Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Cyanate ester resins toughened with epoxy-terminated and fluorine-containing polyaryletherketone

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EXPERIMENTAL PART

MATERIALS AND METHODS

Materials.

Bisphenol A cyanate ester (BADCy, density 1.171 g/cm^3, molecular weight 278.31 g/mol) was received from Jiangsu Wuqiao Resin Factory Co., Ltd. (Jiangsu, China). Bisphenol AF (BPAF, 98%), N-Methylpyrrolidone (NMP, ≥99.0%), and benzyl triethyl ammonium chloride (TEBAC, >98.0%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Difluorobenzophenone (DFBP, 99%) and epichlorohydrin (ECH) were purchased from Macklin Reagent Co., Ltd. (Shanghai, China). Anhydrous potassium carbonate (K_2CO_3) and sodium hydroxide (NaOH) were bought from Komeo Chemical Reagent Co., Ltd. (Tianjin, China). All the chemicals were used as received without further treatment.

Methods.

^{1}H and ^{13}C nuclear magnetic resonance (NMR): The ^{1}H and ^{13}C NMR spectra of the samples were measured by Bruker Avance 400 MHz NMR instrument (Bruker, Germany) with tetramethylsilane (TMS) containing $CDCl_3$ as a solvent. The average molar mass based on NMR ($M_{\text{n, NMR}}$) of FPAEK and EFPAEK was calculated by applying the peak of the underlined proton in -C$\underline{\boldsymbol{H}}$-O-$CH_2$- of the epoxy group of EFPAEK (peak g in **Figure 1(b)**) as internal reference. Its integration was set as 1 (meaning 1 proton). The integrations of all the other peaks in the spectrum were then obtained. The number of repeat units of FPAEK and EFPAEK can be obtained by calculating the ratio of the integrations of the protons from benzene rings and peak g.

Fourier transform infrared spectroscopy (FTIR): The FTIR spectra of the samples were measured on Bruker Tensor 27 infrared spectrometer (Bruker, Germany) applying potassium bromide (KBr) tablet compression method with the test wave number range of 4000-400 cm^{-1}.

Size exclusion chromatography (SEC): The number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (PDI) of samples were determined using waters1515 (Waters Technology Co., China.) size exclusion chromatography with tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL min^{-1} (35°C). The column system was calibrated with polystyrene standards (ranging from 1100 to 138600 g mol^{-1}). Samples were diluted to a concentration about 10 mg mL^{-1} and filtered through 0.45 μm Nylon syringe filters before injection.

Differential scanning calorimetry (DSC): The curing process of EFPAEK/BADCy resin was measured by DSC1 of Mettler-Toledo (Mettler, Switzerland) at heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min under nitrogen atmosphere. The weight of each sample used was 5 mg.

Thermal gravimetric analysis (TGA): TGA was performed by STA 449F3 (NETZSCH Co., Germany) thermal gravimetric analyzer. The test temperature range was 40-800°C, and the heating rate was 10°C/min under argon atmosphere. The mass was about 5 mg for each sample.

Scanning electron microscopy (SEM): SEM was carried on a VEGA3-LMH equipment (TESCAN Co., Czech Republic) to analyze the fracture morphology of the resin. The scanning voltage was 20 kV and the sample was sprayed with gold before testing.

Energy dispersive X-Ray spectroscopy (EDS): EDS of the samples was analyzed by Verios G4 (FEI Co., America).

Dielectric property: Dielectric constant (ε) and dielectric loss tangent ($\tan\delta$) values of the samples were measured using a Novocontrol Technologies Alpha-N high resolution dielectric analyzer (Novocontrol, Germany) at room temperature, and the corresponding dimension of the specimens was 15 mm × 15 mm × 1 mm. The samples used for the analysis of dielectric property were made applying the same procedure with the preparation of EFPAEK/BADCy resin (please see below for details). A layer of conductive silver paste was coated on the surface of the sample and then dried in an oven for two hours at 40°C before testing.

Mechanical property: The flexural strength of the samples was tested by SANS2CMT5105 electronic universal testing machine (Shenzhen New Sansi Co., China) according to ISO 178-2010 standard. The impact strength of the samples was tested by XCJ-40 impact testing machine (Chengde Materials Testing Co., China) according to ISO 179-2010 standard. The samples used for the mechanical property were prepared applying the same procedure with the preparation of EFPAEK/BADCy resin (please see below for details). The sample sizes for flexural and impact strength tests were 80 mm×15 mm×4 mm and 80 mm × 10 mm × 4 mm, respectively.

