Piezoelectric Properties and Temperature Stability of Poly(Vinylidene Fluoride-Trifluoroethylene) Copolymers

G. M. STACK AND R. Y. TING

Abstract—Piezoelectric measurements were made on several copolymers of vinylidene fluoride and trifluoroethylene having a vinylidene fluoride concentration in the range of 65 to 75 percent. The hydrostatic $g$ constant showed only a slight dependence on pressure, and pressures up to 35 MegaPascal (MPa) caused no apparent loss of the piezoelectric activity. A significant increase in the value of the hydrostatic $g$ constant was observed both at temperatures above and considerably below the room temperature. The anomalous result obtained upon cooling below the room temperature may be attributed to the glass transition temperature of the trifluoroethylene comonomer. Temperature aging studies were performed at high temperatures using films of these copolymers. A significant loss of piezoelectric activity occurred after long-time exposure. Isothermal studies at various aging temperatures revealed that this decay continued over a long time span. The aging behavior characteristically followed a linear dependence on the logarithm of aging time.

I. INTRODUCTION

COPOLYMERS of vinylidene fluoride (VF$_2$) and trifluoroethylene (TrFE) are presently being considered for many piezoelectric applications. These copolymers exist in a crystal phase that yields large piezoelectric coefficients upon poling [1]. In contrast, the proper crystal phase can only be attained in poly(vinylidene fluoride) (PVDF) homopolymer by poling extruded and stretched films [2]. The stretching process causes an asymmetry in the film that has been shown to cause complications in the design of piezoelectric devices such as sonar arrays. Therefore, the copolymer systems are likely to be more useful for such applications.

A great deal of work has been done on the piezoelectric properties of PVDF homopolymer. Its piezoelectric coefficients have been found to have a strong temperature dependence [2], [3]. At very low temperatures, below the glass transition temperature of PVDF, the piezoelectric coefficients are almost independent of temperature. A large increase in piezoelectric activity occurs when the temperature is raised through this glass transition region. Further increases in temperature only lead to a small additional increase in the piezoelectric coefficients. But, long-term exposure of the PVDF films at these higher temperatures has been shown to result in a reduction in piezoelectric activity [4], [5]. This loss of activity depends on the logarithm of the aging time and continues over many decades of aging time [5]. The application of large hydrostatic pressures also decreases the activity of a sample, but no irreversible loss is seen except in the case of highly voided samples [6].

In contrast to the work on PVDF, little has been reported on the effects of pressure and temperature on the piezoelectric coefficients of copolymers of vinylidene fluoride and trifluoroethylene. The glass transition temperature of polytrifluoroethylene is just slightly below room temperature, but much higher than that of PVDF. One may therefore expect that the temperature dependence of these copolymers is likely to be more complex than that of PVDF homopolymer. The measurement of dynamic mechanical properties of these copolymers showed that separate relaxation processes occurred near the glass transition temperatures of each of the corresponding homopolymers [7]. Furthermore, in all of the published temperature studies only the measurement of the piezoelectric $d_{31}$ constant was reported. In general, a continuous increase in the value of $d_{31}$ was observed with increasing temperature [1], [8]. In this report, the results of hydrostatic-mode measurements on the piezoelectric properties of vinylidene fluoride and trifluoroethylene copolymers having different compositions are presented. The effects of pressure, temperature and extended thermal aging on the piezoelectric properties of the copolymers are also investigated.

II. EXPERIMENTAL

Copolymers of vinylidene fluoride and trifluoroethylene with compositions ranging from 65- to 75-percent of VF$_2$ were obtained from the Pennwalt Corporation. The piezoelectric and dielectric constants of the copolymer samples, once poled, were measured with an acoustic reciprocity technique that has been described previously [9]. Samples were placed in a castor-oil-filled acoustic coupler with temperature and static pressure controlled to within 0.1°C and 0.02 MPa, and a sinusoidal acoustic pressure was applied at 1-kHz. The adiabatic hydrostatic piezo-
electric \( d \) and \( g \) coefficients were measured. These coefficients are defined as
\[
d = \left( \frac{\partial D}{\partial T} \right)_E, \quad g = \left( \frac{\partial E}{\partial T} \right)_D.
\]
These coefficients, therefore, give the relationships between charge density \( D \), electric field \( E \), and mechanical stress \( T \). The relative dielectric constant \( K_{33}^f \) was calculated from 1-kHz capacitance measurements while the sample was in the coupler.

