A highly scalable dielectric metamaterial with superior capacitor performance over a broad temperature

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Although many polymers exhibit excellent dielectric performance including high energy density with high efficiency at room temperature, their electric and dielectric performance deteriorates at high temperatures (~150°C). Here, we show that nanofillers at very low volume content in high-temperature (high–glass transition temperature) semicrystalline dipolar polymer, poly(arylene ether urea), can generate local structural changes, leading to a marked increase in both dielectric constant and breakdown field, and substantially reduce conduction losses at high electric fields and over a broad temperature range. Consequently, the polymer with a low nanofiller loading (0.2 volume %) generates a high discharged energy density of ca. 5 J/cm³ with high efficiency at 150°C. The experimental data reveal microstructure changes in the nanocomposites, which, at 0.2 volume % nanofiller loading, reduce constraints on dipole motions locally in the glassy state of the polymer, reduce the mean free path for the mobile charges, and enhance the deep trap level.

INTRODUCTION

Dielectric materials play a key role in electronic and electric devices and systems for controlling and storing charge and electric energy. For example, they are widely used for improving the power efficiency such as in hybrid electric vehicles (HEVs), electric grids, and networks and for energy storage in pulse power systems. Compared with inorganic dielectrics, polymers are attractive for their low dielectric loss, low manufacturing cost because of their thin-film roll-to-roll fabrication process, high breakdown strength, and graceful failure mode, which ensures high reliability when operating at high electric fields (1–7). A key figure of merit for dielectric materials is the energy density $U_c$

$$U_c = \frac{1}{2} K \varepsilon_0 E^2$$

where $E$ is the applied electric field, $K$ is the dielectric constant, and $\varepsilon_0$ is the vacuum permittivity ($=8.85 \times 10^{-12}$ F/m). Hence, a dielectric material with high $K$ and high breakdown field $E$ is highly desirable, in addition to low cost. Moreover, the charge/discharge (C/D) efficiency of a dielectric material at high electric fields, which measures how efficiently the material can store, control, and deliver charges and energy is directly linked to the high-field dielectric loss (see fig. S1A), is another critical performance parameter. In dielectric polymers, the conduction loss, which is negligible at low fields, could become high at high fields (and high temperatures) because most conduction losses increase exponentially with electric field and temperature (8, 9). High loss at high field will also cause heating in dielectric devices, which may lead to failure of the devices. Hence, evaluating and comparing $U_c$ of dielectric materials should take the electric field $E$ at which the dielectric can maintain a high C/D efficiency (low loss) into consideration.

Therefore, despite its low $K$ (=2.2), the exceptionally high breakdown field (~700 MV/m), low loss, and low cost of biaxially oriented polypropylene (BOPP) films enable BOPP film capacitors to reach a relatively high energy density (~3 J/cm³) with high C/D efficiency, which makes it the capacitor of choice for a wide range of applications such as HEV and high-voltage electric networks (3, 4, 10). On the other hand, the low operation temperatures of BOPP (<80°C) require external cooling to maintain safe operation temperature of these capacitors, because many applications are in hot environments (to 150°C) (5, 6, 11). This external cooling increases system size and cost.

To meet the demand of increased energy and power levels, increased functionality with limited volume, and miniaturization of the modern electronic and electrical devices and systems, there are urgent needs to (i) improve the energy density while developing strategies to maintain low loss so that a higher energy can be stored and delivered efficiently without increasing the device volume [because for many electric and electronic devices and products, capacitors can occupy more than 30% of the volume and weight (12)] and (ii) raise the operation temperature of polymer capacitors to above 150°C, for high-temperature applications and for eliminating external cooling in many polymer capacitor applications (5, 6).

