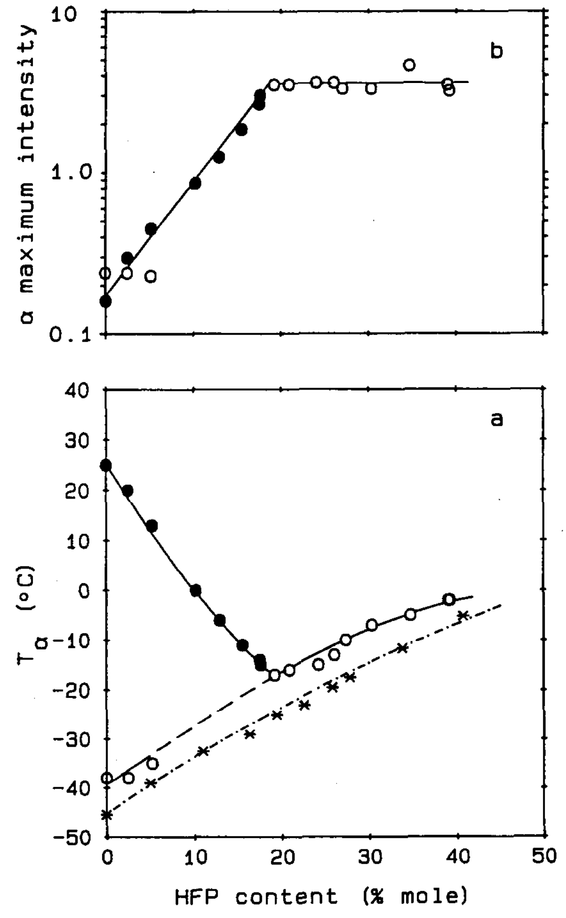

Figure 9 (a) α Relaxation temperature and (b) its intensity as a function of composition for copolymers: ○, $T_{\alpha,L}$; ●, $T_{\alpha,U}$; ∗, d.s.c. data from Reference 3; — · — · —, calculated by the Fox' equation (see text)

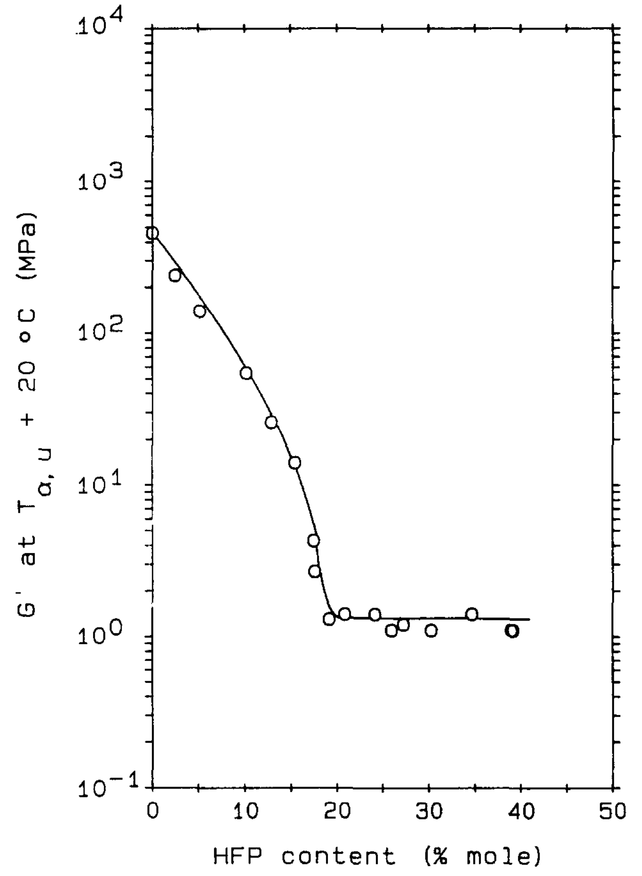

Figure 10 Trend of storage modulus G' at $T_{\alpha,\mathrm{U}}+20°\mathrm{C}$ as a function of composition for copolymers

sensitive even at very low crystallinities, where other methods fail or are affected by large errors. A good example is given by a study on the crystallinity of polyvinylchloride[18]. The relaxed modulus data were conventionally measured at a reduced temperature $T_{\alpha,\mathrm{U}}+20°\mathrm{C}$ or at $T_\alpha+20°\mathrm{C}$, when only a maximum is observed; they are plotted in *Figure 10* as a function of the HFP molar concentration. It can be seen that the storage shear modulus reaches the typical value for a rubbery plateau for a concentration >19–20 mol%.

