

## Mechanical Relaxations of Poly(vinylidene Fluoride) and Some of its Copolymers

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### Synopsis

The dynamic mechanical properties of poly(vinylidene fluoride) have been studied under isochronal conditions and the effect of thermal treatment examined. The results are compared with a product of different molecular weight distribution. The study also included the mechanical relaxation spectra of copolymers of vinylidene fluoride and chlorotrifluoroethylene at four compositions and four frequencies as a function of temperature. The thermodynamic parameters associated with the main relaxations were determined and the results discussed on the basis of available information on the degree of crystallinity, copolymer heterogeneity, and main chain flexibility.

### INTRODUCTION

Poly(vinylidene fluoride),  $\text{-(CH}_2\text{-CF}_2\text{)}_n\text{-}$  (PVF<sub>2</sub>), is a relatively new high-performance plastic useful in applications requiring high tensile and impact strength. Its abrasion resistance combined with high dielectric strength and chemical stability under ionizing irradiation are also noteworthy. Melt-spun fibers have excellent properties compared to other commercial fibers.<sup>1</sup>

Copolymerization with other fluorine-containing monomers, such as hexafluoropropylene,  $\text{CF}_3\text{CF=CF}_2$  (HFP), and chlorotrifluoroethylene,  $\text{CF}_2\text{=CFCl}$  (CTFE), yields products of varying degree of flexibility depending on the percentage of methylene groups present. It is reported<sup>2</sup> that varying the amount of vinylidene fluoride comonomer leads to an interesting array of polymeric materials covering the complete spectrum of rheological behavior, i.e., plastic, soluble resin, elastomer. Of particular importance are the thermally stable (up to 200°C) elastomers obtained when the mole percentage of the incorporated  $\text{CF}_2\text{=CH}_2$  is in the range of 47-75.

In this report, the dynamic mechanical behavior of PVF<sub>2</sub> and its copolymers with CTFE at four representative compositions was investigated as a function of temperature and frequency. Though the dielectric prop-

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erties of the homopolymer have been thoroughly examined,<sup>3,4</sup> dynamic mechanical data are limited.<sup>3</sup> It was also of interest to compare our results with a PVF<sub>2</sub> from a different source (Kynar, from Pennwalt Corp.) for which a preliminary investigation had been made.<sup>5</sup> A comparative study on the physicochemical differences between the two homopolymers is available.<sup>1</sup> The effect of thermal history was also studied to determine the influence of the degree of crystallinity on the mechanical relaxations. For the copolymers the frequency shift of the relaxation maxima allowed an estimate of the activation parameters associated with the primary relaxations. We are not aware of any similar work in the literature.

### EXPERIMENTAL

The direct-reading viscoelastometer (Vibron, Model DDVII from Toyo Measuring Instruments, Co., Ltd., Tokyo, Japan) utilizes the forced vibration technique and has been developed by Takayanagi.<sup>6</sup> The measurement chamber was kept moisture free by a stream of precooled nitrogen gas.

The complex modulus and loss tangent,  $E^*$  and  $\tan \delta$ , respectively, were determined between  $-90^\circ$  and  $180^\circ\text{C}$  at 110 Hz for PVF<sub>2</sub>. The pellets of the pure homopolymer (Dalvor 8200, Diamond Alkali, Co.) were hot pressed under 3000 psi at  $190^\circ\text{C}$  for 5 min and quenched in ice. For the annealed specimens, a higher temperature ( $220^\circ\text{C}$ ) was used and the specimens were cooled under reduced pressure (100 psi) to room temperature within 2 hr approximately.

The copolymers with 25, 50, and 70 mole-% VF<sub>2</sub> (Minnesota Mining and Manufacturing Co.) were hot pressed under 3000 psi at  $170$ – $180^\circ\text{C}$  for 7 min. For the 3 mole-% VF<sub>2</sub> copolymer, more severe conditions were required (5000 psi at  $265^\circ\text{C}$  for 15 min) to obtain transparent, stress-free films. Samples quenched in ice and annealed by slow cooling were examined.

