High Dielectric Constant Dipolar Glass Polymer Based on Sulfonylated Poly(ether ether ketone)

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ABSTRACT: In this work, a new kind of dipolar glass polymer, containing strongly

polar sulfonyl groups, was synthesized by post functionalization of the corresponding

poly(ether ether ketone) containing carboxyl groups (PEEK-COOH). The sulfonylated

PEEK (PEEK-SO₂) exhibited strong β transition at -100 °C and 1 Hz due to the large

dipole moment (4.25 D) of the side-chain sulfonyl groups, which were attached to the

backbone via flexible ester bonds. Because of this strong β dipole relaxation, the glassy

PEEK-SO₂ exhibited a high dielectric constant of 5.0 at 25 °C and 1 Hz, nearly 32%

higher than that of PEEK-COOH. From an electric displacement-electric field loop

study, PEEK-SO₂ exhibited a relative high discharge energy density of 2.35 J/cm³ at

300 MV/m and room temperature, which was 1.4 times that of PEEK-COOH. However,

the hysteresis loss was only 0.008 at 100 Hz and 25 °C. This work further reveals that

dipolar glass polymers with high mobile dipolar side groups are suitable for high energy

density and low loss dielectric applications.

Keywords: dipolar glass polymer, dipole relaxation, poly(ether ether ketone)

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1. Introduction

Dielectric polymers with high breakdown strength, high energy density, high temperature resistance, and low loss tangent are highly needed for a variety of practical applications, especially in power and electrical devices [1-5]. Among these, dipolar glass polymers (DGPs) are promising substitutes for the state-of-the art polymer dielectric material, biaxially oriented polypropylene (BOPP), due to their relatively high dielectric constant (4-15).[6-11] Besides, compared with ferroelectric poly(vinylidene fluoride) (PVDF)-based copolymers, DGPs with isolated molecular dipoles also have relatively low dielectric loss because of weak dipole-dipole interactions. The first example DGP is poly(2-(methylsulfonyl)ethyl methacrylate) (PMSEMA), which exhibited a high dielectric constant of 11.4 and a relatively low dissipation factor of 0.02 at 25 °C and 1 Hz due to the large dipole moment (4.25 D) and the small size of the side sulfonyl groups.[7] The second sample is sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) (SO₂-PPO), which was synthesized via postpolymer functionalization. The discharged energy density of SO₂-PPO reached as high as 22 J·cm⁻³ and the low dissipation factor was 0.003 with high T_g of 220 °C due to efficient rotation of highly polar methylsulfonyl side groups.[6] From these reports, we found that methylsulfonyl group is a stable and effective molecular dipole for DGPs. In addition, post-polymer functionalization is a promising method to obtain advanced DGPs, which can overcome the difficulty from polymerization of monomers.

Although the dielectric properties of the above DGPs are good, their mechanical properties are not ideal. For example, the polymer dielectric needs to be flexible and tough for film capacitors. Due to the rigid structure of SO₂-PPO, the solution-cast film was very brittle. For PMSEMA, the film was also lack of toughness because of relatively low molecular weight. In conventional radical polymerization in solution, the molecular weight of PMSEMA is difficult to be high, possibly due to chain transfer to the methyl sulfonyl groups and solvent.

In this work, we report synthesis and dielectric properties of side-chain sulfonylated poly(ether ether ketone) (PEEK-SO₂). Due to the rigid molecular framework and flexible ether linkage, PEEK-SO₂ exhibited better flexibility and toughness. Meanwhile, highly dipolar methylsulfonyl side groups boosted the orientational polarization. Therefore, a rather high dielectric constant of 5.0 and a low dielectric loss of 0.008 were observed for PEEK-SO₂ at room temperature and 1 Hz. The window from the β to α transition was as wide as ca 200 °C. Therefore, PEEK-SO₂ has practical significance for the film capacitor field.

2. EXPERIMENTAL SECTION

2.1. Materials

4,4-Bis(4-hydroxyphenyl)pentanoic acid (DPA), potassium carbonate (K₂CO₃), potassium hydroxide (KOH), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidinone (NMP), dichloromethane (DCM). 4,4'-difluorobenzophenone, and thionyl chloride were purchased from Shanghai Aladdin Biochemical Polytron Technologies, Inc., China. Toluene was obtained from Tianjin Bodi Chemical Holding Co. Ltd., China. 2-(Methanesulfonyl)ethanol was purchased from Tokyo Chemical

Industry Co. Ltd., Japan. All chemicals were used as received without further purification.

