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RADIATION RESPONSE AND ELECTRICAL PROPERTIES OF POLYMER ENERGY-STORAGE CAPACITORS: PVF_2, POLYSULFONE, AND MYLAR*

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SUMMARY

Sandia National Laboratories is currently interested in the development of a polymer film capacitor that is tolerant to radiation. The capacitors are to be utilized in a high voltage-pulse discharge application.

Radiation response data at high dose/dose rate levels are presented for polyvinylidene fluoride (PVF_2), polysulfone, and Mylar.† The results show that PVF_2 is the most radiation tolerant while Mylar is the least tolerant. The data also show that the radiation response is quite dependent on operating electric stress.

Although PVF_2 has good radiation tolerance and a dielectric constant which is a factor of three larger than Mylar and polysulfone, PVF_2 has properties which complicate its use as a capacitor dielectric. Electrical properties of these materials will be presented and discussed.

INTRODUCTION

The motivation for this work is the development of pulse discharge, energy storage capacitors which are tolerant to high dose rate and high dose radiation environments where a recharge option is not available. The capacitance and voltage ranges of interest are, respectively, 0.1-3 μF and 2.5-6 kV. In general, the effect of radiation on a capacitor is a charge or voltage loss. This charge loss is the result of radiation-induced conductivity in the capacitor dielectric.[1] The absorption of radiation in a dielectric results in the creation of electron-hole pairs in conduction states. (The number of charge carriers created is dependent on the atomic cross sections of the dielectric.) The excited carriers will travel toward the electrodes because of the electric field and effectively reduce the charge on the electrodes. The mechanism which impedes the charged carrier displacement in a solid dielectric is the interaction of the carriers with traps. In a given radiation environment, a dielectric which has a high trap density will exhibit less charge loss than one with a low trap density. The radiation-induced conductivity is very material dependent. It is a function of composition, impurities, and structural defects. For a solid dielectric, a theoretical prediction of the magnitude of the radiation response is not tractable; the response is best determined by experiment.

For the past 10 years, Sandia National Laboratories has been active in developing the technology for utilizing polymer films as the dielectric in pulse discharge, energy storage capacitors. The primary focus has been on developing Mylar both in dry and wet[2] configurations. Mylar is an excellent dielectric; however, in a high dose rate, high dose radiation environment [10^{12} Rad(Si)/sec, 10^5 Rad(Si)], Mylar exhibits a high radiation-induced conductivity. A part of the current effort on polymer dielectrics is to examine other commercially-available plastic films which may have better radiation tolerance.

The liquid-impregnated, plastic film (wet) capacitor technology that has been successful in dramatically improving the energy density[2] unfortunately, cannot be used in a high dose radiation environment. A liquid dielectric generally exhibits a large radiation-induced conductivity because a liquid, as opposed to a solid dielectric, does not have carrier traps to impede charge carrier displacement. A dry design capacitor, at the outset, will have a better radiation tolerance.

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†Mylar is a trade name of the DuPont Company for polyethylene terephthalate.

DISCLAIMER

Preliminary low dose radiation studies on polymer films have shown that both polysulfone and polyvinylidene fluoride (PVF_2) are superior to Mylar.[3] The data presented here extend these results to the high dose [10^5 Rad(Si)] regime. PVF_2 is also attractive because of its high dielectric constant of 10 as compared to 3 for Mylar and polysulfone. On the other hand, PVF_2 has been shown to exhibit ferroelectricity,[4] which may have a detrimental effect on high electric field applications. Obviously, there are trade-offs that must be considered in the development of specialized capacitors.

The data presented in this paper will focus on the radiation response and electrical properties of PVF_2. Some data on polysulfone and Mylar will also be given for comparison.

CAPACITOR DESIGN

The dielectrics used were commercially-available, capacitor-grade films.* For the present studies, either 2-12 μm or 1-25 μm layers were employed for the dielectric pad. The capacitor design is a dry, foil-wound, tapewrapped, epoxy end encapsulation construction and is shown in Figure 1. The end margins were varied between 0.250 and 0.50 in. The capacitor rolls were wound on a precision, tension-controlled winder,[2] with polysulfone being the most difficult to wind.

The processing consists of a drying cycle followed by end sealing. The capacitor rolls are dried (in dry nitrogen) at 71°C for 24 hours and then at 80-100°C for another 24 hours. The rolls are cooled to 71°C and maintained at this temperature during the end sealing process. The end seals are made with mica-loaded epoxy.