Terpolymers. All the samples examined show, over all the compositional ranges studied here, only a single relaxation process related to the glass transition. *Figures 11a,b* show, respectively, the trend of T_α and of its intensity as a function of composition. It can be observed from both *Figure 2b* and *Figure 11a* that the maximum is shifted towards higher temperatures with increasing TFE content. The intensity at first remains constant, then begins to decrease for TFE concentrations >20% (*Figure 11b*); such a behaviour would suggest an increasing presence of ordered structures. In agreement with this hypothesis the G' value above T increases above this critical concentration (*Figure 2a*). The relationship between the pseudo-plateau value of the storage modulus, measured at a reduced temperature $T=T_\alpha+20°\mathrm{C}$, and the CF_2 pentad concentration is shown in *Figure 12*.

The α_c maximum and melting

These relaxation processes are observed only for VDF/HFP copolymers. Pure PVDF shows a crystal disorder transition[9,12] which is generally called α_c and occurs at about 75°C at 1 Hz. The introduction of a comonomeric moiety lowers the temperature of this maximum, which disappears at very low HFP concentration (see *Table 1*).

The melting point onset, which can be found either from the sudden drop of G' or from a maximum in Δ (at least for low HFP content), decreases rapidly, as expected, with HFP concentration.

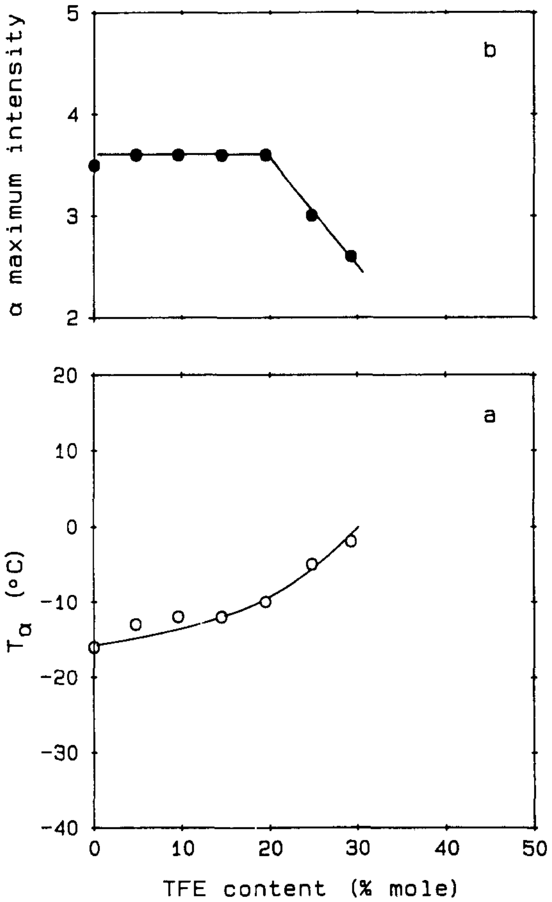

Figure 11 (a) α Relaxation temperature and (b) its intensity as a function of TFE content for terpolymers

