

# High-Temperature Poly(phthalazinone ether ketone) Thin Films for Dielectric Energy Storage

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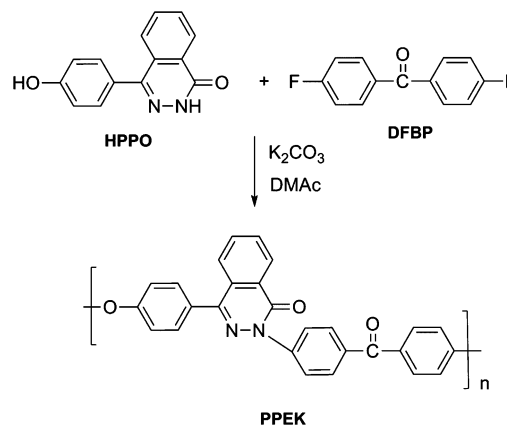
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**ABSTRACT** The synthesis and characterization of poly(phthalazinone ether ketone) (PPEK) for high-temperature electric energy storage applications is described. It was found that PPEK displayed excellent stability of the dielectric properties over a broad frequency and temperature range. Little change in the breakdown field and discharge time has been observed in PPEK with the increase of temperature up to 190 °C. A linear correlation between the AC conductance and the angular frequency implied that the hopping as a dominant conduction process contributed to the dielectric loss. Superior energy densities, remarkable breakdown strengths, and fast discharge speeds have been demonstrated in PPEK at various temperatures.

**KEYWORDS:** polymers • dielectric properties • capacitors • energy density • high-temperature materials • breakdown strength

The increasing demand for lightweight, flexible, and processable energy storage materials has motivated the development of dielectric polymers that are capable of storing high-density electric energy (1, 2). Dielectric polymers have potential manufacturing advantages over traditional electronic ceramics, including solution processing and large-scale fabrication with reduced cost. Furthermore, because the energy density of dielectric materials has a quadratic dependence on the applied electric field, polymers can lead to high charge storage capacity because of their higher breakdown strength relative to those of ceramic counterparts. Remarkable energy densities and fast discharge speed have been recently achieved in poly(vinylidene fluoride)-based ferroelectric polymers (3). However, the dielectric properties of these polymers often vary significantly with increasing temperature (4), limiting their utility at temperatures below 100 °C. Polymers with dielectric properties that are stable at elevated temperatures are particularly interesting for hybrid electric vehicle and aerospace applications (5). The ever-shrinking microelectronic devices also call for high temperature capacitors, as heat dissipation increases nonlinearly with miniaturization of electronic circuits (6). Recent examples on high-temperature polymer capacitors such as polycarbonate, polyetherimide (PEI), Teflon perfluoroalkoxy, and polyphenylene sulfide (PPS) not only illustrate the promising progress made in this area but also reveal limitations in the classes of high-

## Scheme 1. Synthesis of PPEK



performance polymers investigated (7–11). In this contribution, we report on the synthesis and characterization of poly(phthalazinone ether ketone) (PPEK) thin films for high-temperature capacitor applications. The dielectric properties, discharged energy density, breakdown strength, and discharge time of PPEK have been examined at various temperatures.

It has been demonstrated that incorporation of the rigid asymmetric phenyl phthalazinone moiety into the polymer backbone yields the engineering polymers with high glass transition temperatures, excellent mechanical properties, and outstanding thermo-oxidative stability (12). For this study, as depicted in Scheme 1, PPEK was readily synthesized by polycondensation of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one (HPPO) and 4,4'-difluorobenzophenone (DFBP) in dimethylacetamide (DMAc) at 190 °C (13). The phenolate and aza-nitrogen anions, which were formed via deprotonation of HPPO by potassium carbonate, underwent a nucleophilic displacement reaction with activated difluoro

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monomer DFBP to afford high-molecular-weight PPEK. The structure of the resulting PPEK was confirmed by spectroscopic studies and elemental analysis. The lack of resonances at 12.8 and 9.7 ppm corresponding to phthalazinone N–H and phenolic O–H protons and the presence of six peaks from 7.18 to 8.65 ppm assigned to the aromatic protons were evident in the  $^1\text{H}$  NMR spectrum. The FTIR spectrum of the resulting PPEK revealed characteristic absorption at about 1666 (C=O), 1595 and 1498 (aromatic C=C), and 1240  $\text{cm}^{-1}$  (C–O–C), respectively. The absorption bands for –NH and –OH in the range of 3100–3400  $\text{cm}^{-1}$  was not observed, further implying that the polycondensation occurred as expected. The prepared PPEK had an inherent viscosity of 0.3 dL/g in 98% concentrated  $\text{H}_2\text{SO}_4$  at 30 °C and was soluble in chloroform and *N*-methylpyrrolidinone (NMP) at room temperature. The glass transition temperature and the decomposition temperature related to 5% weight loss under nitrogen of PPEK were 250 and 490 °C, respectively, determined by differential scanning calorimetry and thermogravimetric analysis.