Adhesion property: The lap shear test of the modified resin was carried out at room temperature using SANS2CMT5105 electronic universal testing machine (Shenzhen New Sansi Co., China) according to the ISO 4587-2003 standard. The aluminum alloy model used was 2A12. The aluminum alloy was washed sequentially with acetone and ethanol, and then soaked in the aqueous solution of sodium hydroxide/sodium carbonate (20 mg/mL for both) for one minute at 50°C. The aluminum alloy was then rinsed with deionized water, followed by soaking into a solution of nitric acid (4.8 mol/L) for 2 minutes at room temperature. Finally, the aluminum alloy was rinsed with deionized water and dried in an oven for one hour at 50°C.

Contact angles: Contact angles between the samples and water were measured using a CA100B (Shanghai Innuo Precision Instruments Co., China) at room temperature.

Water absorption: Water absorption of samples was tested at room temperature according to ISO 64-2008 standard.

Synthesis of FPAEK and EFPAEK

Synthesis of FPAEK: BPAF (0.036 mol, 12.104 g), DFBP (0.03 mol, 6.546 g), and K_2CO_3 (0.039 mol, 5.39 g) were added into a three-necked flask containing NMP (30 mL), and then the flask was placed in an oil bath at 160^{o}C to allow the mixture to react for 1.5 hours. Then the temperature was raised to 180^{o}C to react for another 3 hours.[1] Finally, the hot reaction mixture was slowly poured into 200 mL ethanol. The obtained crude product was repeatedly washed with 200 mL ethanol and 200 mL deionized water, respectively. The obtained product was then dried at 60^{o}C for 12 hours to afford a light gray solid, namely bisphenol AF polyaryletherketone with hydroxyl terminal group (FPAEK), with the yield of about 72%.

Synthesis of EFPAEK: FPAEK (9.7 g, 1 mmol) and TEBAC (0.485 g, 5% of FPAEK mass) were added into a three-necked flask containing 20 mL ECH. The mixture was then reacted at 80^{o}C under reflux for 40 minutes. Then 0.59 mL of 15 wt% NaOH (2 mmol) aqueous solution was added to the above reaction mixture and reacted at 80^{o}C for another 3 hours. Finally, the reaction mixture was poured into 200 mL ethanol and filtered to remove the excess ECH. The obtained crude product was repeatedly washed with 200 mL ethanol and 200 mL deionized water, respectively, and was then dried at 60^{o}C for 12 hours. The light-yellow solid, namely EFPAEK, was obtained with the yield of about 95%.

Preparation of EFPAEK/BADCy resin

BADCy was heated at 120^{o}C to melt and a certain amount of EFPAEK was slowly added and stirred evenly. Then the temperature was raised to 160^{o}C and the mixture was continuously stirred for 1 hour. After that, the mixture was poured into a preheated mold (preheated at 120°C for 3 hours) and degassed in a vacuum oven at 120°C for 30 minutes. Then the mixture was cured according to the procedure of 180°C/2 hours+200°C/6 hours+220°C/2 hours to obtain EFPAEK/BADCy resin.

