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Mechanical properties of functionalized SEBS based inorganic hybrid materials

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Summary

Functional triblock copolymer [polystyrene-*b*-poly(ethylene-*ran*-butylene)-*b*-polystyrene] or SEBS elastomer was used to synthesize flexible organic-inorganic hybrid materials. Modification of elastomer was first achieved via nitration to produce nitrofunctionalized copolymer and its subsequent reduction forming aminofunctionalized copolymer. IR, ^{1}H NMR and ^{13}C NMR spectroscopic analyses provided an evidence of their modified structures. Modified SEBS based hybrid materials were then prepared through solution intercalation technique using layered silicates and in-situ polymerization of metal alkoxides via sol-gel process. In the first attempt, hybrids were prepared by the reinforcement of aminofunctionalized SEBS with organophilic montmorillonite to establish compatibility between organic matrix and inorganic phase. Reinforcement of the modified copolymer was secondly achieved by hydrolytic condensation of tetraethoxysilane using 3-glycidyloxypropyl trimethoxysilane (as a coupling agent) yielding hybrid materials. The chemical interactions between the organic polymer chains and the inorganic networks produced in-situ led to better properties of modified elastomer. Mechanical properties of thin transparent films of these hybrids were measured. Tensile strength of hybrids shows a considerable improvement over pure SEBS as well as aminofunctionalized copolymer in all the systems, which shows an increased interfacial interaction between organic and inorganic phases.

Introduction

Polymer intercalation from solution provides a novel synthetic approach for polymer-clay hybrid materials. It involves dispersion of preswelled clay in the polymer solution at molecular level and long polymer chains thus adjust themselves in the interlayer spaces of organophilic clay. An important prerequisite is to modify interparticle chemistry so as to promote organophilicity rather than the natural hydrophilic character. Proper polymer-clay solvent system and removal of solvent after formation of the composites is also desirable. Recently nanocomposites have received considerable interest due to enhanced properties which are presumably due to the synergistic effects of nanoscale structure and interaction of fillers with polymers. The

polyamide-6 and clay nanocomposites have been reported with improved heat resistance and toughness over ordinary polyamide-6 and used in polyamide timing belt covers [1]. Polystyrene-clay nanocomposites with 7.5-wt. % of organoclay showed the greatest improvement in mechanical properties as compared with pure polystyrene [2, 3]. The storage modulus of polypropylene-clay nanocomposites (intercalative polymerization and melt intercalation) with 8.1-wt. % clay was about three times that of the pure polymer [4-6]. The fracture toughness of epoxy-clay nanocomposites was also investigated [7, 8]. Polyimide-clay hybrid with only 2-wt.% of clay loading brought gas permeability to value less than half of that polyimide [9]. The sol-gel technique [10-17] has also been extended to synthesize hybrid materials by in-situ hydrolytic condensation [18] of metal alkoxides in the polymer matrices. Covalent bonding between organic phase and inorganic network can be introduced using coupling agent [19-21]. Polyimide-silica hybrids prepared by sol-gel process were reported with largest increase in rigidity and strength and also better mechanical properties at high temperatures [17, 22-27]. Tensile and impact performance of polypropylene and SEBS hybrid composites were investigated [28-33]. Zulfiqar and coworkers reported SEBS-g-MA based hybrids that showed increase in mechanical data [34]. Hybrids of titanium and zirconium oxides with poly (dimethylsiloxane) and poly (tetramethylene oxide) have also been reported [35, 36]. Huang and coworkers [37] synthesized hybrids of styrene-ethylene-butadiene-styrene (rubbery elastomer) with silica and titania via sol-gel process and reported higher storage modulus and better optical properties of the hybrids than pure elastomer.

