

Supporting Information

Toward simultaneous toughening and reinforcing of trifunctional epoxies by a low loading flexible reactive triblock copolymers

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Experimental

Synthesis of reactive triblock copolymer

Reactive GPG with different reactive block lengths were synthesized by using a two-step protocol. Firstly, the difunctional macroinitiator was synthesized by the complete acylation of HO-PPG-OH with BIB at a molar ratio of [PPG]:[BIB]:[Et₃N] of 1:3:3 for 2 days at room temperature. Secondly, according to a typical ATRP procedure,[1] the Br-PPG-Br difunctional macroinitiator obtained was used to polymerize GMA in solution at 40 °C using a CuBr/PMDETA catalytic system at a molar ratio of [Br-PPG-Br]/[CuBr]/[PMDETA]=1:2:2. Two kinds of reactive triblock copolymers were obtained by controlling the monomer feed ratio and polymerization time

¹H NMR spectra were recorded by a 600 MHz Bruker Fourier Transform AVANCE 600 spectrometer in CDCl₃. GPC measurements were performed on a Breeze™ 2 HPLC System at room temperature. Tetrahydrofuran was employed as the eluent at a flow rate of 1.0 mL/min, and monodispersed polystyrene was used as the calibration standards.

Characterization of reactive triblock copolymers

The structures of macroinitiator and reactive PGMA-PPG-PGMA triblock

copolymers synthesized were characterized by ^1H NMR. As shown in Figure S 1a, the chemical shifts of macroinitiator Br-PPG-Br at 1.13, 1.14 and 1.15 ppm (**1**) are assigned to the protons of the methyl group, which split in to three peaks. The chemical shift at $\delta=1.93$ ppm (**4**) is attributed to $-\text{C}(\text{Br})-(\text{CH}_3)_2$. Those chemical shifts at $\delta=3.3$ - 3.4 ppm (**2**) and 3.5 - 3.6 ppm (**3**) are related to $-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-$ and $-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-$, respectively. Otherwise, the signal of hydroxyl $\delta=3.8$ ppm of HO-PPG-OH is disappeared, indicating the complete acylation of HO-PPG-OH with BIB. The average number molecular weight of Br-PPG-Br is estimated to be 2300 g/mol by the integral area ratios of 1:0.1 for protons of (**1**) and (**4**), corresponding well to the data provided by the supplier ($M_n=2000$ g/mol).

As to GPG (Figure S 1b), the additional signals of chemical shifts from the PGMA blocks were detected at $\delta=0.94$ - 1.10 ppm (a), $\delta=1.84$ (b), 2.64, 2.84 ppm (c), $\delta=3.24$ ppm (d) and $\delta=3.81$, 4.3 ppm, which were attributed the methyl group of PGMA blocks, methylene of PGMA backbone, methylene of lateral groups of PGMA blocks and protons of the oxirane ring, respectively. Moreover, the peak area ratio of a, d and c was 2.92:1:1.99, which was close to 3:1:2. These results indicated that the epoxy rings in the PGMA remained intact during the polymerization of GMA.

The molecular weights and polydispersity indices (PDI) of macroinitiator Br-PPG-Br and GPG triblock copolymers were listed in Table 1. Based on the GPC and NMR results, the polymerization degree of each reactive block for two GPG copolymers is determined to be 34 and 81. More detail, the $\text{PGMA}_{34}\text{-PPG}_{34}\text{-PGMA}_{34}$ with short reactive blocks (short L_{reactive}) possessed a similar weight fraction of epoxy-philic blocks (GPG83, $w_{\text{PGMA}}=83$ wt.%) with $\text{PEG}_{76}\text{-PPG}_{29}\text{-PEG}_{76}$ (nonreactive EPE80, $w_{\text{PEG}}=80$ wt.%). And, the polymerization degree of the $\text{PGMA}_{81}\text{-PPG}_{34}\text{-PGMA}_{81}$ (GPG92, $w_{\text{PGMA}}=92$ wt.%) with a long L_{reactive} was similar with that of EPE80.