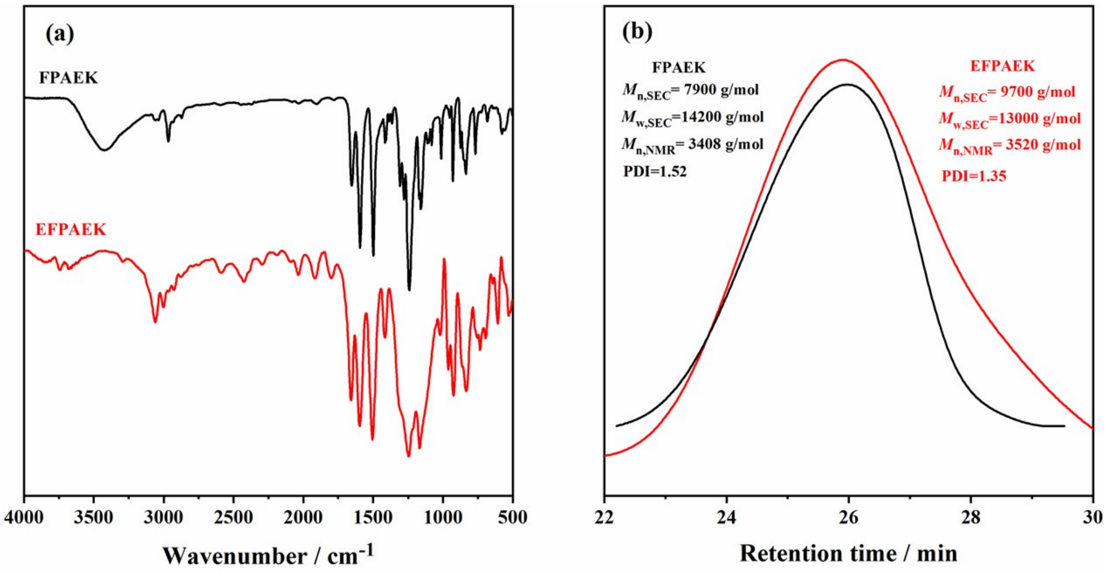


Figure S1. FTIR spectra (a) and SEC curves (b) of FPAEK and EFPAEK

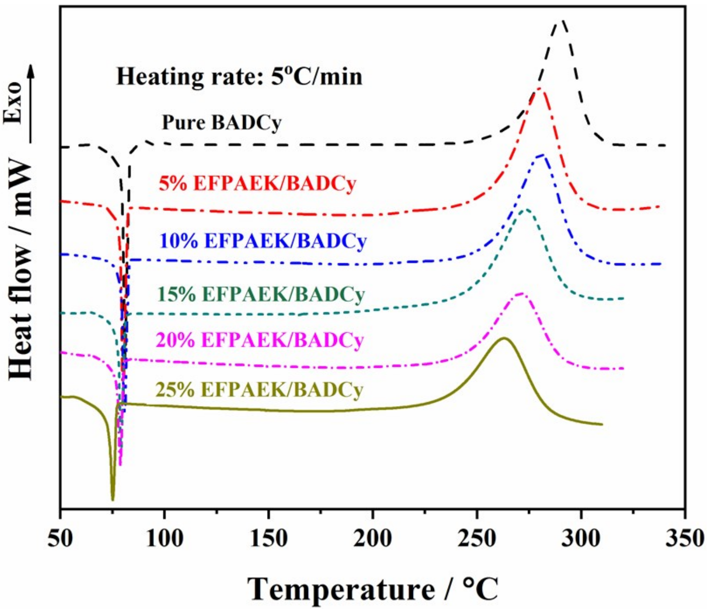


Figure S2. DSC curves of EFPAEK/BADCy resin with different mass fractions of EFPAEK at the heating rate of 5°C/min

