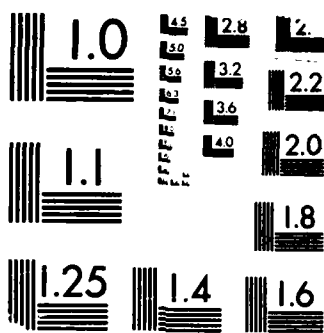


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Piezoelectric measurements were made on several copolymers of vinylidene fluoride and trifluoroethylene having a vinylidene fluoride concentration in the range of 65 to 75%. The hydrostatic g constant showed only a slight dependence on pressure, and pressures up to 35 MPa caused no apparent loss of the piezoelectric activity. A significant increase in the value of the hydrostatic g constant occurred with an increase in temperature. Anomalous results obtained upon cooling below 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 behaviour characteristically followed a linear dependence on the logarithm of aging time.

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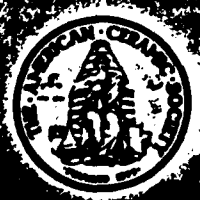
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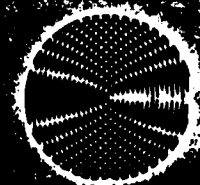
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SYMPOSIUM OVERVIEW

The 1986 IEEE International Symposium on the Applications of Ferroelectrics was held at Lehigh University from June 8 to 10, 1986. More than three hundred seventy scientists and engineers participated in the twenty-eight oral and poster sessions. It is heartening to note that the participants included over eighty students as these young workers constitute the future of our profession. Researchers from industrial, university and government laboratories provided a good balance of perspectives. The eighty-two participants from eighteen countries outside the U.S. verify the truly international character of this meeting. The many spirited technical discussions — both in the meeting rooms and corridors — testify to the value of this Symposium for the interchange of technical information on ferroelectric materials and their applications.

This Symposium was the sixth in a series begun in 1968 organized by the IEEE Committee on Ferroelectrics. Each symposium has been larger and more vigorous than the preceeding, thereby recording the growth and dynamism in ferroelectrics research. 1986 marked a particularly significant milestone in the maturation process: the emergence of the IEEE Ultrasonics, Ferroelectrics, and Frequency Control Society from its predecessor, the IEEE Group on Sonics and Ultrasonics. In a brief ceremonial session at this meeting the Certificate of Recognition of the IEEE Committee on Ferroelectrics was presented to Cecil E. Land in recognition of both his scientific contributions in ferroelectrics research and of the key role he played in bringing the *ferroelectrics community* to full partnership in the IEEE Ultrasonics, Ferroelectrics, and Frequency Control Society.

The Symposium began on Sunday afternoon with an educational session comprising introductory lectures by R.E. Newnham, R.C. Pohanka and A.M. Glass. This was the first time for such tutorial overviews to start our meeting. The response was enthusiastic — nearly one hundred fifty persons attended. Monday through Wednesday, the technical sessions, both poster and oral, proceeded in two parallel streams in adjacent buildings. The grassy mall between the auditoriums provided a beautiful site for coffee breaks and informal technical discussions. The lunches, a reception, a picnic and a banquet provided further opportunities for the informal dialogue that accomplishes the main purpose of scientific meetings: information interchange. All participants are indebted to Lehigh's Local Arrangements Committee, headed by Martin Harmer, for smoothly orchestrating these events; they added much to the productivity and enjoyment of the Symposium.

The Call for Papers elicited over two hundred abstracts from every domain of ferroelectric material and device research. The submissions were coherently organized into oral and poster sessions by the Program Committee under Robert Newnham's leadership. Each of the oral sessions began with an invited talk that provided a unifying theme for the session, either by reviewing past work or providing timely new results. The bulk of the contributed papers were presented in six poster sessions. Every poster was up for an entire day with two hours specifically set aside for poster discussions. Often discussions extended well beyond the allotted time; the international ferroelectrics community is experienced and comfortable with this style of technical session.

These Proceedings contain manuscripts representing more than eighty percent of the two hundred and one papers presented at the Symposium. Under the guidance of the Proceedings Editor, Van Wood, each of these manuscripts was reviewed during the meeting; the session chairmen distributed the manuscripts to participants who swiftly provided critical comments and evaluations of their colleagues' work. Many hours of diligent work stand behind the fine record of the Symposium contained in these Proceedings.