2.2. Synthesis of PEEK-COOH

PEEK-COOH was synthesized by an aromatic nucleophilic substitution reaction, as shown in Scheme 1. Similar processes for the synthesis of polymer was described in previous literature.[12] Into a 250 mL round-bottom flask equipped with a stirring bar and nitrogen inlet, K₂CO₃ (52.8 mmol), DPA (35.3 mmol), KOH (17.6 mmol), toluene (27 mL), and NMP (81 mL) were charged. The mixture solution was stirred at 145 °C for 1.5 h. After cooling, 4,4'-difluorobenzophenone (35.3 mmol) was added into the round-bottom flask. The condensation polymerization was then carried out at 145 °C for 1.5 h and at 190 °C until the viscosity was high enough. The water byproduct and toluene were continuously removed using a Dean-Stark trap. Finally, the viscous solution was precipitated in a 10% HCl aqueous solution. After drying, the product was dissolved in DMF, and the solution was added dropwise into deionized water with magnetic stirring. Then, the white precipitate was washed three cycles with hot deionized water. After being dried in a vacuum oven for 48 hours, the purified polymer was obtained.

2.3. Synthesis of PEEK-SO₂

A 100 mL round-bottom flask was charged with 2 g of PEEK-COOH, 10 mL SOCl₂, and two drops of DMF under Argon protection. The flask was sealed by a rubber stopper with magnetic stirring for 24 h. The unreacted SOCl₂ was removed by rotary evaporation. Then, 10 mL of 2-(methanesulfonyl)ethanol and 20 mL of DCM were added into the reaction system, and the mixture was stirred for another 24 h. After that, the solution was precipitated in ethanol. After drying, the product was dissolved in DMF, and the solution was added dropwise to deionized water with magnetic stirring. Finally, the purified PEEK-SO₂ was dried under vacuum at 80 °C for 2 d.

2.4. Film Preparation

Polymer film samples were prepared by solution-casting. For example, PEEK-COOH (1 g) was dissolved in DMF (10 mL), and the solution was poured onto glass substrates. The glass substrates were then placed in an air-circulating oven, and the temperature was stepwise ramped to 160 °C at hourly intervals at 90, 100, 120, 140, and 160 °C, respectively. Afterwards, they were naturally cooled to room temperature (RT = 25 °C, i.e., room conditions). The thickness of the films varied from 30 to 50 μ m. Both obtained films were tough, flexible, and transparent.

2.5. Characterization and Instrumentation

Transmission Fourier transform infrared (FTIR) spectrum was recorded on a Bruker Tensor 27 FTIR spectrophotometer (Billerica, MA) with a resolution of 4 cm⁻¹. KBr window was used as substrate. Proton nuclear magnetic resonance (¹H NMR) spectrum was recorded at 600 MHz on a Bruker NMR spectrometer using CDCl₃ or DMSO-d₆ as solvent with an internal reference of tetramethylsilane. The thermal

property of films was studied using a TA Instruments (New Castle, DE) Q100 differential scanning calorimeter (DSC). The scanning rate was 10 °C/min, and about 3 mg of sample was used to avoid possible thermal lag. Thermogravimetric analysis (TGA) was recorded on a TA Instruments Q50 thermogravimetric analyzer at a heating rate of 20 °C/min.

Broadband dielectric spectroscopy (BDS) measurements were performed on a Novocontrol Concept 80 broadband dielectric spectrometer (Montabaur, Germany) with precise temperature control. The applied voltage was 1 V_{rms} (rms means root mean square) with the frequency ranging from 0.01 to 10^7 Hz and the temperature from -145 to 200 °C. The as-prepared films were coated with aluminum electrodes on both sides using a Denton Vacuum Benchtop Turbo evaporator (Moorestown, NJ) with an electrode area of about 0.785 cm².

Electric displacement-electric field (D-E) loops were measured using a Radiant Technology Premiere II ferroelectric tester at a frequency of 10 Hz using a sinusoidal wave function. Gold electrodes (10 nm thick) were sputter-coated on both sides of the film with a diameter of 2.5 mm. Samples were immersed in a silicone oil bath to avoid corona discharge in air. The maximum electric field was increased stepwise at increment of 50 MV/m until dielectric breakdown. The discharged energy density ($U_{e,dis}$) and the discharge efficiency could be calculated based on the area of D-E loop.

