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Polyisobutylene Modified Bisphenol A Diglycidyl Ether Based Epoxy Resins Possessing Improved Mechanical Properties

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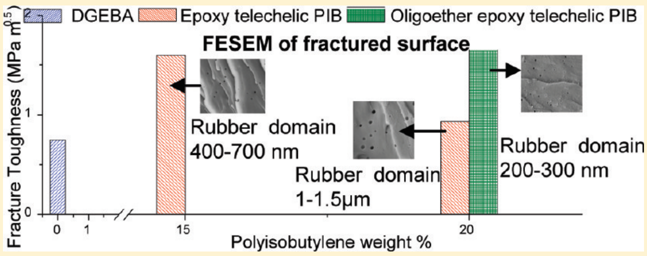
S *Supporting Information*

ABSTRACT: Epoxy telechelic polyisobutylenes (EP-PIB-EP), potentially useful to obtain flexible epoxies, were synthesized by reacting bromoallyl end-functional PIB with glycidol in the presence of NaH. The epoxy end-capped macromonomers were mixed with bisphenol A diglycidyl ether (DGEBA) and triethylenetetramine as curing agent and cured at elevated temperature. Field emission scanning electron microscopy (FESEM) indicated nanophase segregation of rubbery domains at EP-PIB-EP ≤ 15 wt %, and the fracture toughness increased by 100% relative to the unmodified epoxy network, while the tensile and flexural strengths remained adequate. However, at EP-PIB-EP ≥ 20 wt % macrophase separation resulted in a drastic reduction in toughness along with other mechanical properties. Use of oligo(tetramethylene oxide) modified epoxy telechelic PIB (EP-oTHF-PIB-oTHF-EP) as soft segment significantly improved the miscibility, and cured materials with excellent fracture toughness were obtained even at 40 wt % rubber content. Thermal stability of the amine cured epoxy resin was not affected by the incorporation of PIB. These flexible networks possess superior mechanical properties compared to poly(ethylene glycol)/DGEBA networks commercialized by Dow Chemical Company.



INTRODUCTION

Epoxy resins are a versatile group of thermoset polymers possessing excellent combination of stiffness, strength, chemical resistance, insulating properties, adhesion to substrate, and environmental stability. Thus, these materials find widespread applications in the field of construction, electronics, adhesives, and coatings.[1] One of the important applications of epoxy resins is sealing electronics components, which requires excellent adhesion, dimensional stability and barrier properties, and low shrinkage combined with sufficient flexibility to accommodate expansion and contraction.[2] However, the major limitations associated with the available high performance resins are their inherent brittleness and poor resistance to crack propagation, which limits their industrial applications.[3] Numerous attempts were made for improving the brittleness and fracture energy of conventional epoxy resins by blending with functionalized elastomers.[4] The advantage of reactive functionalized elastomers is that the blends are homogeneous in the uncured state and undergo complete phase separation in nano- to micrometer range after curing. These phase separated microdomains of rubber particles lead to shear yielding of matrix and are responsible for energy dissipation and toughness enhancement.[5] The size of the segregated rubber phase is crucial to achieve maximum toughness without sacrificing other mechanical properties.[6] At high rubber concentration the network loses a significant amount of other mechanical properties such as modulus and strength due to heterogeneous nature of the matrix.[7] There is a strong dependence of particle size on enhancement of fracture toughness and that the optimum dispersed rubber particle sizes of 1−5 μm were essential, whereas particle sizes greater than 20 μm were ineffective.[8] Kim et al. had identified the lower limit of 0.2 μm for the rubber particles to achieve effective toughening.[9] The compatibility between liquid rubber and resin must be matched carefully to achieve the desired phase separation during curing and produce sufficient interfacial adhesion.[10] Various reactive functionalized butadiene-*co*-acrylonitrile rubbers such as carboxyl-terminated butadiene acrylonitrile (CTBN), amine-terminated butadiene acrylonitrile (ATBN), and epoxy-terminated butadiene acrylonitrile (ETBN) were widely used as modifiers for epoxy resin, especially for diglycidyl ether of bisphenol A (DGEBA) resin.[11] Kinloch and co-workers reported the enhancement of fracture toughness of CTBN modified thermosets, but sacrificing other mechanical properties such as modulus and yield strength.[12] Chikhi and co-workers used ATBN as a liquid rubber, thus increasing the critical stress intensity factor (K_{IC}) from 0.9 to 1.49 MPa m$^{1/2}$ (about 1.5 times) and with minimal increase in elongation at break.[13] However, the increase in toughness was accompanied by severe reduction of tensile strength and modulus. Further, it was observed that at ATBN concentration above 12.5 parts per hundred resins (phr) the dispersed rubber particles coalesce, thereby drastically reducing the mechanical properties.

Thermoplastic modifiers like poly(ether sulfone), poly(ether imide), poly(ether ether ketone), and polystyrene were also

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Scheme 1. Schematic Representation of Hybrid Cured Networks Comprising EP-PIB-EP (Soft Segments) and Bisphenol A Diglycidyl Ether (DGEBA) Cured with Triethylenetetramine (TETA)

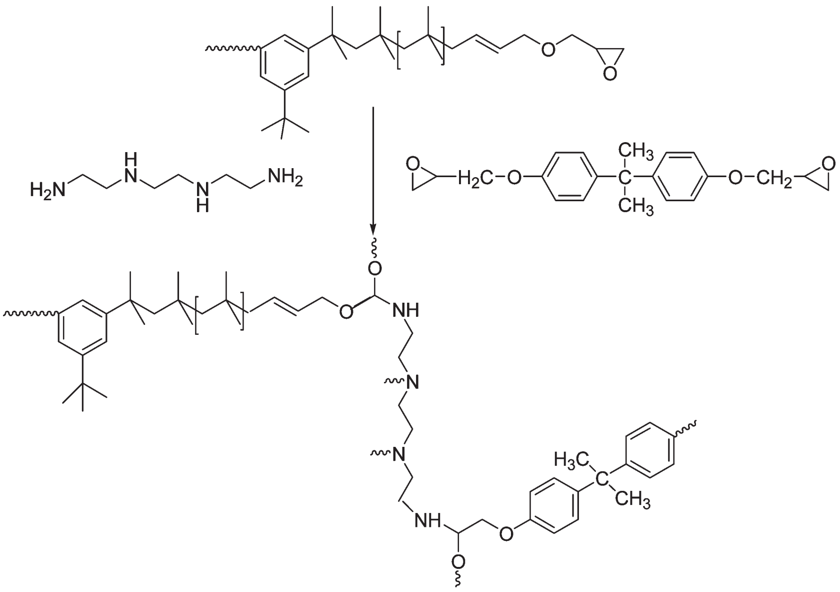


Table 1. Mechanical Properties of Unmodified Cured Hybrid Resins

sample	DGEBA (wt %)	PIB (wt %)	flexural modulus (MPa)	flexural strength (MPa)	fracture toughness (MPa $m^{0.5}$)	tensile strength (MPa)	elongation at break (%)
1[a]	100	0	2700	120	0.75	70	3
2[a]	98	2	1850	100	0.96	59	9
3[a]	95	5	1571	80	1	55	10
4[a]	90	10	1450	67	1.11	50	12
5[a]	85	15	1400	58	1.6	43	13
6[a]	80	20	850	43	0.93	40	14
7[a]	60	40	700	32	0.35	19	15
8[b]	98	2	1760	75	0.9	55	9
9[b]	95	5	1457	65	1.05	45	10
10[b]	90	10	1350	50	1.1	40	12
11[b]	85	15	1250	45	1.4	38	12
12[b]	80	20	710	38	1.04	26	13
13[b]	60	40	620	32	0.30	20	15

