Polyarylene Ether Nitrile and Titanium Dioxide Hybrids as Thermal Resistant Dielectrics

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With the expanding application of capacitors, thermal resistant dielectric materials are in high demand due to the increasing harsh environments where the capacitors are needed and the heat generated by the capacitors. In this work, we present polyarylene ether nitrile and titanium dioxide hybrids which can be used as thermal resistant dielectrics for these capacitors. Phthalonitrile modified titanium dioxide (TiO$_2$-CN) and phthalonitrile end-capped polyarylene ether nitrile (PEN-Ph) are firstly prepared. After being cast into TiO$_2$-CN/PEN nanocomposite films, these composites self-crosslink upon heating at 320 °C for 4 h, forming the polyarylene ether nitrile and titanium dioxide hybrids (TiO$_2$-PEN). Improved dielectric constants which are stable from room temperature to 200 °C of these hybrids are observed, indicating the potential application of the hybrids as thermal resistant dielectrics.

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3.5, which is not high enough for the high energy storage capacitors. It has been widely reported that the dielectric constant of the polymers can be effectively improved by introducing additives with high permittivity and/or conductive fillers.\textsuperscript{[4,22]} The dielectric constant of PEN has also been improved by incorporating fillers such as BaTiO\textsubscript{3},\textsuperscript{[23–25]} ZnO,\textsuperscript{[26]} CNT,\textsuperscript{[27]} graphene oxide,\textsuperscript{[28]} polyaniline,\textsuperscript{[29]} and others.\textsuperscript{[20,30,31]} However, the dielectric loss of the obtained composites increases spontaneously due to the incompatibility of nanofillers in PEN matrix.\textsuperscript{[19,23–26]} Especially, the dielectric loss is more obvious at high temperature even the nanofillers are modified. The dielectric loss caused by incompatibility can be effectively repressed by the preparation of organic-inorganic hybrid materials in which the nanofillers are chemically bonded with the polymeric matrix.\textsuperscript{[20,31]} Definitely, the chemical bond connecting the nanofillers and polymeric matrix should be strong enough to make sure the application of the hybrid at high temperature. Herein, we present the preparation of polyarylene ether nitrile and titanium dioxide hybrids (TiO\textsubscript{2}-PEN) with high dielectric constant and low dielectric loss that are stable from room temperature to 200 °C.

**EXPERIMENTAL**

**Materials**

Titanium dioxide (TiO\textsubscript{2}) nanoparticles (20–30 nm) were purchased from Aladdin chemical Co, Shanghai, China. Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), N-methylpyrrolidone (NMP), and N,N-dimethylformamide (DMF) were brought from Kelong Reagent, Chengdu, China. Potassium carbonate (K\textsubscript{2}CO\textsubscript{3}) was purchased from Kelong Reagent, Chengdu, China. Toluene, dichlorobenzonitrile (DCBN), biphenyldiol (BP), hydroquinone (HQ) and 4-nitrophthalonitrile were supplied by Changzheng Reagent, Chengdu, China. Other chemicals and reagents were commercially available products and used without further purification.

**Synthesis of PEN-Ph**

The phthalonitrile end-capped polyarylene ether nitrile (PEN-Ph) was synthesized in our laboratory according to the previous procedure.\textsuperscript{[19]} Specifically, PEN-Ph was used in this study was synthesized by DCBN, BP and HQ in polar NMP and toluene solution in the condition of the presence of K\textsubscript{2}CO\textsubscript{3}. When the viscosity was no longer increasing, 4-nitrophthalonitrile was added into the solution to obtain PEN-Ph.

**Synthesis of TiO\textsubscript{2}-CN Nanoparticles**

TiO\textsubscript{2} nanoparticles (2 g) were added in 100 mL of H\textsubscript{2}O\textsubscript{2} solution and stirring for 4 h under reflux condition. Drying in vacuum condition at 80 °C for 12 h after washed with deionized water for several times offered the TiO\textsubscript{2}-OH nanoparticles. TiO\textsubscript{2}-OH (0.4 g) prepared above was added with 0.4 g of 4-nitrophthalonitrile and 0.24 g of K\textsubscript{2}CO\textsubscript{3} in 100 mL of DMF, and the mixture was reacted at 105 °C for 6 h under stirring condition. Washing with DMF and deionized water for several times respectively and drying in vacuum condition at 100 °C for 12 h offered the final products.