The aging experiments were carried out in situ by aging the samples directly in the coupler. The same sample was heated to progressively higher temperatures and held for a specified period of time at each aging temperature. Measurements were made both as a function of time at the aging temperature and after subsequent cooling to room temperature. A minimum equilibration period of 12 h was allowed before the subsequent room-temperature measurements were made.

III. RESULTS AND DISCUSSIONS

The hydrostatic \( g \) coefficients, \( g_h \), of each of the copolymers are plotted as a function of hydrostatic pressure in Fig. 1. It is clear from this figure that the \( g_h \) coefficients of these copolymers have only a very small dependence on hydrostatic pressure. For example, as the pressure was increased from 1 to 35 MPa, the hydrostatic \( g \) coefficient for a 68-percent \( \text{VF}_2 \) sample decreased from 148 to 142 mV-m/N, a less than 0.5-dB reduction. In each of these copolymers, when the pressure was lowered back to 1 MPa, the samples returned to their initial level of activity with no irreversible degradation.

The temperature dependence of the hydrostatic \( g \) coefficient is shown in Fig. 2 for a 75-percent \( \text{VF}_2 \) copolymer. A significant increase in the hydrostatic \( g \) coefficient occurs when the temperature is raised above room temperature. Similar behavior has been observed for the piezoelectric \( d_{31} \) coefficient in previous studies of these \( \text{VF}_2/\text{TrFE} \) copolymers [1], [8]. This behavior has been attributed to the increased mobility of the amorphous segments as the temperature is raised further above the glass transition temperature. Above 60°C is the temperature region where degradation of the sample's piezoelectric property takes place. The high-temperature stability of the copolymers will be discussed in detail below. A more striking observation is the large increase in the hydrostatic \( g \) coefficient found when cooling below room temperature. Such an increase at low temperatures has not been reported previously in either the \( d \) or \( g \) coefficients of these copolymers or PVDF homopolymer. To examine this behavior more closely, the hydrostatic \( d \) coefficient, \( d_h \), and the relative dielectric constant \( K_{33}^f \) of this 75-percent \( \text{VF}_2 \) copolymer are plotted as a function of temperature in Figs. 3 and 4.

Examination of Fig. 3 indicates that the \( d_h \) coefficient continuously decreases as the temperature is lowered. The observed increase in the \( g_h \) therefore does not correspond to an actual increase in the sample's piezoelectric activity. Rather, the increase in \( g_h \) is caused by the decrease of the dielectric constant as the temperature is lowered. As shown in Fig. 4, this decrease of the dielectric constant becomes more pronounced in the low temperature region where \( g_h \) begins to increase. This rapid decrease in \( K_{33}^f \) with temperature causes the observed increase in the \( g_h \), even though the hydrostatic \( d \) coefficient is also decreasing. The temperature region where this anomalous behavior occurs coincides with that where these copolymers undergo the mechanical transition associated with the glass transition of the trifluoroethylene component [7]. It is very likely that the large decrease in the dielectric constant is a manifestation of the polymer being taken through this glass transition.

The temperature dependence described for the 75-percent \( \text{VF}_2 \) copolymer also was found in the copolymers of other compositions. As the \( \text{VF}_2 \) content was decreased to 68 percent, the \( g_h \) coefficient reached a low temperature maximum at -17°C and then started to decrease again at temperatures below this value. For the 65-percent \( \text{VF}_2 \) copolymer, the \( g_h \) coefficient initially remained constant as the temperature was lowered from room temperature. It began to show a decrease with temperature only below -19°C. In all of these copolymers the hydrostatic \( d \) and \( K_{33}^f \) continuously decreased as the temperature was lowered. It appears that the behavior of the \( g_h \) depends on the relative rate of decrease of the \( d \) and \( K_{33}^f \) constants.

Upon heating these copolymers to temperatures above 60°C, a reduction in the sample's piezoelectric activity became evident. To monitor this loss of activity, the piezoelectric coefficients were measured as a function of time as the samples were maintained at the high temper-
ture in the coupler. In Fig. 5, the hydrostatic $g$ coefficient of a 70-percent VF$_2$ copolymer is plotted as a function of the logarithm of aging time at 85°C.

