INVESTIGATION OF DIELECTRIC BREAKDOWN OF POLYVINYLIDENE FLUORIDE USING AC AND DC METHODS

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ABSTRACT - The dielectric breakdown strength of polyvinylidene fluoride (PVDF) has been investigated using both ac and dc methods. The dc breakdown strength of PVDF is in the range of 720 to 770 MV/m which is as good as or better than the capacitor grade polypropylene film. The ac breakdown strength (rms value) of PVDF is 220 to 233 MV/m. The ac to dc ratio of breakdown strengths for PVDF is significantly lower than that for other polymers. This observation is discussed in terms of the specific dielectric properties of PVDF, namely, its ferroelectricity.

INTRODUCTION

Polyvinylidene fluoride (PVDF) and its copolymers are ferroelectrics. The discovery of strong piezoelectricity in PVDF by Kawai [1] in 1969 has attracted much attention to these polymers. Also reported are findings of pyroelectricity and second harmonic generation [2]; observations of electric displacement (D) vs electric field (E) hysteresis loops and fast switching phenomena [3-4]; evidence of possible reorientation of crystalline dipoles induced by poling [5-6]; and efforts to understand the basic mechanism of piezoelectric effects [7-9]. The technical applications of these materials in electromechanical and pyroelectric devices are numerous [10].

The high dielectric constants (ϵ') of PVDF and its copolymers also make them potential candidates for energy storage devices [11-12]. The electrostatic energy that can be stored in a dielectric material is proportional to the dielectric constant of the material and the square of the voltage that is applied to the material. Therefore, it is desirable for dielectric materials to possess high dielectric strength. Commercial PVDF films have been available for some time. However, high energy density capacitors using PVDF have not been successfully commercialized. This prompted us to investigate the dielectric properties, especially the breakdown strength of PVDF. Comparisons with other polymers are also reported.

EXPERIMENTAL

The PVDF film - the biaxially oriented KF film from Kureha, was used as received. It is a mixture of α and β phases. Also used as received were non-ferroelectric polymer films including polypropylene (PP) - 12 μ m from Hercules, polycarbonate (PC) - 10 μ m from Steiner, polyester (PET) - 12 μ m from Hoechst, polyimide (PI) - 25.4 μ m Kapton 100HN from DuPont, and syndiotactic polystyrene (PS) from Dow Chemical.

The dielectric strengths of the films were tested under dc and ac conditions using 6.35 mm (1/4 inch) brass electrodes in air and/or in impregnants. The impregnants used were silicon oil and dioctyl phthalate (DOP). The breakdown strength values reported here were average values from nine or more tests. Hipotronics Model OC 60D was used for ac tests. Hipotronics Model 260 TS or Spellman RMP DC power supply was used for dc

tests. The rate of voltage rise was 500 V/sec for dc tests and 460 V/sec (rms) for ac tests. The frequency of the ac voltage was 60 Hz. The dielectric constant (ϵ') and the dissipation factor ($\tan \delta$) of various films were measured using a Hewlett-Packard 4284A LCR meter.

RESULTS AND DISCUSSION

dc Breakdown Strength

The average values of dc breakdown strength ($E_{b,dc}$) of various films are listed in Table I. The values shown in parentheses are the standard deviations. The maximum electrostatic energy density (U_m) that can be stored in each polymer is defined as one half of the multiplication of the dielectric constant and the square of the breakdown strength of each polymer. These values and the ϵ' values of various polymers are also included in Table I for comparisons.

TABLE I
DIELECTRIC CONSTANT (ϵ'), dc BREAKDOWN STRENGTH ($E_{b,dc}$)
AND MAXIMUM ELECTROSTATIC ENERGY DENSITY (U_m)
OF POLYMERS

Polymer	ϵ'	$E_{b,dc}$ (MV/m)	U_m (joules/cc)
PVDF ^{a)}	11.0	770(83)	28.9
PVDF ^{b)}	11.0	771(95)	28.9
PVDF ^{c)}	11.0	720(74)	25.2
PP ^{d)}	2.2	730(33)	5.2
PET ^{e)}	3.5	594(65)	5.5
PI ^{f)}	3.6	470(13)	5.2
PC ^{g)}	2.9	720(19)	6.7
PS ^{h)}	2.6	450(53)	2.3