[a] Molecular weight of soft segment (EP-PIB-EP) M_n = 1600. [b] Molecular weight of soft segment (EP-PIB-EP) M_n = 2500.

utilized for improving brittleness of epoxy resin in order to avoid the compromise between toughness and thermal stability associated with rubber toughening of thermosets.[14] However, no significant enhancement in toughness was noticed due to poor interfacial adhesion between the phases. Besides, solvent resistance and creep properties of the materials were also not great. End-functional thermoplastics were also employed with the intention of obtaining a chemical linkage between the phases that may increase the toughness of brittle thermosets, but with limited success.[15,16]

Polyisobutylene (PIBs) based networks possess excellent flexibility and strong adherence to substrate such as wood, fiber glass, metals like aluminum and stainless steel, rubbers, electronic or electro-optic devices, good damping and barrier properties, thermal stability, and excellent chemical and solvent resistance.[17] The above properties can be effectively used for various coating applications.[18] To the best of our knowledge, epoxy resins incorporating end-functional PIBs as reactive liquid rubbers have not been reported in the literature. The current work describes the modification of diglycidyl ether of bisphenol A (DGEBA) based epoxy resins with PIB and oligo tetrahydrofuran end modified PIB. We envisaged that oligo tetrahydrofuran end modified PIB will possess better miscibility with DGEBA. Scanning electron microscopy (SEM) was used to characterize the fractured surfaces to understand the failure of the epoxy networks.

■ EXPERIMENTAL SECTION

Materials. Epichlorohydrin (Aldrich, 98%), bisphenol A diglycidyl ether (DGEBA, Aldrich,), bisphenol A diglycidyl ether (DGEBA[1], DER 332, Fluka), poly(ethylene glycol) diglycidyl ether (PEG-DGE, DER Resin 732, Aldrich), triethylenetetramine (TETA, Aldrich, 60%), oligo tetrahydrofuran (oTHF, Aldrich, M_n = 250, PDI: 1.29), 18-crown-6 (Aldrich,) tetra-*n*-butylammonium bromide (TBAB, Aldrich, 99%), sodium hydride (NaH Aldrich, 60% dispersion in mineral oil), potassium hydroxide (KOH, Aldrich), sodium sulfate (Na_2SO_4, Aldrich), 1,4-benzoquinone (Aldrich, 98%), and methanol (Doe & Ingals, Technical grade) were used as received. Hexanes (Hex, Doe & Ingals, Technical grade) was purified by refluxing over sulfuric acid for 24 h followed by washing with aqueous solution of KOH 3 times followed by distilled water. It was stored over sodium sulfate overnight at room temperature and finally distilled over CaH_2 under a nitrogen atmosphere before use. Tetrahydrofuran (THF, Aldrich, 99%) was refluxed over sodium metal and benzophenone overnight and distilled under a nitrogen atmosphere prior to use. The detailed synthesis of EP-PIB-EP is reported elsewhere.[19]

Characterization. ^1H and ^{13}C NMR spectroscopies for structural analysis were carried out on a Bruker 500 MHz spectrometer using $CDCl_3$ (Cambridge Isotope laboratories, Inc.) as a solvent. ^1H or ^{13}C NMR spectra of solution in $CDCl_3$ were calibrated to tetramethylsilane (TMS) as internal standard (δ H or δ C 0.00).

Molecular weights were measured with a Waters HPLC system equipped with a model 515 HPLC pump, model 2410 differential refractometer, model 2487 absorbance detector, online multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology

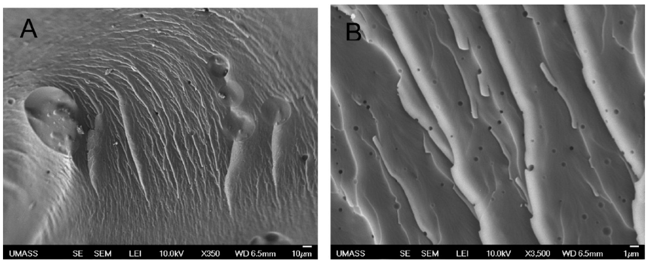


Figure 1. SEM micrograph of fractured surface of cured hybrid epoxy resins: (A) 15 wt % of EP-PIB-EP (soft segment) at 350×; (B) 15 wt % of EP-PIB-EP (soft segment) at 3500×.

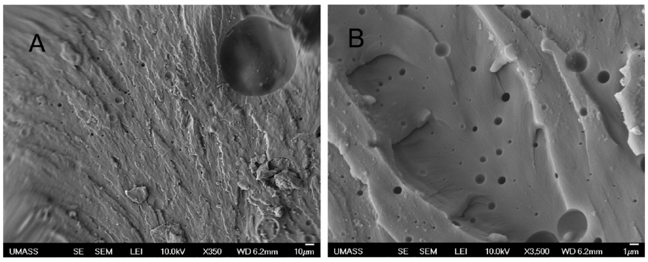


Figure 2. SEM micrograph of fractured surface of cured hybrid epoxy resins: (A) 20 wt % of EP-PIB-EP (soft segment) at 350×; (B) 20 wt % of EP-PIB-EP (soft segment) at 3500×.

Inc.), on-line differential viscometer (ViscoStar, Wyatt Technology Inc.), Model 717 plus sample processor, and five Styragel HR GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as an eluant at a flow rate of 1 mL/min. The molecular weight was calculated using Universal Calibration curve (UCAL). The UCAL curve was constructed by injecting a series of narrow polystyrene standards of known molecular weight.

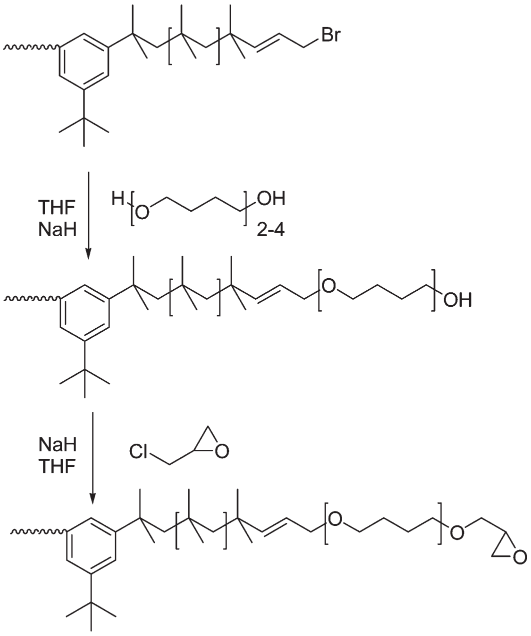
The tensile tests were performed at room temperature (~25 °C) and atmospheric conditions with a 200 N load cell on an Instron Model 4400R testing machine, at a crosshead speed of 1 mm/min, according to ASTM D 638. The specimens were cut from cured sheets using a fine band saw to dimensions of 60 × 7 × 1.6 mm^3. The values were taken from an average of at least three specimens.