Several approaches have been investigated in the past to raise the dielectric constant $K$ of polymer-based dielectrics and hence improve the energy density. For example, nanocomposites in which high volume loading (>15 volume %) of high–dielectric constant nanofillers ($K > 1000$) is added to a polymer matrix have been widely studied to raise the dielectric constant (7, 13–15). The rationale for this approach is based on the assumption that the composites can maintain high breakdown field $E$ of the polymer matrix, and hence, a high $U_c$ can be obtained. However, the large dielectric contrast between the nanofillers and polymer matrix and high volume loading of nanofillers required to raise $K$ of the composites result in the intensification of local electric fields in the polymer matrix, leading to a large reduction of the electric breakdown strength (15–17). To mitigate this local field effect, the surfaces of high-$K$ nanofillers have been modified, for example, to form core-shell structures that reduce the local field strength so that the breakdown strength of the nanocomposites approaches that of the polymer matrix (18, 19). By integrating nanocomposite layers with different nanofiller morphologies into multilayered films, both the dielectric constant and breakdown field can be improved compared with the polymer matrix (20, 21).

On the other hand, these studies have not addressed the issues of
improving the C/D efficiency at high fields and raising the operation temperature to 125°C or even 150°C. For dielectric materials, low cost is one of the most important factors to consider in developing new dielectric approaches. The composite approaches developed increase complications and cost in fabricating polymer films (typically below 5 μm in polymer capacitors), which are not compatible with large-scale/low-cost roll-to-roll processes (7).

During the past decade, dielectric polymers with high glass transition temperatures (Tg > 150°C) have been examined for high-temperature polymer capacitors (5, 11, 22, 23). It was found that although these high-Tg polymers have low dielectric loss (<1%) at low electric fields (<10 MV/m), large conduction loss at high electric fields (>300 MV/m) at high temperature causes high loss and a large reduction of the breakdown field, resulting in a low Uc at high temperatures (5, 6, 11, 24). Recently, Li et al. (6) show that nanocomposites of cross-linked high-Tg polymer BCB [divinyltetramethyldisiloxane-bis(benzocyclobutene)] with 10 volume % boron nitride (BN) nanosheets can substantially reduce the conduction loss at high temperature while achieving high breakdown field. As a result, the discharged energy density Ue ~ 2.2 J/cm³ with 90% C/D efficiency of a highly scalable and low-cost dielectric metamaterial film. Alumina (Al₂O₃) nanoparticles (K = 9.1; size, 20 nm; gamma phase), which have been widely used in nanocomposites, are chosen as the nanofiller. The films were fabricated using a solution casting method (see Materials and Methods for details).

RESULTS

Dielectric properties of PEEU nanocomposites

The dielectric constant K at 1 kHz of PEEU films at room temperature with various low nanofiller loading is presented in Fig. 1A, showing a dielectric enhancement peak K = 7.4 at ca. 0.21 volume %.

In nanocomposites, even small amount of nanofillers can generate large interface areas and boundaries and induce substantial effects in polymers (26, 27). For instance, in PEI, a high-temperature (Tg > 217°C) amorphous dipolar polymer that has been considered as a promising candidate for high-temperature capacitor applications (5, 11), it was observed that very low volume loading (<0.5 volume %) of nanofillers can lead to more than 50% increase in the dielectric constant K (28). However, as will be shown here, the presence of nanofillers in PEI films does not reduce the conduction loss at high fields and hence does not enhance the breakdown fields and does not generate a large improvement in the high-temperature performance.

In contrast to amorphous polymers, polymer single crystals exhibit very low electric conductivity because of the large bandgap (>7 eV) (9). Simulations by Xu et al. (29) show that the presence of crystallinity in semicrystalline polymers can substantially reduce the high-field conduction loss. Our current paper reports the development of a highly scalable and low-cost dielectric metamaterial approach, in which nanoparticles at very low loading volume (~0.2 volume %) substantially enhance the energy density, C/D efficiency, and breakdown field of high-temperature semicrystalline dipolar polymers. Specifically, we show that in poly(arylene ether urea) (PEEU), which is a high-Tg (>250°C) semicrystalline dipolar polymer, ca. 0.2 volume % of 20-nm-sized alumina nanofiller increases both the dielectric constant K and breakdown field E over a broad temperature range to >150°C. The dielectric constant K is raised from K = 4.7 of the base PEEU to 7.4. At 150°C, the nanocomposite films exhibit a breakdown field of 600 MV/m, increased from 400 MV/m of the base PEEU films. Moreover, the nanofiller at such a low loading also substantially reduces the high-field conduction loss. As a result, the PEEU films deliver a discharged Ue of 5 J/cm³ with a high C/D efficiency (>90%) at 150°C [see fig. S2A for the synthesis and chemical structure of PEEU (22)]. We chose PEEU for this study because its urea unit has a high dipole moment of 4.56 D, which can serve as deep traps and reduce the conduction loss (9, 30).