In the present article, a thermoplastic triblock copolymer SEBS was modified via nitration to produce a yellow colored nitrofunctionalized-SEBS (SEBS-A) and subsequent reduction of SEBS-A yielded an orange brown colored aminofunctionalized-SEBS (SEBS-B). Spectroscopic techniques IR, ^{13}C NMR and ^{1}H NMR were employed to characterize both SEBS-A and SEBS-B. The aminofunctionalized copolymer i.e. SEBS-B was reinforced with inorganic fillers such as layered silicates (clay) and silica using solution intercalation and sol-gel techniques respectively. In this regard, copolymer based inorganic hybrids were prepared either dispersing organophilic montmorillonite or producing in-situ silica network through tetraethoxysilane in the matrix using tetrahydrofuran as a solvent. Thin transparent hybrid films were cast by evaporating the solvent. These films were further dried and analyzed for their mechanical measurements.

Experimental

Materials

SEBS elastomer with 28 % styrene content and molecular weight 118,000 supplied by Aldrich was used in the synthesis of hybrid materials. Tetraethoxysilane (TEOS) (99%), 3-glycidyloxypropyl tri-methoxysilane (GOTMS) (98%), anhydrous calcium chloride (99%), anhydrous calcium oxide (99%), anhydrous tin(II) chloride (99%) montmorillonite K-10 and dodecylamine (98%) procured from Aldrich were used as received. Benzophenone (99%), sodium metal (stored in kerosene), ethanol (99%) and hydrochloric acid (99%) obtained from Fluka were used as such. Sodium hydroxide (98%), methanol (99%), nitric acid (65%) and sulfuric acid (98%) supplied by Merck were used as received. Tetrahydrofuran (THF) supplied by Merck was used after drying by reflux procedure using sodium wire with benzophenone as an indicator.

Chloroform provided by Lab-scan was dried by the addition of anhydrous calcium chloride and distilling at constant boiling temperature. The filtrate was then refluxed and collected at 60°C and used in the present work.
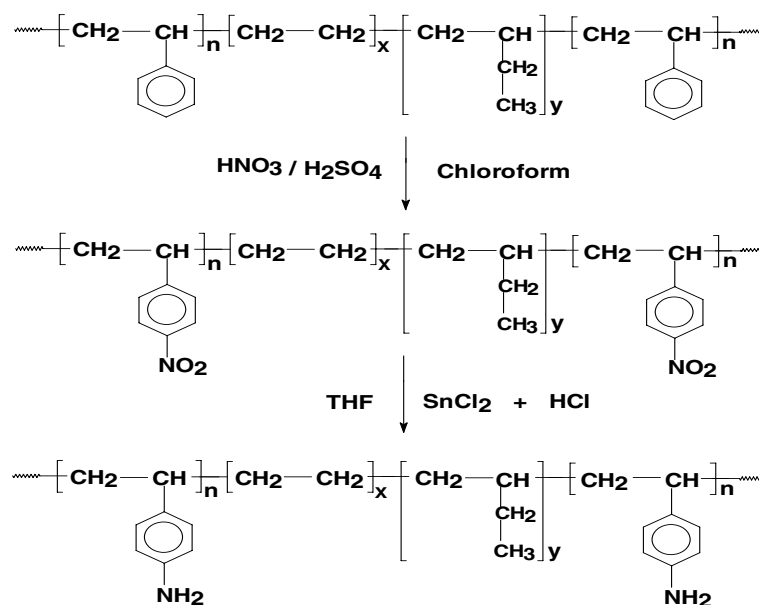
Functionalized SEBS synthesis

Nitrofunctionalization of SEBS

Nitration of SEBS elastomer first involves the dissolution of 10.0g of SEBS in 50.0ml of dried $CHCl_3$ with constant stirring for 24hr. Nitrating mixture (70.0ml fuming nitric acid and 30.0ml concentrated sulfuric acid) was added drop wise to the stock solution. The mixture was then cooled to 0°C in an ice bath and stirred at 60°C for 1hr till two layers became visible in the reaction container. A 30% (w/w) solution of NaOH was added to neutralize the mixture. The oily layer was washed with distilled water until the mixture became clear. The chloroform layer was poured into methanol. The bright yellow colored copolymer (SEBS-A) obtained was dried under vacuum for 36hr.