Note:

- a) 12 μ m, Kureha KF film, tested in air
- b) 12 μ m, Kureha KF film, tested in DOP
- c) 12 μ m, Kureha KF film, tested in silicon oil
- d) 12 μ m, Hercules, tested in DOP
- e) 12 μ m, tested in DOP
- f) 25.4 μ m, DuPont Kapton 100HN, tested in air
- g) 10 μ m, Steiner, tested in air
- h) 4 μ m, syndiotactic, Dow Chemical, tested in air

We note that $E_{b,dc}$ values of PVDF are the highest among all polymers tested except PP which shows similar values. PVDF's high ϵ' and high $E_{b,dc}$ values makes it the highest energy density polymeric dielectric. However, the commercial success of developing PVDF as dielectric for energy storage capacitors is lacking.

Although there is no report available on this aspect, its potential problems can be speculated as follows: 1) PVDF is difficult to be cleared under high voltage since it contains no oxygen, 2) PVDF emits

hydrogen fluoride (HF) under high voltage [13] which may deteriorate impregnant, 3) PVDF's high dissipation factor is not desirable (see Table II), 4) PVDF is not efficient due to its hysteresis heat loss.

ac Breakdown Strength and α Values

Since dielectric behavior of ferroelectric PVDF varies with the field, the ac breakdown test appears to be the most proper method to observe the effect of its intrinsic properties on the breakdown strength of ferroelectric materials.

The root-mean-square values of ac breakdown strength ($E_{b,ac-rms}$) and the zero to peak values of ac breakdown strength ($E_{b,ac-0p}$) of PVDF tested in air, silicon oil and DOP are listed in Table II. The α value, defined as the ratios of $E_{b,ac-0p}$ to $E_{b,dc}$, is created to express the ac breakdown strength of a material relative to its dc breakdown strength. The ac breakdown strength and α value of other polymers are also listed in Table II for comparisons. $E_{b,dc}$ values in Table I were used to calculate α .

TABLE II
ROOT-MEAN-SQUARE (rms) AND ZERO-PEAK (0p) OF
ac BREAKDOWN AND α VALUES OF POLYMERS

Polymer	$E_{b,ac-rms}$ (MV/m)	$E_{b,ac-0p}$ (MV/m)	α
PVDF	220(83)	310	0.40
PVDF	233(6.6)	330	0.43
PVDF	233(9)	330	0.46
PP	493(26)	695	0.95
PET	289(20)	408	0.69
PI	300(4)	429	0.89
PC	400(20)	570	0.79
PS	350(53)	495	1.10

The $E_{b,ac-rms}$ values of PVDF are 220- 233 MV/m which are the lowest among polymers tested. We also note that α values of PVDF are particularly low at about 0.4 to 0.46 when compared to other polymers which have α values at 0.7 to 0.95. Table II also suggests that linear polymers such as PP and PS have α values close to 1. The polar polymers such as PET, PI and PC show α values from 0.7 to 0.9.

With its high dc breakdown strength and dielectric constant, PVDF should be ideal for use in energy storage discharge capacitors. However, the low ac breakdown strength of PVDF suggests that it is undesirable to use this material in an ac environment. When energy storage capacitors are discharged under oscillatory condition (low load), a voltage reversal will occur, again resulting in undesirable ac-like oscillations.

Dielectric Breakdown Mechanism of PVDF

The possible breakdown mechanisms of solids generally include: 1) thermal breakdown, 2) electromechanical breakdown, 3) electronic breakdown, and 4) breakdown due to space charge effect. The breakdown strength, in reality, is affected by many factors, such as morphology, crystallinity, impurities, and microvoids, etc. Therefore, films of the same chemical composition may have different breakdown strengths. The films selected for our test were of

highest quality available commercially.