Dynamic mechanical properties of the film samples were characterized using a TA DMA Q800 dynamic mechanical analysis (DMA, TA Instruments). The film samples were cut into a rectangular shape with a width of 5.3 mm and a thickness of 35 μ m. The characterization was taken under tension film mode with a gauge length of \sim 10 mm at an oscillation frequency of 1 Hz and amplitude of 15 μ m. The heating rate was 3 °C/min.

Tensile tests of the film samples were carried out using an Instron 5965 uniaxial stretcher. The film samples were cut into a rectangular shape with a width of \sim 6 mm and a thickness of \sim 30 μ m. The stretching was taken with a gauge length of \sim 10 mm at 60 mm/min at room temperature.

3. RESULTS AND DISCUSSION

The synthetic route of PEEK-COOH is showed in Scheme 1 by condensation polymerization. The PEEK-SO₂ was synthesized by reacting PEEK-COOH with SOCl₂ in the presence of DMF first, then reacting with 2-(methanesulfonyl)ethanol in DCM. The structure of the purified PEEK-COOH and PEEK-SO₂ were confirmed by ¹H NMR spectroscopy. Figs. 1A and B show ¹H NMR spectra of PEEK-COOH and PEEK-SO₂, respectively. By comparing the ¹H NMR spectra with polymer structures, all protons and their integral area for both PEEK-COOH and PEEK-SO₂ can be successfully assigned.

Scheme 1. The synthesis route for PEEK-COOH and PEEK-SO₂.

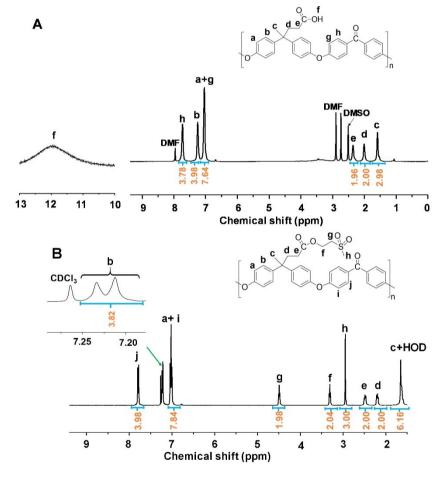


Fig. 1. ¹H NMR spectra of (A) PEEK-COOH and (B) PEEK-SO₂. The solvent is DMSO-*d*₆ and CDCl₃, respectively. Peak assignments are indicated with indication of solvent (DMF and CHCl₃) and water peaks.

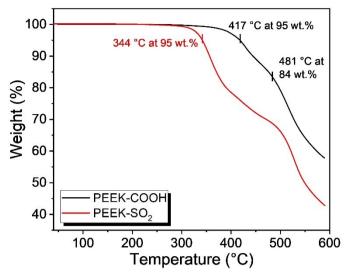


Fig. 2. TGA curves of PEEK-COOH and PEEK-SO₂, respectively.

The TGA results in Fig. 2 showed that 5 wt.% degradation of PEEK-COOH started at ca. 417 °C. There were obviously two-step degradation processes for both polymers. The first step degradation was around 430 °C. The second degradation process was obvious and around 516 °C. Considering the structure of PEEK-COOH, the first degradation process should originate from the degradation of pendant -(CH₂)₂COOH group, whose weight fraction is about 16.2%. Indeed, the weight loss at 481 °C was about 16 wt.%. The second weight loss process was attributed to the thermal degradation of the backbone. Compared with PEEK-COOH, the 5 wt.% degradation of PEEK-SO₂ started at a lower temperature of 344 °C. The major reason for this difference was attributed to the fact that the thermal stability of -(CH₂)₂-COOH in PEEK-COOH was higher than that of -(CH₂)₂COO(CH₂)₂SO₂CH₃ in PEEK-SO₂. Basically, upon thermal degradation, CH₂=CHSO₂CH₃ was eliminated followed by the loss of the -(CH₂)₂COOH group.

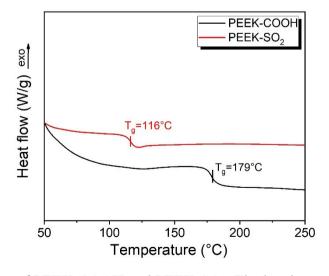


Fig. 3. DSC curves of PEEK-COOH and PEEK-SO₂. The heating rate was 10 °C/min.