Aminofunctionalization of SEBS-A

SEBS-A (10.0g) was dissolved in 60.0g of dried THF with constant stirring for 24hr. Reducing mixture was prepared by dissolving 120.0g of anhydrous stannous chloride in 120.0ml of hydrochloric acid with stirring at 60°C. Copolymer solution and the reducing mixture were mixed and refluxed at 80°C for 2hr and then neutralized with 10% (w/w) NaOH. The orange brown polymer obtained (Scheme 1) was poured into methanol and dried under vacuum for 24hr.

**Scheme 1.** Synthesis of Aminofunctionalized SEBS

Composite synthesis

Modified SEBS and Clay Hybrids

Clay was intercalated using 8.82g of dodecylamine and 4.8ml of concentrated HCl in 100ml of distilled water. This solution was heated at 80°C. In a separate beaker, 20g of Na-montmorillonite was dispersed in distilled water at 80°C. This dispersed clay was added to the solution of ammonium salt of dodecylamine and the resulting mixture was vigorously stirred for 3hr at 60°C. The white precipitates were filtered, washed with 400ml of hot water and finally dried in vacuum oven at 60°C for 24hr. A stock solution of modified copolymer was prepared by dissolving 10.0g of SEBS-B in 50.0g of dried THF with constant stirring for 24hr. SEBS-B/clay hybrids (Scheme 2) were prepared by mixing different concentrations of intercalated clay (2-18 wt. %) to the stock solution. Thin transparent dark brown colored films were cast in teflon petri dishes by evaporating solvent at room temperature (25°C). Hybrid films having thickness (0.2-0.3mm) were dried at 45-50°C for at least 24hr. Finally these films were dried under vacuum for 72 hr to a constant weight.

Modified SEBS and Silica Hybrids

SEBS-B and silica unbonded hybrids were prepared by mixing TEOS concentration varied from 0-12.5 wt. % with appropriate amount of the stock solution. For the hydrolytic condensation distilled water and diluted HCl were added to the reaction
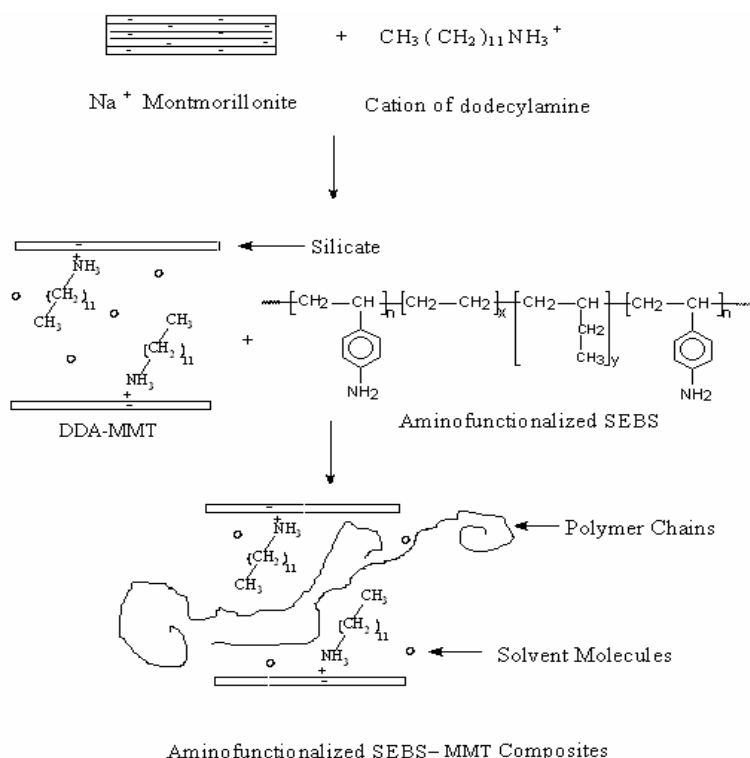
Scheme 2. Preparation of modified SEBS-Clay Hybrids
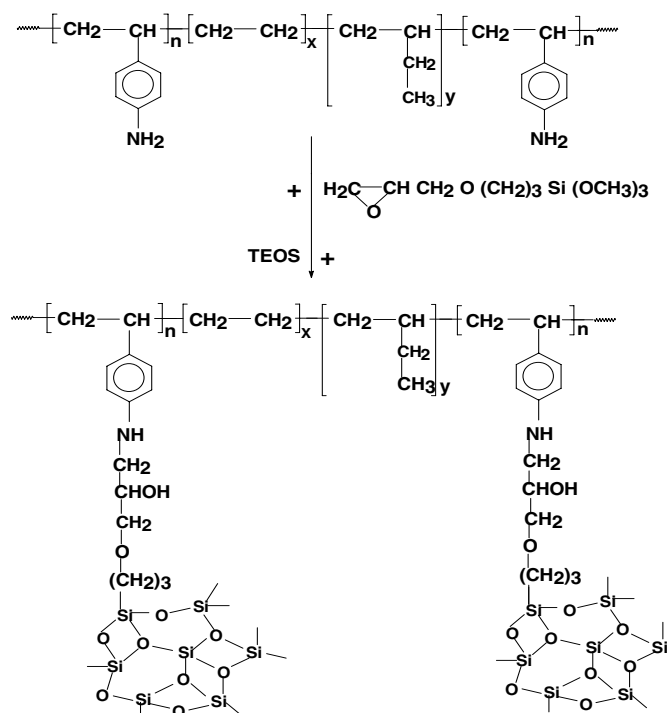
Scheme 3. Preparation of modified SEBS-Silica Hybrids