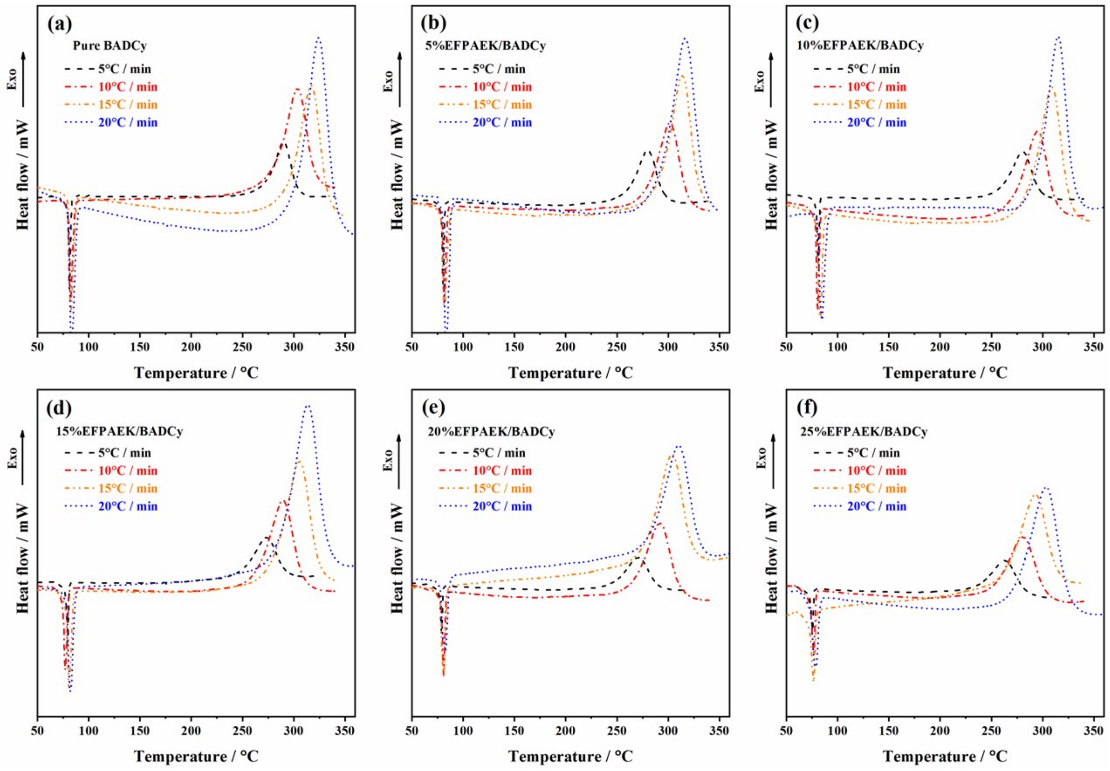


Figure S3. DSC curves of EFPAEK/BADCy resins with 0 (a), 5 (b), 10 (c), 15 (d), 20 (e), and 25 wt% (f) of EFPAEK at different heating rates

Table S1 Peak temperature of EFPAEK/BADCy resin system with different mass fractions of EFPAEK at different heating rate

Samples	**Peak temperature/°C**			
	5°C/min	**10°C/min**	**15°C/min**	**20°C/min**
Pure BADCy	289.8	303.5	316.9	323.8
5%EFPAEK/BADCy	285.1	301.8	311.9	316.8
10%EFPAEK/BADCy	280.1	296.4	308.8	315.2
15%EFPAEK/BADCy	272.3	290.9	305.8	313.7
20%EFPAEK/BADCy	271.0	290.0	304.0	311.0
25%EFPAEK/BADCy	262.9	280.8	294.7	305.1

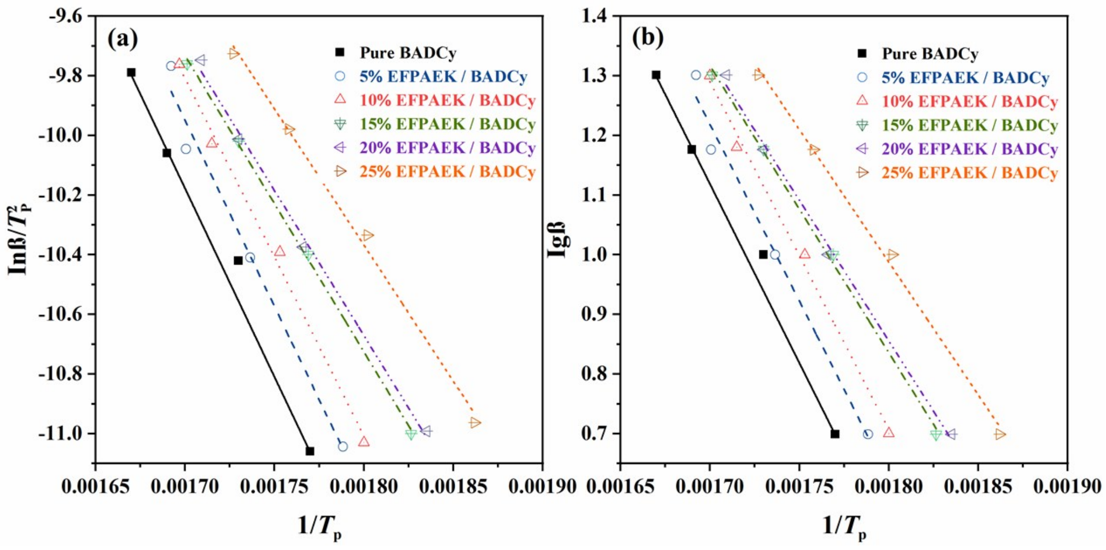
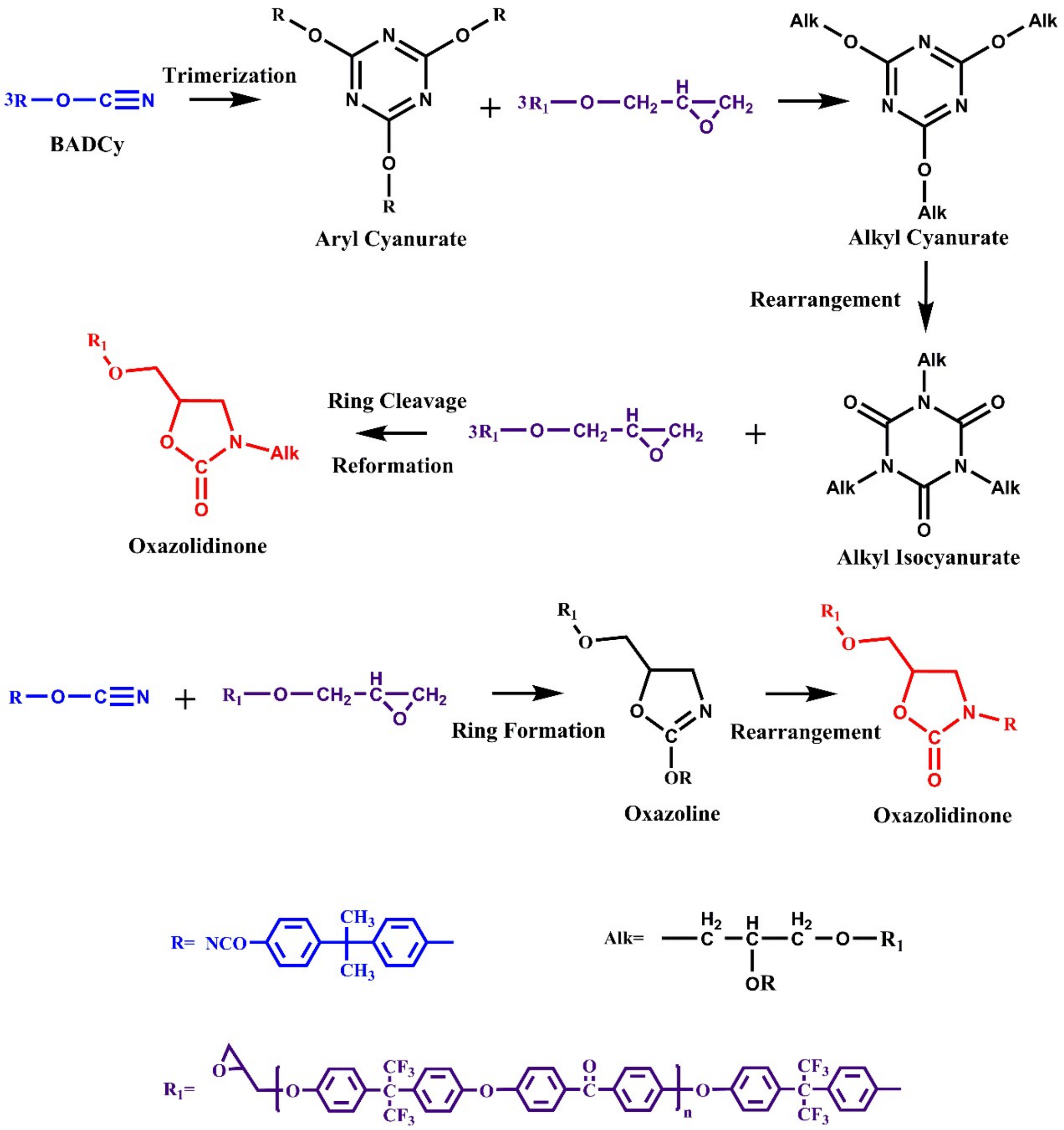