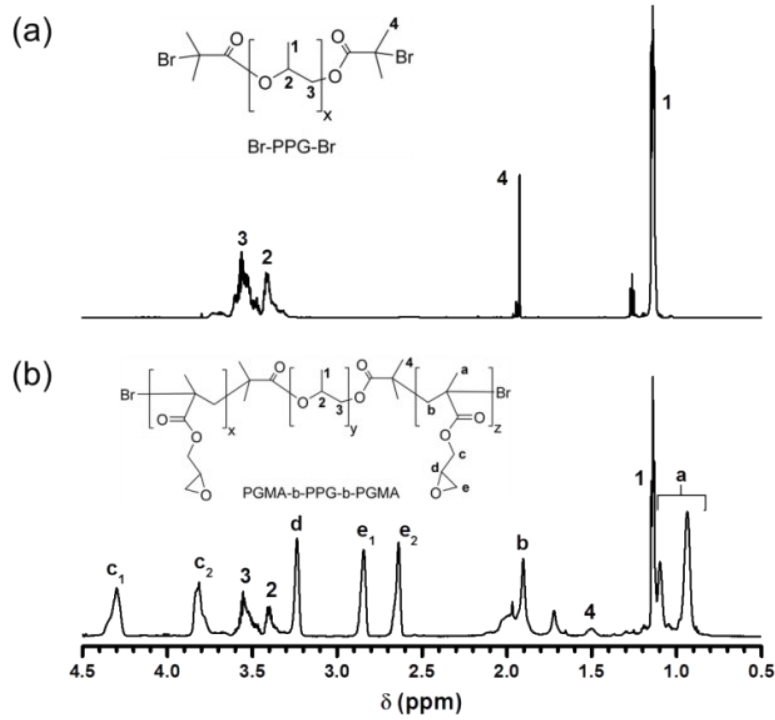


Figure S 1 ^1H NMR spectra (600 MHz in CDCl_3) of (a) macroinitiator Br-PPG-Br and (b) PGMA-PPG-PGMA.

Calculation of fracture toughness

Mode-1 critical stress intensity factor (K_{1c}) and critical strain energy release rate (G_{1c}) were calculated according (1) to (2) and, respectively [2].

$$K_{1c} = \frac{P_Q}{B\sqrt{W}} f(x) \quad \text{\textbackslash* MERGEFORMAT (1)}$$

where P_Q is the maximum loading force in the SENB test, B and W are specimen thickness and width, respectively, as defined in ASTM D5045-99. $f(x)$ is the geometric factor, defined as

$$f(x) = 6x^{1/2} \frac{\left[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2) \right]}{(1+2x)(1-x)^{3/2}} \quad \text{\textbackslash*}$$

MERGEFORMAT (2)

where $x = a/W$ and a is the initial notch length including the precrack. The mode-1 critical strain energy release rate is defined as

$$G_{1c} = \frac{(1-\nu^2)K_{1c}^2}{E} \quad \backslash * \text{MERGEFORMAT (3)}$$

where E is the elastic modulus acquired from the tensile test and ν is Poisson ratio of the TDE-85 epoxy, which is taken to be 0.33 [3].

Verification of the plain strain condition

The validity of calculated K_{1c} was checked by following equation:

$$B, a, (W - a) > 2.5 \left(\frac{K_{1c}}{\sigma_y} \right)^2 \quad \backslash * \text{MERGEFORMAT (4)}$$

where B is the sample thickness, a is the precrack length and W is the sample width, and σ_y is the material yield stress determined from a tensile test. So the maximum

limits value of the $2.5 \left(\frac{K_{1c}}{\sigma_y} \right)^2$ part can be calculated from the experiment data in this study. Otherwise, it should be pointed out that the yield stress could not be obtained as the tensile samples fractured before yielding. Then the tensile yield stress might be ascertained from the measured compression yield stress, σ_{yc} , from[4]:

$$\sigma_y = \sigma_{yc} \frac{(\sqrt{3} - \mu_m)}{(\sqrt{3} + \mu_m)} \quad \backslash * \text{MERGEFORMAT (5)}$$

where μ_m is a material constant which has a value of 0.2. Then equation * MERGEFORMAT (5) can be simplified:

$$\sigma_y = 0.793\sigma_{yc} \quad \backslash * \text{MERGEFORMAT (6)}$$

From the compression test curves (Figure S2), with the loading of BCPs increase, the σ_{yc} values are gradually decreased. So the lowest σ_{yc} value, 175 MPa, is obtained when 5 wt.% EPE80 was added. Then $\sigma_{y,\min} = 138$ MPa. The maximum K_{1c} is 1.62

MPa·m^{1/2} (Table S2) when 2.5 wt.% GPG83 was added. So $\left[2.5 \left(\frac{K_{Ic}}{\sigma_y} \right)^2 \right]_{\max} = 0.3445$

mm. For this specimen, B = 5 mm, W = 10 mm, a = 5 mm, these data are fulfill with the equation* MERGEFORMAT (6). Therefore, the validity of calculated K_{Ic} values were confirmed in this work.