In addition, the crystalline phase in PEEU is sensitive to processing conditions, which may be exploited for tuning the dielectric properties in dielectric metamaterials (22). Alumina (Al₂O₃) nanoparticles (K = 9.1; size, 20 nm; gamma phase), which have been widely used in nanocomposites, are chosen as the nanofiller. The films were fabricated using a solution casting method (see Materials and Methods for details).

Fig. 1. Dielectric properties. (A) Summary of dielectric constant at 1 kHz versus the nanofiller loading, showing a dielectric enhancement at ca. 0.2 volume % filler loading. (B) Dielectric properties as functions of frequency of the PEEU nanocomposites with different nanofiller loadings measured at room temperature. (C) Dielectric properties at 1 kHz of the base PEEU and nanocomposite films with 0.21 volume % filler loading versus temperature.
The films containing nanofillers display very similar dielectric loss and frequency dispersion as that of PEEU (see Fig. 1B). Figure 1C presents the dielectric performance of the films with nanofillers to high temperature, showing thermal stability with low dielectric loss to 200°C.

For dielectric materials such as polymers, the losses at high electric fields and high temperatures (such as at 150°C) are caused mainly by high-field conduction, which can be much higher than that at low fields (<10 MV/m, for example). High conduction loss at high electric field results in a low C/D efficiency, which lowers the energy density $U_e$ and may cause a low breakdown field (6). The C/D behavior from the films at room temperature and high electric fields was examined first at compositions of interest. The data for PEEU films with different nanofiller loadings at room temperature are shown in Fig. 2 (A to C). Distinctly different from the PEI nanocomposites (28), PEEU films with 0.21 volume % filler exhibits 50% higher breakdown field (900 MV/m) than the base PEEU (600 MV/m). The C/D efficiency $\eta$ at high fields (conduction loss $= 1 - \eta$) is deduced from the C/D data (see fig. S1A). Owing to enhancement in both the dielectric constant $K$ and breakdown field $E_b$, the PEEU films with 0.21 volume % nanofiller loading deliver a discharged energy density of 27 J/cm$^3$ with a C/D efficiency of >90% under 900 MV/m, compared with 8.2 J/cm$^3$ of the base PEEU under 600 MV/m, as shown in Fig. 2B. At higher nanofiller loading, the breakdown field of the PEEU films becomes similar to or even lower than that of the base PEEU (see Fig. 2C). That is, the enhancements in both the dielectric constant and breakdown field in PEEU occur in a narrow nanofiller composition range. Figure 2C summarizes the breakdown field $E_b$, which is the highest field measured from the C/D curve, versus the filler loading at room temperature, showing a peak at ca. 0.21 volume %. For room temperature, the electric fields $E_{CD}$ at 90% C/D efficiency of the nanocomposites are the same as the highest breakdown field $E_b$ measured.