mixture. Partially cracked hybrid films were obtained. SEBS-B and silica chemically bonded hybrid films (Scheme 3) were also prepared by mixing 2.5-30 wt. % of TEOS to the copolymer solution with the addition of 1-wt. % of GOTMS to promote chemical interactions between copolymer matrix and silica. Transparent and flexible films of orange brown color were cast by solvent evaporation technique. Films were first dried at 55°C for 36hr and then under vacuum for 96hr to a constant weight.

Instruments and measurements

FTIR, ^{1}H NMR and ^{13}C NMR spectroscopic analyses were employed on thin films of block copolymers (SEBS-A and SEBS-B) to confirm their modified structures. Stress-strain response of the hybrid samples with varying thicknesses, widths and fixed lengths as adjusted by instrument was monitored according to DIN procedure 53455 having a crosshead speed of 5 mm/min using Testometric Universal Testing Machine M350/500. Standard procedures and formulae were applied to calculate various tensile properties including stress, strain, young's modulus and toughness.

Results and discussion

FTIR and NMR analyses of modified SEBS

FTIR spectrum (SEBS-A film): N=O asymmetrical vibration at 1521cm^{-1} and N=O symmetrical vibration at 1346 cm^{-1} indicates the presence of nitro group. Peak at
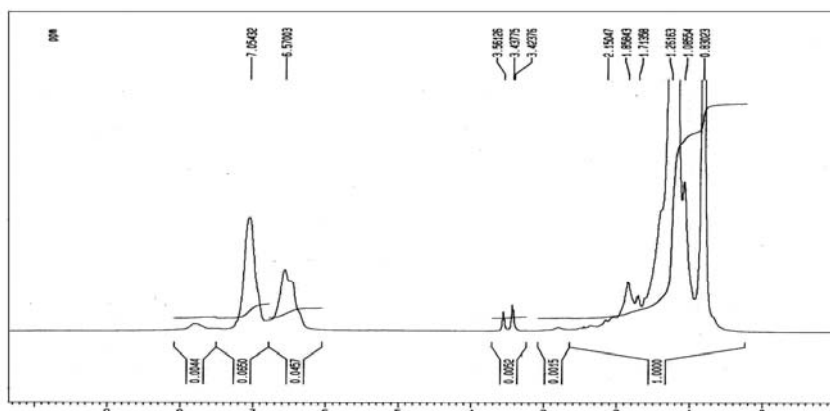
Figure 1. ^{1}H NMR Spectrum of SEBS-A

853 cm^{-1} shows 1,4-disubstitution on benzene ring. Aromatic C=C vibrations at 1599 and 1456 cm^{-1} were also observed. FTIR spectrum (SEBS-B film): N-H stretching vibration at 3375 cm^{-1} and N-H bending vibration at 1640 cm^{-1} were present. Aromatic amine (C-N) vibration was also observed at 1305 cm^{-1}. Peak at 826 cm^{-1} shows 1,4-disubstitution on benzene ring. Aromatic C=C vibrations appeared at 1601 cm^{-1} and 1374 cm^{-1}.

