Polyisobutylene-Toughened Poly(methyl methacrylate). 1. Synthesis, Characterization, and Tensile Properties of PMMA-*l*-PIB Networks

Joseph P. Kennedy* **and G. Caywood Richard**

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

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ABSTRACT: A series of new polyisobutylene (PIB)-toughened poly(methyl methacrylate) (PMMA) networks have been prepared in which the PIB domains are covalently bonded to a PMMA matrix. The synthesis involves free-radical solution copolymerization of methyl methacrylate (MMA) and methacrylate tritelechelic PIB [PIB-(OCOC(CH_3)=CH_2)$_3$, PIB-(MA)$_3$]. Three different molecular weight ($\bar{M}_n$) PIB-(MA)$_3$s (6500, 18 000, and 37 000 g/mol) were prepared by living carbocationic polymerization followed by end functionalization and copolymerized with various amounts of MMA. A two-stage cure was developed to ensure the retention of microdomain morphology. Selective solvent extraction indicates that these materials represent a new type of semisimultaneous interpenetrating network. Differential scanning calorimetry and dynamic mechanical thermal analysis support a two-phase morphology for the compositions synthesized. The effect of PIB $\bar{M}_n$ and weight percent (wt %) on tensile strength, yield strength, elongation, Young's modulus, and relative toughness was studied by uniaxial tensile testing. Shear yielding is the dominant energy-absorbing mechanism in the networks containing 6500 g/mol PIB-(MA)$_3$, while crazing dominates in those containing 18 000 g/mol PIB-(MA)$_3$. Networks containing 37 000 g/mol PIB-(MA)$_3$ are relatively weak. The networks containing 18 000 g/mol PIB-(MA)$_3$ showed optimum behavior, with the 20 wt % composition behaving the toughest.

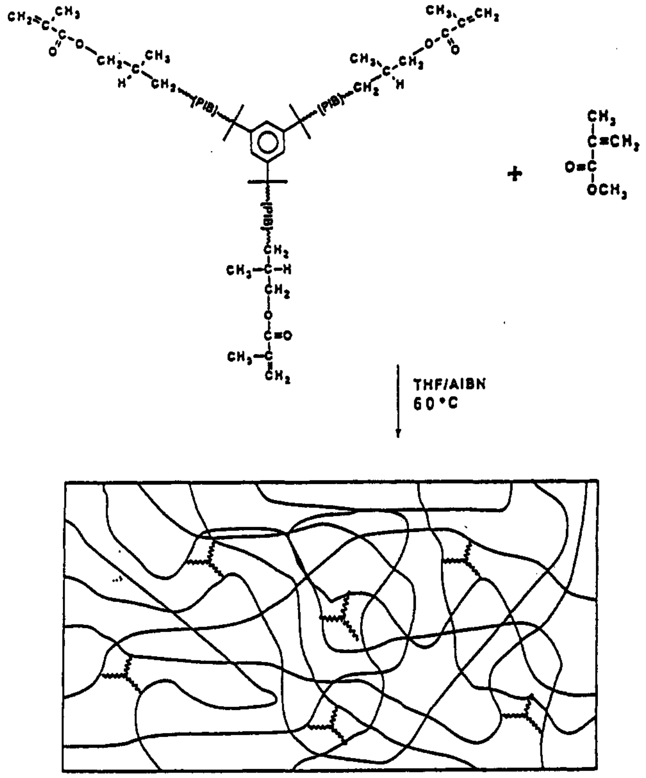
Introduction

The recent discovery of living carbocationic polymerization[1,2] led to the synthesis of controlled molecular weight ($\bar{M}_n$) polyisobutylene (PIB) telechelics. Functionalization of such materials to methacrylate-terminated PIBs[3-5] allows for the synthesis of unique rubber-toughened poly(methyl methacrylate) (PMMA) networks in which the PIB is covalently bound to the PMMA matrix. A series of PIB-toughened PMMAs containing 5, 10, 20, and 30 wt % of each of three different $\bar{M}_n$ PIB-(MA)$_3$s was prepared was prepared by copolymerization of PIB-(MA)$_3$ with MMA. Scheme I helps to visualize the ingredients employed and the network which results. With these products in hand, the effect of PIB $\bar{M}_n$ on the mechanical properties of rubber-toughened PMMA networks could be investigated.

