New Hybrid Materials Incorporating Tetrabutyl Titanate and Tetraethoxysilane with Functional SEBS Elastomer via the Sol–Gel Process: Synthesis and Characterization

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ABSTRACT: New flexible hybrid materials were prepared by incorporating amino-functionalized styrene–ethylene–butylene–styrene block copolymer (SEBS elastomer) with tetrabutyl titanate and tetraethoxysilane. SEBS was modified via nitration and subsequent reduction, giving the product SEBS II bearing amino groups in the hard segments. The trimethoxylsilane functionalization was then achieved by the addition of coupling agent, 3-glycidyloxypropyl trimethoxysilane (GOTMS) in the sol–gel processing. The hydrolytic condensation of these trimethoxylsilane groups on SEBS II with metal alkoxide led to the formation of covalent bonds between the organic polymer chains and the inorganic networks produced *in situ* to prevent macrophase separation, resulting in better optical properties. Electron micrographs clearly show that the size of dispersed inorganic phase can be reduced by the use of trimethoxyl silane functionalization. The results of dynamic mechanical analysis are also discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 853–860, 1997

Key words: hybrid material; sol-gel process; SEBS elastomer; tetrabutyl titanate; tetraethoxysilane; 3-glycidyloxypropyl trimethoxysilane

INTRODUCTION

The sol–gel process develops a novel route of preparing organic/inorganic hybrid materials with its associated mild conditions, such as low temperature and pressure.[1–4] As reported in previous publications, these novel materials lead to transparent systems that exhibit interesting property behavior. The composition and homogeneity of the hybrid materials can be controlled at the molecular level.[5] The incorporation of organic polymers (elastomers in particular) would be expected to impart flexibility to the inorganic glasses. On the other hand, the introduction of the inorganic component can improve the properties of organic polymers, such as hardness and modulus. These would make it possible to prepare crack-free structures which could be treated to obtain the hybrid materials in electrical, structural, or coating applications.

Basically, the sol–gel reaction can be viewed as a two-step network-forming process in which the metal alkoxide is hydrolyzed to produce an intermediate species, metal hydroxides. The three-dimensional network then forms by poly-

condensation of the hydroxyl groups.[6] Tetraethoxysilane (TEOS) has been employed in most cases as the inorganic component due to its relatively slow and controllable rate of reaction. For making multicomponent hybrid material, however, other types of metal alkoxides based on aluminum, titanium, and zirconium (all three of which show relatively fast hydrolysis rates) can be employed. The homogeneous product can be obtained with almost any composition, with some modification of the reaction procedure. Sur and Mark[7] have infused crosslinked polydimethylsiloxane films with TEOS and precipitated silica particles by means of the sol−gel process. Wilkes and colleagues[8,9] produced the hybrid polymer materials from solution mixture of TEOS with hydroxy-terminated polydimethxylsiloxane and poly(tetramethylene oxide)(PTMO). Furthermore, the hybrid systems based on ZrO_2−PTMO and TiO_2−PTMO can be synthesized.[10,11] The introduction of titania or zirconia into the hybrid system improves the modulus and stress at break of the hybrids.[12]

In this article, we describe the preparation of hybrid materials incorporating tetrabutyl titanate and TEOS with functionalized styrene-ethylene-butylene-styrene block copolymer (SEBS elastomer) by the sol−gel process. The sol−gel process produces the mixture of organic polymers and inorganic glasses. The compatibility of the two phases affects the properties of the materials. Macrophase separation can be prevented by promoting reactions or strong physical interactions between polymer chains and the inorganic network, either directly or via a coupling agent.[13−16] First the amino-functionalized SEBS elastomer was prepared, and then the functionalized SEBS polymer chains were covalently connected with the inorganic network by the sol−gel process. The hybrids with different SiO_2 contents and mixed TiO_2−SiO_2 components were obtained with various components. The properties of these materials were also determined.