^{1}H NMR (SEBS-A in CDCl$_3$): Peaks for aliphatic protons were observed from 0.5-2 ppm and for aromatic protons in the region of 6-8 ppm (Figure 1). Appearance of two signals at 6.57 and 7.05 ppm confirms para substitution on benzene ring. ^{1}H NMR (SEBS-B in CDCl$_3$): Sharp peaks at 3.53 and 3.57 ppm for N-H were observed in this case (Figure 2). Para substitution on aromatic ring was confirmed by peaks at 6.42 and 7.04 ppm. Signals for aliphatic and aromatic protons appeared at 0-2.5 ppm and 6-8 ppm respectively.

^{13}C NMR (SEBS-A in CDCl$_3$): Peaks at 125.6, 127.6, 127.9 and 145.1 ppm for 1,4-disubstitution on aromatic ring were observed. Several intense peaks from 20-45ppm

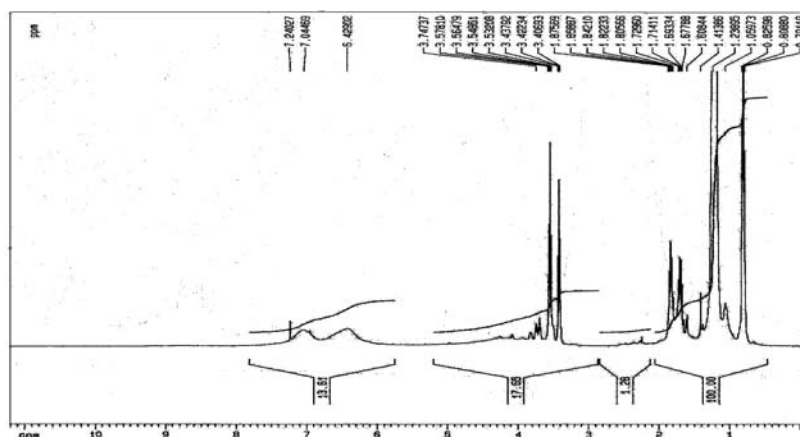**Figure 2.** ^{1}H NMR spectrum of SEBS-B

for sp^3 carbons and from 30-60 ppm for aliphatic carbons were also present. Similar peaks for ^{13}C NMR of SEBS-B in CDCl$_3$ were observed.

FTIR and ^{1}H NMR indicates the conversion of nitro group into NH$_2$ group, however, ^{13}C NMR is least helpful due to complex copolymer network. In copolymer and silica hybrids trimethoxysilane groups were introduced on SEBS-B using a coupling agent GOTMS. These groups are unstable and easily hydrolyzed to form silanol which made difficult to characterize trimethoxysilane functionalized SEBS by FTIR and NMR.

Mechanical analysis

The mechanical data obtained from these hybrid materials with 2 to 18-wt. % clay contents is given in Table 1. The stress-strain behavior for various proportions of clay loading shows a comparison of tensile properties of pure SEBS-B and SEBS-B/clay hybrids (Figure 3). The maximum stress was found to increase initially with increase in the clay contents, and then at 14-wt. % clay showed a maximum value of 15.41 MPa (relative to the 6.89 MPa of pure copolymer), which represents improvements in tensile strength. Further addition of clay decreases the strength because of increasing embrittlement. The elongation at break of the hybrid materials increases up to 10.67 with 14-wt. % clay contents in the matrix and then decreases. Modulus shows an increase up to 80 MPa with 10-wt. % clay relative to pure SEBS-B (43 MPa). Toughness of these hybrids shows increase in this specific property with increase in inorganic contents up to 12-wt. %. There is overall improvement in the mechanical properties in the present case up to 14-wt. %, presumably from the compatibility between the copolymer and clay. Maximum interaction between organic and inorganic phases can be achieved when silicate layers are fully dispersed homogenously through out the matrix. When the amount of clay in the polymer matrix increases beyond certain limits, the silicate sheets may stack together and form aggregates (large size particle). With the decrease in interlayer spacing of silicates compatibility between the organic chains and inorganic network also decreases. Hence these particles degrade the tensile properties of composites.