The flexural strength and modulus were also performed with rectangular samples according to ASTM D 790 using an Instron Model 4400R testing machine, fitted with a three-point bending fixture at a crosshead speed of 2 mm/min. The dimension of the specimens were 50.8 × 12.7 × 1.6 mm^3, and the span to thickness ratio was set at L/D = 32:1. The results, expressed in megapascals(MPa), are the averages from three samples.

Plane-strain fracture toughness testing was conducted in accordance with ASTM D 399 on single edge notched (SEN) specimens in a three-point-bend (3PB) test configuration. The sample geometry was 60 × 8 × 4 mm^3. A notch was machined into the samples using a fine band saw, and then precracks were introduced by tapping a liquid nitrogen dipped razor blade into the samples. The 3PB tests were conducted using a standard 3PB test fixture with the load applied using an Instron 4410 screw driven mechanical testing machine. A crosshead speed of 1 mm/min was used. The maximum load was obtained from the load−deflection plots, and the average crack length was obtained by measuring the crack length at three locations on the fracture surface of failed SEN specimens with engineering calipers. The K_{IC} values were calculated in accordance to the ASTM D 399 method:

$$K_{\text{IC}} = \frac{P}{BW^{1/2}} f\left(\frac{a}{W}\right)$$

Scheme 2. Synthesis of OH-oTHF-PIB-oTHF-OH and EP-oTHF-PIB-oTHF-EP Obtained by Reaction of Polyisobutylene−Allyl Bromide with Nucleophiles



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

$$x = \frac{a}{W}$$

where P is the critical load for crack propagation in kN, B is the specimen thickness in cm, W is the specimen width in cm, a is the average crack length in cm, and $f(a/W)$ is the nondimensional shape factor.

Fractured ASTM D 399 SEN-3PB specimens were examined using a JEOL Model JSM 7401F field emission scanning electron microscope at an accelerating voltage of 10 kV. 350× and 3500× magnification were used to record the micrographs. Surface morphology was observed on gold sputter-coated samples using a Denton Vacuum Desk IV cold cathode sputter coater. The samples were sputter-coated for 2.0 min at 25% power, corresponding to a thickness of ~75 Å of gold.

A TA Q-50 thermal gravimetric analyzer was used to investigate the decomposition temperature of cured epoxy resins. The cured samples (8−10 mg) were heated under a nitrogen atmosphere from ambient temperature to 700 °C at the heating rate of 10 °C/min in all cases. The thermal degradation temperature was taken as the onset temperature at which 5 wt % of weight loss occurs.

Synthesis of oTHF-PIB-oTHF. Bromoallyl telechelic PIB (M_n = 2200, PDI = 1.2, 200 mg, 0.09 mmol) was dissolved in dry THF (15 mL). Oligotetrahydrofuran (1.36 g, 5 mmol), NaH (80 mg, 3.33 mmol), and TBAB (1.61 g, 5 mmol) were added to it. The mixture was refluxed under a dry nitrogen atmosphere for 12 h. The polymers were purified by precipitation from hexane/methanol. Finally, the precipitate was dried under vacuum at room temperature for 12 h. Gravimetric yield: 95%. ^{1}H NMR (CDCl_3, ppm, δ): 3.95 (d, 2H, $-\text{CH}{=}\text{CH}\textit{CH}_2\text{O}-$), 5.54(m, 1H, $-\text{CH}{=}\textit{CH}\ \text{CH}_2-$, 5.72 (m, 1H, $-\textit{CH}{=}\text{CHCH}_2-$, 3.6 (d, 2H, $-\text{O}(\text{CH}_2\text{CH}_2\text{CH}_2\textit{CH}_2\text{OH})$, 3.48 (m, 10H, $-(\textit{CH}_2\text{CH}_2\text{CH}_2\textit{CH}_2)_2-$), 1.75 (m, 12H, $-\text{O}(\text{CH}_2\textit{CH}_2\textit{CH}_2\text{CH}_2)_2-$).

^{13}C NMR ($CDCl_3$, ppm, δ): 149 ($C{=}CH$, Ar), 148.5 ($-C{=}CH$, Ar), 129 ($-CH{=}CHCH_2O-$), 121.5 (($-CH{=}CHCH_2O-$), 118 ($CH{=}C$, Ar), 72 ($-CH{=}CHCH_2O-$), 70.5 ($-O(CH_2CH_2CH_2CH_2)_2O-$), 60.0 ($-O(CH_2CH_2CH_2CH_2OH)$, 26.0 ($-O(CH_2CH_2CH_2CH_2)_2O-$).

Synthesis of EP-oTHF-PIB-oTHF-EP. oTHF-PIB-oTHF (M_n = 2500, PDI: 1.2 200 mg, 0.08 mmol) was dissolved in dry THF (15 mL) and charged into a two-necked glass reactor equipped with an effective condenser. Epichlorohydrin (530 mg, 5.75 mmol), sodium hydride (80 mg, 3.33 mmol), and 18-crown-6 (20 mg, 0.07 mmol) were charged into the reactor under a slow stream of dry nitrogen atmosphere, and the reaction mixture was stirred for 12 h at ambient temperature. THF was evaporated, and the residue was dissolved in hexane and filtered. The polymer was purified by frequent reprecipitation from methanol. Gravimetric yield: 97%. ^{1}H NMR ($CDCl_3$, ppm, δ): 3.95 (d, 2H, $-CH{=}CHCH_2O-$), 5.54 (m, 1H, $-CH{=}CHCH_2O-$), 5.72 (m, 1H, $-CH{=}CHCH_2O-$), 3.6 (d, 2H, $-O(CH_2CH_2CH_2CH_2O-$), 3.48 (m, 10H, $-O(CH_2CH_2CH_2CH_2)_2-$, 1.75 (m, 12H, $-O(CH_2CH_2CH_2CH_2)_2-$), 3.5 and 3.4 (m, 2H, $-CH_2(CHCH_2O)$, 3.3 (m, 1H, $-(CHCH_2O)$), 2.9 and 2.7 (m, 2H, $-(CHCH_2O)$. ^{13}C NMR ($CDCl_3$, ppm, δ): 149 ($-C{=}CH$, Ar), 148.5 ($-C{=}CH$, Ar), 131 ($-CH{=}CHCH_2O-$), 129.5 ($-CH{=}CHCH_2-$), 119 ($CH{=}C$, Ar), 71.0 ($-OCH_2(CHCH_2O)$, 60.0 ($-O(CH_2CH_2CH_2CH_2)_2O-$), 51.0 ($-CH_2(CHCH_2O)$, 48.0 ($-CH_2(CHCH_2O)$, 26.0 ($-O(CH_2CH_2CH_2CH_2)_2O-$).

Synthesis of Flexible Epoxy Coating. EP-PIB-EP (M_n = 1600, PDI = 1.2, 500 mg, 5 wt %) was placed in a small sample vial along with DGEBA (4.5 g, 95 wt %). The mixture was slightly warmed and mixed vigorously to prepare a homogeneous solution. To the above solution triethylenetetraamine (0.745 g, 0.38 mol %) was added and mixed using a high-speed mixer. The resulting blend of epoxy and amine was degassed for 1 h. The samples were then poured into a mold (15 cm × 15 cm), which was preheated to 100 °C in a vacuum oven. The samples were then cured at 100 °C for 2 h. Postcure was conducted at 100 °C for 12 h. After the postcure, the oven was switched off and allowed to cool slowly to room temperature to avoid crack formation.