RADIATION PROPERTIES

The radiation response data were obtained on a high-intensity-flash x-ray machine.[5] This machine is capable of producing up to 10^5 Rad(Si) at a rate of 10^{12} Rad(Si)/sec with a photon energy spectrum between 60 keV and 10 MeV. The radiation pulse width is 50 nsec. The

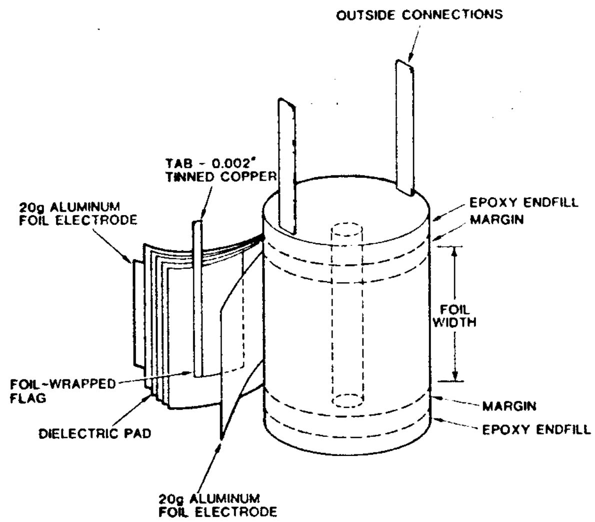

Figure 1. Capacitor design used in this study.

quantity of interest is the fraction of voltage loss on the capacitor at a given dose. The fraction of voltage loss is defined as the ratio of the actual voltage loss to the initial applied voltage. (Hereafter, the term voltage loss will be synonymous with fraction of voltage loss.) The voltage-loss data presented reflects both the prompt and delayed radiation-induced conductivity components. All data were recorded at 20° to 25°C, and no dose memory effects were observed.

The radiation response as a function of dose for the three polymer dielectrics is shown in Figure 2. As is expected, the voltage loss in all cases increases with increasing dose. It is observed that PVF_2 has the best radiation tolerance, Mylar is the poorest, and polysulfone is intermediate. For PVF_2 and polysulfone, the radiation response is represented by families of curves. This shows that the voltage loss is electric stress dependent. The electric stress dependence is shown more clearly in Figure 3 where the voltage loss is plotted as a function of the electric stress at a constant dose of 100 KRad(Si). Similar plots can be made at say 10 or 50 KRad(Si), but these plots will show essentially the same behavior except that the voltage loss will be scaled down proportionately. This type of data representation exemplifies the relative ranking of the dielectrics.

*Polysulfone is marketed by Kimberly-Clark Corp. under the trademark of Kimfone. Polyvinylidene flouride (PVF_2) is marketed by Kureha Chemical Industry Co. under the name of KF film.

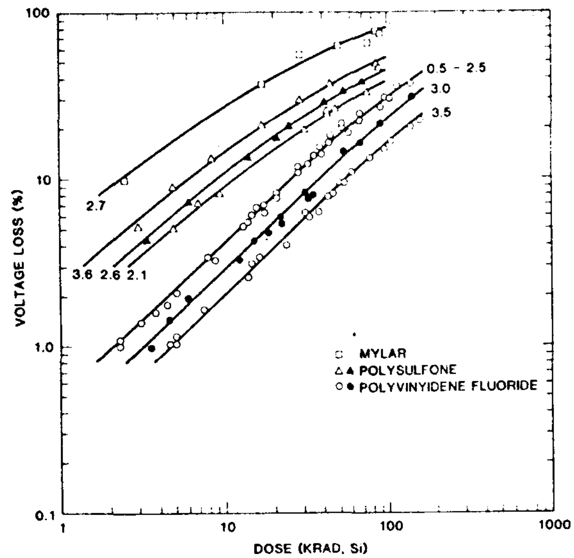

Figure 2. The basic radiation response data. The numbers associated with each of the curves are the electric stresses in kV/mil.

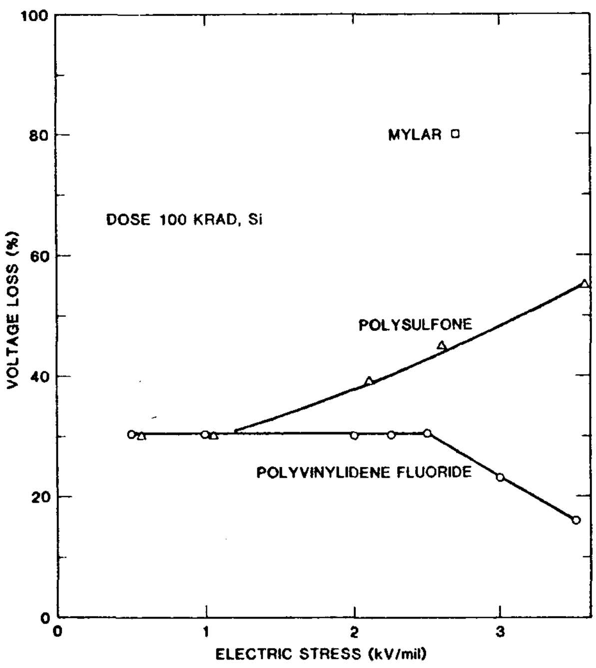

Figure 3. The electric stress dependence of the radiation response.