EXPERIMENTAL

Materials

The SEBS elastomer used in this study was Kraton® G1650 (29 wt % styrene content, Shell Chemical Company, Canada). A high purity grade of 3-glycidyloxypropyl trimethoxysilane (GOTMS) was received from Nanjing University Chemical Fac-
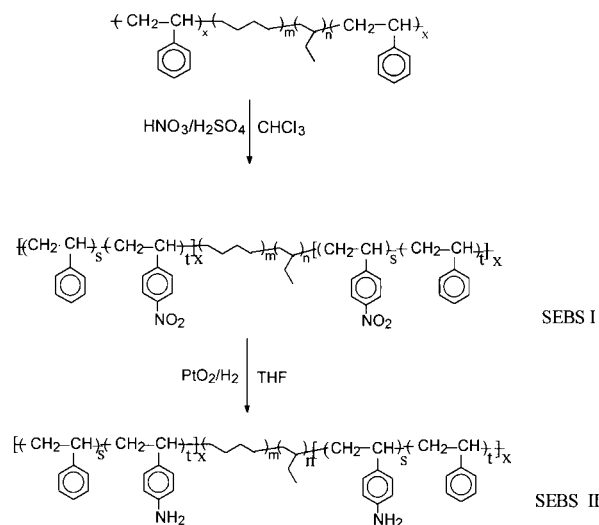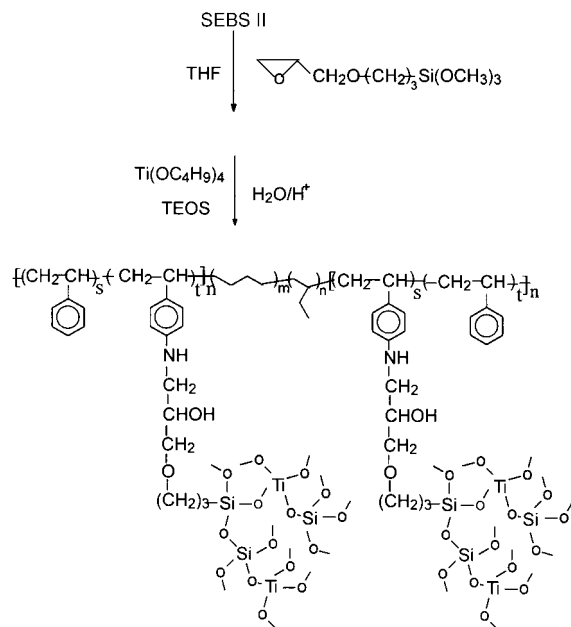

Scheme 1

tory, Nanjing, China. TEOS, $Si(OC_2H_5)_4$, was obtained from Union Chimque Belge, S.A., Belgium. Tetrabutyl titanate, $Ti(OC_4H_9)_4$, was purchased from Beijing 8994 reagent factory, Beijing, and used as obtained. Distilled water was used to induce the hydrolytic reactions in the alkoxysilane or tetrabutyl titanate component using HCl acid as catalyst and distilled tetrahydrofuran (THF) as solvent. Platinum dioxide (PtO_2) was prepared from hydrogen hexachloroplatinate (H_2PtCl_6) according to the procedures in literature.[17] The hydrogen hexachloroplatinate reagent was from Beijing Chemical Factory, Beijing. The other reagents were used as received.

Synthesis

Functionalization of SEBS Elastomer (Scheme 1)

Nitration of SEBS (SEBS I). To a solution of 30 g SEBS and 50 mL dry $CHCl_3$ was added dropwise the mixture of 9 mL fuming nitric acid and 9 mL concentrated sulfuric acid at room temperature. The mixture was stirred at temperatures below 55°C for 1 h. A solution of 5% (w/w) NaOH was then added to neutralize the mixture. The oil layer was washed by distilled water until the mixture became neutral. The $CHCl_3$ layer was poured into methanol and the yellow polymer was obtained and dried under vacuum. FTIR spectrum (film): 2959−2852 cm^{-1} (C—H stretching); 1601, 1454 cm^{-1} (C=C of benzene ring); 1520, 1378 cm^{-1} (NO_2 stretching); 860 cm^{-1} (para disubstituted benzene ring).

Scheme 2

^{1}H-NMR (ppm, in CDCl$_3$): 7.4–8.2 (aromatic H in *p*-NO$_2$ PSt), 7.1 and 6.5 (Ar-H in PSt), 2.5–0.8 (aliphatic H).

From both the integration ratio of *p*-NO$_2$ PSt over unsubstituted PSt and the elemental analysis results (Table I), the conversion of nitration is estimated at 77%.

Amino-functionalization of SEBS (SEBS II). To a solution of 60 g SEBS and 250 mL THF were added 10 mL acetic acid and 0.11 g PtO$_2$ catalyst. After degassing by nitrogen, a flow of hydrogen was led to the reactive solution, and the mixture was stirred at room temperature for 2 h. Then the Pt black in the solution was filtered out, and the solution was poured into methanol and filtered. The obtained polymer was dried under vacuum.

FTIR (film): 2959–2852 cm^{-1} (C—H stretching); 1601, 1454 cm^{-1} (C=C of aromatic ring).
^{1}H-NMR (ppm, in CDCl$_3$): 7.7–8.1 (*p*-NO$_2$ PSt); 7.1–6.5 (Ar-H for both PSt and *p*-NH$_2$ PSt); 3.5 (N—H); 2.5–0.8 (aliphatic H).