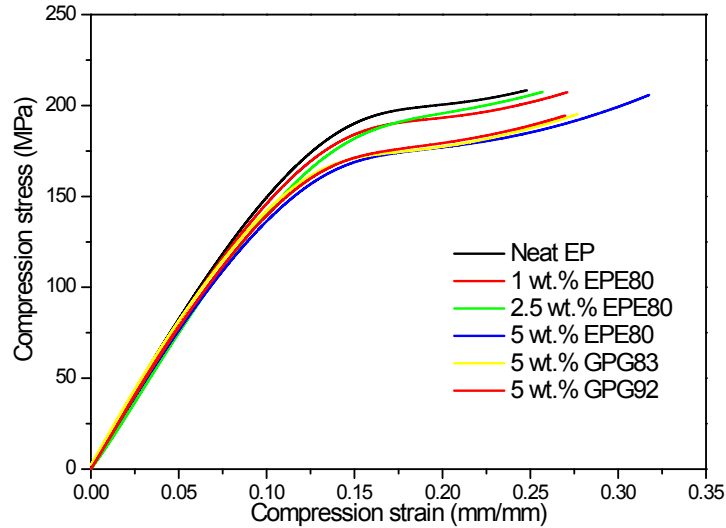


Figure S2. Representative compression stress versus strain curves of the neat and modified epoxy thermosets.

Density of the modified thermosets

The densities of the samples were measured by the Pycnometer Test Method at room temperature according to GB/T 4472-2011. The media of test is water, which has a known density of 0.9977 g/cm³. The density was calculated using the equation:

$$\rho = \frac{m_s}{m_s + m_1 - m_2} \rho_w \quad \text{* MERGEFORMAT (7)}$$

where m_s is the weight of sample, m_1 is the weight of full water pycnometer, m_2 is the weight of full water pycnometer and sample, ρ_w is the density of water. To estimate the density of the sample at rubbery plateau, the dimension of sample at room and evaluated temperature was measured by rheometer (ARES from TA instruments, USA).

Characterization of epoxy thermosets by FTIR

FTIR were characterized by a Nicolet 6700 spectrometer (Thermo Fisher Scientific) in the transmission or reflection mode in a wavelength range from 4000 to 650 cm^{-1} .

Results and discussion

Table S1 Tensile properties of epoxy thermosets with various loadings of BCPs.

Samples	BCP loading (wt.%)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	G (MJ/m^3)
Neat EP	0	105.4±5.9	3.46±0.07	5.27±0.48	3.07±0.42
EPE80	1	123.6±7.5	3.32±0.05	7.55±0.96	5.81±1.17
	2.5	116.2±4.6	3.32±0.08	6.66±0.36	4.76±0.52
	5	112.5±4.9	3.13±0.08	7.27±0.95	5.2±1.02
GPG83	1	135.3±8.4	3.48±0.07	7.82±1.50	6.53±2.05
	2.5	138.1±9.7	3.50±0.07	7.69±1.33	6.78±1.75
	5	126.4±9.0	3.51±0.05	5.96±0.80	4.55±0.95
GPG92	1	115.8±2.9	3.50±0.03	6.05±0.29	4.67±0.37
	2.5	115.0±8.3	3.48±0.08	4.95±0.61	3.82±0.71
	5	105.9±8.7	3.53±0.03	5.10±0.69	3.22±0.87

Table S2 Fracture toughness properties of epoxy thermosets with various loadings of BCPs.

Samples	BCPs loading (wt.%)	K_{Ic} ($\text{MPa}\cdot\text{m}^{1/2}$)	G_{Ic} (J/m^2)
Neat EP	0	1.05±0.21	286.3±117.9
EPE80	1	1.38±0.12	505.8±78.7
	2.5	1.53±0.07	619.1±39.7
	5	1.56±0.06	687.1±39.5
GPG83	1	1.47±0.11	548.5±72.8
	2.5	1.62±0.11	660.7±81.7
	5	1.52±0.05	579.0±31.5
GPG92	1	1.39±0.13	488.5±89.8
	2.5	1.32±0.15	442.7±93.5

5	1.28±0.16	411.1±104.2
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Table S 3 The densities of samples at room temperature and rubbery plateau.