In the case of polysulfone, the voltage loss is observed to increase with increasing electric field. Low dose data on Mylar also show the same electric stress dependence.[3] The electric stress dependence for PVF_2 is rather unique. The voltage loss is observed to be independent of the electric stress up to 2.5 kV/mil and then decreases rather dramatically at higher stresses.

The radiation response of a polymer-film dielectric depends on the number of free carriers generated per unit dose and the free carrier mobility-lifetime product. The electric stress dependence is usually observed to be in the above factors. All of the films in this study have similar densities and are all composed of low atomic number elements. This implies that the photon absorption cross section should be similar for all of the films. (Calculations bear this out.) Thus the number of carrier pairs created per unit dose should be nearly equal for these films. The number of free carriers that will participate in conduction, however, will be less than the number of carriers initially created by the radiation. This is due to geminate recombination effects. Initially, it takes time for the electric stress to disperse (or penetrate) the space charge clouds; and it is during this time that recombination takes place. This process is electric stress dependent. The number of free carriers available for conduction is a strong function of electric stress, increasing with the stress.[1] Therefore, it is expected that the voltage loss at a given dose should increase with increasing electric stress. This effect is observed in both Mylar and polysulfone; however, in PVF_2 there must be another competing mechanism. This will be discussed at the end of this section.

The second factor which affects the radiation response is the carrier mobility-lifetime product. This product is electric stress dependent; however, it has been shown that most of the stress dependence is in the number of free carriers generated.[1] The carrier lifetime is dependent on the trap structure and trap density of a given film. A film which, for example, has a high trap density will probably have a short lifetime. Thus a film with a high trap density should exhibit a lower voltage loss at a given dose than a film with a low trap density. It is felt that the difference in the relative radiation responses of these films is due to differences in the trap structure and trap density.[3] Both the mobility and lifetime are difficult quantities to determine in polymer films.

As is observed in Figure 3, the electric stress dependence of the voltage loss in PVF_2 is quite different than in Mylar and polysulfone. It is possible that this behavior is related to the ferroelectric/structural properties of PVF_2. The biaxially stretched PVF_2 film is approximately half amorphous and half crystalline in structure. It has been reported that the crystalline structure of the biaxially oriented film contains both a polar and an antipolar phase, and there is a field-induced phase transition for electric stresses above 2.5 kV/mil.[6] It is possible that this field-induced phase transition could result in an increase in trap density.[7] This, in turn, would result in a decrease in the voltage loss. The plausibility of this explanation is being pursued further.

ELECTRICAL PROPERTIES

Both Mylar and polysulfone are linear dielectrics up to high voltages (i.e., the relation, Q = CV, is valid). PVF_2, by virtue of the ferroelectric behavior, is a nonlinear dielectric, especially at high electric stresses. The ferroelectric data were obtained by standard looping techniques. The results are shown in Figure 4. At 25°C, the polarization is fairly linear up to 1.5 kV/mil, and above 2.5 kV/mil, the polarization increases very rapidly with electric stress. The loops below 1.5 kV/mil were observed to be quite narrow. At -55°C, there is a dramatic decrease in the polarization. This behavior will influence or limit capacitor design and application.

The temperature and frequency dependence of the small signal dielectric properties of PVF_2 are shown in Figures 5 and 6. In Figure 5, it is observed that the capacitance (or dielectric constant) is very temperature and frequency dependent, especially at low temperatures. This is consistent with the low temperature ferroelectric data. The dissipation factor is also very temperature and frequency dependent. It should be noted that the dissipation factor becomes very significant (19 percent) at 100 kHz and 0°C. The observed low temperature behavior in PVF_2 is associated with the glass transition. Mylar and polysulfone, in contrast, exhibit a much subdued temperature and frequency dependence. Also, the magnitude of the dissipation factor is much less for these materials. For example, over a frequency range of 1 to 100 kHz and a temperature range of -55° to 70°C, the dissipation factor of Mylar varies only from 0.2 to 4.5 percent.