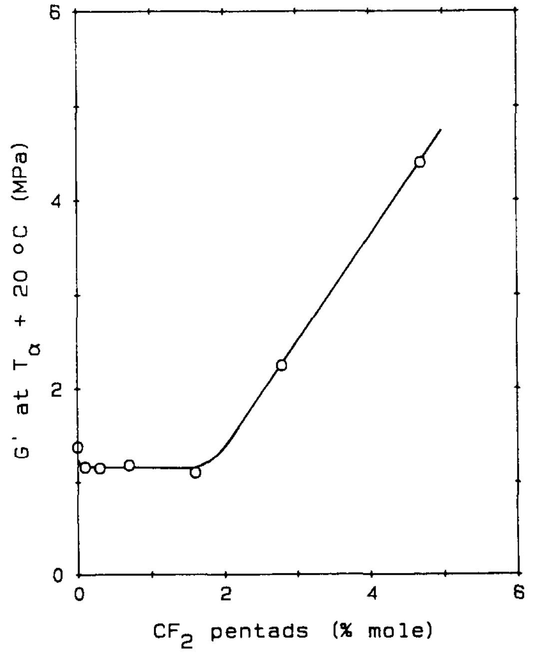

Figure 12 Trend of the storage modulus G' at $T_\alpha+20°\mathrm{C}$ for terpolymers as a function of CF_2 pentad concentration

DISCUSSION

The experimental results show clearly that dynamic-mechanical properties of VDF/HFP copolymers and VDF/HFP/TFE terpolymers are strongly influenced by the presence of ordered structures. Previous work on copolymers[2,3] demonstrated that crystallinity and order do decrease with HFP concentration. Wide angle X-ray (WAXR) measurements allow, for example, extrapolation of the HFP molar concentration for a zero degree of crystallinity at about 19%. The probability of long VDF sequences, as calculated by Markovian statistics and confirmed by n.m.r. analysis, decreases quickly with HFP[4].

All these results are not only in a very good agreement with the measured values of the relaxed storage modulus for copolymers but also with the trend of the intensities of the α and β transitions, which reach a maximum and constant value only above the same critical composition.

The dynamic-mechanical and n.m.r. investigations also allowed detection of the critical value of TFE sequences (or TFE molar content) for the occurrence of ordered structures in terpolymers; the TFE molar concentration is $\approx 20\%$. The degree of crystallinity can be roughly estimated to be $\leqslant 2$–3% for the highest TFE concentration, on the basis of a cross-correlation of moduli data obtained in this work and WAXR data[2] for copolymers.

As mentioned above, both α and β relaxation processes are typical of the amorphous phase; their composition dependence shows peculiarities which will be now discussed.

For the β transition of copolymers it seems strange at first that substitution of linear VDF units with those of HFP, having a bulky side group, does not affect T_β, even at large concentration, when the content of alternate structures increases. The insensitivity of the β relaxation to the comonomer content is very similar to that of ethylene–propylene (E–P) copolymers, where the γ relaxation temperature is unaffected by propylene content over a large compositional range[14,19]; McCrum observed that for TFE–HFP copolymers the γ relaxation temperature, which is related to local motions as the β process considered here, was unaffected by comonomer content up to 14 mol% HFP[20].

Schatzki discussed, on the basis of his well known crankshaft model, the possibility of rotation around the chain axis of a short segment of a polyethylene chain carrying a $-CH_3$ side group[19]. He demonstrated that the rotation is not hindered only if there are at least three methylene groups between the substituted groups. The example given is that of the hydrogenated hevea rubber, which shows a γ relaxation at the same temperature as for linear polyethylene. For random E–P copolymers the segmental rotation is prevented by two adjacent propylene units and the loss intensity accordingly decreases with increasing propylene molar fraction.

Since for VDF–HFP copolymers the presence of two adjacent HFP units is completely excluded, both on the basis of n.m.r. data[4] and because of the reactivity ratios of comonomers, the insensitivity observed of the loss maximum to the composition seems to be justified for the amorphous copolymers on the basis of the Schatzki's model and on the experimental observation of an identical loss intensity for hydrogenated hevea and polyethylene.