Based on the integration ratio and elemental analysis, the conversion of nitro groups to amino groups was estimated at 65%.

Preparation of Hybrid Materials (Scheme 2)

About 0.3 g SEBS II polymer was added to a 100-mL round-bottom flask followed by 12 mL dry

THF, and about 0.018 mL GOTMS was added after the SEBS II polymer completely dissolved in THF. It was refluxed for 1 h. After the mixture was cooled to room temperature, appropriate amounts of Ti(OC$_4$H$_9$)$_4$, TEOS, distilled H$_2$O, hydrochloric acid, and THF were added. By vigorous stirring for 30 min, a transparent homogeneous solution was obtained and poured into a glass mold. It was covered with parafilm for 20 days to allow the evaporation of the solvents and water produced in the condensation. All obtained hybrid samples are listed in Table II.

Nomenclature

The hybrid materials obtained from SEBS elastomer (SEBS II) with tetrabutyl titanate, TEOS, and mixed metal alkoxide, and the coupling agent GOTMS are expressed as SEBS-G/TiO$_2$, SEBS-G/SiO$_2$, and SEBS-G/TiO$_2$–SiO$_2$, respectively. The hybrid material incorporating SEBS elastomer with tetrabutyl titanate and TEOS in the absence of the coupling agent GOTMS is expressed as SEBS/TiO$_2$–SiO$_2$.

Measurements

The FTIR study was carried out on thin films by using a Nicolet Magna-IR 750 instrument. ^{1}H-NMR spectra of the samples were recorded using a Varian ARX400 spectrometer at room temperature with CDCl$_3$ as solvent and tetramethylsilane as internal standard.

The fracture surfaces of the hybrids were examined on an AMRAY 1910FE Field Emission Scanning Electron Microscope.

Dynamic mechanical behavior was studied in a DDV-II-EA (Toyo Baldwin Co., Japan) Dynamic Mechanical Thermal Analyzer at the temperature range of −150 to 150°C with a heating rate of 2°C/

Table I Elemental Analysis Results of SEBS, SEBS I, and SEBS II

Element	Percent Content (Experimental Data)		
	SEBS	SEBS I	SEBS II
C	87.16	68.85	79.47
H	12.70	10.05	11.33
N	0	2.47	2.80

Table II   Sample Preparation and Composition

Sample	$Ti(OC_4H_9)_4$ (wt %)	$Si(OC_2H_5)_4$ (wt %)	Product Description
SEBS-G/TiO$_2$	10	0	Transparent film
SEBS-G/TiO$_2$	20	0	Transparent film
SEBS-G/TiO$_2$	33	0	Transparent film
SEBS-G/TiO$_2$	50	0	Translucent film
SEBS-G/TiO$_2$–SiO$_2$[a]	6.2	3.8	Transparent film
SEBS-G/TiO$_2$–SiO$_2$[a]	12.4	7.6	Transparent film
SEBS-G/TiO$_2$–SiO$_2$[a]	20.5	12.5	Transparent film
SEBS-G/TiO$_2$–SiO$_2$[a]	31.0	19.0	Transparent film
SEBS-G/TiO$_2$–SiO$_2$[b]	15.3	4.7	Transparent film
SEBS-G/TiO$_2$–SiO$_2$[c]	9.0	11.0	Transparent film
SEBS/TiO$_2$–SiO$_2$[a]	12.4	7.6	Opaque film
SEBS-G/SiO$_2$	0	20	Translucent film

Preparation conditions: $[H_2O]/\{[Ti(OC_4H_9)_4] + [TEOS]\} = 1 : 1$ (mol. ratio); $[HCl]/\{[Ti(OC_4H_9)_4] + [TEOS]\} = 0.06$ (mol. ratio).
[a] $[Ti(OC_4H_9)_4] : [TEOS] = 1 : 1$ (mol. ratio).
[b] $[Ti(OC_4H_9)_4] : [TEOS] = 2 : 1$ (mol. ratio).
[c] $[Ti(OC_4H_9)_4] : [TEOS] = 1 : 2$ (mol. ratio).

min. A frequency of 3.5 Hz was selected for all the dynamic mechanical experiments.