Figure S4. Kinetic curves of different EFPAEK/BADCy resin systems calculated by Kissinger method (a) and Ozawa method (b)

Table S2 Apparent activation energy and reaction order of EFPAEK/BADCy resins with different mass fractions of EFPAEK

Samples	**Apparent activation energy/kJ·mol^{-1}**		**Reaction order**
	Kissinger	**Ozawa**	**n**
Pure BADCy	105.1	109.3	0.91
5%EFPAEK/BADCy	103.9	107.8	0.91
10%EFPAEK/BADCy	99.8	106.2	0.90
15%EFPAEK/BADCy	82.5	87.6	0.90
20%EFPAEK/BADCy	81.1	85.9	0.90
25%EFPAEK/BADCy	75.9	81.0	0.89



Scheme S1. The reaction mechanisms of EFPAEK with BADCy

Table S3 Comparison of properties of CE resins modified by different epoxy resins

Samples	ε	tanδ	Flexural strength / MPa	Impact strength / kJ·m^2
Our present work	**2.64**	**0.006**	**131.8**	**30.6**
G-POSS-7/CE[2]	3.15	0.0092	118.29	23.76
CE/ER/PR (70:15:15)[3]	3.0	0.008	134.5	16.7
AEAF-BADCy[4]	2.49	0.0048	126.5	15.2
ESi/BCE[5]	--	--	123.93	14.49
0.2 PreEP/CE[6]	--	--	105.8	18.3
3 wt.% Al_2O_3/E51-BCE[7]	--	--	172.3	24.2
EP-POSS/QFs/CE[8]	2.48	0.002	--	--

BA-a/BADCy/E_{44}[9]	3.85	0.0040	158.9	22.8

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