The objective of rubber-toughening of glassy plastics is to convert stiff, brittle materials into tougher products. The presence of the rubber allows for a new energy-dissipative mechanism (i.e., crazing or shear yielding) to occur.[6] The elastomeric component must meet several requirements for effective toughening:[7] Its glass transition temperature (T_g) must be well below the use temperature of the glassy matrix to allow it to function as a stress concentrator. It must be immiscible with the matrix to allow dispersion with a well-controlled morphology. Interface adhesion between the elastomer and the glassy phase must be strong; otherwise, significant energy dissipation will not occur. Finally, the microdomain morphology must be preserved. Conventionally, this has been done by cross-linking the elastomer phase once the desired morphology is obtained. However, for a saturated elastomer (such as PIB) other means of morphology preservation must be developed.

The goal of this research was the synthesis and characterization of a series of new PIB-toughened PMMAs suitable for biomedical use. In these materials, PIB is covalently attached to the PMMA matrix. A trifunctional initiator was used to produce trifunctional PIB-(MA)$_3$s allowing three points of attachment of PIB to the matrix for high interface strength. According to results of selective solvent extraction, our materials are semisimultaneous interpenetrating networks (semi-SINs).[8,9] Both PMMA homopolymer and a network composed of PMMA-*linked by*-PIB (PMMA-*l*-PIB)[10] are formed simultaneously. The effect of PIB-(MA)$_3$ $\bar{M}_n$ and wt % on tensile properties and relative toughness ("work of rupture") of these PMMA-*l*-PIB semi-SINs was determined.

Scheme I



Experimental Procedures

Materials. The synthesis and purification of methacrylate-capped PIBs have been described.[1-5] THF was refluxed and distilled from CaH_2 under a N_2 atmosphere. MMA (Aldrich

Table I
Characterization Data for PIB-$(MA)_3$ Macromonomers

		$\bar{F}_n$	
$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	^{1}H NMR	FTIR
6 500	1.32	2.90 ± 0.15	2.93 ± 0.10
18 500	1.28	2.85 ± 0.15	2.92 ± 0.10
37 000	1.26	2.75 ± 0.15	2.80 ± 0.10

Chemical Co.) was washed twice with 5% aqueous, NaOH and twice with H_2O, dried over $MgSO_4$, refluxed, and partially vacuum distilled from CaH_2 before use. 2,2′-Azobis(isobutyronitrile) (Eastman Chemical Co.) was recrystallized from CH_3OH. Methylmagnesium bromide, 3.0 M in diethyl ether (Aldrich) was used as received. Reagent grade hexanes, THF, and acetone were used for extraction studies.

To assure that samples suitable for tensile testing could be obtained, a Teflon mold of 5.5 in. × 3.5 in. × 0.5 in. was used to form rectangular plates of about 1-mm thickness for each composition. From these plates, a minimum of three tensile test pieces were machined with the following dimensions: 11.5-cm overall length, 6.3-cm neck length, 6-mm neck width. Uniaxial tensile testing was conducted on an Instron tensile tester, employing an extensometer for accurate elongation measurement. Test conditions: gauge length, 2.54 cm; strain rate, 1.27 cm/min. Relative toughness was calculated as work of rupture (U) (i.e., area under the stress–strain curve in J/m^3) using the cut-and-weigh method.