PEEK-COOH and PEEK-SO₂ were amorphous polymers and showed T_g around 179 and 116 °C at a heating rate of 10 °C/min (see Fig. 3). Due to the rigid backbone structure of PEEK-COOH and hydrogen-bonding, PEEK-COOH had a higher T_g than the PEEK based on 1,4-bis-(4-chlorobenzoyl)benzene and bisphenol A (T_g = 167 °C) and another PEEK based on 1,3-bis-(4-fluorobenzoyl)benzene and bisphenol A (PEEK-BPA, T_g = 155 °C).[13,14] Although the polarity of -SO₂CH₃ in PEEK-SO₂ was higher than -COOH in PEEK-COOH, T_g of PEEK-SO₂ was much lower than that of PEEK-COOH. The reason was attributed to the much longer side chain length in PEEK-SO₂, which was 8 atoms long.[15, 16]

Dielectric Properties

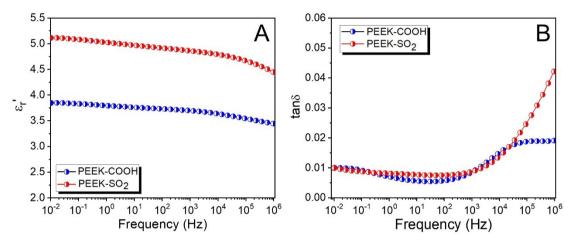


Fig. 4. Frequency-scan BDS results of (A) real relative permittivity (ε_r ') and (B) dissipation factor (tan δ) for PEEK-COOH and PEEK-SO₂ at room temperature.

PEEK-COOH is a polar amorphous polymer showing a relatively high permittivity of 3.75 at 1 Hz, which was 25% higher than that of neat PEEK (\sim 3) (Fig. 4A).[17-19] After functionalization of PEEK-COOH, the dielectric constant of PEEK-SO₂ increased about 32% (i.e., $\epsilon_r = 5.0$ at RT). From Fig. 4B, the relaxation frequencies for the -CH₂CH₂COOH and -CH₂CH₂COOCH₂CH₂SO₂CH₃ groups were above 10⁵ Hz, after which the dielectric loss of PEEK-SO₂ was much higher than that of PEEK-COOH. This indicated that the relaxation process of dipoles always led to a higher dielectric loss as a result of intermolecular friction.[20-22] Meanwhile, the dielectric constant started to decrease due to dipolar relaxation around 10⁵ Hz. Therefore, these DGPs should be only suitable for power conditioning at low frequencies (<10⁴ Hz), and not suitable for high frequency (>10⁹ Hz) applications.

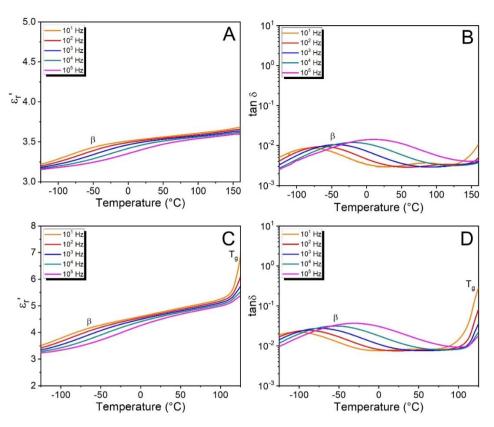


Fig. 5. Temperature-scan BDS results of (A, C) the real relative permittivity (ε_r) and (B, D) dissipation factor ($\tan \delta$) at various frequencies for (A, B) PEEK-COOH and (C, D) PEEK-SO₂.

PEEK-COOH exhibited an obvious sub- T_g (i.e., β) transition around -75 °C at 10 Hz in the tan δ plot (Fig. 5B), which might be due to the orientational polarization of side-chain (-COOH) in the electric field. Besides, the β transition shifted to higher temperatures with frequency increasing. Between -125 to 160 °C at 10 Hz, the dielectric constant gradually improved from 3.2 to 3.6 (Fig. 5A). Note that the temperature-scan ε_r values in Fig. 5 were slightly lower (4-6%) than the frequency-scan values in Fig. 4A under the same test conditions. The difference should originate from the error in film thickness measurement, considering i) non-uniformity in thickness for solution-cast films and ii) error in the film thickness gauge ($\pm 0.5 \, \mu m$).