Transparent PPEK films were prepared by hot-pressing the polymer power at 345 °C under 2500 psi in a Carver hydraulic press with heated plates. The typical film thickness in this investigation was between 20 and 40  $\mu\text{m}$ . Gold electrodes with a diameter of 2.6 mm and thickness of 30 nm were sputtered at both sides of the films for the electrical measurements. The dielectric properties were characterized at different frequencies and temperatures using an Agilent multifrequency LCR meter equipped with a computer-controlled temperature chamber. Figure 1 presents the frequency and temperature dependence of the dielectric constant and loss of PPEK under a 1 V bias. PPEK exhibited a dielectric constant of 3.5 and a dielectric loss of 0.0063 at 1 kHz and room temperature. The dielectric constant and loss tangent of PPEK was found to remain almost constant in the frequency range of 100 Hz to 1 MHz and temperatures up to 240 °C. The considerable stability of the dielectric properties at high frequencies has been attributed to formation of long-range polaron delocalization in the aromatic structures (14). The dielectric loss displayed a sharp increase at temperatures greater than 240 °C. This onset temperature lies in the neighborhood of the glass transition temperature of PPEK, indicating that the increased loss is directly correlated to structural relaxation ( $\alpha$ -process) of the polymer (15).

The discharged energy density and energy storage efficiency of the films were determined from the unipolar polarization-electric field ( $P$ – $E$ ) loops that were recorded using a modified Sawyer–Tower circuit at various temperatures. The loop duration was 0.01s. The stored and discharged energy densities are the integration from the lower and upper branches the  $P$ – $E$  curve, respectively. The discharged efficiency is given by the ratio of the discharged energy density versus the stored energy density. The discharged energy densities and efficiency measured at different temperatures are summarized in Figure 2. At an applied field of 450 MV/m, PPEK exhibited the discharged energy

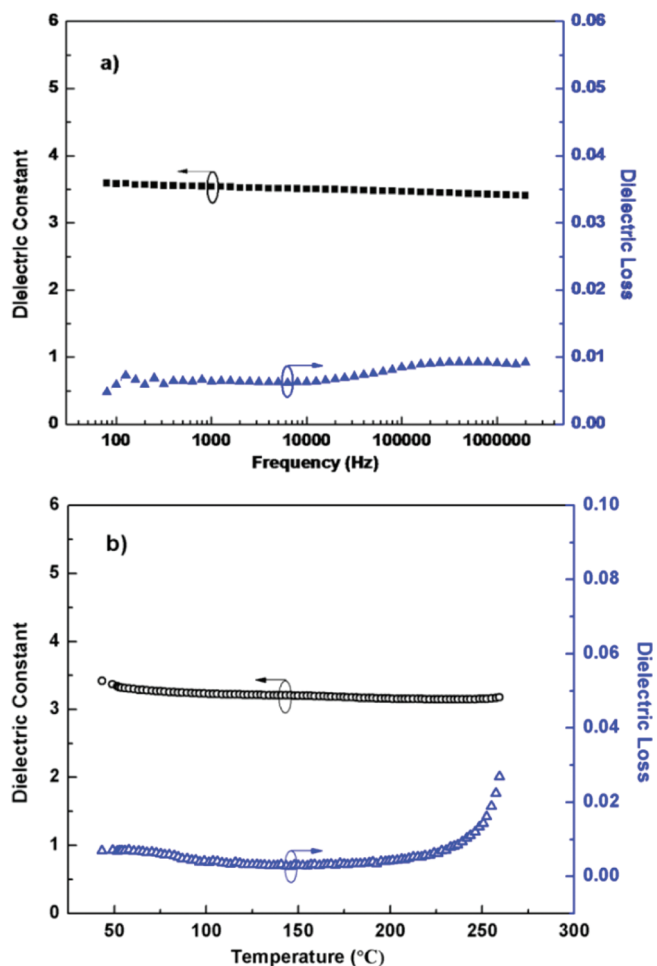


FIGURE 1. (a) Frequency dependence of the dielectric properties of PPEK at room temperature. (b) Temperature dependence of the dielectric properties of PPEK at 1 kHz.

densities of 3.9, 3.5, 3.1, 2.8, 2.4, and 2.1  $\text{J}/\text{cm}^3$  at 22, 70, 100, 130, 160, and 190 °C, respectively. Encouragingly, these values, especially at high temperatures, are significant and suggest a respectable improvement over what has been reported in the past with the high-performance polymers (7). It is also noteworthy that PPEK possessed high discharged efficiencies (>80%) over a wide temperature and field range. Both the energy density and discharge efficiency decreased rapidly under the field above 400 MV/m and temperature above 130 °C. This reduction is mainly ascribed to the increased conduction loss under high electric field and elevated temperature.