The stress-strain data for the copolymer-silica composite films having no interphase bonding (Table 2) were also analyzed. The maximum stress for the pure copolymer is

Table 1. Mechanical properties of SEBS-B-clay hybrid materials

Sample No.	Clay Contents (%)	Maximum Stress (MPa) ± 0.03	Maximum Strain ± 0.02	Young's Modulus (MPa) ± 0.02	Toughness (MPa) ± 0.05
1	0.0	6.89	4.47	43	10.93
2	2.0	8.53	5.65	55	31.64
3	4.0	9.06	5.84	59	32.46
4	6.0	10.14	7.75	67	47.24
5	8.0	10.47	9.86	76	53.16
6	10.0	12.79	9.89	80	66.36
7	12.0	13.78	10.05	71	68.45
8	14.0	15.41	10.67	66	52.45
9	16.0	9.21	7.12	53	41.17
10	18.0	8.65	5.87	39	31.77
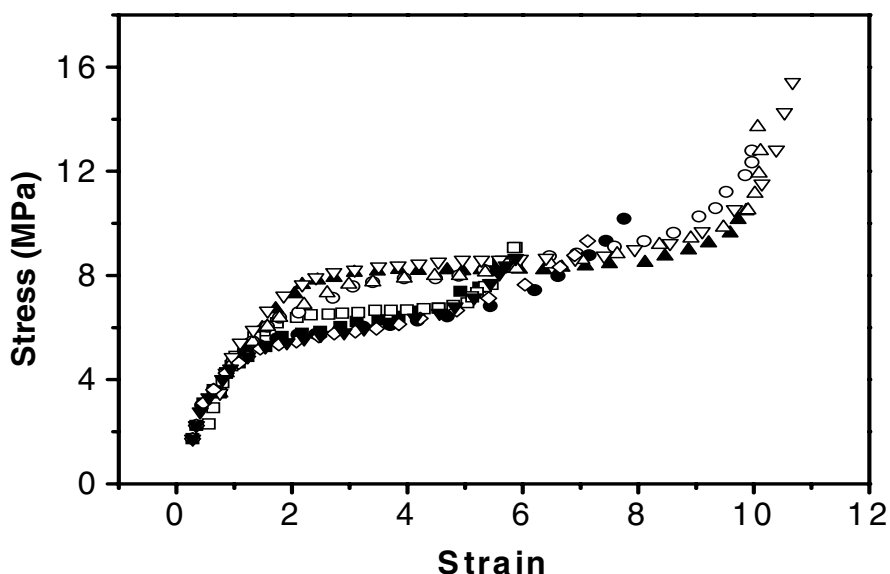
Figure 3. Stress-strain curves of SEBS-B-clay hybrids; clay % in matrix 0 (◆), 2 (■), 4 (□), 6 (●), 8 (▲), 10 (○), 12 (△), 14(▽), 16 (◇), 18.0 (▼).

Table 2. Mechanical properties of SEBS-B-silica hybrid materials

Sample No.	Silica Contents (%)	Maximum Stress (MPa) ± 0.03	Maximum strain ±0.02	Young's Modulus (MPa) ± 0.02	Toughness (MPa) ± 0.05
1	0.0	6.89	4.47	43	10.93
2	2.5	6.62	4.13	39	17.91
3	5.0	6.18	3.72	34	12.18
4	7.5	5.90	3.35	24	11.21
5	10.0	5.57	2.99	13	9.74
6	12.5	5.49	2.54	11	7.15