Compared to PEEK-COOH, PEEK-SO₂ had a higher dielectric constant, from 3.5 to 6.8 between -125 to 125 °C at 10 Hz (Fig. 5C). Besides, PEEK-SO₂ also had an obvious β transition around -100 and 10 Hz (Fig. 5D). This transition was ascribed to switching of side-chain sulfonyl dipoles.[23-25] The peak temperature for the β relaxation was lower, indicating that the switching of side-chain sulfonyl dipoles was easier than the rotation of side-chain COOH groups. It was considered that the hydrogen bonding among COOH diploes restricted their motion. From these tan δ plots, the lowest dissipation factors reached 0.003 for PEEK-COOH (25 - 145 °C) and 0.008 for PEEK-SO₂ (0 - 90 °C) at 100 Hz. The tan δ for PEEK-COOH started to increase when the temperature was above 150 °C at 10 Hz (Fig. 5B). For PEEK-SO₂, tan δ started to rise around 100 °C at 10 Hz (Fig. 5D). The temperatures of increased tan δ for both PEEK-

COOH and PEEK-SO₂ were close their T_g s, around which the motion of impurity ions in the free volume became stronger.[26-28] Therefore, the increase of $\tan\delta$ around T_g could be attributed to both cooperative segmental motion of the polymers and subsequent migration of impurity ions. Below T_g , DGPs, such as PEEK-COOH and PEEK-SO₂, have a lower dielectric loss than that of ferroelectric polymers due to their frozen main chains.

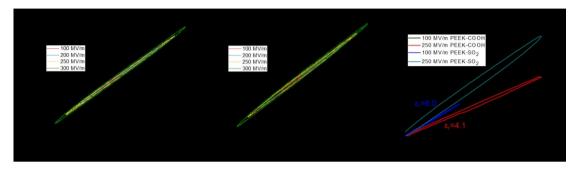


Fig. 6. Bipolar D-E loops for (A) PEEK-COOH and (B) PEEK-SO₂ at 10 Hz and room temperature. (C) Unipolar D-E loops for PEEK-COOH and PEEK-SO₂ at 200 Hz and 100 °C.

High-field dielectric properties of these modified PEEK films at different temperatures were studied by D-E loop measurements. At 10 Hz and RT, both PEEK-COOH and PEEK-SO₂ showed narrow loops below 300 MV/m (Figs. 6A and B). At 200 Hz and high temperatures (Fig. 6C), PEEK-COOH showed relatively narrow D-E loops at 250 MV/m. Besides, the loop loss for PEEK-SO₂ became higher at higher fields due to the enhanced AC electronic conduction. When compared with PEEK-COOH, PEEK-SO₂ could show narrow D-E loops at RT and 10 Hz under 300 MV/m (Fig. 6B). The apparent ϵ_r of both polymers could be calculated from the slope in the range of the straight line of the loops, i.e., 4.2 for PEEK-COOH and 6.1 for PEEK-SO₂. These values are somewhat higher than the BDS results in Fig. 4A. This could be attributed to the higher dipolar polarization under enhanced electric fields. From the linear D-E loops for PEEK-COOH and PEEK-SO₂, it came to a conclusion that no ferroelectric domains formed in the high-field.[29] This is beneficial for electric energy storage applications.

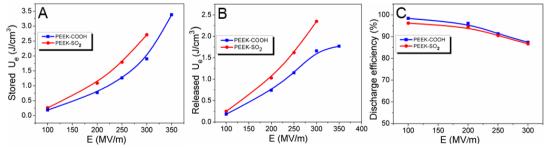


Fig. 7. (A) Stored $(U_{e,st})$ and (B) discharged $(U_{e,dis})$ energy densities, and (C) discharge efficiency as a function of the electric field for PEEK-COOH and PEEK-SO₂ at 10 Hz and room temperature, respectively.

The stored (U_{e,st}) and discharged energy densities (U_{e,dis}) were obtained from the bipolar D-E loops in Fig. 6. Upon increasing the applied electric field, the U_{e,st} and U_{e,dis} of PEEK-COOH increased to 3.38 and 1.77 J/cm⁻³ at 350 MV/m, respectively (Fig. 7A). Meanwhile, the U_{e,st} and U_{e,dis} of PEEK-SO₂ increased faster than those of PEEK-COOH, reaching 2.70 and 2.35 J/cm⁻³ at 300 MV/m (Fig. 7B). This could be attributed to the higher dielectric constant for PEEK-SO₂. However, PEEK-COOH showed a slightly higher discharged efficiency than PEEK-SO₂ below 300 MV/m (Fig. 7C).

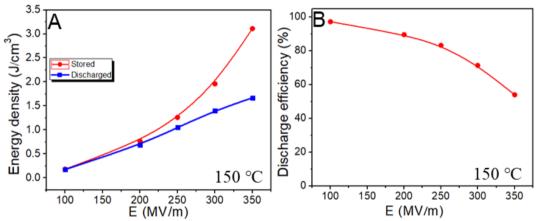


Fig. 8. (A) Stored $(U_{e,st})$ and discharged energy $(U_{e,dis})$ densities and (B) discharge efficiency as a function of the electric field for PEEK-COOH at 200 Hz and 150 °C.