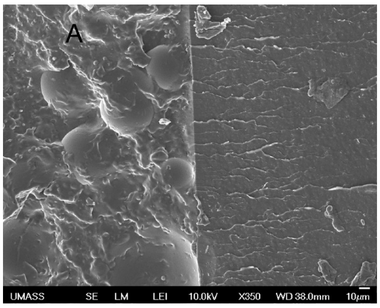


Figure 3. SEM micrograph of fractured surface of cured hybrid epoxy resins: 40 wt % of EP-PIB-EP (soft segment) at 350×.

■ RESULTS AND DISCUSSION

Synthesis of Epoxy Telechelic PIB. Epoxy telechelic PIBs (EP-PIB-EP) with different M_n (1600 or 2500) were synthesized by reacting bromoallyl telechelic PIB with glycidol using NaH in THF under reflux. Addition of a phase transfer catalyst such as TBAB increased the homogeneity of the reaction mixture, and the substitution was complete in 6 h. The detailed synthesis and characterization of EP-PIB-EP were reported previously.[19] The quantitative end-functionality was confirmed using ^{1}H NMR and MALDI-TOF MS spectroscopic analysis. The GPC-RI traces of the macromonomers were similar to the precursor Br-Allyl-PIB-Allyl-Br, indicating that the end groups are unaffected during the synthesis and purification (Figures 6 and 7). The thermal curing of the above macromers and DGEBA in various weight proportions were carried out in presence of triethylenetetraamine at 100 °C to obtain flexible uniform films. The schematic representation of the network formed is shown in Scheme 1.

Flexural Properties. In the series of epoxy resins consisting of EP-PIB-EP (M_n = 1600) and DGEBA in various wt % (100−60 wt %), the flexural modulus decreased from 2700 to 700 MPa

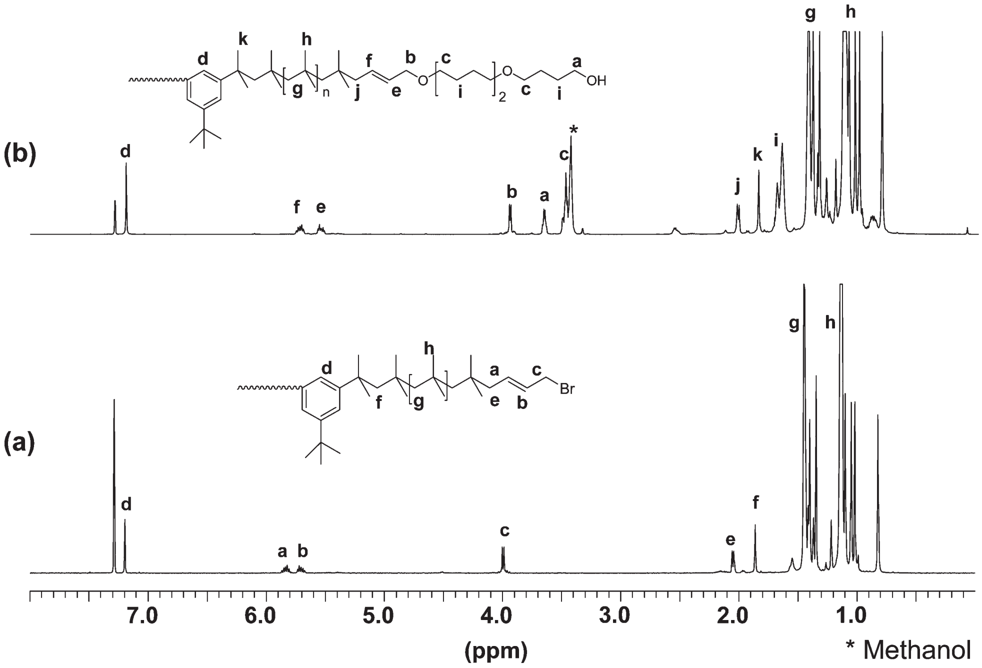


Figure 4. ^{1}H NMR spectra of (a) Br-Allyl-PIB-Allyl-Br and (b) OH-oTHF-PIB-oTHF-OH.

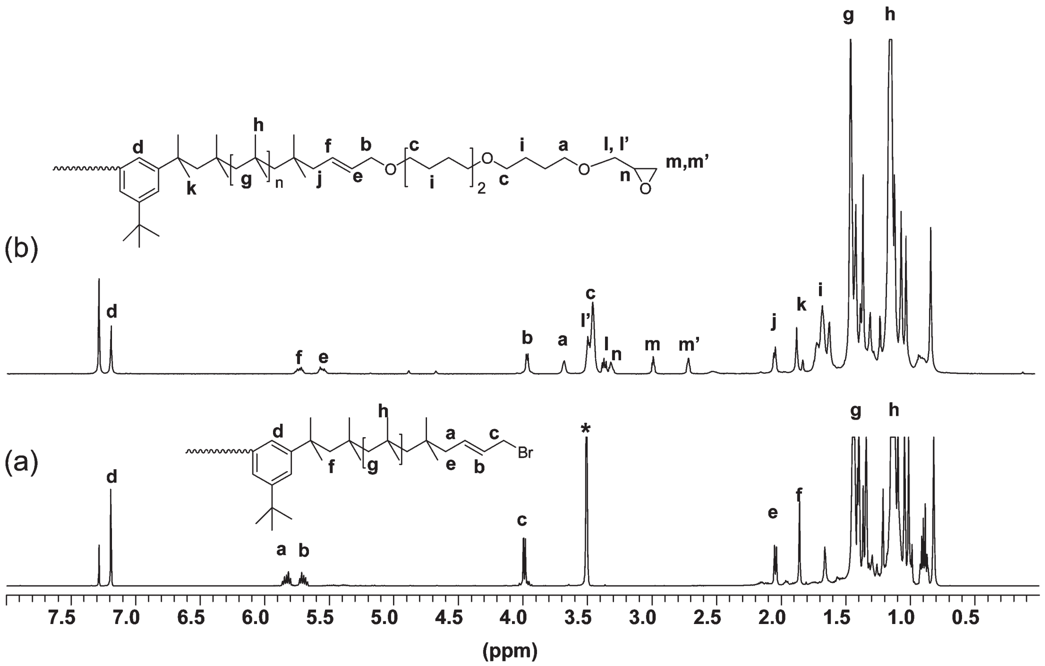


Figure 5. ^{1}H NMR spectra of (a) Br-Allyl-PIB-Allyl-Br and (b) EP-oTHF-PIB-oTHF-EP.

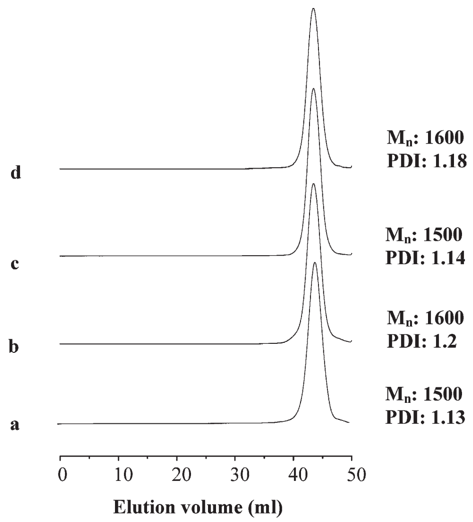


Figure 6. GPC-RI traces of (a) Br-PIB-Br, (b) EP-PIB-EP, (c) oTHF-PIB-oTHF, and (d) EP-oTHF-PIB-oTHF-EP.

with the increase in EP-PIB-EP content from 0 to 40 wt % (Table 1). The flexural strength also decreased by up to 73%.