Procedure. 1,3,5-Tris(2-methoxy-2-propyl)benzene (tricumyl methyl ether, TCME) was prepared according to a two-step route as opposed to the three-step route previously described.[11] 1,3,5-Triacetylbenzene (Aldrich) was converted to 1,3,5-tris(2-hydroxy-2-propyl)benzene by Grignard reaction as follows: A THF solution of 1,3,5-triacetylbenzene was added to methylmagnesium bromide in diethyl ether (80% excess of Grignard reagent per functional group). The addition rate was controlled to allow a mild reflux of ether. After stirring overnight, the thick suspension was hydrolyzed by addition to an ice/salt bath and stirred for 1 h. The resulting mixture was extracted five times with diethyl ether, the extract dried overnight, and nearly all solvent removed to provide crude 1,3,5-tris(2-hydroxy-2-propyl)benzene. This material was triturated in toluene, resulting in the precipitation of fine, white solids. Recrystallization from ethyl acetate at room temperature afforded 75% of pure product, mp 148–150 °C. This material was converted to TCME according to the established procedure.[11] The TCME prepared according to this route provided initiator efficiencies of 94% or greater.

The synthesis of narrow molecular weight distribution (MWD) three-arm star PIBs carrying *tert*-chlorine endgroups was carried out by living carbocationic polymerization.[1,2] This was followed by quantitative dehydrochlorination,[3] hydroboration/oxidation,[4] and esterification[5] to form PIB-$(MA)_3$s. Table I provides $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and functionality ($\bar{F}_n$) information for the three tritelechelic macromonomers prepared. Number-average end functionality ($\bar{F}_n$) was analyzed by ^{1}H NMR (Varian Gemini-200 instrument) and FTIR (Beckman FT100 instrument) spectroscopies. Tritelechelic macromonomer molecular weights were determined by GPC (Waters high-pressure instrument, Model 6000A pump) using a series of μ-Styragel columns (100, 500, 10^3, 10^4, 10^5 Å) calibrated against narrow MWD PIB standards, a differential refractometer (Model 410), and a WISP (710B) automatic sampler. Flow rate was 1 mL of THF/min. Further details have been described elsewhere.[12]

Copolymerization of PIB-$(MA)_3$s with MMA. The first stage of copolymerization was conducted in a 100-mL round-bottom flask under N_2. A series of 12 compositions were prepared using 5, 10, 20, and 30 wt % of each of the three different $\bar{M}_n$ PIB-$(MA)_3$s. A monomer concentration of 30 wt % in THF solution was employed. An initiator concentration of 0.5 mol % (based on total moles of MA functional groups) was used. PIB-$(MA)_3$, THF, MMA, and AIBN were codissolved in the flask and polymerized under stirring at 60 °C under N_2 until the onset of gelation. At this point, heating was discontinued and the sealed flask transferred into a N_2-flushed inert atmosphere bag containing a rectangular Teflon cavity mold (see Materials for mold specifications). The contents of the flask were poured into the mold, the mold was sealed, and the assembly was removed from the bag, clamped closed, and cured in a controlled-temperature curing oven at 55 °C for 72 h. The resulting plates of PMMA-*l*-PIB were allowed to dry slowly (several days) before removal from the mold, followed by vacuum drying at 70 °C for 5 days. In this manner, rectangular plates of PMMA-*l*-PIB suitable for machining into mechanical test specimens were obtained. Table II shows sample compositions and identification codes together with reagent concentrations employed in the preparation of the samples.