6.89 MPa that decrease up to 5.49 MPa with 12.5-wt. % of silica in the copolymer matrix. The stress values of this system show a decreasing pattern with increasing silica concentration. The elongation at rupture in pure copolymer is 4.47 that decrease with further addition of silica contents in the hybrids. The toughness values of hybrids also show no increase with respect to original SEBS-B. The pure copolymer had a value of tensile modulus 43 MPa that decreased to a minimum value 11 MPa with 12.5-wt. % silica. The results show no increase in the tensile strength of the hybrid materials relative to the pure SEBS-B polymer as illustrated in stress-strain curves of various concentrations of silica (Figure 4). The films of copolymer-silica hybrids containing silica up to 12.5-wt. % were partially cracked in texture. Further addition of silica beyond this concentration resulted in cracked and ruptured hybrid films which were not suitable for mechanical analysis.

In another related attempt, to improve the compatibility between disparate phases, 3-glycidyloxypropyltrimethoxy silane was used to act as coupling agent between
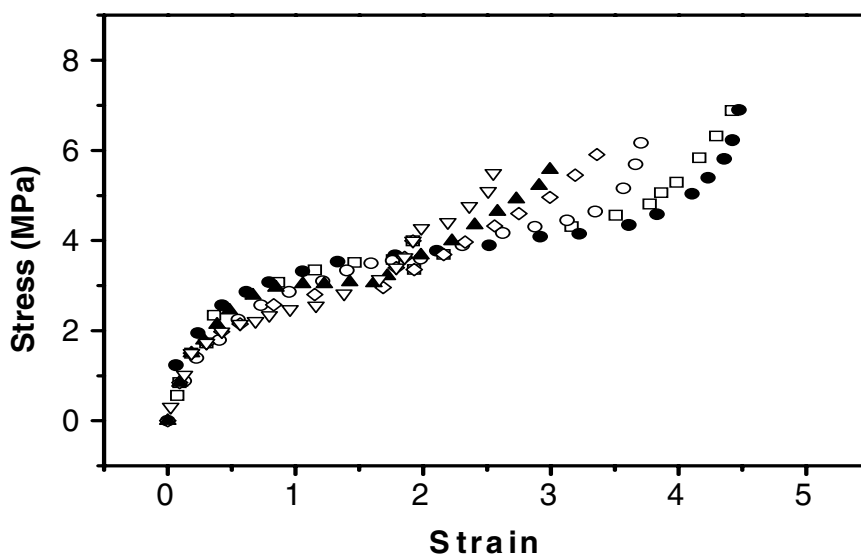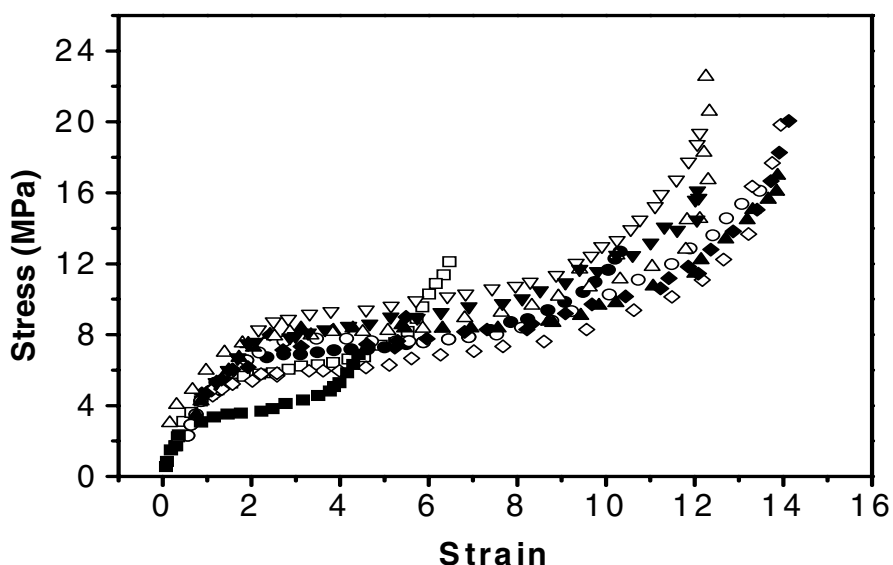
Figure 4. Stress-strain curves of unbonded SEBS-B-silica hybrids; silica % in matrix 0 (□), 2.5 (●), 5 (○), 7.5 (◇), 10 (▲), 12.5 (▽).