Similar phenomena were also observed in systems prepared with EP-PIB-EP having M_n = 2500. The flexural modulus decreased from 1760 to 620 MPa as the DGEBA content decreased from 98 to 60 wt %, and the flexural strength also decreased by ~50% (Table 1). The phase-separated low modulus rubber domains impart reduction in modulus as well as flexural strength. At low concentration up to 15 wt % the soft phase (EP-PIB-EP) is well dispersed in the hard phase (DGEBA) and thereby flexibilizes the thermoset network. The SEM micrograph of fractured surface of network at 15 wt % of soft segments (EP-PIB-EP, Figure 1) clearly showed that PIB is completely dispersed in the hard phase forming a single coherent network. However, increasing the soft segment concentration above 15 wt % resulted in macrophase separations, which decreased the flexural properties drastically. The FESEM micrograph observed in Figure 3 (SEM micrographs of fractured surface with 40 wt % EP-PIB-EP) shows the presence of two macrophases in the network. Previous works on rubber modified epoxies support this observation.[20]

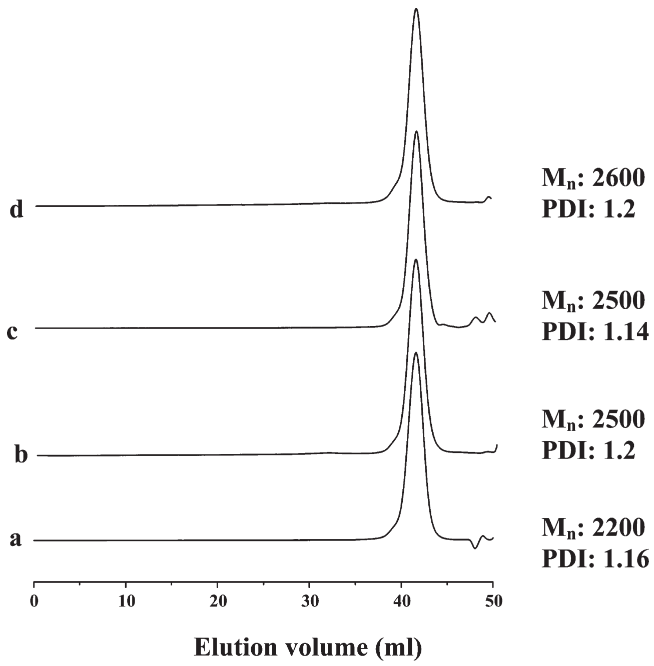


Figure 7. GPC-RI traces of (a) Br-PIB-Br, (b) EP-PIB-EP, (c) oTHF-PIB-oTHF, and (d) EP-oTHF-PIB-oTHF-EP.

Tensile Properties. The tensile strength of the resins continued to decrease with increase in PIB wt % from 2 to 40 in the

Scheme 3. Schematic Representation of Hybrid Cured Networks Comprising EP-oTHF-PIB-oTHF-EP (Soft Segments) and Bisphenol A Diglycidyl Ether (DGEBA) Cured with Triethylenetetramine (TETA)

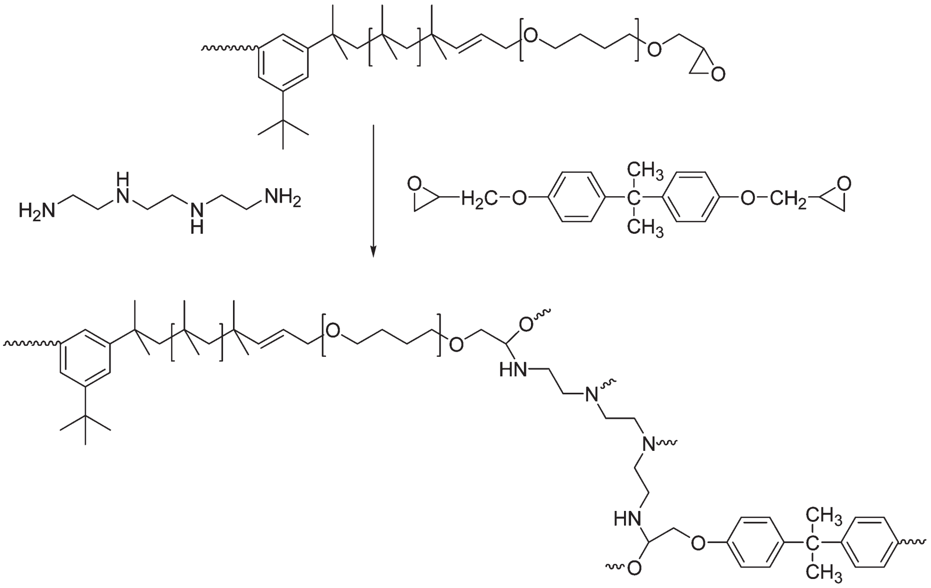


Table 2. Mechanical Properties of Modified Cured Hybrid Resins

sample	DGEBA (wt %)	PIB (wt %)	flexural modulus (MPa)	flexural strength (MPa)	fracture toughness (MPa m$^{0.5}$)	tensile strength (MPa)	elongation at break (%)
1[a]	98	2	1825	100	0.8	59	9
2[a]	95	5	1500	80	0.94	55	10
3[a]	90	10	1400	58	0.98	50	12
4[a]	85	15	1350	54	1.1	42	12
5[a]	80	20	1600	70	1.65	44	13
6[a]	60	40	1600	55	1.35	42	14
7[c]	70	0	1800	71	1.1	40	4
8[d]	70	0	1850	55	0.7	38	5
9[b]	98	2	1500	70	0.8	55	8
10[b]	95	5	1150	60	0.92	46	10
11[b]	90	10	1080	50	0.96	40	11
12[b]	85	15	1070	39	1.2	43	14
13[b]	80	20	1350	58	1.5	35	14
14[b]	60	40	1380	46	1.3	35	15

[a] Molecular weight of soft segment (EP-oTHF-PIB-oTHF-EP) M_n = 1600. [b] Molecular weight of soft segment (EP-oTHF-PIB-oTHF-EP) M_n = 2600. [c] DGEBA: 70 wt %; PEG-DGE: 30 wt %. [d] DGEBA[1]: 70 wt %; PEG-DGE: 30 wt %.

resin (Table 1). The ultimate tensile strength (UTS) continuously decreased from 70 to 19 MPa with an increase in EP-PIB-EP wt % from 2 to 40 wt % in case of the series of resins prepared using EP-PIB-EP having M_n = 1600. The elongation at break increased from 3 to 15% with an increase in soft segment (EP-PIB-EP) from 0 to 40% as expected. Generally, addition of a rubber modifier to a thermoset resin decreases the tensile strength significantly. A similar phenomenon was also observed by various authors when different rubber modifiers such as CTBN, ATBN, or ETBN were used for toughening epoxy resins.[11] The M_n of PIB segment has little effect on the tensile properties as the resins prepared with EP-PIB-EP (M_n = 2500) also exhibited similar change in UTS and elongation at break (Table 1). The sharp decrease in tensile strength with incorporation of such rubber modifiers is likely due to decrease in load-bearing capacity of the elastomer. The curing speed of DGEBA and PIB end modified epoxy may differ, thus causing internal stresses, which are responsible for failure on application of external load.

