Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Title

Reinforcement of Ultrahigh Thermoresistant Polybenzimidazole Films by Hard Craters

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Experimental sections

Measurements.

^{13}C NMR spectrum of the copolymer poly(DABA-*co*-ABA) was confirmed at a spinning speed of 8 kHz using a Brucker Avance III spectrometer operating at 125 MHz. Solid-state ^{13}C dipolar decoupled magic angle spinning (DD-MAS) spectrum was recorded using zirconia rotors with 4 mm diameter. The samples were packed in a 7 mm diameter zirconia rotor with a Kel-F cap and spun at 10 kHz. A contact time of 2 ms was used, the period between successive accumulation was 5 s, and the total number of scans was 160,000. Fourier transform infrared (FT-IR) spectra of the pristine poly(DABA-*co*-ABA) film and porous poly(DABA-*co*-ABA) films were recorded in the wavenumber ranging from 4000 to 400 cm^{-1}, using a Perkin-Elmer Spectrum with a diamond-attenuated total reflection (ATR) accessory. The determination of particle size and size distribution of the SiO_2 was carried out by scanning electron microscope (JCM-6000PLUS Versatile Benchtop SEM), which was also explored to investigate surface and cross-sectional morphologies of both the pristine and porous poly(DABA-*co*-ABA) films. Samples were pre-coated with Au powder under vacuum before SEM measurements. The three-dimensional surface morphology of the porous films was obtained from a high-performance scanning probe microscope (SPM-Nanoa™, SHIMADZU Co., Japan). The scanning area of the porous film is 1×1 μm^2.). Wide-angle X-ray diffraction (WAXD; SmartLab; Rigaku Corp., Akishima, Japan) was utilized to investigate the crystallinity and orientation of fabricated films with a graphite-monochromatized Cu Kα radiation beam generated at 100 mA and 40 kV. The tensile test was carried out at an elongation speed of 1 mm min^{-1} using an Instron-3365 mechanical tester instrument at room temperature.

Materials.

3,4-Diaminobenzoic acid (DABA, 99% purity) and 4-aminobenzoic acid (ABA, 99% purity) were purchased from Tokyo Chemical Industry Co., Ltd. Polyphosphoric acid (PPA, 80% purity) was obtained from FUJIFILM Wako Pure Chemical Corp. Spherical silica nanoparticles (seahostar@KE-P30, diameter: 300nm) were purchased from Nippon Shokubai Co., Ltd., Japan. Hydrofluoric acid (HF, 55% purity) was obtained from MORITA CHEMICAL INDUSTRIES CO., LTD. Trifluoroacetic acid (TFA), methanesulfonic acid (MSA), sodium bicarbonate, hydrochloric acid, methanol, acetone, and other chemicals were obtained from Kanto Chemical Co., Inc. All the chemicals and reagents were used as received.

Synthesis of copolymer poly(DABA-*co*-ABA).

A typical synthetic procedure for poly(DABA-*co*-ABA) with a composition of DABA and ABA (85/15; *mol/mol*), which showed ultrahigh thermal resistance as described in our previous research[1], was given below. Poly(phosphoric acid) (PPA, 50 g) was added into a three-necked flask equipped with a magnetic stirrer and heated at 120 ℃ for 1 h in a nitrogen atmosphere. Subsequently, DABA-2HCl (1.91 g, 8.5 mmol) and ABA-HCl (0.26 g, 1.5 mmol) were added to PPA slowly and stirred for 1 h to remove the moisture. After the powder dissolved completely, the solution was stepwise heated at 140 ℃ for 1 h, 160 ℃ for 1 h, and 180 ℃ for 8 h, respectively, until the solution became viscous and then maintained at 220 ℃ for 12 h. During the process, the viscosity of the solution increased significantly with the increasing temperature, and the color of the solution changed from red to dark brown. The resulted viscous solution was precipitated into deionized water (500 ml) and washed with stirring for 12 h. After the collection of the obtained product by filtration, the collected brown solid was dried at 150 ℃ for 12 h.

Finally, the solid was crushed into powder and neutralized with a 5 % $NaHCO_3$ (aq.), followed by repeated washing with deionized water until the pH of the cleaning liquid reached 7 (measured using pH test papers, Macherey-Nagel GmbH & Co. KG, Duren, Germany).

Fabrication of porous poly(DABA-*co*-ABA) films.