TABLE I  
Properties of the Polymers Studied

Polymer, mole-% VF <sub>2</sub> in copolymer	Density, g/cm <sup>3</sup>	$T_g$ , °C	$T_m$ , °C	Crystalline form
0 (PCTFE) <sup>a</sup>	2.107–2.124 <sup>b</sup>	–35	212–224	hexagonal
3 (3VF <sub>2</sub> cop)	2.09–2.12 <sup>b</sup>	~52 <sup>c</sup>	~197 <sup>c</sup>	hexagonal (helical arrangement)
25 (25VF <sub>2</sub> cop)	2.02	—		amorphous
50 (50VF <sub>2</sub> cop)	1.85	0		amorphous
70 (70VF <sub>2</sub> cop)	1.85	–15		amorphous
100 (PVF <sub>2</sub> )	1.776–1.780 <sup>b</sup>	–40	168	quenched $\alpha$ -form (stag- gered conformation) annealed $\beta$ -form (planar zigzag)

<sup>a</sup> A. H. Scott, D. J. Scheiber, A. J. Curtis, J. I. Lauritzen, Jr., and J. D. Hoffman, *J. Res. Nat. Bur. Stand.*, **66A**, 269 (1962).

<sup>b</sup> Indicates higher crystallinity.

<sup>c</sup> Data based on a 4% VF<sub>2</sub> sample; G. C. Adams and R. S. Stein, *J. Polym. Sci. A-2*, **6**, 31 (1968).

Isochronal measurements at 3.5, 11, 35, and 110 Hz were made between  $-90^{\circ}\text{C}$  to the highest temperature before the onset of flow. Table I summarizes the polymers studied and some of their properties. The PCTFE is included for comparison purposes.

## RESULTS AND DISCUSSION

### Homopolymer

Figure 1 shows the mechanical relaxation spectrum of PVF<sub>2</sub> in the annealed and quenched states. Both loss modulus and tangent indicate three relaxations. A very weak one near  $-80^{\circ}\text{C}$  ( $\gamma$ ), the main relaxation at  $-32^{\circ}\text{C}$  ( $\beta$ ), and an additional one at  $40^{\circ}\text{C}$  ( $\alpha$ ). At a comparable frequency the dielectric technique<sup>4</sup> located the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -relaxations at  $68^{\circ}$ ,  $-30^{\circ}$ , and  $-80^{\circ}\text{C}$ , respectively. Kakutani<sup>3</sup> reported a higher temperature for the  $\alpha$ -peak and an additional relaxation near  $0^{\circ}\text{C}$  for which there is evidence in the annealed specimen.

The  $\gamma$ -peak has been attributed to local chain motions below the  $T_g$  while the  $\beta$ -relaxation has been attributed to large segmental main-chain motions at the  $T_g$ . Dilatometric measurements<sup>7</sup> give a  $T_g$  near  $-35^{\circ}\text{C}$ . All relaxations are reduced by annealing. For the  $\alpha$ -peak, this may suggest that its origin lies in the amorphous phase. For an analogous polymer, poly(vinylidene chloride), a peak in the vicinity of  $70^{\circ}\text{C}$  was attributed to motions within strained amorphous regions.<sup>8</sup> This is not consistent with present concepts on the state of the amorphous phase in a semicrystalline polymer. The larger the size and the higher the amount of crystallites pro-

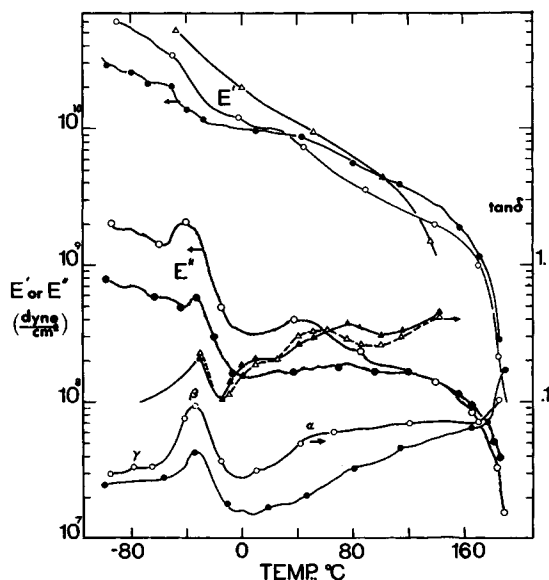


Fig. 1. Dynamic moduli  $E'$ ,  $E''$ , and loss tangent  $\tan \delta$  of PVF<sub>2</sub> at 110 Hz. Effect of thermal treatment: (●) annealed; (○) quenched. Storage modulus ( $\Delta$ ) and loss tangent of annealed (— $\blacktriangle$ —) and quenched (— $\Delta$ —) specimens of Kynar, ref. 5.