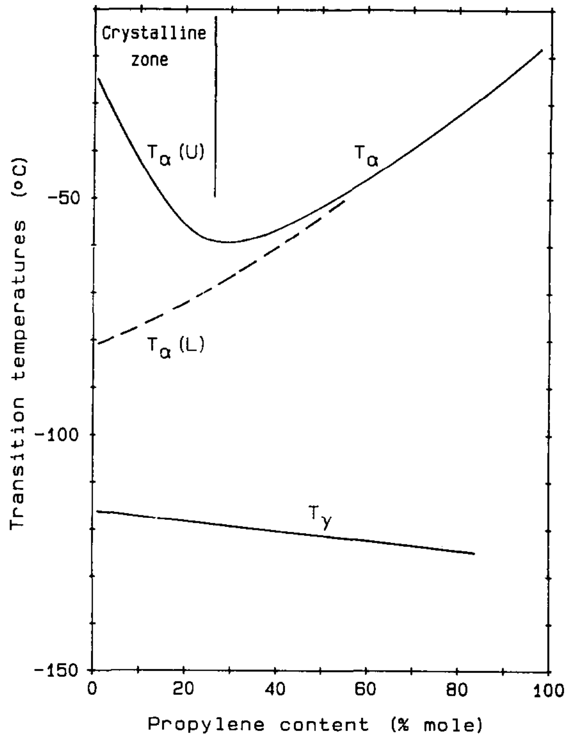

Figure 13 Transitions for ethylene–propylene system (redrawn from Reference 14)

The introduction of a non-polar comonomer like TFE into the copolymeric VDF–HFP chain reduces polar interchain interactions so that the degrees of freedom of the chain segments increase, as shown by the decrease of T_β and the broadening of the spectrum on the low temperature side. It seems reasonable, on the basis of the crankshaft model, that T_β should be directly related to TFE sequences instead of to the gross composition of terpolymers. The Schatzki model requires the rotation of only four carbon atoms around the chain axis. In any case our n.m.r. data show that only a small concentration of adjacent TFE units is sufficient to shift the β transition to temperatures close to that typical of pure PTFE.

As far as the α transition is concerned it is remarkable that the double glass transition behaviour of the VDF–HFP system looks very similar to that of the E–P system (see *Figure 13*). In both cases two transitions are observed only when ordered structures are present, and the upper transition temperature becomes closer to the lower one with decreasing crystallinity.

Then the general explanation given by Boyer for several crystalline polymers (among them there is PVDF) and for E–P copolymers can be directly applied to the system under study. The lower transition is related to disordered chain segments, the motion of which is only weakly restricted by the neighbouring crystalline phase, while the upper transition is related to motions of segments lying at the surface of lamellae with reduced degrees of freedom, such as tie molecules and loose loops. It follows that both are dependent on any factor which is able to influence crystallinity and crystal morphology.

Finally, the trend of T_α towards a limiting value for 1:1 molar composition for copolymers confirms the previous calorimetric work. It was previously shown that T_g cannot be predicted by standard equations, like Fox's equation, by using T_g data fro PVDF and PHFP. Since for 1:1 molar ratio the copolymer is alternate, other more sophisticated equations seemed to be necessary[3].

However, it is shown here that the simple Fox's equation:

$$1/T_g = w_A/T_{gA} + w_B/T_{gB}$$

where w is the weight fraction, and subscripts A and B refer to the A and B monomers, can be used if the copolymer is considered to be composed not by randomly distributed VDF and HFP moieties, but by VDF and $CH_2.CF_2.CF_2.CF(CF_3)$ moieties (where the last unit is that of 1:1 alternate copolymer) and using the corresponding T_g values.

The agreement between calculated and experimental data is very good, as shown in *Figure 9*.

CONCLUDING REMARKS

The results obtained in this study also have some relevance in practice, in that the critical compositions identified for both copolymers and terpolymers can represent a limit for the application of these materials.

For the VDF/HFP system pure elastomeric behaviour can be found for an HFP content >19–20 mol%. In reality the composition of commercial samples is 20–21 mol% HFP, since this represents the best compromise between the requirements of a low T_g and a fully amorphous elastomer.

For the terpolymers studied here a limit is found at about 25 mol% TFE. This should illustrate that high fluorine terpolymers, which are required by industry for their inertness against several chemicals, must be tailored to avoid ordered structures, which are certainly detrimental to good elastomeric behaviour.

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