**Synthesis of TiO\textsubscript{2}-PEN Hybrids**

First of all, a certain amount of TiO\textsubscript{2}-CN nanoparticles were dispersed in 10 mL of NMP under ultrasonic condition. Then, PEN-Ph prepared above was dissolved in NMP in stirring and heating condition. After mixing the two solutions under ultrasonic condition, the solution was cast onto a clean horizontal glass plate and dried in an oven at 80 °C (1 h), 100 °C (1 h), 120 °C (1 h), 160 °C (1 h) and 200 °C (2 h). The final light brown films with the thickness about 50 μm were obtained after cooling to the room temperature. The content of TiO\textsubscript{2}-CN is 0 wt%, 10 wt%, 20 wt%, 30 wt% and 40 wt% of the total mass and named TiO\textsubscript{2}-CN/PEN-0, TiO\textsubscript{2}-CN/PEN-10, TiO\textsubscript{2}-CN/PEN-20, TiO\textsubscript{2}-CN/PEN-30 and TiO\textsubscript{2}-CN/PEN-40, respectively.

Five additional composite films were prepared according to the same method and ratio as above, and treated at 320 °C for 4 h to obtain hybrid films which were named TiO\textsubscript{2}-PEN-0, TiO\textsubscript{2}-PEN-10, TiO\textsubscript{2}-PEN-20, TiO\textsubscript{2}-PEN-30 and TiO\textsubscript{2}-PEN-40, respectively.

**Characterization**

Thermal gravimetric (TGA, TA-Q50) analysis was carried out to measure the thermal stability performance of the nanoparticles and the films at a heating rate of 10 °C/min under nitrogen atmosphere. Thermal properties of nanocomposite films were obtained from differential scanning calorimetry (DSC, TA DSC-Q100) at a heating rate of 10 °C/min. Fourier transform infrared (FTIR) spectroscopy (200SXV, Nicolet) was used to study the structure of the TiO\textsubscript{2} and TiO\textsubscript{2}-CN. X-ray photoelectron spectroscopy (XPS, ESCALab 250X) was used to further identify the composition of TiO\textsubscript{2}-CN. To investigate the morphology of the nanoparticles and films, samples were characterized using a scanning electron microscope (SEM, Jeol JSM-6490LV). Energy spectrum test was measured by energy dispersive spectrometer (EDS) with a field emission transmission electron microscope (TEM, FEI Talos F200S). Mechanical and dielectric properties of the nanocomposite films were investigated through the universal testing machine (SANS CMT6104) and an LCR meter (Tonghui TH2819A), respectively.

**RESULTS AND DISCUSSION**

As shown in Fig. 1, phthalonitrile modified titanium dioxide (TiO\textsubscript{2}-CN) and phthalonitrile end-capped polyarylene ether nitrile (PEN-Ph) are firstly prepared. After being cast into TiO\textsubscript{2}-CN/PEN nanocomposite films, these composites self-crosslink upon heating at 320 °C for 4 h, forming the polyarylene ether nitrile and titanium dioxide hybrids (TiO\textsubscript{2}-PEN). PEN-Ph is synthesized in our laboratory according to the previous procedure.\textsuperscript{[19]} TiO\textsubscript{2}-CN is prepared by the reaction between 4-nitrophthalonitrile and hydroxylated titanium dioxide (TiO\textsubscript{2}-OH), which is obtained by treating TiO\textsubscript{2} nanoparticle with hydrogen peroxide.