The large enhancement in the breakdown field in the PEEU films with 0.21 volume % nanofillers is maintained at high temperatures. The dielectric breakdown strength enhancement peaks at ca. 0.21 volume %, which is the same as that at room temperature. The C/D curves measured at 150°C are shown in Fig. 2D. The base PEEU films display a breakdown field of 400 MV/m, while the PEEU films with 0.21 volume % nanofiller have higher breakdown field, reaching 600 MV/m. Figure 2E compares the discharged energy density and C/D efficiency of the films with 0.21 volume % loading with that of PEEU at 150°C, revealing that the films with 0.21 volume % of nanofillers delivers a discharged energy density of 10.6 J/cm$^3$ at 600 MV/m (highest breakdown field measured), compared with the base PEEU of 2.9 J/cm$^3$ at 400 MV/m. Figure 2F shows how the nanofiller loading influences the high-temperature (e.g., 150°C) C/D efficiency, e.g., the electric field $E_{CD}$ at 90% C/D efficiency. In Fig. 2F, the breakdown field versus the nanofiller loading is also presented. The data reveal that PEEU films with ca. 0.21 volume % filler loading exhibit an $E_{CD}$ of 400 MV/m compared with base PEEU of 200 MV/m. The enhancement in both $K$ and $E_{CD}$ results in a discharged energy density of 5 J/cm$^3$ at 90% C/D efficiency, which is six times of the base PEEU of 0.83 J/cm$^3$ at 150°C. The $U_e$ demonstrated here is more than two times of the state of the art at high temperature (150°C) (6, 24), not to mention the highly scalable and low-cost strategy developed here.

In fig. S1B, we illustrate how the C/D efficiency of PEEU films under a fixed high electric field changes with alumina nanofiller...
loading at both room temperature and 150°C. At room temperature, the efficiency is taken at 600 MV/m. At 150°C, the efficiency is taken at 400 MV/m. The data show that under a given electric field, the films with 0.21 volume % filler loading exhibit a much higher efficiency compared with that of PEEU, reflecting substantially reduced conduction loss of the PEEU films at high electric fields by 0.21 volume % nanoparticles. It should be pointed out that at low fields, nanofillers do not change the dielectric loss of the films, which is expected because of very low nanofiller loading in the films (Fig. 1B). At high fields, the conduction loss shows a strong dependence on the nanofiller loading (loss = 1 – efficiency) and temperature. It is also noted that the C/D efficiency curves in fig. S1B resemble the dielectric breakdown curve, revealing the direct correlation between the charge conduction at high electric field and dielectric breakdown in the PEEU films.

In dielectric materials, the presence of deep traps may reduce the charge conduction at high fields (9). Here, thermally stimulated depolarization current (TSDC) is used to probe the trap states in the PEEU films with different nanofiller loadings (31, 32), and the data recorded are presented in fig. S3. The PEEU films with 0.21 volume % nanofiller display a major discharge peak at 92.5°C, higher than 78°C of the base PEEU and 70°C of the films with 0.43 volume % nanofillers. The higher temperature peak position and shaper peak rising curve indicate that the PEEU films with 0.21 volume % filler have a deeper trap level compared with the PEEU and PEEU films with 0.43 volume % nanofillers (31, 32). The presence of deep traps reduces the charge carrier mobility μ from the trap-free value μ0. Several models have been derived, and in general, it follows that μ = μ0 (exp(ΔE/kBT))−1 (9), where ΔE is the trap level, kB is the Boltzmann constant, and T is the temperature in kelvin. These results are consistent with the direct conduction measurements in PEEU films with nanofillers. Electric conductivity σ measured at 100 MV/m and room temperature shows σ = 1.5 × 10−17 S/cm for PEEU films with 0.21 volume % loading, more than one order of magnitude smaller than PEEU, σ = 2 × 10−16 S/cm.