Fracture Toughness. The fracture toughness of the resins varied with the PIB wt % in the sample. In case of the series of resins prepared using unmodified PIB (EP-PIB-EP) segments (M_n = 1600 or 2500) the toughness increased from 0.75 to ~1.6 with an increase in PIB wt % from 0 to 15% (Table 1). This suggested that at ≤15 wt % EP-PIB-EP there is no macrophase separation with DGEBA and FESEM micrographs supported the fracture data as the fractured surface showed nanophase segregated spherical rubber domains with a diameter of 400−700 nm

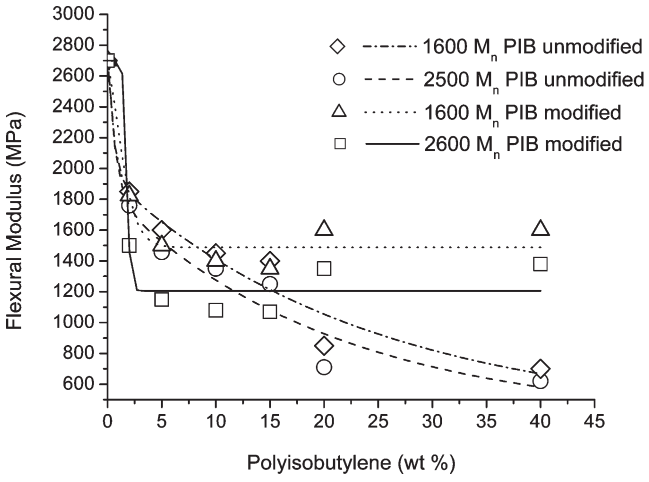


Figure 8. Flexural modulus of cured hybrid epoxy resin at different PIB wt %.

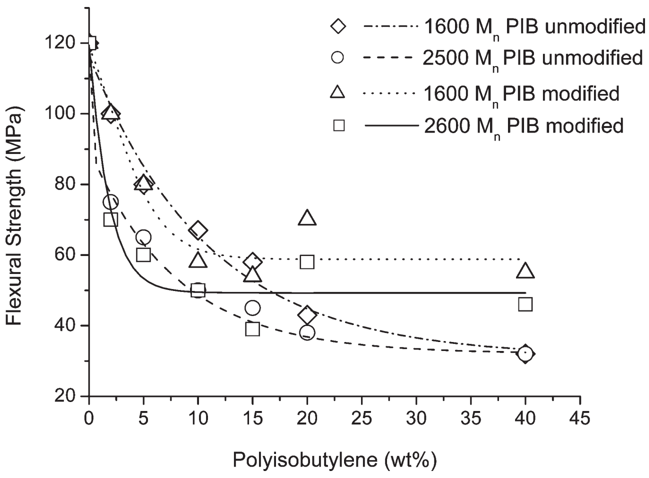


Figure 9. Flexural strength of cured hybrid epoxy resin at different PIB wt %.

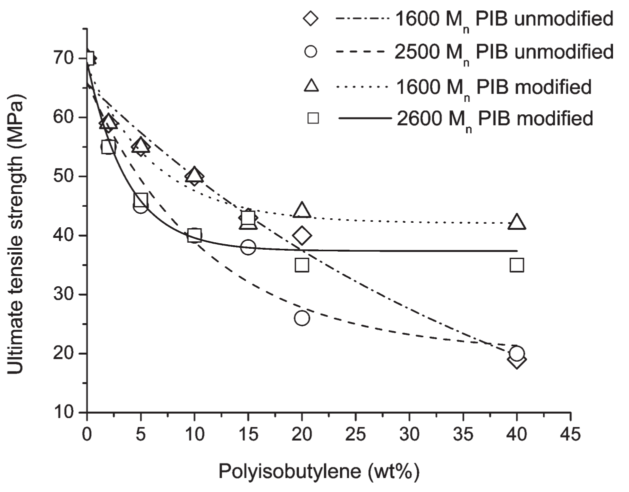


Figure 10. Ultimate tensile strength (MPa) of cured hybrid epoxy resin at different PIB wt %.

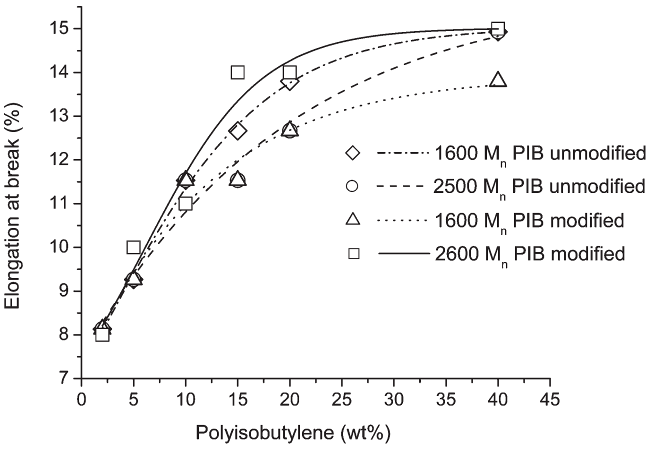


Figure 11. Elongation at break (%) of cured hybrid epoxy resin at different PIB wt %.

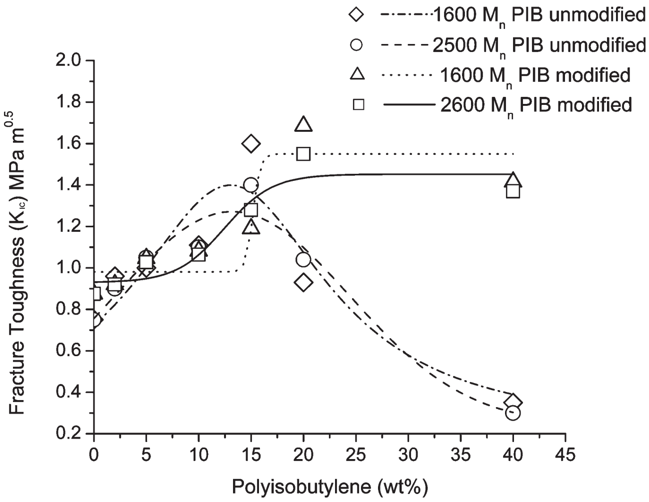


Figure 12. Fracture toughness of cured hybrid epoxy resin at different PIB wt %.

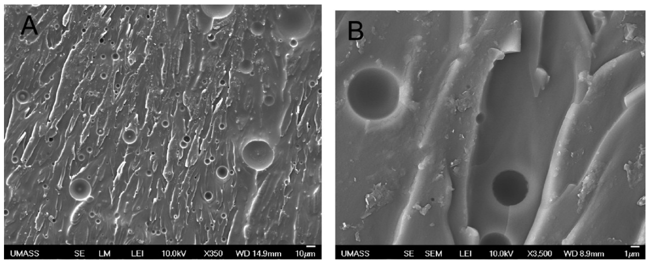


Figure 13. SEM micrograph of fractured surface of cured hybrid epoxy resins: (A)15 wt % of EP-oTHF-PIB-oTHF-EP (soft segment) at 350×; (B) 15 wt % of EP-oTHF-PIB-oTHF-EP (soft segment) at 3500×.