**Characterization of TiO\textsubscript{2}-CN Nanoparticles**

The modification of TiO\textsubscript{2}-CN nanoparticles by organic groups can improve compatibility and dispersion in the PEN matrix, and the phthalonitrile groups can undergo the self-crosslinking reaction at high temperature offering the hybrid materials TiO\textsubscript{2}-PEN. Therefore, it is very important to prepare and characterize the cyanated TiO\textsubscript{2} nanoparticles TiO\textsubscript{2}-CN. Firstly, thermogravimetric analysis (TGA) was employed to characterize TiO\textsubscript{2} nanoparticles before and after modification with phthalonitrile groups. As shown in Fig. 2(a), due to the stable inorganic
composition of TiO$_2$, the residue weight of TiO$_2$ at 800 °C is 98.2 wt%. In comparison, the residue decreases to 90.6 wt% for TiO$_2$-CN, indicating the existence of organic groups at the surface of the nanoparticles. The weight percent of the phthalonitrile groups grafted on TiO$_2$-CN is calculated to be 7.6 wt%. To further characterize the TiO$_2$ nanoparticles before and after modification, these materials were characterized by FTIR spectra, as shown in Fig. 2(b). The curve of infrared spectrum of TiO$_2$ is relatively smooth. After modification with phthalonitrile groups, there is a clear hydroxyl (−OH) band at 3435 cm$^{-1}$, mainly due to the residue hydroxyl groups which are not replaced by phthalonitrile groups.$^{[32]}$ The stretching vibrations of the C−C bonds and C≡N bonds causing bands at 1628 and 2227 cm$^{-1}$ also suggest the successful modification of TiO$_2$. In addition, quantitative analysis of surface elements of TiO$_2$-CN is conducted by XPS measurement (Figs. 2c and 2d). In the wide scan spectrum of TiO$_2$-CN, the distinct peaks at 530.0, 460.0, 402.2 and 285.0 eV correspond to O1s, Ti2p, N1s and C1s.
respectively, demonstrating the presence of O, Ti, N, and C elements in the nanoparticles TiO$_2$-CN. Furthermore, the C1s spectrum can be quantitatively differentiated into three different carbon species located at 288.6 eV (−CN), 286.1 eV (C−O) and 284.5 eV (C−C), illustrating the presence of cyano group and ether group, which are formed due to the successful reaction between TiO$_2$-OH and 4-nitrophthalonitrile.

The energy dispersive spectrometry (EDS) can also reveal elemental composition by using different characteristics of different elements of X-ray photon feature energy. The modified TiO$_2$-CN was also characterized by EDS. Fig. 3(a) is the TEM EDS result of TiO$_2$-CN from the TEM image of TiO$_2$-CN shown in Fig. 3(b). It is obvious that four elements of Ti, O, C and N can be observed from the TEM EDS result. Furthermore, it can be seen from the EDS mapping images (Figs. 3c–3f) and Fig. S1 in the electronic supplementary information, ESI that the distribution of the four elements in the nanoparticles is basically consistent, meaning they are from the same sample. Additional TEM and SEM micro-images of TiO$_2$-CN are shown in Figs. 3(g) and 3(h). The results of the previous TGA, FTIR, XPS, TEM and TEM EDS characterizations indicate that the nanoparticles TiO$_2$-CN have been successfully prepared.

Morphology of TiO$_2$-CN/PEN and TiO$_2$-PEN

After the preparation of PEN-Ph and TiO$_2$-CN, TiO$_2$-CN/PEN nanocomposite films are prepared by casting method. The content of TiO$_2$-CN in the nanocomposite films is 0 wt%, 10 wt%, 20 wt%, 30 wt% and 40 wt% and named TiO$_2$-CN/PEN-0, TiO$_2$-CN/PEN-10, TiO$_2$-CN/PEN-20, TiO$_2$-CN/PEN-30 and TiO$_2$-CN/PEN-40, respectively. Fig. 4 shows cross-sectional SEM images of neat PEN film and TiO$_2$-CN/PEN nanocomposite films at a magnification of 10$^5$ (scale bar 1 μm). SEM test was carried out for reason that the compatibility and dispersion of the inorganic phase with the organic phase would directly affect the mechanical, thermal, dielectric and other properties of the composite film. It can be seen from the figure that the TiO$_2$-CN nanoparticles and the PEN matrix demonstrate favorable compatibility and no obvious agglomeration is observed between them even at TiO$_2$-CN content up to 40 wt%. More SEM micrographs of the TiO$_2$-CN/PEN nanocomposite films are shown in Figs. S2–S5 (in ESI). This could mainly result from the fact that the TiO$_2$ nanoparticles are modified by phthalonitrile groups which promote the compatibility between the nanoparticles and the PEN matrix.[19,20] TiO$_2$-CN/PEN nanocomposite films are further isothermally treated at 320 °C for 4 h during which the phthalonitrile groups self-crosslink offering hybrid films named TiO$_2$-PEN-0, TiO$_2$-PEN-10, TiO$_2$-PEN-20, TiO$_2$-PEN-30 and TiO$_2$-PEN-40, respectively.[21] The gel content of the samples by Soxhlet extraction confirms the formation of the hybrids. The measured gel content of thermally treated TiO$_2$-PEN-40, TiO$_2$-PEN-30 and PEN-Ph is 98.93%, 91.61% and 94.74% respectively.