RESULTS AND DISCUSSION

Functionalization of the SEBS Elastomer

For the purpose of minimizing the phase separation in the hybrid system, it is possible to incorporate functionalized organic polymers with metal alkoxides by *in situ* condensation of the functional groups in organic polymer chains and metal alkoxides.[14] The covalent bond can be formed in the interface of organic polymer chains and metal oxide networks to prevent macrophase separation in the hybrid system. In this work, the NH$_2$ group was first introduced onto polystyrene block of SEBS by a two-step reaction (i.e., nitration and reduction). The structure of the modified block copolymers has been confirmed by FTIR, ^{1}H-NMR, and elemental analysis (Table I). The amino group content in SEBS II was estimated from the integration ratio and elemental analysis data (Table I) and found to be about 0.17 mol/100 g polymer, indicating a low content of functional groups in the SEBS II polymer which would finally restrict the high inorganic content in the hybrid system. It has been found that 77% PSt repeating units have been substituted, mainly *para*-oriented due to the bulky effect, by nitro groups and that 65.6% nitro groups have been converted to amino groups. After reaction of epoxy groups in the coupling agent GOTMS with amino groups in SEBS II, trimethoxyl silane groups were introduced onto the SEBS II; these groups are unstable and are easily hydrolyzed to form silanol groups. This made it very difficult to characterize the trimethoxyl silane-functionalized SEBS by NMR. By *in situ* hydrolytic condensation of the silanol groups with metal alkoxides, the SEBS polymeric chain can be covalently connected with the metal oxide network.

Transparency of Resulting Hybrid Materials

The appearance of SEBS-G/TiO$_2$, SEBS-G/TiO$_2$–SiO$_2$, and SEBS/TiO$_2$–SiO$_2$ hybrid materials obtained are listed in Table II. As literature reported,[18] the optical transparency can be used as an initial criterion for the phase size. When the macrophase separation occurs in the system, the products will show opaque because of the light scattering of large domain size of the inorganic metal oxide. The SEBS-G/TiO$_2$ hybrid materials obtained are transparent films at low Ti(OC$_4$H$_9$)$_4$ contents up to 33 wt %. The Ti(OC$_4$H$_9$)$_4$ content is above 33 wt %, so the film becomes translucent due to the low content of amino-functional groups in the SEBS II polymer. On the other hand, all the SEBS-G/TiO$_2$–SiO$_2$ hybrids produce transparent films.

Table III   Solvent Extraction Results of the Hybrids

Sample	Gel (wt. %) (Anal.)	Gel (wt. %) (Theoretic)[a]	Film Appearance After Extraction for 2 Days
SEBS-G/SiO$_2$ (20 wt % TEOS)	15.2	5.8	Broken into fine particles
SEBS-G/TiO$_2$ [20 wt % Ti(OC$_4$H$_9$)$_4$]	54.1	4.7	Intact and transparent film
SEBS-G/TiO$_2$–SiO$_2$ {[Ti(OC$_4$H$_9$)$_4$] : [TEOS] = 1 : 1}[b]	64.7	5.1	Intact and transparent film
SEBS-G/TiO$_2$–SiO$_2$ {[Ti(OC$_4$H$_9$)$_4$] : [TEOS] = 1 : 2}[b]	45.9	5.3	Intact and transparent film
SEBS-G/TiO$_2$–SiO$_2$ {[Ti(OC$_4$H$_9$)$_4$] : [TEOS] = 2 : 1}[b]	57.4	5.0	Intact and transparent film
SEBS/TiO$_2$–SiO$_2$ {[Ti(OC$_4$H$_9$)$_4$] : [TEOS] = 1 : 1}[b]	5.7	5.1	Broken into fine yellow powder

The solvent for extraction: THF; extraction time: 2 days.

[a] The theoretical gel content is calculated based on the content of TiO$_2$ and SiO$_2$ in Ti(OC$_4$H$_9$)$_4$ and TEOS, respectively, and the SiO$_2$ content from the —Si(OCH$_3$)$_3$ groups of GOTMS is omitted.

[b] Whole inorganic alkoxide content: 20 wt %.

To elucidate the role of covalent bonding between organic polymer chains and inorganic networks: the control test was done by the hydrolytic condensation of metal alkyoxides in the solution of SEBS which does not bear amino groups, producing the SEBS/TiO$_2$–SiO$_2$ hybrid. The SEBS/TiO$_2$–SiO$_2$ hybrid was found to be opaque and nonhomogeneous because the macrophase separation does occur in this hybrid system. It is clearly shown that covalent bonding is essential to prevent macrophase separation in the non-hydrogen bonding hybrid systems.