Table II
Synthesis of PMMA-*l*-PIB Semi-SINs[a]

	PIB-$(MA)_3$						
sample	$\bar{M}_n$ (g/mol)	wt %	PIB (g)	MA endgroup (mol × 10^4)	MMA (g)	MMA (mol)	AIBN (mol × 10^4)
6K5	6 500	5	0.745	3.44	14.16	0.141	7.07
6K10	6 500	10	1.476	6.81	13.30	0.133	6.58
6K20	6 500	20	2.896	13.36	11.61	0.116	5.85
6K30	6 500	30	4.285	19.78	9.98	0.100	5.00
18K5	18 000	5	0.745	1.24	14.16	0.141	7.07
18K10	18 000	10	1.476	2.46	13.30	0.133	6.58
18K20	18 000	20	2.896	4.92	11.61	0.116	5.85
18K30	18 000	30	4.285	7.38	9.98	0.100	5.00
37K5	37 000	5	0.745	0.60	14.16	0.141	7.07
37K10	37 000	10	1.476	1.21	13.30	0.133	6.58
37K20	37 000	20	2.896	2.24	11.61	0.116	5.85
37K30	37 000	30	4.285	3.37	9.98	0.100	5.00
PMMA					15.07	0.151	7.37

[a] 40 mL of THF employed as solvent in all cases.

Selective Solvent Extraction. For determination of free PIB, samples were swelled in THF overnight, air-dried overnight, and extracted with hexanes at room temperature for 48 h. The solvent was replaced with fresh hexanes after 24 h. For determination of PMMA, samples were swelled in THF overnight, air-dried overnight, and extracted with acetone at room temperature for 48 h. The solvent was replaced with fresh acetone after 24 h.

Differential Scanning Calorimetry (DSC). DSC was conducted on a Du Pont 910 DSC module using a Du Pont 9900 computer/thermal analyzer. Samples were vacuum-dried for 4 days at 130 °C. DSC thermograms were run by first preheating the sample to 135 °C for 5 min, rapidly cooling through the T_gs, and collecting data during the second heating run using a 10 °C/min heating rate. The midpoint method was used to obtain the T_gs.

Dynamic Mechanical Thermal Analysis (DMTA). DMTA was conducted using a Polymer Laboratories DMTA instrument. A dual cantilever bean testing mode was used. A heating rate of 4 °C/min, strain cycle frequency of 1 Hz, strain amplitude of 64 μm, and temperature range of −100 to 130 °C were employed. DMTA was conducted on samples containing the lowest amounts of the lowest $\bar{M}_n$ PIB-$(MA)_2$ to ascertain phase separation in these samples.

Results and Discussion

Copolymerization. The synthesis of PIB-toughened PMMAs requires the simultaneous copolymerization *and* cross-linking of an immiscible tritelechelic macromonomer/monomer system (see Scheme I). Therefore, several requirements have to be met to obtain the desired microdomain-separated two-phase system in which the rubber is covalently bound to the glassy matrix. First, the copolymerization conditions must be such that the PIB methacrylate endgroups are freely accessible. This can be accomplished by the use of a compatibilizing solvent that dissolves both reagents. Second, a sufficient PMMA matrix $\bar{M}_n$ must be achieved to obtain good mechanical properties. This is accomplished by controlling the monomer/initiator mole ratio in the system. Third, the tritelechelic macromonomer endgroup and the MMA must be of comparable reactivity. This condition was met by the use of the methacrylate endgroup. Finally, the

Table III
Extraction Results

sample	hexane extract (wt %)	acetone extract (wt %) total wt basis	PMMA basis	gel (wt %)
6K5	0.0	90.6	95.4	9.4
6K10	0.0	26.2	29.1	73.8
6K20	0.0	13.4	16.8	86.6
6K30	1.0	10.5	15.1	89.5
18K5	0.0	95.7	100.0	4.3
18K10	0.5	79.1	88.0	20.9
18K20	0.5	48.5	60.8	51.5
18K30	0.9	26.5	38.0	73.5
37K5	0.0	95.8	100.0	4.2
37K10	0.0	90.1	100.0	9.9
37K20	0.0	64.7	80.9	35.3
37K30	1.8	63.2	90.3	36.8