The reported dielectric breakdown strength varies depending on the testing method. For example, the ac breakdown value of a dielectric is usually lower than the dc breakdown value. Our observation, however, shows that only PVDF has substantially lower ac breakdown strength relative to its dc breakdown strength, or α values. We believe this unusually low value may have related to its intrinsic dielectric properties. Since PVDF is a piezoelectric/ferroelectric polymer, its breakdown mechanism will be considered in terms of its specific properties.

Thermal effects

There are two sources of energy loss: 1) dielectric loss, and 2) hysteresis due to PVDF's ferroelectric nature. The energy loss due to dielectric loss happens when there is a phase lag between the polarization and the applied fields. In ac fields, the energy loss per unit volume per unit time is expressed as [14]

$$H_{av} = E_0^2 \epsilon_0 \epsilon' \omega \tan \delta / 8 \pi, \quad (1)$$

where E_0 is the peak value of the sinusoidal ac field, $\epsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of vacuum, ω is the angular frequency, and $\tan \delta$ is the dissipation factor. The energy loss per unit volume per cycle is

$$H_{av} = E_0^2 \epsilon_0 \epsilon' \tan \delta / 4. \quad (2)$$

The ac breakdown voltage obtained for PVDF was 2.8 kV (rms value) in DOP. Since the ac voltage rate of rise was 460 V/sec, the time required to break PVDF under ac was about 6 sec. The peak field at breakdown was 1.41×2.8 kV/12 μ m, or 330 kV/mm (see Table I). The voltage rise was linear, the peak field of the first cycle, E_{o1} , was approximately 330 (kV/mm)/360 cycles = 914 V/mm. The peak field of the second cycle, E_{o2} , was approximately 2×914 V/mm. Therefore, the total energy loss over 360 cycles before PVDF broke down was

$$H_T = \epsilon_0 \epsilon' \tan \delta (E_{o1}^2 + E_{o2}^2 + \dots + E_{o360}^2) / 4$$

$$= \epsilon_0 \epsilon' \tan \delta (914)^2 (1^2 + 2^2 + \dots + 360^2) / 4 \quad (3)$$

For PVDF, $\epsilon' = 11$ and $\tan \delta = 0.012$, measured at 100 Hz, were used to calculate H_T . Therefore, the calculated H_T was 0.43 joules/cc. Compared to other polymers, the dielectric loss ($\epsilon'' = \epsilon' \tan \delta$) of PVDF is substantially higher as shown in Table III. For example, the ϵ'' value of PVDF is about 220 times higher than that of PP. Nonetheless, we believe that the small amount of heat dissipated due to dielectric loss should not be the reason for PVDF's low ac breakdown strength.

TABLE III
DIELECTRIC CONSTANTS, DISSIPATION FACTORS AND
DIELECTRIC LOSS OF VARIOUS POLYMERS

Polymer	ϵ' (100 Hz)	$\tan \delta$ (100 Hz)	ϵ'' (100 Hz)
PVDF	11.0	1.1×10^{-2}	1.2×10^{-1}
PP	2.2	4.2×10^{-4}	9.2×10^{-4}
PET	3.5	1.7×10^{-3}	6.0×10^{-3}
PI	3.6	2.0×10^{-3}	7.2×10^{-3}
PC	2.9	9.7×10^{-4}	2.8×10^{-3}
PS	2.6	2.6×10^{-4}	7.3×10^{-4}

We should also note that the above calculations are valid for ac fields that are small enough for the effects to be linear. The effect of the non-linearity of the ferroelectric PVDF, especially at high fields, is our major concern. The energy loss in this case equals the area of the polarization (P) versus electric field (E) hysteresis loop. At high fields, the loop area could be estimated from the coercive field (E_c) and the remanent polarization (P_r).

For Kureha PVDF film, P_r saturates around 55 mC/m² with E_c equal to 60 MV/m at fields equal to or higher than 240 MV/m [15]. Therefore, the energy loss for PVDF due to one hysteresis cycle at a field of 240 MV/m is about 3 joules/cc. This value is about one order of magnitude higher than that of the total linear dielectric loss (H_r , see Eq. (3)) in 6 seconds before PVDF breaks down in ac voltages. The average breakdown field of PVDF is 330 MV/m (see Table I), the number of cycles with fields higher than 240 MV/m is about 98. Therefore, the total energy loss for all cycles with ac peak fields higher than 240 MV/m is about 300 joules/cc which is about three orders of magnitude higher than the energy loss due to linear dielectric loss. This energy is substantial enough to heat up PVDF film even though part of the heat may dissipate through the surrounding media.