Some uncertainty in the total exposure time existed because it took several minutes to raise the sample temperature to the new level in the coupler. Within the accuracy of the measurement, it appears that the $g_h$ coefficient decreased linearly as a function of the logarithm of aging time. In general, the copolymers continued to lose activity as aging progressed for as long as 48 h. In the example of Fig. 5, the $g_h$ is clearly continuing to decrease after 24 h of exposure at 85°C.

The piezoelectric coefficients measured after aging at several temperatures cannot be compared directly because of the strong temperature dependence of these properties. To assess the relative degradation resulting from high-temperature aging, the piezoelectric coefficients were measured at the room temperature after high-temperature exposure. In these experiments, the samples were allowed to reequilibrate at room temperature for at least twelve hours before the final piezoelectric measurements were made. The results for a 65-percent VF$_2$ copolymer are summarized in Fig. 6, where the room-temperature $g_h$ is plotted as a function of the aging temperature after 24-h exposures at the aging temperatures. It is evident that at temperatures as low as 50°C some loss of activity has taken place. Aging at progressively higher temperatures resulted in much greater decreases in the value of the $g_h$. 

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**Fig. 2.** Hydrostatic $g$ coefficient as function of temperature for 75-percent VF$_2$ copolymer.

**Fig. 3.** Hydrostatic $d$ coefficient as function of temperature for 75-percent VF$_2$ copolymer.
coefficient. For the example shown in Fig. 6, aging at 84°C lowered the room-temperature value of $g_h$ to 60 percent of its original value.

To compare the thermal stability of the various copolymers, ratios of the room-temperature hydrostatic $g$ coefficients of the aged to those of the original samples were calculated. These ratios are plotted as a function of aging temperature in Fig. 7. These ratios were calculated after 24 h of exposure at each of the aging temperatures. It appears that the thermal stability of these copolymers deteriorates as the VF$_2$ content decreases. These copolymers are known to undergo a solid-state transition to a less ordered phase at a somewhat higher temperature [8], [10]. This transition, which occurs over a broad temperature range, results in a loss of the sample's polarization and piezoelectric activity. Earlier scanning calorimetry studies have found that the peak transition temperature decreases from 130 to 100°C as the VF$_2$ content was decreased from 80 percent to 65 percent [11]. The larger amount of thermal degradation observed in the copolymers with lower VF$_2$ content may be due to their solid-state transition occurring at a lower temperature.

The effects of high temperature exposure on the hydrostatic $d$ coefficient and the dielectric constant $K_{33}^T$ were also examined in this study. The changes in $g_h$, $d_h$, and $K_{33}^T$ induced by aging are listed in Table I for several of the copolymers. In each of these samples comparable changes in $d_h$ and $K_{33}^T$ were observed at the higher aging
temperatures. These changes make approximately equal contributions to the observed reduction in the $g_{h}$ coefficient. At lower aging temperatures, some difference in behavior was found. For the 70-percent VF$_2$ copolymer the initial reduction in $g_{h}$ is caused completely by a reduction in $d_{h}$. In contrast, it is an increase in $K_{33}^3$ that causes the decrease in $g_{h}$ for the 65- and 68-percent VF$_2$ copolymers at the lower aging temperatures. These results differ from the observations made on the aging behavior of PVDF homopolymer [4]. In those studies, the reduction in piezoelectric activity was found to be almost exclusively due to a reduction in the hydrostatic $d$ constant. A slight increase of the dielectric constant was observed, but the increase would cause only a small part of the observed decrease in the hydrostatic $g$ constant.

It was noted in a related study of the effects of thermal aging that the dielectric coefficients would return to their initial values after cooling from the high temperature [12], [13]. This recovery was found to occur slowly over the course of several days. If such a reduction in the dielectric constant occurred, it would result in some increase in the $g_{h}$ coefficient. To investigate this recovery process, room temperature piezoelectric measurements were made over the course of several weeks on a sample of the 70-percent VF$_2$ copolymer that had been aged at 85°C. As shown in Fig. 8, a fairly linear increase in the hydrostatic $g$ coefficient was found to occur over several decades of the logarithm of recovery time. This increase in the $g$ coefficient, although significant, does not result in a return to the sample's initial level of activity. The high-temperature aging

**Fig. 6.** Room-temperature hydrostatic $g$ coefficient for 65-percent VF$_2$ copolymer as function of aging temperature.