As we mentioned before, one major shortcoming of BOPP films is the low operating temperature not higher than 85 °C. It is needed to search for high temperature resistance polymer dielectrics. High temperature dielectric performance for PEEK-COOH was studied by D-E loop tests at 150 °C. The poling electric field was up to 350 MV/m at 200 Hz (note that the loss became too large when the frequency was 10 Hz). Note that this temperature was higher than the T_g of PEEK-SO₂. Therefore, the dielectric performance of PEEK-SO₂ could not be tested at 150 °C. The U_{e,st} and U_{e,dis} for PEEK-COOH are shown in Fig. 8A. When the electric field was below 200 MV/m, the discharge efficiency was above 90% (Fig. 8B). Above 200 MV/m, the discharge efficiency significantly decreased, primarily owing to enhanced AC electronic conduction in the polymer sample at higher temperature. Therefore, PEEK-COOH showed good high temperature performance at 150 °C when the poling electric field was below 200 MV/m.

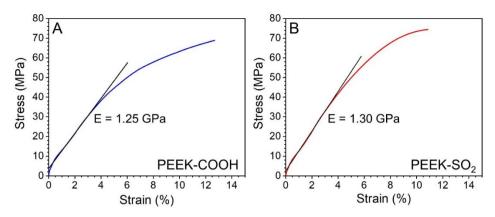


Fig. 9. Stress-strain curves for (A) of PEEK-COOH and (B) PEEK-SO₂ at room temperature. The stretching rate is 60 mm/min.

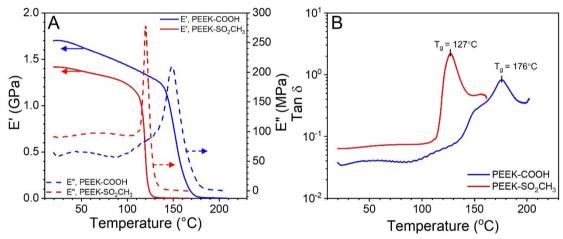


Fig. 10. Temperature-scan (A) storage (E') and loss (E") tensile moduli of PEEK-COOH and PEEK-SO₂ at 1 Hz. (B) Dissipation factor, tanδ, for PEEK-COOH and PEEK-SO₂.

One advantage of these DGPs was their mechanical toughness. Unlike other reported DGPs, they were not brittle at all. Fig. 9 shows the stress-strain curves for PEEK-COOH and PEEK-SO₂ at RT. The Young's moduli were 1.25 and 1.30 GPa, for PEEK-COOH and PEEK-SO₂, respectively. The strength and elongation at break were 70 MPa and 12.5% for PEEK-COOH. The strength and elongation at break were 75 MPa and 11% for PEEK-SO₂. These values are comparable to those of bisphenol A polycarbonate (PC), whose strength and elongation at break are ca. 100 MPa and 20-30%, respectively.[30] Temperature dependence of mechanical property for these DGPs was studied by DMA, as shown in Fig. 10. The T_g values were found around 127 °C for PEEK-SO₂ and 176 °C for PEEK-COOH, respectively (Fig. 10B). Below T_g, the tensile moduli were 1.4 and 1.7 GPa for PEEK-SO₂ and PEEK-COOH at RT (Fig. 10A). The differences in tensile moduli might originate from different measurements and certain experimental error. Given the tough mechanical and good dielectric properties of these DGPs, they are promising for future film capacitor applications.

4. Conclusions

In summary, chemically modified PEEKs, a new type of dipolar glass polymers, were synthesized to demonstrate both mechanical toughness and high dielectric performance (i.e., high $U_{e,dis}$ and discharge efficiency). At RT, the PEEK-SO₂ exhibited a relatively high permittivity of 5.0 as a result of orientational polarization of the highly polar methylsulfonyl side groups (4.5 D). The $U_{e,dis}$ reached 2.35 J/cm³ at 300 MV/m. Meanwhile, the low dielectric loss (tan δ =0.008) at RT could be ascribed to the rigid backbone structure and the large temperature window from the β to α transitions in temperature-scan BDS results. Although PEEK-COOH exhibited a lower dielectric constant (3.75) at RT and 10 Hz, its high temperature performance persisted up to 150 °C when the poling electric field was below 200 MV/m.

Acknowledgements

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