Characterizations of structural changes of PEEU nanocomposites
To examine the possible changes in the polymer morphology in the PEEU films with nanofiller loading, we collected wide-angle x-ray diffraction (XRD) data for the base PEEU and nanocomposites, which are shown in Fig. 3A. PEEU with 0.21 volume % displays a distinctly different x-ray pattern compared with the base PEEU and PEEU with higher alumina loadings. The data were analyzed (see fig. S4) to estimate the crystallinity and the peak position change of the amorphous phase of the base PEEU and nanocomposite films (33). Using the peak position to estimate the mean interchain spacing shows an expansion of the interchain spacing of about 5.8% for films with 0.21 volume % of nanofillers compared with base PEEU and films with higher volume loading (0.43 and 0.63 volume %) (see table S1 for the summary of structural changes deduced from the x-ray data). We also obtained infrared spectra of the PEEU films with different nanofiller loadings and noticed the change in the Fourier transform infrared (FT-IR) data, as presented in Fig. 3B, associated with the hydrogen bonding in PEEU polymer (see fig. S2B for schematics of hydrogen bonding in PEEU polymer). The data show a softening of the hydrogen bonding in the PEEU films with 0.21 volume % nanofiller loading compared with PEEU and PEEU with higher volume loading of nanofillers, indicating that the nanofillers of 0.21 volume % partially disrupt the hydrogen bonding in the polymer, which reduces the constraints on the urea dipoles. Both the weakening of hydrogen bonding and expansion of the interchain spacing, which generates local free space for dipoles, will enhance the dipolar response to the external field and increase the dielectric constant (22).

The data in Fig. 3A also suggest that the films with 0.21 volume % have a relatively smaller amorphous peak area compared with other films. By comparing the peak areas of the broad amorphous peak and relatively sharp peak for the crystalline phase, we estimate the crystallinity of the PEEU films with different nanofiller loadings, which is presented in the inset of Fig. 3A. The data show that there is a slight increase in crystallinity (and reduced crystallite size; see fig. S4D) of the PEEU films with 0.21 volume % compared with the base PEEU. The results suggest that the induced increase in crystallinity and the reduced crystallite size in the PEEU 0.21 volume % nanocomposites of the nanofillers reduce the distance between crystallites, reducing the mean free path for the mobile charges. This may have a positive contribution to the reduced conductivity and enhanced breakdown strength. This mechanism is supported by the experimental results of Wang et al. (34) on low-density polyethylene (LDPE)/alumina nanocomposites, in which 0.5 weight % (wt %) (0.12 volume %) of alumina nanofiller (particles of 30 nm diameter) in LDPE enhances the breakdown field and reduces the conduction loss at high electric field, compared with the neat LDPE and composites with higher nanofiller loadings. The nanofillers at 0.5 wt % also increase the crystallinity of LDPE films.

**Comparison on capacitor performance of PEEU nanocomposites with multiple classic dielectric polymeric composites**

Panels A and B of Fig. 4 compare Uc at the breakdown fields and at fields with 90% C/D efficiency of the PEEU films with 0.21 volume % filler loading with the state-of-the-art high-temperature nanocomposites in the literature, respectively (6, 24). The PEEU nanocomposites deliver a Uc value of 4.8 J/cm² at 150°C at 90% C/D efficiency, which is about six times that of the base PEEU. In addition, we also choose PEI and polyaromatic ether ketone (PAEK) for the comparison. PEI is a high-temperature (Tg = 217°C) amorphous dipolar polymer, and its nanocomposite shows dielectric enhancement from the base PEI K = 3.2 to K = 5 of films with 0.32 volume % of 20-nm-diameter nanoparticles (28). For PEI nanocomposites, an earlier study has shown that nanofillers do not improve the
breakdown field and high-temperature performance (28). PAEK is a commercial high-temperature semicrystalline dipolar polymer ($K = 3.6, T_g = 230°C, T_m = 350°C$) (see fig. S2D for the chemical structure). The PEI and PAEK and their nanocomposite films were prepared here, and measurements were carried out (see figs. S5 and S6). Although the nanofiller of 20 nm size at 0.32 volume % increases the dielectric constant in PEI, the data show that the nanofiller does not improve the C/D efficiency of the PEI films. This is different from the PEEU films. For PAEK, it was found that it is not straightforward to make high-quality films; hence, only one nanocomposite composition (0.35 volume % of 20-nm-sized alumina particles, which is close to the PEI composition showing high dielectric enhancement) was fabricated. Data in fig. S6 show that PAEK films with nanofiller loading display very similar features as observed in PEEU, i.e., nanofillers at this composition enhance both the dielectric constant and breakdown field. $K$ is increased from 3.6 of the base PAEK to 4.3 in the nanocomposite films. Breakdown at room temperature is increased from 400 MV/m of base PAEK to 500 MV/m for the nanocomposite. At 150°C, it is increased from 350 to 400 MV/m. In addition, at 150°C, nanofillers substantially reduce the conduction loss and improve the C/D efficiency, as shown in fig. S6 (D and E).