microdomain morphology must be preserved by suitable polymerization and cure conditions. Preliminary experiments in which the reagents were codissolved and placed in the mold for cure gave macroscopic phase separation. This indicated that the ultimate morphology must be developed and maintained prior to casting into the mold. The two-stage cure (prepolymerization and casting) provided a solution to this problem. Thus, the comonomers were first polymerized at 60 °C to the onset of gelation, and the viscous prepolymer syrup was then transferred to the mold under an inert atmosphere. With the 18K and 37K materials, the charge became opaque early on during the prepolymerization, suggesting that phase separation had occurred. Prepolymerization time varied depending on the $\bar{M}_n$ and wt % of the PIB-(MA)$_3$ "cross-linker" in the mixture. For the 6K series, prepolymerization times were 5–10 h. For the higher $\bar{M}_n$ series, overnight prepolymerization was required. The 6K series was transparent. Samples of the 18K series were transparent except for 18K30, which was slightly opaque. Samples of the 37K series were opaque. Evidently these compositions contain a range of PIB microdomain sizes that varies with PIB $\bar{M}_n$ and wt %. That the PIB domain size increases with increasing PIB $\bar{M}_n$ is also supported by the observation that the prepolymers of the 6K series remained transparent while those of the 18K series became opaque after a few hours of prepolymerization; the 37K series became opaque after 1 h of prepolymerization.

Selective Solvent Extraction. (a) Hexane Extraction. First, the quantity of PIB-(MA)$_3$ covalently bound to the PMMA matrix was determined by extracting with hexanes. Table III shows the results. Evidently, the covalent incorporation of PIB-(MA)$_3$ is enhanced by prepolymerization because macroscopic phase separation is avoided. Extraction of materials prepared without prepolymerization indicated that macroscopic phase separation reduces the accessibility of the PIB methacrylate endgroup, thereby lowering covalent incorporation of PIB into the matrix.

(b) Acetone Extraction. Second, the amount of gel present was determined by acetone extraction. According to the results, these materials consist of a two-component network (PMMA-*l*-PIB) throughout which PMMA homopolymer is interwoven. Table III illustrates the extraction results. PMMA homopolymer is present because of the low molar percentages of PIB-(MA)$_3$ used; therefore, the macromonomer functional group concentration was lower than that required for all polymerizing MMA to be incorporated into a network under these reaction conditions.

Table IV
T_gs of PMMA-*l*-PIB Semi-SINs by DSC

sample	PIB T_g (°C)	PMMA T_g (°C)	sample	PIB T_g (°C)	PMMA T_g (°C)
PIB6K	−63		18K20	−66	116
6K5		108	18K30	−66	115
6K10		117	PIB37K	−65	
6K20	−66	116	37K5		106
6K30	−66	108	37K10		106
PIB18K	−64		37K20	−66	121
18K5		120	37K30	−66	118
18K10		121	PMMA		115

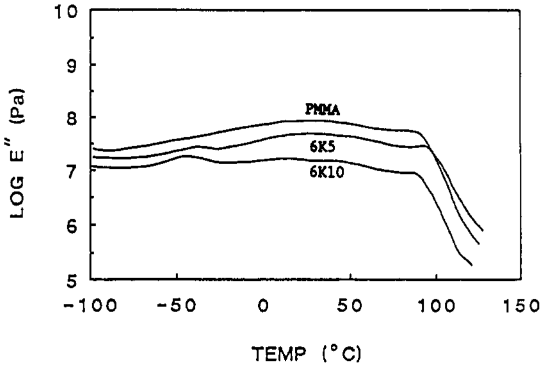


Figure 1. Loss modulus vs temperature curves for samples 6K5, 6K10, and PMMA.