Wallace Arden Smith
Symposium Chairman ISAF '86

PIEZOELECTRIC PROPERTIES AND TEMPERATURE STABILITY
OF POLY (VINYLIDENE FLUORIDE-TRIFLUOROETHYLENE) COPOLYMERS

G. M. STACK and R. Y. TING
Naval Research Laboratory
Underwater Sound Reference Detachment
Orlando, FL 32856

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%. The hydrostatic g constant showed only a slight dependence on pressure, and pressures up to 35 MPa caused no apparent loss of the piezoelectric activity. A significant increase in the value of the hydrostatic g constant occurred with an increase in temperature. Anomalous results obtained upon cooling below 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 behaviour characteristically followed a linear dependence on the logarithm of aging time.

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 temperature dependence of these copolymers is likely to be more complex than that of PVDF homopolymer. The glass transition temperature of polytrifluoroethylene is much higher than that of PVDF and occurs only at slightly below room temperature. Mechanical relaxation studies in these copolymers found that transitions occurred near the glass transition of each of the corresponding homopolymers[7]. All of the published temperature studies have measured only the d_{31} ; constant and in these, a continuous increase in activity is observed with increasing temperature[1,8].

1. Introduction

Copolymers of vinylidene fluoride (VF₂) and trifluoroethylene (TrFE) are presently being considered for many piezoelectric applications. These copolymers exist in a crystal phase which yields large piezoelectric coefficients upon poling[1]. In contrast, the proper crystal phase is attained in poly(vinylidene fluoride) (PVDF) homopolymer only after the film is extruded and poled[2]. The stretching process causes an asymmetry in the film which 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

2. Experimental

Copolymers of vinylidene fluoride and trifluoroethylene with compositions ranging from 65 to 75% of VF₂ were obtained from the Pennwalt Corporation. These samples were either already poled or poled at the Naval Ocean Systems Center (NOSC). The piezoelectric and dielectric constants of these copolymers were measured with an acoustic reciprocity technique which 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 piezoelectric 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} was calculated from 1-kHz

capacitance measurements while the sample was in the coupler.

The aging experiments were performed 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.

3. Results and Discussion

The hydrostatic g coefficients, g_h , of the copolymers were found to have a very small dependence on hydrostatic pressure. For example, as the pressure was increased from 1 to 30 MPa, the hydrostatic g coefficient for a 68% VF_2 sample decreased from 148 to 142 mV-m/N, a less than 0.5-dB reduction. When the pressure was lowered back to 1 MPa, the sample returned to its initial level of activity with no irreversible degradation. This reduction in g_h was observed in each of the copolymer compositions studied. No pressure hysteresis effect was found in either case.

The temperature dependence of the hydrostatic g coefficient is shown in Figure 1 for a 75% VF_2 copolymer.

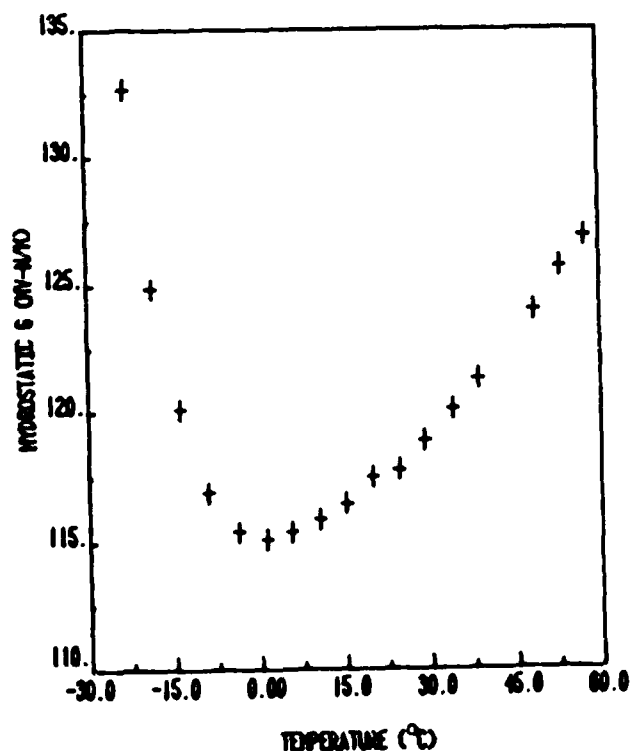


FIGURE 1. The hydrostatic g coefficient as a function of temperature for the 75% VF_2 copolymer.