Hikita et al. [16-17] recently reported lower dc breakdown strength for PVDF at higher temperatures. He also concluded that thermal breakdown is operative in PVDF, based on the facts that the dielectric strength decreases with increasing temperature and increases with increasing field rising rate. Our findings concur with his results.

Electromechanical effects

When the PVDF film is placed between two electrodes and under electric field, three field-related mechanical changes take place. The first is the electrostatic force that acts on PVDF film and is proportional to the square of the field. The second is the electrostriction that is also proportional to the square of the field. The third is the piezoelectric changes that are proportional to the field. The electrostriction and the piezoelectric changes are produced by the materials themselves, while the electrostatic force always exists whenever voltage is applied.

Under electric field, the strain of PVDF exhibits a hysteresis, very much like the hysteresis of its D-E curve. During ac breakdown tests, the PVDF film went through many cycles of sinusoidal voltages. This means that the film went through many cycles of dimensional expansion and contraction. Cookin et al. [18] recently measured strain-field (x-E) loops for PVDF. They found that the loop shows butterfly shape at fields higher than $E_{max}=160$ MV/m with positive strain at the fields around E_c and with negative strain at fields away from E_c . At $E_{max}=260$ MV/m, the maximum positive strain is 0.003 and the maximum negative strain is about -0.013. This is not an insignificant spread.

It seems that the strain of PVDF cycles with field may have impact on the dielectric strength. However, we can not conclude that this causes PVDF to have lower ac breakdown strength. Considering the fact that PVDF is a semicrystalline polymer, the elastic constants of the crystalline and the amorphous parts are different at temperatures much higher than T_g [19]. We believe that heat generated through the hysteresis is enough to heat up the film to a higher temperature and causes much higher internal strain along the crystalline and

amorphous interphase. This may cause the film's breakdown to occur at lower ac voltages.

Effect of charge injection or space charge

The basic mechanisms of the formation of piezoelectricity in PVDF have been reported extensively [7-9, 20]. Wada and Hayakawa [7] suggested that the piezoelectricity of PVDF may arise from the embedded charge (space charge) coupled with the heterogeneity (e.g. mixture of crystalline and amorphous phases). Womes et al [21] and Bihler et al.'s [22] recent studies indicate that the stabilization of the polarization is mediated by charge injection and charge trapping at polarized crystallite surfaces.

During dc breakdown tests, when the voltages were high, extra charges were injected to stabilize the dipole until the polarization saturates. These extra charges may be the reason why PVDF exhibits high dc breakdown voltages.

CONCLUSION

The ac and dc dielectric strength of PVDF and several other polymers were measured. The dielectric strength of solid polymers depends on many factors. We found that $E_{b,ac}$ is an important factor to be considered for dielectrics to be used in energy storage applications. The α value, which measures the relative strength of ac to dc breakdown strength, can be used to indicate the degree of linearity of a material. However, we believe that the substantially low α value of PVDF can be attributed to its specific dielectric properties, namely, the piezoelectricity and ferroelectricity.

The excessive energy loss at high fields resulting from the hysteresis nature of the ferroelectric PVDF during ac breakdown tests is the major cause of breakdown. The lower dielectric strength for PVDF at elevated temperatures as reported by Hikita et al. [16-17] is consistent with our observations. We believe that the large internal strain in PVDF produced at the interphase of the crystalline and the amorphous phases at elevated temperatures may induce the breakdown. PVDF's high dc breakdown strength may be related to its basic mechanism of piezoelectricity, which requires that charges be supplied at high voltages to stabilize the polarization.

Based on the above discussion, we may also conclude, in general, that ferroelectrics, be they polymer or ceramic, depending on the degree of hysteresis, may not be suitable for applications of high field ac or high field dc at oscillatory discharge conditions or at fast repetition rates.

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