For linear dielectric materials, the conduction current can be derived from the  $P$ – $E$  loop as (16):

$$J_c(E) = J - J_d = \frac{dD}{dt} - K\epsilon_0 \frac{dE}{dt} \quad (1)$$

where  $J_c$ ,  $J_d$ , and  $J$  are the conduction, displacement, and total current densities, respectively, and  $K$  is the dielectric constant. As shown in Figure 3, the conduction currents remained negligible at low fields and rose quickly when the field and temperature reached critical levels. In dielectric materials, conduction stems primarily from the charge

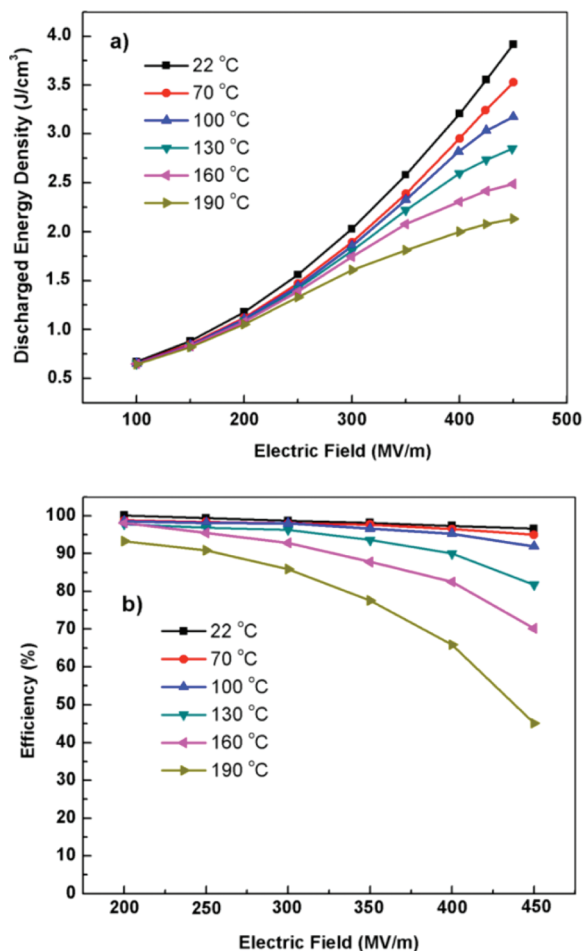


FIGURE 2. (a) Discharged energy density as a function of temperature and the applied field. (b) Efficiency versus temperature under different electric fields.

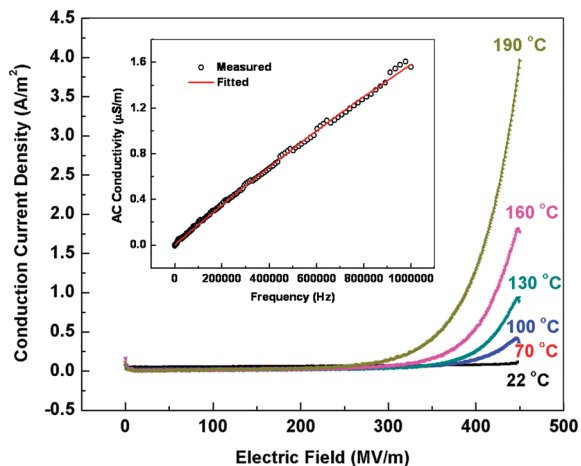


FIGURE 3. Conduction current derived from the  $P$ - $E$  loops at different temperatures. Inset: the measured and theoretically fitted ac conductance of PPEK.