Panels A and B of fig. S7 present the discharged energy density $U_e$ of the base polymers at the breakdown electric fields and fields with 90% C/D efficiency, respectively, from which the enhancement ratios of $U_e$ of composites to their base polymers in Fig. 4 (A and B) are derived. As can be seen, the high-temperature semicrystalline polymers, e.g., PEEU and PAEK, exhibit a high enhancement ratio at 150°C compared with the other polymers, indicating the effectiveness of nanofillers at low volume loading in these polymers in reducing the conduction loss at high temperature. Figure S7 (C and D) presents another view of Fig. 4, e.g., the enhancement ratio of composite film $U_e$/base polymer $U_e$ as the vertical axis and $U_e$ of the nanocomposite as the horizontal axis, showing superior capacitance performance of PEEU nanocomposites.

In addition to the results presented here, we note that in several widely used low-temperature (e.g., $T_g$ near or below room temperature) semicrystalline polymers such as LDPE, polypropylene (PP), and tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride (THV) terpolymer, early studies have also shown that nanofillers at very low volume loading (<0.5 volume %) enhance the breakdown field and reduce the high-field conduction loss at room temperature (34–36). On the other hand, no enhancement in the dielectric constant was observed in these low-temperature dielectric polymers. The enhancements of capacitance performance from nanocomposites with low nanofiller volume loading are summarized in table S2, including high-temperature polymers of PEEU, PEI, and PAEK and low-temperature polymers of LDPE and PP.

**DISCUSSION**

This paper reports that low volume loading of nanofillers (<0.5 volume %) in high-$T_g$ semicrystalline dipolar polymers, PEEU and PAEK, can increase the dielectric constant, reduce the high-field conduction loss, and enhance the breakdown field over a broad temperature range. The experimental data on PEEU show that nanofillers at such a low volume content generate local and nanostructure changes that weaken the hydrogen bonding and expand the interchain spacing, hence creating local “free volume” and reducing the local constraints on polymer dipoles in the glassy state. These contribute to the increase in the dielectric constant. In addition, nanofillers at 0.21 volume % loading in PEEU films enhance the deep trap level, increase crystallinity, and reduce the crystallite size, which may have positive contributions to the reduced conduction loss and enhanced breakdown field.

We note that dielectric metamaterials have been studied quite extensively in the past decades for high-frequency applications (from microwave to optical frequencies). In these dielectric metamaterials, local structures and interfaces, rather than averaged structures, play a substantial role in enhancing the material performance and generating new material responses, which are not found in natural materials (37). The results presented here demonstrate that such a dielectric metamaterial strategy can also be explored at low frequencies for controlling and storing charges and electric energy in dielectric composites. The low cost and highly scalable approach demonstrated here pave the way for the development of a totally new class of dielectric metamaterial with superior capacitance performance over a broad temperature range.
Preparation of PEEU nanocomposites

PEEU powder was synthesized by Key Synthesis LLC, following the synthesis process as shown in fig. S2A. The $^1$H nuclear magnetic resonance spectrum of PEEU is presented in fig. S2B. The molecular weight $M_n$ is around 20,000. Alumina (Al$_2$O$_3$) nanoparticles (gamma phase) with a mean particle diameter of 20 nm were purchased from US-Nano. To prepare the nanocomposite solution, a proper amount of PEEU powder was dissolved in dimethylformamide (DMF) at 60°C and stirred overnight to obtain a homogeneous solution. Alumina nanoparticles with selected weight percentage were dispersed in DMF at room temperature using Elma “P” Series Ultrasonics (250 W) for 1 hour. Afterward, the PEEU solution was poured into this suspension and sonicated for 6 hours. Then, the solution was cast onto a silicon plate and kept in a vacuum oven for 4 hours and dried at 80°C for 12 hours to remove the solvent. The obtained film was heated to 180°C for 24 hours to further remove the solvent. Platinum (Pt) electrodes of 4 mm diameters were sputtered on the composite films for the dielectric characterization. The thickness of PEEU and its nanocomposites is in the range of 2 to 3 μm. It was found that long ultrasonication time is critical to ensure uniform nanocomposite films. Relatively small fluctuations in filler content could compromise the homogeneity of the final product.