According to Sperling's definition, if one of the components is in network form and the other is linear, a semi-interpenetrating network (semi-IPN) results.[9] If the homopolymer and macromonomer polymerize simultaneously and independently of each other, a semisimultaneous interpenetrating network (semi-SIN) is obtained.[9] Our semi-SINs differ from conventional semi-SINs because the PIB-(MA)$_3$ and MMA do not homopolymerize but copolymerize to form a network. Thus, a system composed of a two-component network (PMMA-*l*-PIB) plus a homopolymer (PMMA) is formed. This represents a new class of semi-SIN. According to the data in Table III, the series of PMMA-*l*-PIB semi-SINs prepared in this research ranges from nearly complete networks (6K30) to those containing very little network (37K5).

Differential Scanning Calorimetry. PMMA-*l*-PIB semi-SINs are expected to show domain separation due to the incompatibility of the PIB and PMMA phases. While two T_gs were expected, the simultaneous existence of PMMA homopolymer and PMMA-*l*-PIB network may broaden the T_g of the matrix. The results of DSC analyses are shown in Table IV. A T_g for PIB-(MA)$_3$ could not be discerned in materials containing only 5 and 10 wt % PIB-(MA)$_3$. The 20 and 30 wt % PIB-(MA)$_3$ samples showed two T_gs, similar in value to the homopolymers, indicating phase separation.

Dynamic Mechanical Thermal Analysis. DMTA was conducted to demonstrate that the materials containing 5 and 10 wt % of the lowest $\bar{M}_n$ PIB-(MA)$_3$ employed are also phase-separated. Figure 1 shows the loss modulus (E'') vs temperature traces for samples 6K5, 6K10, and a PMMA control.

The appearance of a small energy-absorbing transition (β-transition) at ca. −50 °C is seen in samples 6K5 and 6K10 but is not seen in the trace of the PMMA. Since the β-transition is due to the T_g of PIB, the samples containing PIB are phase-separated.

The combined DSC and DMTA results indicate that all of the PMMA-*l*-PIB semi-SINs synthesized exhibit phase separation.

Uniaxial Tensile Testing. After this new family of PIB-toughened PMMAs was synthesized and characterized, the first task was to determine fundamental material

Table V
Uniaxial Tensile Test Results[a]

sample	E (1%) (MPa)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)	U (J/m^3) × 10^{-6}
6K5	3390 ± 66	38.4 ± 0.8	32.9 ± 4.0	6.4 ± 4.7	2.15 ± 1.58
6K10	3080 ± 320	37.8 ± 0.3	30.0 ± 4.3	8.0 ± 3.0	2.65 ± 0.96
6K20	970 ± 49	23.6 ± 0.8	14.2 ± 0.1	20.1 ± 3.4	4.11 ± 0.75
6K30	1530 ± 186	22.6 ± 0.6	18.7 ± 4.6	5.0 ± 1.4	0.94 ± 0.30
18K5	3040	32.3 ± 0.2	32.2 ± 0.2	0.8 ± 0.1	0.202 ± 0.014
18K10	2880 ± 62	31.2 ± 0.3	28.8 ± 0.6	1.8 ± 0.8	0.485 ± 0.185
18K20	2450 ± 20	24.7 ± 0.1	18.4 ± 0.3	32.9 ± 9.5	6.76 ± 1.85
18K30	1660 ± 57	23.7 ± 0.3	16.7 ± 1.2	18.2 ± 1.7	3.61 ± 0.344
37K5	3240 ± 210	34.3 ± 1.8	34.3 ± 1.8	1.1 ± 0.5	0.340 ± 0.020
37K10	3000 ± 100	32.0 ± 0.5	31.9 ± 0.5	1.3 ± 0.5	0.347 ± 0.150
37K20	2220 ± 170	25.7 ± 0.2	25.1 ± 0.7	2.2 ± 0.1	0.489 ± 0.009
37K30	1770 ± 80	19.2 ± 0.4	19.0 ± 0.3	2.1 ± 0.4	0.362 ± 0.020

[a] Averages of at least three determinations.