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Thermal Properties of TiO$_2$-CN/PEN and TiO$_2$-PEN

Fig. 5(a) shows the TGA curves of TiO$_2$-CN/PEN nanocomposite films with different TiO$_2$-CN contents. It can be seen from the figure that the composite films have excellent thermal stability as the decomposition temperature is higher than 500 °C. The 5 wt% decomposition temperature ($T_{\text{5\%}}$) of TiO$_2$-PEN-0 is 504.8 °C, 516.9 °C and 529.2 °C, respectively (Table 1). After adding nanoparticles, the decomposition temperature of the composite films rises. This is mainly because the decomposition temperature of the inorganic filler is inherently higher than that of the polymer matrix. Analogously, the TGA curves of TiO$_2$-PEN hybrid films are showed in Fig. 5(b). The phthalonitrile groups at the end of PEN-Ph and the surface of TiO$_2$-CN self-crosslink upon treating at 320 °C, resulting in the transition of the system from...
more conducive to the high temperature application of these dielectric materials. For the amorphous polymeric dielectrics, the glass transition temperature ($T_g$) is an important parameter for their application at high temperature because the dielectric constant and loss increase abruptly around their $T_g$.\cite{34} Fig. 6(a) is the DSC results of the TiO$_2$-CN/PEN nanocomposites. Due to the rigid structure of PEN backbone, its $T_g$ is ~195 °C, which shows preferable ability for high temperature application. With the increased content of TiO$_2$-CN, the $T_g$ of the TiO$_2$-CN/PEN nanocomposites increases gradually, which is owing to the added TiO$_2$-CN nanoparticles that impede the movement of the macromolecular chains.\cite{19,23} The $T_g$ of the TiO$_2$-PEN hybrids is shown in Fig. 6(b). Compared with the results of TiO$_2$-CN/PEN nanocomposites, the $T_g$ of the TiO$_2$-PEN hybrids increases to 217.9, 218.1, 221.7, 224.9 and 229.6 °C at the filler content of 0 wt%, 10 wt%, 20 wt%, 30 wt% and 40 wt%, respectively. The main reason for this trend of $T_g$ is that the TiO$_2$ and PEN matrix are linked together by chemical bonds which depresses the movement in the system. This high $T_g$ of the TiO$_2$-PEN hybrids confirms their application at up to 200 °C atmosphere.

**Mechanical Properties of TiO$_2$-CN/PEN and TiO$_2$-PEN**

Tensile strength refers to the resistance of the material to the maximum uniform plastic deformation, which reflects the fracture resistance of the material. Commonly, tensile strength is an important indicator of the mechanical properties of materials, and it is useful to evaluate the mechanical properties of materials.\cite{37} As shown in Fig. 7(a), the tensile strength is 90.8, 87.4, 83.8, 81.3 and 74.3 MPa for TiO$_2$-CN/PEN-0, TiO$_2$-CN/PEN-10, TiO$_2$-CN/PEN-20, TiO$_2$-CN/PEN-30 and TiO$_2$-CN/PEN-40, respectively. The tensile strength decreases with the addition of TiO$_2$-CN nanoparticles because the TiO$_2$-CN nanoparticles do not contribute to the tensile strength. Fortunately, the tensile strength of the TiO$_2$-CN/PEN composites is higher than that of most universal polymers.\cite{34} Fig. 7(b) is the tensile strength of the TiO$_2$-PEN hybrids. Compared with TiO$_2$-CN/PEN composites, tensile strength of the TiO$_2$-PEN hybrids increases and is 100.2,
Dielectric Properties of TiO$_2$-CN/PEN and TiO$_2$-PEN

The dielectric constant and loss of TiO$_2$-CN/PEN composite films at different frequencies and temperatures are studied. Before the investigation of the dielectric properties of PEN based composites, their coefficient of thermal expansion (CTE) were measured using a dynamic mechanical analyzer (DMA) in extension mode. The CTE decreases with the increasing content of TiO$_2$-CN and crosslinking of the system (Tables S1 and S2 in ESI). Fig. 8(a) shows the dielectric property at different frequency, and dielectric constant of all samples slightly declines with the increase of the frequency which is due to the frequency dependence of the dielectric materials.\cite{34,35} At 1 kHz, the dielectric constant of TiO$_2$-CN/PEN-0, TiO$_2$-CN/PEN-10, TiO$_2$-CN/PEN-20, TiO$_2$-CN/PEN-30 and TiO$_2$-CN/PEN-40 at room temperature (RT) is 3.52, 4.06, 4.44, 6.18 and 7.57, respectively. The dielectric constant of TiO$_2$-CN/PEN increases with the increasing content of TiO$_2$-CN nanoparticles, indicating that TiO$_2$ can be used as high permittivity filler to improve the dielectric constant of polymer dielectrics.\cite{35} Dielectric loss of TiO$_2$-CN/PEN is also shown in Fig. 8(a). In general, the addition of inorganic fillers will result in increasing of dielectric loss.\cite{19,20,36}