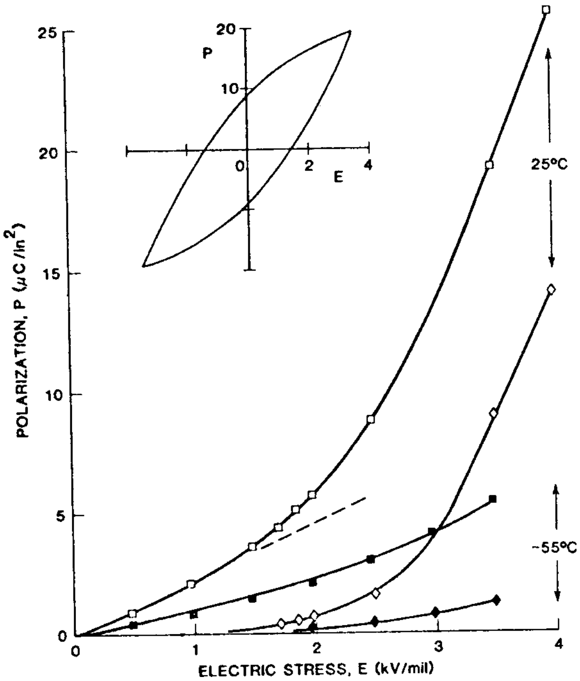

Figure 4. The ferroelectric data for PVF_2, biaxially stretched film. The polarization and remnant polarization at 25°C are represented by □ and ◊, respectively. The solid symbols represent the same data at -55°C. The inset is a typical hysteresis loop at 25°C.

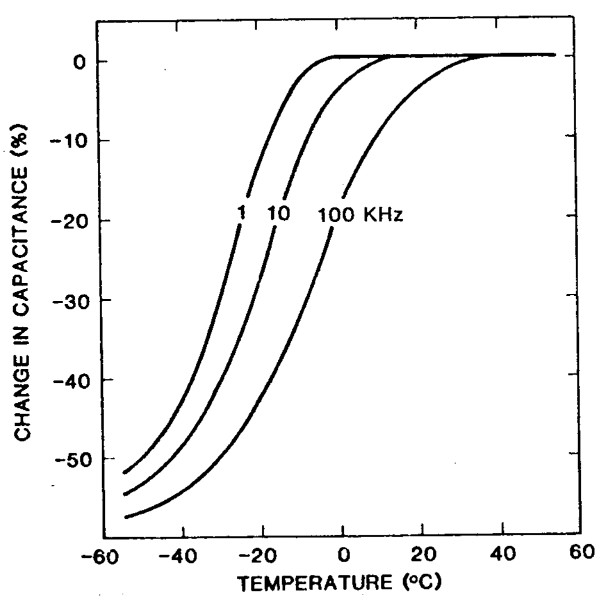

Figure 5. The temperature and frequency dependence of the capacitance (or dielectric constant) for PVF_2.

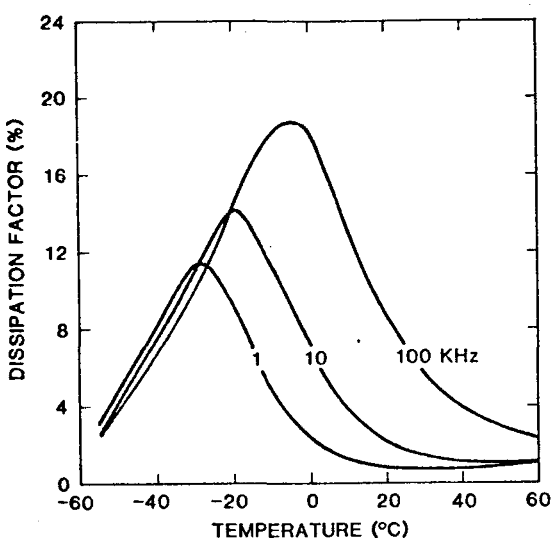

Figure 6. The temperature and frequency dependence of the dissipation factor for PVF_2.

The short-term dielectric breakdown of PVF_2 at 20° to 25°C is similar to that observed for Mylar in the same capacitor design configuration. For end margins greater than or equal to 0.375 in, average breakdown stress was 8 kV/mil with a standard deviation of 1 kV/mil. Additional data are needed at low and high temperatures.

The ambient temperature insulation resistance of PVF_2, polysulfone, and Mylar are, respectively, 823; 13,300; and 266,000 MΩ-μF. The value for PVF_2 is adequate for pulse discharge application; however, there is evidence that the insulation resistance decreases with increasing temperature. We have observed, for a 1 μF capacitor at 3 kV/mil, thermal runaway at 80°C.

CONCLUSIONS

The radiation tolerance and high dielectric constant of PVF_2 make it an attractive candidate for our current applications. However, PVF_2 has some interesting properties which complicate its use as a capacitor dielectric. The ferroelectric behavior will probably limit the design stress to ~ 2.5 kV/mil. The dielectric constant and dissipation factor will influence low-temperature usage while the insulation resistance will govern the high-temperature limit. Further research is still necessary to better define the limits of this film.

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