organic and inorganic phases. The copolymer thus was chemically combined to silica network structures produced in-situ by the hydrolysis/condensation of TEOS. These hybrid films of copolymer-silica containing up to 30-wt. % were light orange brown, transparent and not cracked. The variation of tensile strength for the copolymer-silica composite films having interphase bonding was studied as compared to unbonded system (Table 3 and Figure 5). The pure copolymer had a value of tensile modulus 43 MPa that increased to a maximum value 74 MPa with 2.5-wt. % silica. Maximum stress increases up to 22.55 MPa with 20-wt. % silica and then decreases up to 16.11 MPa with 30-wt. % loading of silica in the composites.

Increase in stress values of SEBS-B/silica bonded materials showed considerable improvement over pure copolymer. The elongation at break also increases with the

Table 3. Mechanical properties of bonded SEBS-B-silica hybrid materials

Sample No.	Silica Contents (%)	Maximum Stress (MPa) ± 0.03	Maximum Strain ± 0.02	Young's Modulus (MPa) ±0.02	Toughness (MPa) ±0.05
1	0.0	6.89	4.47	43	10.93
2	2.5	12.11	6.46	74	32.91
3	5.0	13.12	10.39	69	79.47
4	7.5	16.01	13.97	65	119.0
5	10.0	18.04	13.89	62	144.1
6	12.5	19.84	13.94	60	97.77
7	15.0	20.01	13.70	56	69.29
8	20.0	22.55	12.25	55	41.25
9	25.0	19.39	12.11	55	33.66
10	30.0	16.11	12.06	38	28.66

Figure 5. Stress-strain curves of bonded SEBS-B-silica hybrids; silica % in matrix: 0 (■), 2.5 (□), 5(●), 7.5 (○), 10(▲), 12.5(◇), 15(◆), 20(△), 25 (▽), 30(▼).

addition of silica contents up to13.94 with 15-wt. % then under goes a decrease with 30-wt. % addition of silica. Toughness of these materials were measured by integrating the area under stress-strain curves up to their maximum extension, which corresponds to the energy or work required for rupture. The values initially increase up to 144.1 MPa with 10-wt. % silica and then decreased to minimum value of 28.66 MPa for 30-wt. % silica contents. The better mechanical behavior of bonded SEBS-B/silica hybrids is due to the chemical linkage of silica network with organic matrix. Similar results were found in our previously studied research work [38]. However, the addition of large amounts of silica decreases tensile properties presumably due to the aggregation of silica particles which decreases the compatibility between silica and SEBS-B. The relative increase in tensile strength of copolymer-silica bonded hybrid system is much larger than that of the un-bonded system. The incorporation of a coupling agent results in better cohesion between the disparate phases and enhances tensile strength of the copolymer-silica bonded system as compared to un-bonded system. This may be due to the large number of bonding sites available due to the addition of coupling agent in the organic matrix, which are chemically combined with silica network and this inorganic network provides much reinforcement to hybrid materials.

Conclusions

Modification of a thermoplastic elastomer was successfully carried out to produce nitrofunctionalized SEBS and aminofunctionalized SEBS and their structures were confirmed by spectroscopic analyses. SEBS-B based organic/inorganic hybrid materials were synthesized by the dispersion of organoclay in the copolymer matrix. Hybrids from the same copolymer were also synthesized by incorporation of inorganic sol-gel networks (silica) into polymer structure with and without coupling agent as well. The transparency of the compatibilized hybrids was better relative to the

corresponding systems in which the inorganic network was not bonded to organic phase. Enhancement of mechanical properties in SEBS-B-clay hybrids over pure copolymer was observed. Improvement in mechanical strength was also observed in the chemically bonded SEBS-B/silica hybrid system as compared to un-bonded system. However, improvement in clay hybrids is less pronounced as compared to chemically bonded silica hybrids suggesting enhanced interactions among copolymer and inorganic network via covalent connections.

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