A significant increase in the hydrostatic g coefficient occurs when the temperature is raised above room temperature. Similar behaviour has been observed for the piezoelectric d_{31} coefficient in previous studies of these VF_2/TrFE copolymers[1,8]. This behaviour has been attributed to the increased mobility of the amorphous segments as the temperature is raised further above the glass transition temperature. Above 80°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 temperature has not been reported previously in either the g coefficients of these copolymers or in any other polymer. To examine this behaviour more fully, the hydrostatic d coefficient d_h and the piezoelectric constant K_{33} of this 75% VF_2 copolymer are plotted as a function of temperature in Figures 2 and 3.

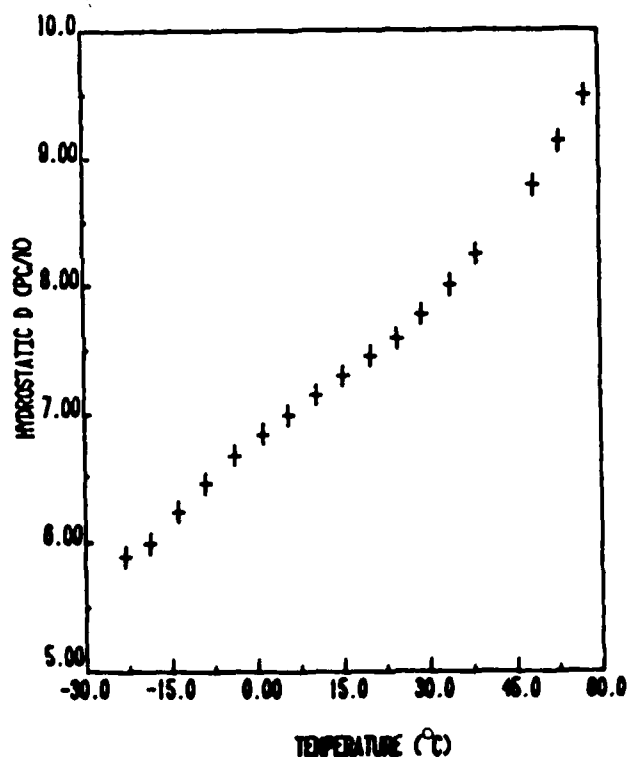


FIGURE 2. The hydrostatic d coefficient as a function of temperature for the 75% VF_2 copolymer.

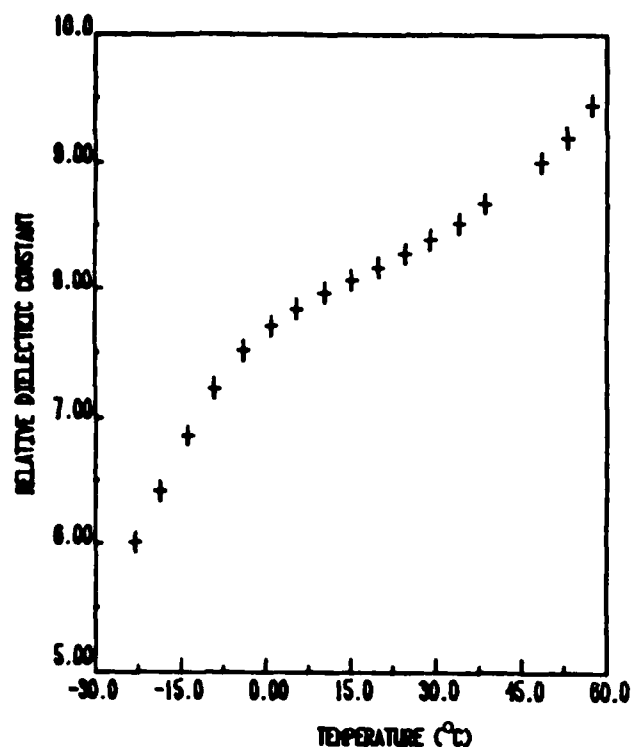


FIGURE 3. The relative dielectric constant K^T_{33} as a function of temperature for the 75% VF_2 copolymer.