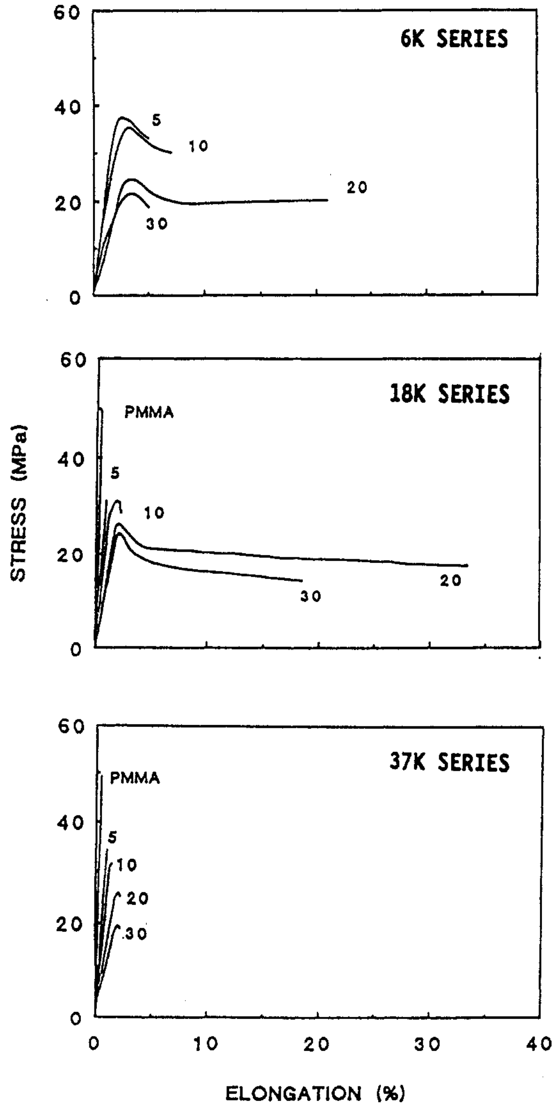


Figure 2. Stress–strain curves for (top) 6K, (middle) 18K, and (bottom) 37K series PMMA-l-PIB semi-SINs.

properties and relative toughness. The task of testing the toughest compositions in a formulation for a specific application would then follow (see subsequent paper in this series and ref 13).[13]

Table V lists Young's modulus at 1% elongation [E(1%)], yield strength (σ_y), ultimate tensile strength (σ_b), elongation at break (ϵ_b), and work of rupture (U) of the 12 materials prepared in this research. Representative stress–strain curves are in Figure 2. With regard to the 6K series, σ_y and E generally decrease with increasing PIB content (the reason for the low value obtained with 6K20 remains obscure). An optimum for ϵ_b and U was noted with sample 6K20. According to the results shown in Figure 2 (top), even 5 wt % of PIB-(MA)$_3$ of $\bar{M}_n$ = 6500 g/mol is sufficient to result in yielding. Increasing the PIB content to 20 wt % increases the extensibility. At some point between 20 and 30 wt % PIB a transition to weaker behavior occurs, as evidenced by the 5% elongation of sample 6K30. This suggests that the optimum PIB domain size for most effective toughening has been crossed on passing from 20 to 30 wt % PIB. Sample 6K30 also behaved as a weak and "overfilled" material when broken. The decrease in tensile properties of sample 6K30 suggests that at this composition we have possibly exceeded an optimum domain size and are approaching the onset of phase inversion where a semicontinuous PIB may exist, i.e., a composition in which some rubbery domains are connected. Small-angle X-ray scattering studies support this conclusion.[8] Such a morphology would not result in effective rubber toughening.

Visual observations on the behavior of these materials under uniaxial tensile test conditions also provided important clues as to the microstructure. Significant necking without stress whitening occurred rather early in the test. Since the samples were transparent, the presence of stress whitening would have been readily observed. This type of behavior is similar to that of a rubber-toughened PVC and suggests that, in the mechanism balance of shear yielding vs crazing, shear yielding may be the major energy-absorbing mechanism.