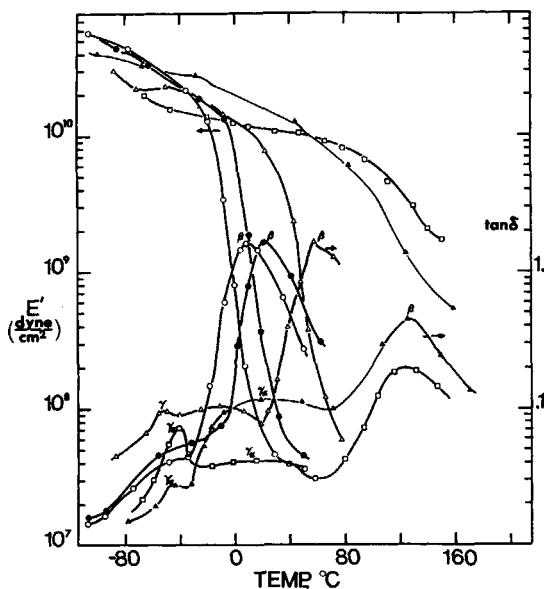


Fig. 2. Storage modulus  $E'$  and loss tangent  $\tan \delta$  of CTFE- $\text{VF}_2$  copolymers at 110 Hz: 3  $\text{VF}_2$  cop (▲) quenched, (□) annealed; (Δ) 25  $\text{VF}_2$  cop; (●) 50  $\text{VF}_2$  cop; (○) 70  $\text{VF}_2$  cop.

duced by annealing, the more the intervening amorphous phase will be strained. A more recent view attributes the origin of the  $\alpha$ -relaxation to molecular motions in the chain-folded surfaces of the lamellae. As the single crystals thicken by annealing, a decrease in the number of folds causes a decrease of the relaxation magnitude. The mechanism is thoroughly discussed by Hoffman and co-workers.<sup>9</sup>

It is of interest to note the lower modulus of the more crystalline sample below  $T_g$ . Similar behavior has been observed for the case of PCTFE of different degrees of crystallinity.<sup>10</sup> This should rather be attributed to the larger size of crystallites formed causing defects and weakening the crystal lattice. In cases where a microcrystalline structure is formed, as in polypropylene and polyethylene,<sup>11</sup> crystallinity reinforced the polymer also below the  $T_g$ . At higher temperatures, the reinforcing action of the crystallites predominates giving a higher modulus to the annealed specimen. The same remark applies for the annealed and quenched semi-crystalline specimen of 3 $\text{VF}_2$  copolymer (see Fig. 2).

In Figure 1 it is seen that one of the main differences between the two types of  $\text{PVF}_2$  is the higher modulus of our sample at elevated temperatures. This is attributed to its higher crystallinity caused by a narrow Gaussian-type MW distribution.<sup>1</sup> The lower overall crystallinity attained by the other sample explains its higher level of damping for the annealed or quenched specimens. There also seems to be an extra relaxation around 0°C due to the crystalline region. It is possible that the bimodal distribution of MW for this product gives rise to two types of lamellae differing in their  $\alpha$ -relaxation behavior.

### Copolymers

The relaxation spectra are shown in Figure 2. A small amount of vinylidene units does not disrupt the crystalline structure of PCTFE significantly. Adams and Stein<sup>12</sup> report that a copolymer with 4 mole-% VF<sub>2</sub> crystallizes in the hexagonal system, though at a lower rate. This is further supported by electron diffraction studies<sup>13</sup> indicating that crystallinity persists up to 16 mole-% VF<sub>2</sub> and that the crystallizing component is PCTFE. Therefore, we would expect that the relaxation spectrum will have the characteristic features of those of PCTFE homopolymer. The main relaxation,  $\beta$ , at 105°C (3.5 Hz) is close to that reported by McCrum<sup>10</sup> (100°C at 1 Hz). Two other relaxations below  $T_g$  were attributed to the amorphous ( $\gamma_a$ ) and crystalline ( $\gamma_c$ ) regions. The annealed sample indicates indeed that such an assignment is correct. It is noteworthy that the equilibrium  $T_g$  (52°C) or  $E_{\max}''$  is significantly lower than  $\tan \delta_{\max}$ . This is due to the shift to higher temperatures of the ratio  $(E''/E')_{\max} = \tan \delta_{\max}$  because of the action of crystallinity and polarity enhancing the value of  $E'$ . The origin of the relaxation has not been clarified. Though it has been suggested<sup>14</sup> that it arises from motions within the chain backbone, the loosening of an intermolecular packing could be another alternative.<sup>15</sup> This is plausible in view of the polar nature of the polymer chain.