(Figure 1). The fracture toughness decreased dramatically to 0.93 and 0.3 with further increase of PIB content to 20 and 40 wt %, respectively. This large decrease in fracture toughness indicated macrophase separation, and in fact, the FESEM images of the fractured surface of the resin prepared by blending 20 wt % EP-PIB-EP and 80 wt % DGEBA showed large domain sizes (1000−1500 nm, Figure 2) and broad size distribution. The large rubber particles obtained at high rubber content would result in high stress intensities around the particle, thereby decreasing

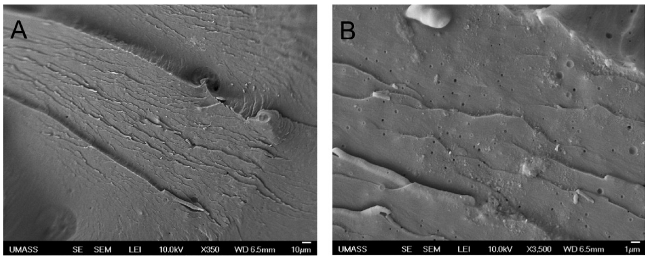


Figure 14. SEM micrograph of fractured surface of cured hybrid epoxy resins: (A) 20 wt % of EP-oTHF-PIB-oTHF-EP (soft segment) at 350×; (B) 20 wt % of EP-oTHF-PIB-oTHF-EP (soft segment) at 3500×.

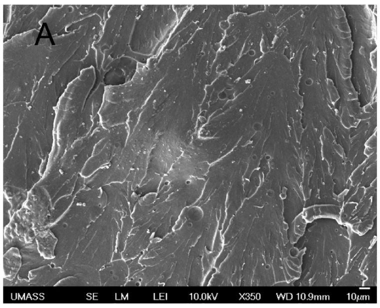


Figure 15. SEM micrograph of fractured surface of cured hybrid epoxy resins: 40 wt % of EP-oTHF-PIB-oTHF-EP (soft segment) at 350×.

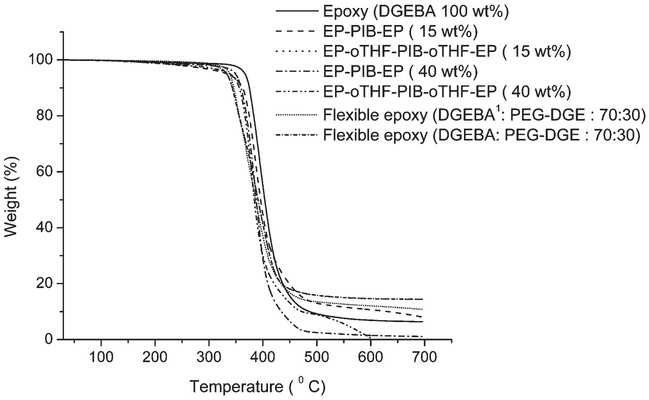


Figure 16. TGA curves of various cured hybrid epoxies.

the toughness.[21] At even higher EP-PIB-EP content of 40 wt % the two phases became immiscible, and two separate layers were observed which can be clearly seen in the FESEM micrograph (Figure 3).

Synthesis of Modified Epoxy Telechelic PIB (EP-oTHF-PIB-oTHF-EP). To increase miscibility, Br-allyl-PIB-allyl-Br was end-modified with HO-oTHF-OH under basic conditions to produce the oTHF end-capped PIB (HO-oTHF-PIB-oTHF−OH). The synthetic Scheme 2 summarizes the different transformations to obtain modified epoxy telechelic PIB. ^{1}H NMR spectroscopy showed the disappearance of peaks at 4.0, 5.7, and 5.75 ppm assigned to the bromomethylene and bromoallylmethine protons and new signals at 3.95, 5.54, and 5.72 ppm assigned to $-\mathrm{CH{=}CHC}\mathit{H}_2-$, $-\mathrm{CH{=}C}\mathit{H}\mathrm{CH}_2-$, and $-\mathrm{C}\mathit{H}\mathrm{{=}CHCH}_2-$ appeared, indicating quantitative conversion (Figure 4b). New peaks at 3.6, 3.48, and 1.75 ppm appeared for $-\mathrm{O(CH_2CH_2CH_2C}\mathit{H}_2\mathrm{O}-)$, $-\mathrm{O(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2)_2\mathrm{O}-$, and $-\mathrm{O(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)_2O}-$. In the ^{13}C NMR spectrum signals at 72 and 70.5 ppm for $-\mathrm{CH{=}CHCH_2O}-$ and $-\mathrm{O(CH_2CH_2CH_2CH_2)_2O}-$ were observed, whereas $-\mathrm{O(CH_2CH_2CH_2CH_2OH)}-$ and $-\mathrm{O(CH_2CH_2CH_2CH_2)_2O}-$ resonated at 60.0 and 26.0 ppm, respectively (Supporting Information Figure 1). The HO-oTHF-PIB-oTHF-OH was treated with epichlorohydrin in the presence of NaH to obtain the corresponding epoxy end-capped macromer (EP-oTHF-PIB-oTHF-EP). Quantitative conversion was achieved in 12 h under reflux. ^{1}H and ^{13}C NMR spectroscopies were used to characterize the product (Figure 5b and Supporting Information Figure 2). The ^{1}H NMR spectrum shows the appearance of new signals at 3.5 and 3.4 ppm which was assigned to $-\mathrm{OC}\mathit{H}\mathit{H}_2$ $\mathrm{(CHCH_2O)}$, whereas the methylene group of the epoxy ring also showed two peaks at 2.9 and 2.7 ppm (Figure 5b). In the ^{13}C NMR spectrum the olefinic carbons resonated at 131 and 129.5 ppm, and new signals for $-\mathrm{OCH_2(CHCH_2O)}$, $-\mathrm{O(CH_2CH_2CH_2CH_2)_2O}-$, $-\mathrm{CH_2}$-$\mathrm{(CHCH_2O)}$, $-\mathrm{CH_2(CHCH_2O)}$, and $-\mathrm{O(CH_2CH_2CH_2CH_2)_2O}-$ appeared at 71.0, 60.0, 51.0, 48.0, and 26.0 ppm, respectively (Supporting Information Figure 2). The GPC-RI traces of the macromonomers were similar to the precursor Br-Allyl-PIB-Allyl-Br, indicating that the end groups are unaffected during the synthesis and purification (Figures 6 and 7). The thermal curing of the above macromers and DGEBA in various weight proportions were carried out in presence of triethylenetetramine at 100 °C to obtain flexible uniform films (Scheme 3).