Tensile results for the 18K series are listed in Table V, with representative stress–strain curves shown in Figure 2 (middle). The σ_y, σ_b, and E(1%) values decreased with increasing wt % PIB. For maximum toughness and ϵ_b, an optimum was again noted at ~20 wt % PIB (18K20). This sample showed excellent toughness; it was ~60% tougher than sample 6K20 and ~85% tougher than sample 18K30.

With $\bar{M}_n$ = 18 000 g/mol PIB-(MA)$_3$, 5 wt % was insufficient to cause yielding, while yielding was observed with the 10% sample. While extensibility steadily improves with up to 20 wt % PIB, at some point between 20 and 30 wt % PIB a transition to a slightly weaker behavior is noted. Sample 18K30 exhibits only about 55% of the extension of sample 18K20 and behaves as a weak, overfilled material when broken.

As with the 6K series, these results support the possible onset of a semicontinuous PIB phase occurring at 30 wt % PIB. This conclusion is again supported by SAXS results.[8] The onset of opacity with sample 18K30 also indicates an increase in domain size.

The 18K series behaves differently under uniaxial tension from the 6K series. While stress whitening was exhibited by all samples, its extent was highest with 18K10 and 18K20, and the entire 2.5-in. sample neck slowly became completely white. This was followed by a highly localized small secondary necking immediately before rupture. This behavior is reminiscent of the behavior of ABS resins and suggests crazing to be the major energy-dissipative mechanism.

Results for the 37K series of opaque materials are listed in Table V, with representative stress-strain curves shown in Figure 2 (bottom). As with the other materials, a steady decrease in E, σ_y, and σ_b with increasing PIB content was noted. However, the ϵ_b and U values for this series were very low. At this $\bar{M}_n$, approximately 20 wt % PIB-(MA)$_3$ was necessary to produce yielding, in contrast to 5 and 10% with the 6K and 18K PIBs, respectively.

A slight optimum in toughness may be noted for sample 37K20; however, all samples of the series behaved poorly. When broken, these materials behaved weakly, as if overfilled with PIB. The dramatic drop in properties, combined with the opacity of the materials, indicates that the PIB domains formed with this $\bar{M}_n$ PIB are too large for effective toughening. SAXS results support this conclusion.[8] Evidently, the samples failed before significant crazing or yielding occurred.

Conclusions

Greatest toughness enhancement was found with samples containing 20 wt % PIB-(MA)$_3$ for all PIB $\bar{M}_n$s employed. Sample 18K20 showed surprisingly high toughness and provided the highest work of rupture of all the samples examined. Samples 6K20 and 18K30 behaved quite well; however, their strengths were lower than that of 18K20, most likely because of the lower PIB $\bar{M}_n$ and the higher wt % PIB, respectively.

The toughness of rubber-toughened glassy materials usually increases with increasing $\bar{M}_n$ of the rubber phase until a plateau is reached.[6] An optimum $\bar{M}_n$ region for toughness enhancement, like the one evidenced here for the 18K series, has not previously been observed. This maximum is most likely due to the novel manner in which these materials have been prepared (i.e., the use of end-functionalized rubber as macromonomer) as opposed to conventional rubber-toughened polymers. Because of this, it seems reasonable that the size [i.e., radius of gyration of one PIB-(MA)$_3$ molecule] may relate to the PIB domain size, thereby resulting in an optimum PIB $\bar{M}_n$ for toughness enhancement. In conventional solution polymerization systems, factors such as rate of stirring determine rubber domain size.

The tensile behavior of these PMMA-*l*-PIB semi-SINs indicates that while the $\bar{M}_n$ of the covalently bound PIB-(MA)$_3$ is a major factor in determining PIB microdomain size, the wt % PIB-(MA)$_3$ is also a factor. The effect of PIB microdomain size on mechanical properties is clearly illustrated by the results of uniaxial tensile testing.

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