As the number of the vinylidene units increases, the chain flexibility is enhanced and the  $\beta$ -relaxation is moved to lower temperatures and its magnitude increased. This amorphous character is caused by the disorder of the crystalline lattice brought about by substituents of the carbon atom with very different dimensions. All the copolymers show a  $\gamma$ -relaxation to which their good impact strength properties can be attributed. The broad mechanical spectrum of the 25 VF<sub>2</sub> copolymer indicates considerable structural heterogeneity. Annealing and further purification (by reprecipitation from an acetone solution) did not alter the results. The reactivity ratios for the system CTFE(1)-VF<sub>2</sub>(2) are  $r_1 = k_{11}/k_{12} = 0.52$  and  $r_2 = k_{22}/k_{21} = 0.17$ . Thus, CTFE monomer units would predominate during the initial stages of polymerization but with a strong overall tendency for alternation ( $r_1 r_2 = 0.088$ ). At higher degrees of conversion, the VF<sub>2</sub> sequences are expected to increase. It is therefore possible to have copolymer heterogeneity depending on the degree of conversion. It is pertinent to note that the copolymer is compatible with both PCTFE and PVF<sub>2</sub>.

The various mechanical relaxation data obtained are given in Table II. Their frequency dependence allowed the determination of the activation energy using the standard expression

$$\Delta H = -R \frac{\partial \ln w_{\max}}{\partial(1/T)} \quad (1)$$

where  $w$  is the angular frequency of oscillation. For the elastomers, a small curvature was observed and the corresponding maximum variation is indicated. Because of considerable broadening, the  $\gamma$ -relaxation shift

TABLE II  
Primary Relaxations and Their Activation Parameters of the Polymers Studied<sup>a</sup>

Polymer, mole-% VF <sub>2</sub>	Fre- quency, Hz	$\beta$ -Relaxation				$\gamma$ -Relaxation			
		$\tan \delta_{\max}$ , °K	$E_{\max}$ , °K	$\Delta H$ , kcal/mole	$\Delta S$ , e.u.	$\tan \delta_{\max}$ , °K	$E_{\max}$ , °K	$\Delta H$ , kcal/mole	$\Delta S$ , e.u.
0 <sup>b</sup>	—	—	—	50(av)	—	—	15	—	—
3	3.5	379.5	363.0	48	74	271.0	248.0	31	62
	11	386.0	369.0			278.0	253.0		
	35	390.0	373.0			281.0	263.0		
	110	400.0	379.0			288.0	268.0		
25	3.5	320.0	300.0	70	166	248.0	—	~37	~97
	11	324.5	304.0			—	—		
	35	328.0	307.0			256.5	—		
	110	331.0	315.0			260.0	221.0		
50	3.5	280.2	270.0	49-32	87(av) <sup>c</sup>	—	197.0	32	97
	11	284.0	273.0			218.0	206.0		
	35	287.5	275.0			223.0	220.0		
	110	294.5	280.0			225.0	—		
70	3.5	266.0	255.0	36-28	72(av) <sup>c</sup>	255.0	198.0	19	25(av) <sup>c</sup>
	11	270.0	257.0			257.0	—		
	35	275.5	261.0			261.0	203.0		
	110	282.0	263.0			263.0	213.0		
100	110	241.0	233.0	30(av) <sup>d</sup>	84(av) <sup>c</sup>	193.0	—	—	—

<sup>a</sup> Specimens quenched.

<sup>b</sup> A. H. Scott, D. J. Scheiber, A. J. Curtis, J. I. Lauritzen, Jr., and J. D. Hoffman, *J. Res. Nat. Bur. Stand.*, **66A**, 269 (1962).

<sup>c</sup> Average values.

<sup>d</sup> S. Yano, *J. Polym. Sci. A-2*, **8**, 1057 (1970).

could not be determined accurately in all cases. Application of the Absolute Reaction Rate Theory<sup>16</sup> gives also the entropy of the relaxation  $\Delta S$ , which is indicative of the degree of disorder attained. Use was made of the following relationship<sup>17</sup> applicable to a single relaxation time model

$$\tan \delta = 2(\tan \delta)_{\max} \left( \frac{w}{1 + w^2 \tau^2} \right). \quad (2)$$

The condition for maximum is  $w\tau = 1$ , where  $\tau$  is the average relaxation time. The fundamental rate equation<sup>16</sup>

$$k = \frac{RT}{Nh} e^{\Delta S/R} e^{-\Delta H/RT} \quad (3)$$

can be solved for  $\Delta S$  with  $k = 1/\tau$ . It is seen that for all copolymers except the 25 VF<sub>2</sub> copolymer, because of structure similarity, the entropy increase and the required activation energy is fairly similar. For the heterogeneous copolymer, a large activation energy is required for the relaxation since it is essentially a cooperative segmental motion.

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