Flexural Properties. With the modified epoxy end-capped PIB based macromer (EP-oTHF-PIB-oTHF-EP, $M_n = 1600$) the resulting networks exhibited a marginal decrease in the flexural modulus from 1825 to 1600 MPa with the increase in EP-oTHF-PIB-oTHF-EP content from 2 to 40 wt % (Table 2). Similarly, the flexural strength decreased from 100 to 55 MPa with an increase in wt % of soft segment (EP-oTHF-PIB-oTHF-EP) from 2 to 40 wt % (Table 2). The flexural modulus decreased ~25% by adding 15 wt % of EP-oTHF-PIB-oTHF-EP. Interestingly, upon a further increase of the soft segment content the flexural modulus remained unchanged. The flexural strength followed a similar trend, first decreasing by 50% by adding 15 wt % of EP-oTHF-PIB-oTHF-EP, and remained unaffected with further increase of rubber content. The series of resins prepared using the modified PIB macromer (EP-oTHF-PIB-oTHF-EP, $M_n = 2600$, Table 2) also exhibited similar properties.

At ≤ 15 wt % of rubber both EP-oTHF-PIB-oTHF-EP and EP-PIB-EP exhibit similar flexural properties. Above 15 wt % of EP-PIB-EP there is a drastic decrease in flexural property due to macrophase separation. In comparison improved the miscibility of resulting EP-oTHF-PIB-oTHF-EP with DGEBA resulted in better flexural properties at the same rubber content (Figures 8 and 9). The flexural modulus and strength of PEG-DGEBA based resins commercialized by Dow Chemical Co. exhibited similar properties to that of PIB modified DGEBA networks.

Tensile Properties. The tensile strength of the networks continuously decreased with an increase in PIB wt % in the resin (Table 2). The M_n of the soft segment had no discernible effect on the tensile properties of the cured resin. As expected, the elongation at break increased from 3% to 15% with an increase of EP-oTHF-PIB-oTHF-EP content from 0 to 40 wt % (Figure 11).

The UTS vs PIB wt % plot showed two distinct patterns for the resins prepared with unmodified and modified PIB segments (Figure 10). Up to 15 wt % both the modified and unmodified PIB behave similarly since macrophase separation is absent.

Table 3. Temperature of Degradation (T_d) of Various Cured Epoxy Resins

sample	DGEBA (wt %)	PIB (wt %)	PEG-DGE[c] (wt %)	DGEBA[d] (wt %)	temp of degradation (T_d)[e] (°C)
1	100	0	0	0	366
2	85	15[a]	0	0	332
3	85	15[b]	0	0	328
4	60	40[a]	0	0	344
5	60	40[b]	0	0	338
6	0	0	30	70	333
7	70	0	30	0	335

[a] Molecular weight of soft segment (EP-PIB-EP) M_n = 1600. [b] Molecular weight of soft segment (EP-oTHF-PIB-oTHF-EP) M_n = 1600. [c] Poly(ethylene glycol) diglycidyl ether (PEG-DGE, DER 732, Aldrich). [d] Bisphenol A diglycidyl ether (DER 332, Fluka). [e] Thermal degradation temperature (T_d), the onset temperature at which 5 wt % of weight loss occurs.

By further increasing the EP-PIB-EP wt % in the epoxy network the UTS decreases considerably due to immiscibility. This decrease is absent with EP-oTHF-PIB-oTHF-EP attributed to the increased miscibility. Thus, elongation at break up to 15% and UTS up to 40 MPa can be achieved. The tensile strength of the PIB modified epoxies is similar to that of PEG-DGEBA based resins commercialized by Dow Chemical Co., whereas the elongation of PIB modified epoxies are superior to PEG-DGEBA resins.

Fracture Toughness. The fracture toughness of DGEBA based resins increased with incorporation of PIB soft segments up to 15 wt % as shown in Table 1.[22] However, upon further increase of PIB content macrophase separation occurred, and the fracture toughness decreased. Hence, to avoid large scale macrophase separation with DGEBA at ≥20 wt % of PIB segments, modified PIB based macromers (EP-oTHF-PIB-oTHF-EP) were used.

As expected, in the case of resins prepared with modified PIB segments (EP-oTHF-PIB-oTHF-EP) the fracture toughness increased from 0.75 to 1.65 MPa $m^{0.5}$ at 20 wt % of PIB and remained almost constant with further increase in PIB wt % up to 40 (Table 2). The enhancement in fracture toughness may be explained on the basis of change in morphological character. With rubber concentration at 20 wt %, FESEM micrographs (Figure 14) showed spherical domain of elastomer with approximately 200−300 nm diameter. These elastomeric particles in nanodimensions are well dispersed within the cross-linked matrix that is responsible for the improvement of fracture properties. The fracture toughness decreased marginally to 1.35 MPa $m^{0.5}$ with further increase in soft segment to 40 wt %. The FESEM of fractured surface revealed micrometer size distributed rubber domains of 1−3 μm diameters (Figure 15). The fracture toughness vs PIB wt % plot (Figure 12) showed the M_n of the soft segments had minimal effect on the fracture toughness of the cured resin. Interestingly, the unmodified or modified PIB-DGEBA cured resins exhibited superior fracture toughness than PEG-DGEBA resins of Dow Chemical Co.

Thermogravimetric Analysis (TGA). According to previous literature, incorporation of rubbery segments affects thermal stability of rigid networks.[14] To estimate the change in thermal stability of the networks, upon incorporation of PIB based soft segments TGA was conducted for all the compositions under a nitrogen atmosphere. Interestingly, all the samples exhibited similar degradation behavior (Figure 16). The degradation temperatures (T_d) of all the samples are listed in Table 3. The T_d = 366 °C of epoxy resin with DGEBA:PIB = 100:0 (wt:wt) was similar to the $T_d \approx 340$ °C of hybrid epoxy resins (DGEBA:PIB = 60:40, wt:wt). Further, the thermal stabilities of resins prepared with EP-PIB-EP (T_d = 344 °C) and EP-oTHF-PIB-oTHF-EP (T_d = 338 °C) were also similar, indicating the end-modification of PIB has little effect on T_d of resulting materials. PEG-DGEBA based resins commercialized by Dow Chemical Co. also exhibited similar degradation characteristics (Table 3).

CONCLUSION

Flexible coatings involving epoxy end-capped PIB segments and DGEBA can be prepared using triethylenetetramine as the curing agent under thermal conditions. With EP-PIB-EP ≤ 15 wt % good fracture properties with adequate tensile and flexural properties can be obtained. However, cured resins with more than 20 wt % EP-PIB-EP possess inadequate mechanical properties due to macrophase segregation of PIB and DGEBA segments. Because of increased miscibility of EP-oTHF-PIB-oTHF-EP with DGEBA the cured products are flexible, transparent and possess adequate mechanical properties along with improved fracture toughness even with 20−40 wt % EP-oTHF-PIB-oTHF-EP. The PEG-DGEBA flexible resin (Dow Chemical Co.) possess inferior fracture toughness and elongation at break compared to PIB modified epoxies, whereas the tensile and flexural properties of PIB modified epoxy networks are comparable to commercial epoxy thermosets. TGA analysis indicated that upper use temperature of these flexible epoxy hybrid coatings are not sacrificed at the cost of superior mechanical properties.

ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{13}C NMR spectra of HO-oTHF-PIB-oTHF-OH and EP-oTHF-PIB-oTHF-EP; integrated proton NMR spectrum of HO-oTHF-PIB-oTHF-OH and Br-PIB-Br. This material is available free of charge via the Internet at http://pubs.acs.org.

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