Examination of Figure 2 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 Figure 3, 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^T_{33} 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 behaviour 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% VF_2 copolymer also was found in the other copolymers. As the VF_2 content was decreased to 68%, the g_h coefficient reached a low temperature maximum at $-17^\circ C$ and then started to decrease again at temperatures below this value. For the 65% 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 temperatures only below $-19^\circ C$. In all of these copolymers the hydrostatic d and K^T_{33}

continuously decreased as the temperature was lowered. It appears that the behaviour of the g_h depends on the relative rate of decrease of the d and K^T_{33} constants.

Upon heating these copolymers to temperatures above $80^\circ C$, 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 being exposed to the high temperature. In Figure 4, the hydrostatic g coefficient of a 70% VF_2 copolymer is plotted as a function of the logarithm of aging time at $85^\circ C$.

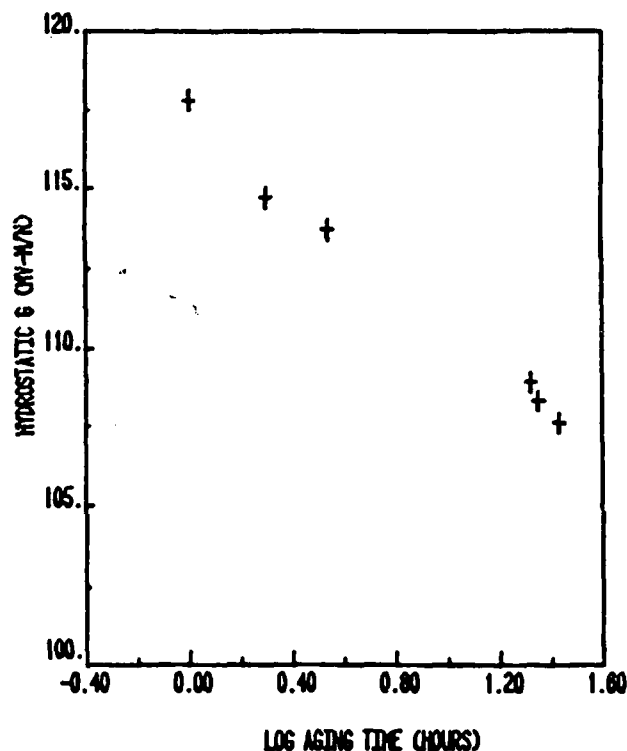


FIGURE 4. The hydrostatic g constant of the 70% VF_2 copolymer as a function of the logarithm of aging time at $85^\circ C$.

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 hours. In the example of Figure 4, the g_h is clearly continuing to decrease after 24 hours of exposure at $85^\circ C$.

The piezoelectric coefficients measured after aging at several temperatures can not 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 at room temperature were measured after high

temperature exposure. This result for a 65% VF_2 copolymer is summarized in Figure 5, where the room-temperature g_h is plotted as a function of the aging temperature after a 24-hour exposure.

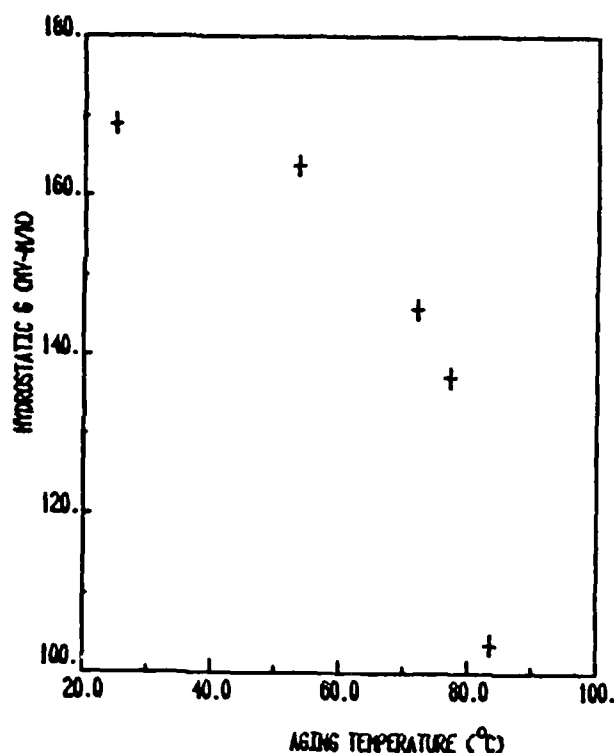


FIGURE 5. The room-temperature hydrostatic g coefficient for the 65% VF_2 copolymer as a function of aging temperature.