injection from metal electrode into dielectric films and the detrapping of charge species from localized states or traps. In both cases, the rate of charge transportation is governed by the probability for the carrier to overcome energy barrier (17). It has been suggested that the significant increase of conduction current with the increase in field and temperature is mainly due to the reduction of the width and height

of energy barriers (16), which in turn results in large conduction loss and reduces the discharged energy density and the efficiency. The total conductance of materials consists of zero-frequency (i.e., dc) conductivity and frequency-dependent (i.e., ac) conductivity. It was observed in PPEK that the signal of ac conductivity was several orders of magnitude higher than the dc conductivity under low fields. To investigate the transport mechanism of carriers, the frequency dependence of ac conductivity of PPEKs was measured in a range of 100 Hz to 1 MHz at room temperature as shown in the inset of Figure 3. The ac conductance could be expressed as (14)

$$\sigma(\omega) = \varepsilon_r(\omega)\varepsilon_0 \tan \delta(\omega) \quad (2)$$

where  $\varepsilon_r$  is the real part of the dielectric constant,  $\varepsilon_0$  is the permittivity of vacuum ( $\varepsilon_0 = 8.85 \times 10^{-14}$  F/cm),  $\tan \delta$  is the dielectric loss tangent, and  $\omega$  is the angular frequency. It was found the ac conductivity revealed in PPEK samples followed the empirical law given as

$$\sigma = A + B\omega^n \quad (3)$$

where  $A$  and  $B$  are constants related to the dc conductivity and  $n$  is a fitting parameter. As shown in the inset of Figure 3, a fitting curve with  $n = 1$  agreed well with the experimental data, which implies that the hopping conduction process may dominate the dielectric loss (18).

An electrostatic pull-down method was employed to study the dielectric strength of PPEK as a function of temperature, where a linear ramp voltage at a rate of 500 V/s was applied between a rounded electrode and the gold-coated polymer film (19). The breakdown fields were measured over 15 samples and evaluated by the Weibull distribution function. It was found that the characteristic dielectric strength of PPEK only decreased slightly from 470 MV/m at room temperature to 441 MV/m at 190 °C. Concurrently, the  $\beta$  value, a shape parameter that evaluates the scatter of data, increased from 12 to 17.4 from room temperature to 190 °C, which suggests the decrease of variation of breakdown field with temperature. The obtained breakdown fields at high temperatures rivals or exceeds those reported for high-temperature dielectric polymers (10, 20). For instance, Teflon perfluoroalkoxy exhibits a dielectric strength of  $\sim 280$  MV/m at 125 °C (8). A dielectric field below 270 MV/m has been reported on PPS at 127 °C (21). The extraordinary breakdown strength of PPEK would enable efficient operation of capacitors at temperatures well beyond 100 °C.

For many electric energy storage applications such as pulsed power film capacitors, a fast discharge time is required. The discharged speed of PPEK was measured by using a specially designed capacitor discharge circuit (3). A representative discharge profile measured at 130 °C from a 20 kilohm load is presented in Figure 4, where the discharge time is defined as the time for the discharge energy in a load resistor to reach 95% of the final value. It was found that PPEK released the stored energy at a rate of

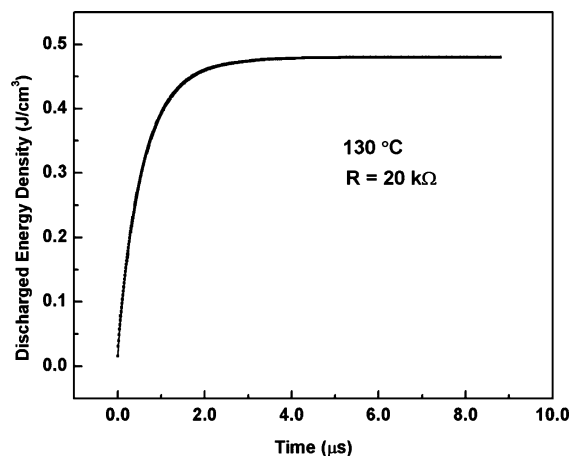


FIGURE 4. Discharge energy density as a function of time measured from direct discharge of PPEK to a load resistor of 20 k $\Omega$  at 130 °C. The applied field is 150 MV/m.

microseconds, which is comparable to the state-of-the-art pulsed power capacitors made from biaxially oriented polypropylene (BOPP) (2). In addition, the discharge speed of PPEK was not greatly affected by operating temperature. The discharge times were determined to be 1.78, 1.84, and 1.85  $\mu$ s at 22, 130, and 145 °C, respectively. The high discharging speed of PPEK may be ascribed to fast orientation and reversal of the polarized  $\pi$  electrons.

In conclusion, we have demonstrated that the phenyl phthalazinone containing polymer, PPEK, exhibited impressive dielectric properties with very small dielectric dispersion over a broad frequency and temperature range. The hopping conduction was identified to be mainly responsible for the reduction in the discharged energy and efficiency at high fields and elevated temperatures. The combination of superior discharged energy density, remarkable breakdown strength, and fast discharge speed at various temperatures makes this class of polymers very attractive for applications in dielectric energy storage at high temperatures.

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**Supporting Information Available:** Experimental details for the synthesis and characterization (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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