Fortunately, the dielectric loss of all composites is lower than 0.03 at 1 kHz due to the modification of TiO$_2$. The dielectric constant at 1 kHz and RT is 3.25, 4.02, 4.40, 6.10 and 7.45 for TiO$_2$-PEN-0, TiO$_2$-PEN-10, TiO$_2$-PEN-20, TiO$_2$-PEN-30 and TiO$_2$-PEN-40, respectively, as shown in Fig. 8(b). The reason why the dielectric constant decreases from TiO$_2$ to TiO$_2$-CN is that the crosslinking points limit the movement of the molecular chains, thereby weakening its polarization.\cite{34} Based on the same reasons, dielectric loss of TiO$_2$-PEN hybrids also decreases.

Temperature dependence of dielectric constant and dielectric loss of TiO$_2$-CN/PEN nanocomposites and TiO$_2$-PEN hybrids are shown in Figs. 9(a) and 9(b). The test of the dielectric properties with the change of temperature is performed at a frequency of 1 kHz. According to our previous results, the dielectric constant and loss of PEN based composites are stable from RT to its $T_g$, while increase abruptly when the temperature is around or higher than its $T_g$.\cite{34} When the temperature reaches the glass transition temperature of PEN, its molecular chain begins to move, further increases the polarization in the system, which in turn leads to improved dielectric properties. In this study, similar results are also observed for TiO$_2$-CN/PEN nanocomposites and TiO$_2$-PEN hybrids. The dielectric constant and dielectric loss increase abruptly around 200 and 220 °C for TiO$_2$-CN/PEN and TiO$_2$-PEN, re-

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**Fig. 8** Frequency dependence of dielectric constant and loss of TiO$_2$-CN/PEN nanocomposites (a) and TiO$_2$-PEN hybrids (b).

Due to the crosslinking in the TiO$_2$-PEN hybrids, the dielectric constant of TiO$_2$-PEN hybrids can bear a higher temperature than that of TiO$_2$-CN/PEN nanocomposites. More importantly, the dielectric loss of the TiO$_2$-PEN hybrids is lower than 0.03 even at 200 °C, indicating the potential application of the TiO$_2$-PEN hybrids as thermal resistant dielectrics.

In addition, titanium dioxide particles with the diameter of ~100 nm are also selected as fillers to repeat the experiment in the study. Fig. S8 (in ESI) shows temperature dependence of dielectric constant and loss of TiO$_2$-PEN hybrids made from titanium dioxide particles with the diameter of ~100 nm as fillers. The hybrid materials prepared from such particles show almost the same results of dielectric properties as those prepared by titanium dioxide particles with the diameter of 20–30 nm as fillers.

**CONCLUSIONS**

In summary, TiO$_2$-PEN hybrids are prepared for thermal resistant dielectrics. Hydrogen peroxide treated TiO$_2$ nanoparticles reacted with 4-nitrophthalonitrile yielding TiO$_2$-CN which was characterized by TGA, FTIR, XPS and TEM. TiO$_2$-CN was then incorporated into PEN-Ph matrix to obtain TiO$_2$-CN/PEN nanocomposite films. TiO$_2$-PEN hybrids were finally prepared through the self-crosslinking reaction of phthalonitrile groups from TiO$_2$-CN and PEN-Ph upon heating at 320 °C for 4 h. $T_g$ and $T_{10\%}$ of TiO$_2$-PEN hybrids are higher than 215 and 520 °C, respectively. The dielectric constant of TiO$_2$-PEN-40 is improved to be 7.45 at 1 kHz and is stable from RT to 200 °C, while the dielectric loss of it remains lower than 0.03, indicating its potential application as thermal resistant dielectrics.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at [http://dx.doi.org/10.1007/s10118-020-2481-z](http://dx.doi.org/10.1007/s10118-020-2481-z).

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