It is evident that at temperatures as low as 50°C some loss of activity has taken place. Aging at progressively higher temperatures results in much greater decreases in the value of the g_h coefficient. For the example shown in Figure 5, aging at 84°C lowers the room-temperature value of g_h to 60% of its original value. [It has been noted in a related study of the effects of thermal aging that the dielectric coefficients will return to their initial values after cooling from the high temperature (10-14 days) [12,13]. If such a reduction in the dielectric constant occurred, it would result in some increase in the g_h coefficient. However, the g_h coefficient would not return to its original value because of the reduction of d_p shown in Table 1. In our experiments the room temperature measurements were made 12 hours after the sample was cooled from the aging temperature.]

To compare the thermal stability of the various copolymers, ratios of the 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 Figure 6. These ratios were calculated after 24 hours of exposure at each of the aging temperatures.

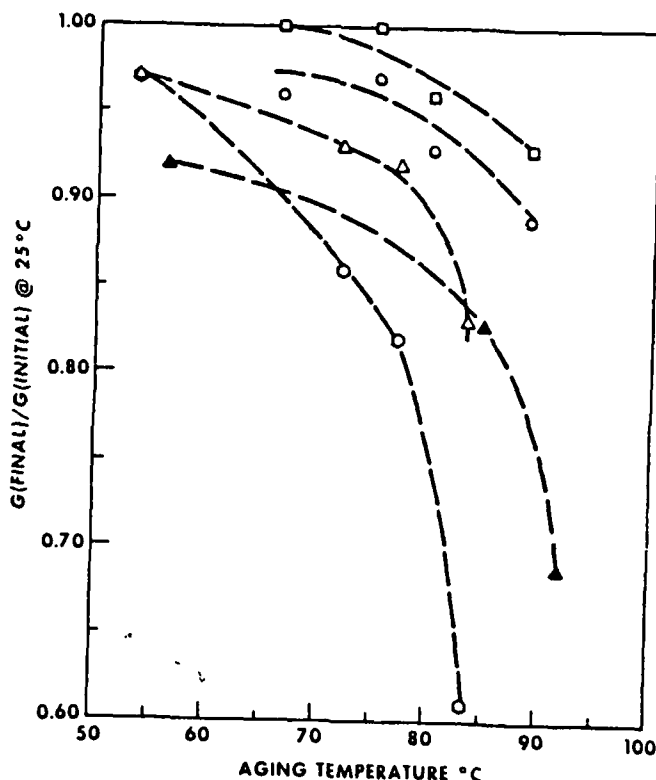


FIGURE 6. The room temperature hydrostatic g coefficients as a function of aging temperature for the copolymers having VF_2 contents of: $\circ$ 65%, $\triangle$ 68%, $\square$ 70%, $\diamond$ 75%.

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. Our scanning calorimetry studies have found that the peak transition temperature decreases from 130 to 100°C as the VF_2 content is decreased to 65% [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} were also examined in this study. The changes in g_h , d_p , and K_{33} induced by aging are listed in Table I for several of the copolymers.

Table 1. The effect of aging on the room temperature piezoelectric properties of vinylidene fluoride-trifluoroethylene copolymers.

VF_2	AGING TEMPERATURE °C	$K_{33}^T/K_{33}^T(\text{INITIAL})$	$D_h/D_h(\text{INITIAL})$	$G_h/G_h(\text{INITIAL})$
70	56.4	1.0	0.92	0.92
70	85.0	1.07	0.89	0.83
70	92.0	1.18	0.82	0.69
68	53.5	1.04	1.00	0.97
68	72.2	1.09	1.00	0.93
68	77.2	1.11	1.00	0.92
68	83.5	1.12	0.92	0.83
65	53.5	1.05	1.00	0.97
65	72.2	1.16	1.00	0.86
65	77.2	1.22	0.99	0.82
65	83.5	1.32	0.81	0.61

In each of these samples comparable changes in d_h and K_{33}^T are observed at the higher aging temperatures. These changes will make approximately equal contributions to the observed reduction in the g_h coefficient. At lower aging temperatures, some difference in behaviour is observed. For the 70% 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}^T that causes the decrease in g_h for the 65 and 68% VF_2 copolymers at the lower aging temperatures. These results differ from the observations made on the aging behaviour 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.

4. Acknowledgments

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