Poly(DABA-*co*-ABA) powder (100mg) was dissolved in TFA (10ml) and two drops MSA (2%-3%) to prepare pristine poly(DABA-*co*-ABA) film. As for the fabrication of porous poly(DABA-*co*-ABA) films, SiO_2 nanoparticles were dispersed in TFA homogeneously by ultrasonication at room temperature for 1h before being added into a well-dissolved solution of poly(DABA-*co*-ABA) powder and TFA/MSA solution. Poly(DABA-*co*-ABA) films with various porosity were fabricated using the above-mentioned two solutions. The weight percent of SiO_2 nanoparticles was calculated as below,

$$X\% = \frac{W_{SiO_2}}{W_{SiO_2} + W_{polymer}} \times 100\%$$

and the prepared porous films were named poly(DABA-*co*-ABA)-X%, where X means the weight percent of SiO_2 nanoparticles. As for the film casting process, the mixture solutions of poly(DABA-*co*-ABA)-SiO_2 solution were coated onto a glass substrate and then evaporated at room temperature. Afterwards, the obtained composite films were immersed in a 40% HF solution to remove SiO_2 nanoparticles from the films. After being soaked in deionized water for 24 h and repeated washing three times, the obtained porous poly(DABA-*co*-ABA) films were further dried under a vacuum.

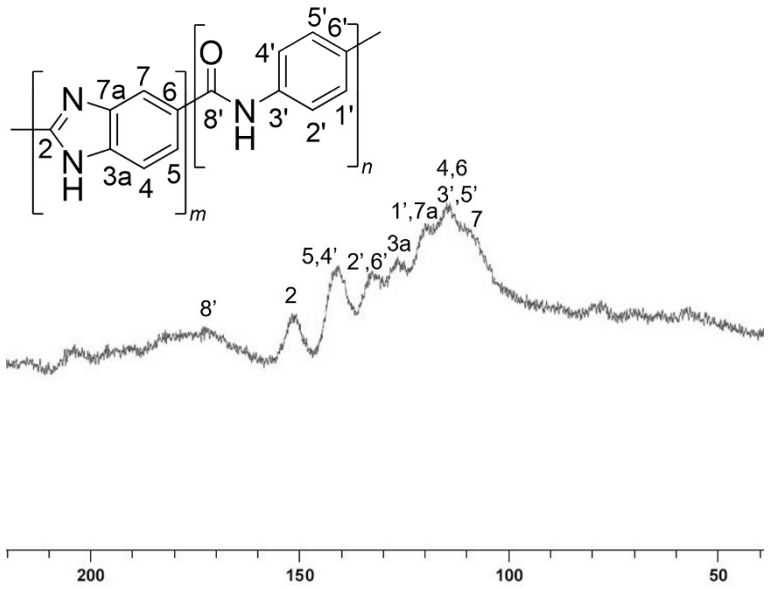

Figure S1. Solid-state ^{13}C-NMR spectrum (dipolar decoupled magic angle spinning; DD-MAS) of copolymer poly(DABA-*co*-ABA).

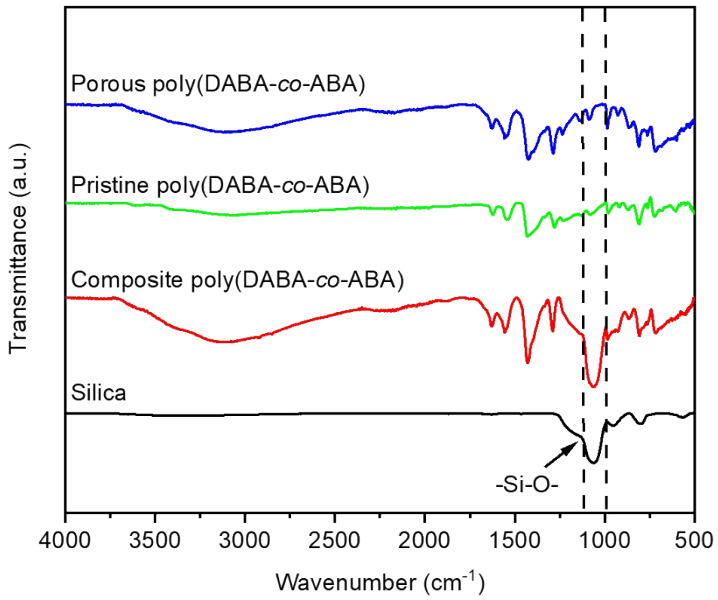

Figure S2. FT-IR spectra of silica nanoparticles (black line), poly(DABA-*co*-ABA)-SiO_2 composite (red line), pristine poly(DABA-*co*-ABA) (green line) and porous poly(DABA-*co*-ABA) film (blue line).