Sample	Density at room temperature	Density at rubbery plateau
	(g/cm ³)	(g/cm ³)
Neat EP	1.362	1.318
1 wt.% EPE80	1.355	1.298
2.5 wt.% EPE80	1.353	1.295
5 wt.% EPE80	1.350	1.292
1 wt.% GPG83	1.360	1.329
2.5 wt.% GPG83	1.356	1.325
5 wt.% GPG83	1.360	1.328
1 wt.% GPG92	1.358	1.300
2.5 wt.% GPG92	1.349	1.290
5 wt.% GPG92	1.356	1.296

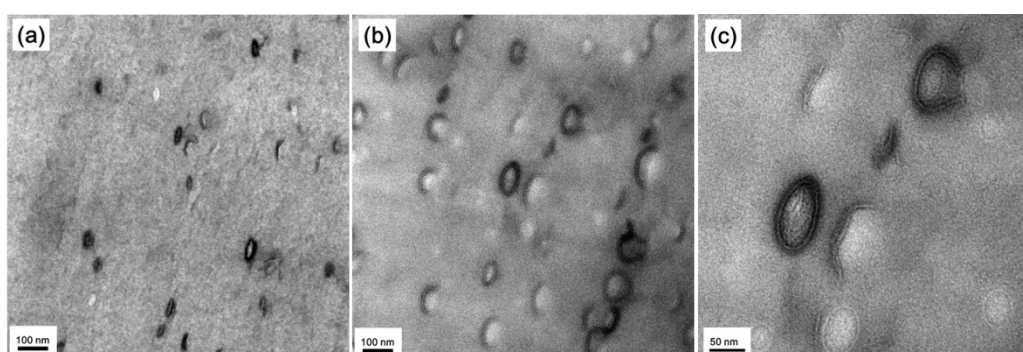


Figure S3. TEM micrographs of (a) 1 wt.%, (b) 5 wt.% EPE80 and (c) higher magnification of 5wt.% EPE80 modified thermosets.

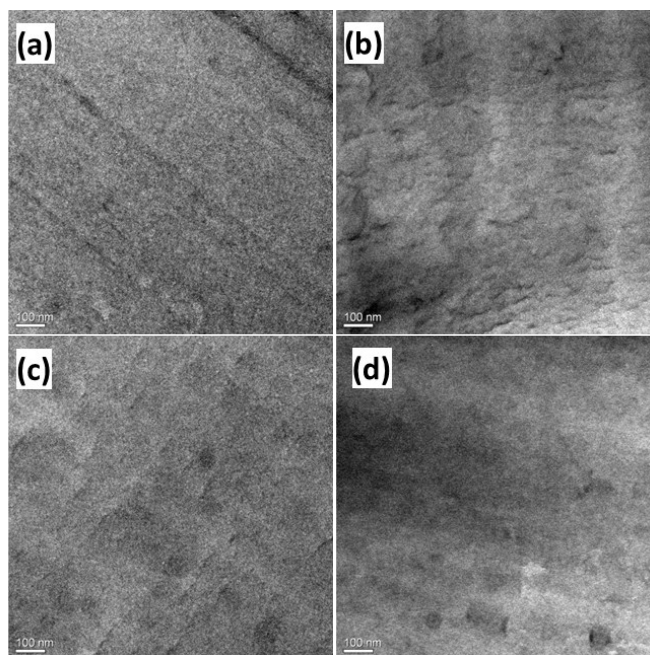


Figure S 4 Additional TEM images of (a)-(b) GPG83 and (c)-(d) GPG92. Scale bar in images are 100nm.