**Fig. 7.** Room-temperature hydrostatic $g$ coefficients as function of aging temperature for copolymers having VF$_2$ contents of: ○ 65 percent, △ 68 percent, ▲ 70 percent, ◆ 70 percent, and □ 75 percent.

<table>
<thead>
<tr>
<th>Percent VF$_2$</th>
<th>Temperature (°C)</th>
<th>$K_{33}^3/K_{33}^T$ (Initial)</th>
<th>$d_{h}/d_{h}$ (Initial)</th>
<th>$g_{h}/g_{h}$ (Initial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>56.4</td>
<td>1.0</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>70</td>
<td>85.0</td>
<td>1.07</td>
<td>0.89</td>
<td>0.83</td>
</tr>
<tr>
<td>70</td>
<td>92.0</td>
<td>1.18</td>
<td>0.92</td>
<td>0.69</td>
</tr>
<tr>
<td>68</td>
<td>53.5</td>
<td>1.04</td>
<td>1.00</td>
<td>0.97</td>
</tr>
<tr>
<td>68</td>
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<td>1.00</td>
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</tr>
<tr>
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<td>68</td>
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<td>0.92</td>
<td>0.83</td>
</tr>
<tr>
<td>65</td>
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<td>1.00</td>
<td>0.97</td>
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</tr>
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<td>65</td>
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<td>0.81</td>
<td>0.61</td>
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</table>
for 24 h resulted in a reduction of the $g$ coefficient from 143 to 119 mV-m/N. During the subsequent 10 weeks at room temperature the $g$ coefficient had only increased back up to 124 mV-m/N. The changes in the relative dielectric constant and the hydrostatic $d$ coefficient over the course of the recovery period are shown in Figs. 9 and 10. The relative dielectric constant recovers by decreasing linearly as a function of the logarithm of the recovery time. This decrease in the dielectric constant explains the observed increase in the hydrostatic $g$ coefficient. In fact, larger increase in the $g$ coefficient should have occurred due to the recovery of the dielectric constant. However, a small decrease in the hydrostatic $d$ coefficient also occurred during the recovery period as shown in Fig. 10.

It is therefore clear that some minor recovery in properties does occur over a long time, but this recovery does not significantly affect the aging results presented above. The changes are quite small and a significant part of the observed recovery takes place at the beginning of the recovery period. Therefore, the room temperature measurements made after 12 h would not be significantly different from the results that would be measured after much longer recovery times.

IV. CONCLUSION

These copolymers with VF$_2$ contents in the range from 65-percent to 80-percent appear to be promising piezoelectric materials. The poled samples of each of these copolymers were found to have large hydrostatic $g$ coefficients greater than 100 mV-m/N. These hydrostatic $g$ coefficients showed little change with hydrostatic pressure and pressures up to 35 MPa caused no irreversible loss of
activity. In contrast, a greater variation of the hydrostatic $g$ coefficient occurs with changes in temperature. At temperatures above $60^\circ C$ a permanent loss of activity occurs. This decay is found to depend logarithmically on the time that the sample is maintained at the high temperature. On cooling, some recovery of the piezoelectric properties occurs but the original level of activity is not attained.

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REFERENCES


Gary M. Stack was born on November 12, 1956, in New Orleans, LA. He received his B.S. degree in chemistry from the University of New Orleans in 1978 and the Ph.D. degree in physical chemistry from Florida State University, Tallahassee, in 1983.

He held the position of Postdoctoral Research Assistant at the University of Massachusetts from 1983 to 1984 and is currently employed in the Acoustic Materials Branch at the Naval Research Laboratory's Underwater Sound Reference Detachment in Orlando, FL.

Dr. Stack is a member of the American Chemical Society and a recipient of a Proctor and Gamble fellowship from Florida State University.

Robert Y. Ting was born on March 8, 1942, in Kwai-Yang, China. He received his B.S. degree from the National Taiwan University in 1964, and the M.S. degree from the Massachusetts Institute of Technology, Cambridge, MA, in 1967, and the Ph.D. degree from the University of California at San Diego in 1971. He has been employed by the Naval Research Laboratory (NRL) since 1971 and is presently the Head of the Acoustic Materials Branch of NRL's Underwater Sound Reference Detachment in Orlando, FL. In this position, he is in charge of the basic research and exploratory development of underwater acoustic materials.

Dr. Ting is a member of the Acoustical Society of America and the American Chemical Society, and is listed in the American Men and Women of Science and Who's Who in Frontiers of Science and Technology.