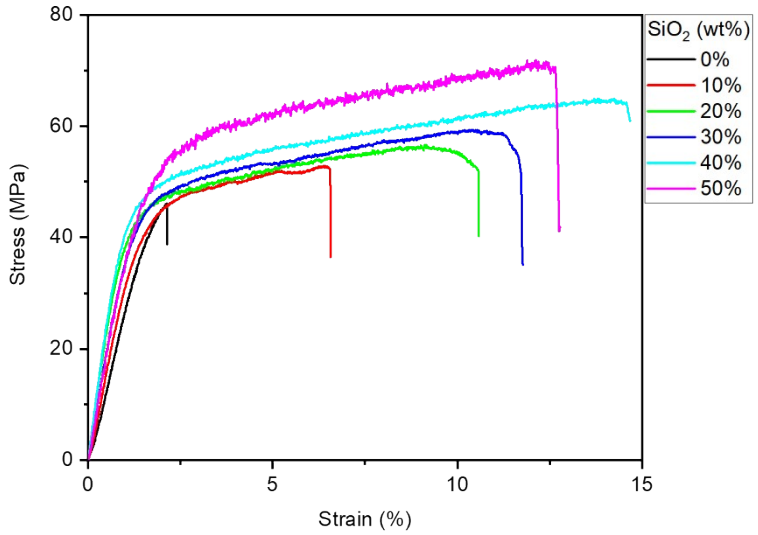

Figure S3. Stress-strain curves of pristine poly(DABA-*co*-ABA) film and porous poly(DABA-*co*-ABA) film with different SiO_2 compositions (0-50%).

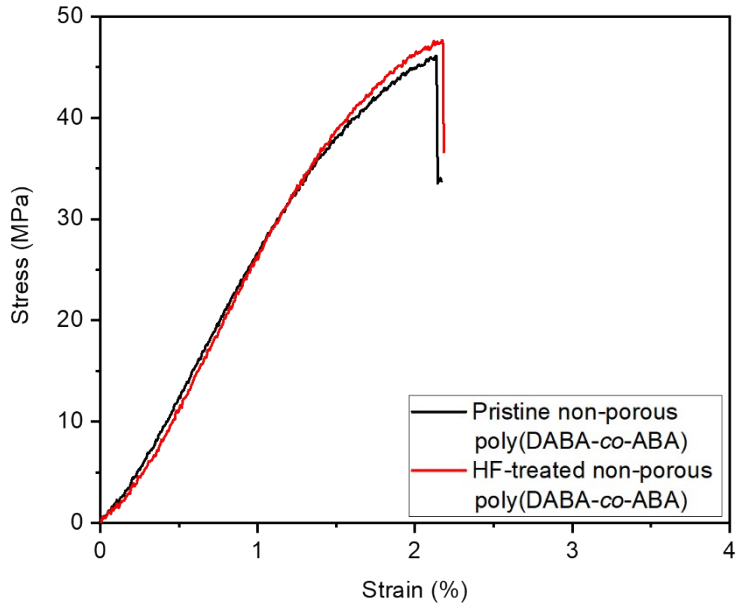

Figure S4. Stress-strain curves of pristine non-porous poly(DABA-*co*-ABA) (black line) and HF-treated non-porous poly(DABA-*co*-ABA) (red line) film.

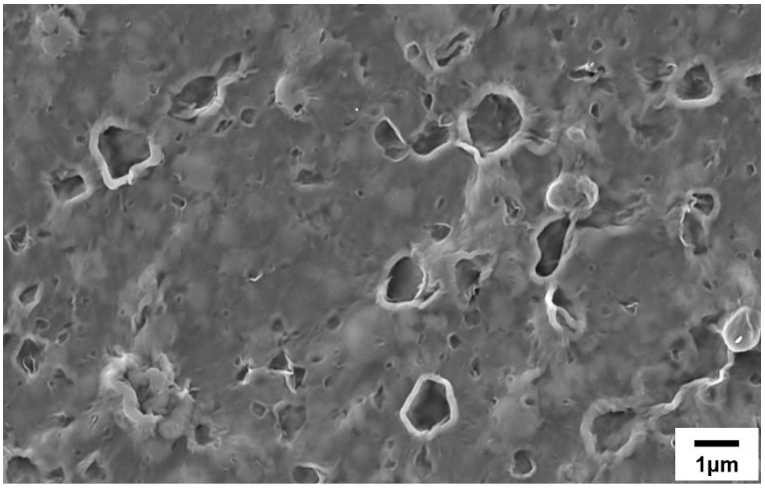

Figure S5. SEM image of fabricated porous poly(DABA-*co*-ABA) film with SiO_2 nanoparticles of a diameter of 20 nm.

Notes and references

1. Nag, A.; Ali, M.A.; Kawaguchi, H.; Saito, S.; Kawasaki, Y.; Miyazaki, S.; Kawamoto, H.; Adi, D.T.N.; Yoshihara, K.; Masuo, S.; Katsuyama, Y.; Kondo, A.; Ogino, C.; Takaya, N.; Kaneko, T.; Ohnishi, Y. Ultrahigh Thermoresistant Lightweight Bioplastics Developed from Fermentation Products of Cellulosic Feedstock. *Adv. Sustainable Syst*., **2021,** *5(1)*, 2000193.