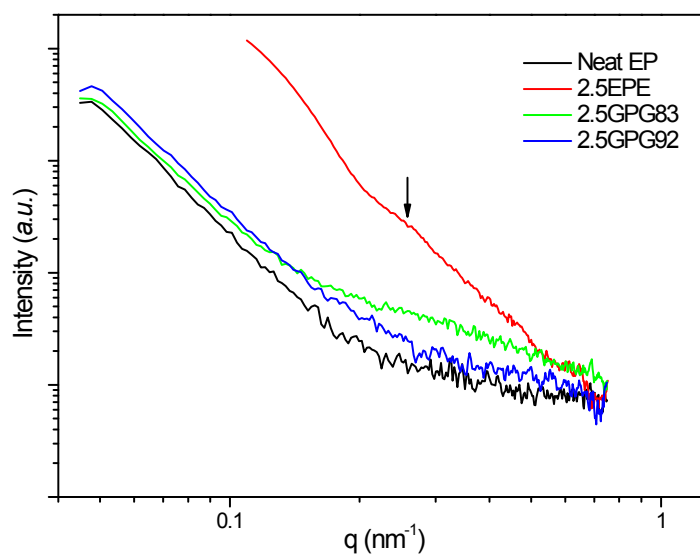


Figure S 5 SAXS curves of neat EP and 2.5 wt.% BCP-modified epoxy thermosets

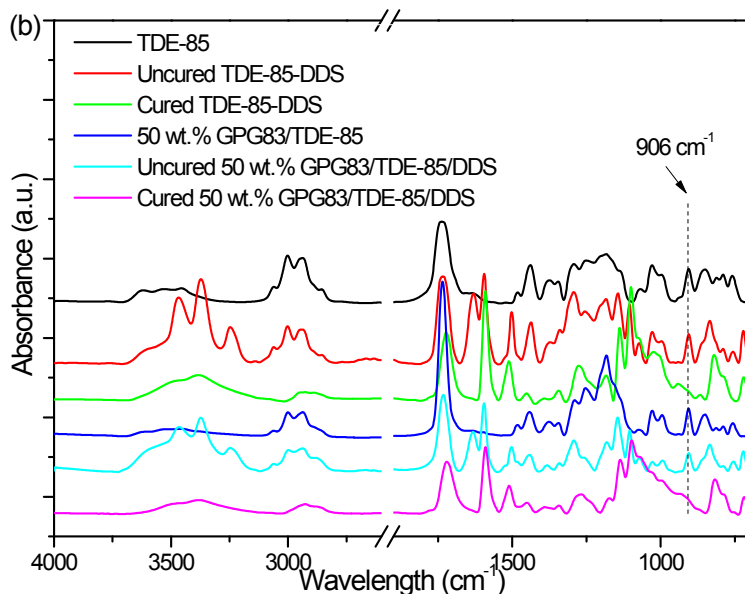


Figure S 6 Represent FTIR spectra of Uncured and cured of neat GPG83, TDE-85, 50 wt.% GPG83 modified TDE-85 blends.

Table S 4 Normalized intensity of epoxy group of GPG

Sample	Normalized intensity of epoxy group (a.u), 906 cm ⁻¹ ^a
Uncured GPG83	0.818/0.643= 1.27
Cured GPG83	0.0523/0.23 = 0.23
Uncured GPG92	0.67/0.45 = 1.47
Cured GPG92	0.034/0.12 = 0.28

^a the values were calculated from the area of epoxy group (906 cm⁻¹) / sulfonyl group (1100 cm⁻¹)

Sulfonyl group was taken as internal standard because it was not affected in the curing process.[5]

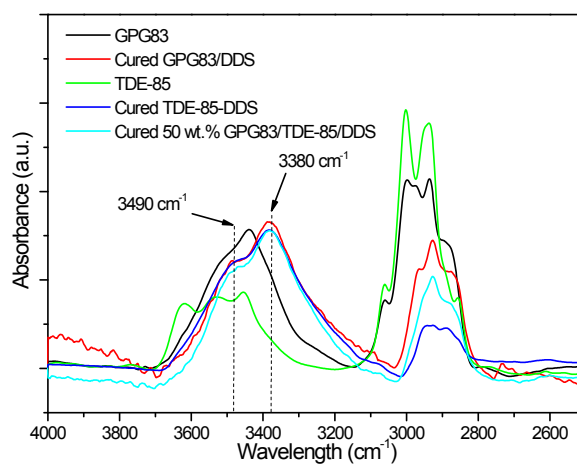


Figure S 7 Represent FTIR spectra of Uncured and cured of neat GPG83, TDE-85, 50 wt.%

GPG83 modified TDE-85 blends at 2500-4000 cm^{-1} .

Reference

- [1] Dayananda K, Dhamodharan R. ATRP of methyl methacrylate using a novel binol ester-based bifunctional initiator. *Journal of Polymer Science Part A: Polymer Chemistry*. 2004;42(4):902-915.
- [2] Park YT, Qian Y, Chan C, Suh T, Nejhad MG, Macosko CW, et al. Epoxy Toughening with Low Graphene Loading. *Adv Funct Mater*. 2015;25(4):575-585.
- [3] Qu Y, Zhang Y, Qu J. Micro-Driving behavior of carbon-fiber-reinforced epoxy resin for standing-wave ultrasonic motor. *Polym Composite*. 2016;37(7):2152-2159.
- [4] Hsieh TH, Kinloch AJ, Masania K, Taylor AC, Sprenger S. The mechanisms and mechanics of the toughening of epoxy polymers modified with silica nanoparticles. *Polymer*. 2010;51(26):6284-6294.
- [5] Edwards ER, Kostov KG, Botelho EC. Evaluation of the chemical interaction between carbon nanotubes functionalized with TGDDM tetrafunctional resin and hardener DDS. *Composites Part B: Engineering*. 2013;51:197-203.