Preparation of PEI nanocomposites

Ultrem 1000 PEI polymer resin was purchased from PolyK Technologies. To prepare the nanocomposite solution, a proper amount of PEI powder was dissolved in DMF at 60°C and stirred overnight to obtain a homogeneous solution. Alumina nanoparticles at 1 wt % were dispersed in DMF at room temperature using Elma “P” Series Ultrasonics (250 W) for 1 hour. Afterward, the PEI solution was poured into this suspension and sonicated for 12 hours. The solution was then cast onto a clean glass slide. The solution cast films were kept in a drying oven at 70°C for 12 hours to remove the solvent and then heated to 100° and 150°C for 1 hour and to 200°C for 12 hours, followed by a final drying step at 225°C for 2 hours. Afterward, the films were kept in a vacuum oven at 200°C for 1 day to further remove any residual solvent. The film was peeled off from the glass substrate by placing it in the deionized (DI) water; then, the film was dried at 70°C in a vacuum oven. The thickness of PEI and its nanocomposite films is in the range of 7 to 8 μm.

Preparation of PAEK nanocomposites

PAEK resin (P7000) was provided by Polymics Ltd. (State College). To prepare the nanocomposite solution, a proper amount of PAEK powder was dissolved in N-methyl pyrrolidone (NMP) at 150°C and stirred overnight to obtain a homogeneous solution. The alumina nanoparticles at 1 wt % were dispersed in NMP at room temperature using Elma “P” Series Ultrasonics (250 W) for 1 hour. Afterward, the PAEK solution was poured into this suspension and sonicated for 12 hours. The solution was then cast onto a clean glass slide. The solution cast films were kept in a drying oven at 70°C for 20 hours to remove the solvent and then heated to 150°C for 12 hours. Afterward, the films were kept in a vacuum oven at 150°C for 1 day to further remove any residual solvent. The film was peeled off from the glass substrate by placing it in the deionized (DI) water; then, the films were dried at 70°C in a vacuum oven. The thickness of PAEK and its nanocomposites is from 10 to 15 μm.

Electrical measurements

Dielectric properties at different temperature were characterized by an HP 4284 LCR meter connected to a Delta 9023 environment chamber. The polarization–electric field unipolar loops (P-E loops) and breakdown strength at various temperatures were measured with a modified Sawyer-Tower circuit at 10 Hz; the area of the electrode is 4.52 mm$^2$. The Weibull distribution on the dielectric breakdown of PEEU nanocomposites with 0.21 volume % alumina is presented in fig. S8. The XRD data for PEEU nanocomposites were collected at room temperature using a PANalytical XPer Pro MPD diffractometer. The TSDC test was characterized using an HP 4140B pA meter, which was connected to a Trek high-voltage amplifier (model 609 D-6) and an environment test chamber (Delta 9023). To perform TSDC test, these samples were poled at a poling field of 10 MV/m (120°C poling temperature for 10 min). Then, the samples were cooled down to ~80°C, and the field was removed. The depolarization currents were measured at a constant heating rate of 5°C/min. The high-field conductivity was measured on a Cascade Microtech probe station with an HP 4140B pA meter/dc voltage source and a Kepco bipolar operational power supply/amplifier (model BOP 1000M). The measurement was carried out under an electric field of 100 MV/m. FT-IR spectra measurement was carried out at room temperature using a Bruker VERTEX 70 spectrophotometer with attenuated total reflectance absorption; the resolution was 2 cm$^{-1}$.
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