Solvent Extraction Analysis of the Hybrids

A good solvent for the organic polymer should dissolve the free polymer and leave the inorganic oxides phase as particles or gel, so the solvent extraction of the hybrid materials can be used to determine the gel content in the hybrid system. If the two phases are connected with a covalent bond, the gel content in the hybrid materials would be high. The measured gel contents of the hybrid films are summarized in Table III. After extraction in THF for 2 days the SEBS/TiO$_2$–SiO$_2$ broke into small, opaque flakes; while the SEBS-G/TiO$_2$ and SEBS-G/TiO$_2$–SiO$_2$ samples maintained intact and transparent films. The gel content of the SEBS/TiO$_2$–SiO$_2$ film is about 5.7 wt %, which is approximately comparable to the theoretical value; those of the SEBS-G/TiO$_2$ and SEBS-G/TiO$_2$–SiO$_2$ samples are much higher than the theoretical values. This difference clearly shows the effect of the bond between the organic polymer chains and metal oxides network on the transparency of hybrid materials.

Morphology of the Hybrids

The fracture surfaces of the hybrid materials were observed by scanning electron microscopy (SEM), which can reflect morphology of the hybrids. The SEM micrograph in Figure 1 clearly shows the compatibility of SEBS-G/TiO$_2$–SiO$_2$ hybrid material prepared in the presence of GOTMS, which could brings about a covalent bond between the organic polymer chain and the inorganic network. It indicates that the macrophase separation has been prevented in this hybrid system. On the other hand, the aggregate metal oxide particles
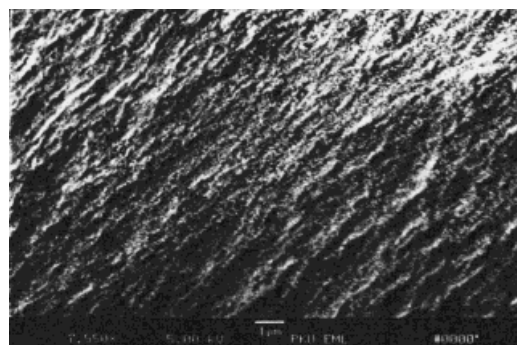

Figure 1   Scanning electron micrograph of fractured surface of SEBS-G/TiO$_2$–SiO$_2$ hybrid material. Whole alkoxide content: 33 wt %.
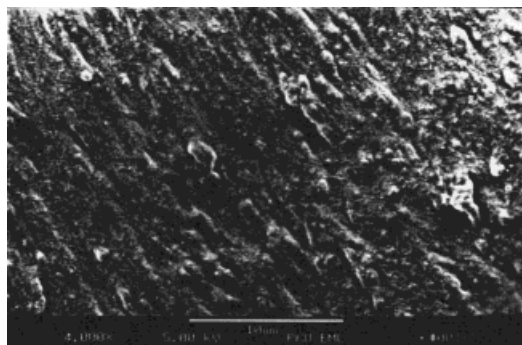
Figure 2 Scanning electron micrograph of fractured surface of SEBS/TiO_2–SiO_2 hybrid material. Whole alkoxide content: 20 wt %.

dispersed in the polymer matrix were observed in the SEM micrograph of the SEBS/TiO_2–SiO_2, the control sample of hybrid material (Fig. 2). Because of the existence of these particles with large domain size (about 0.5 μm), the hybrid shows optical opaque.

Figure 3 is the SEM micrograph of the SEBS-G/TiO_2 hybrid, in which the particles with large domain size cannot be observed. Unlike SEBS-G/TiO_2–SiO_2, there are many small particles dispersing in the polymer matrix, as can be seen in Figure 3 and much more clearly in the magnified micrograph (Fig. 4). Apparently, metal oxide particles with the domain size of about 49 nm disperse in the polymer matrix. The small size of the inorganic particles shows that no macrophase separation occurs in the SEBS-G/TiO_2 hybrid prepared in the presence of GOTMS.

Dynamic Mechanical Behaviors of the Hybrids

In accordance with the above discussion, the SEBS/TiO_2–SiO_2 hybrid would show macrophase
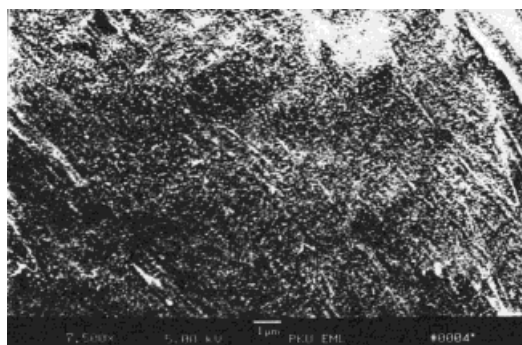

Figure 3 Scanning electron micrograph of fractured surface of SEBS-G/TiO_2 hybrid material. Alkoxide content: 20 wt %.
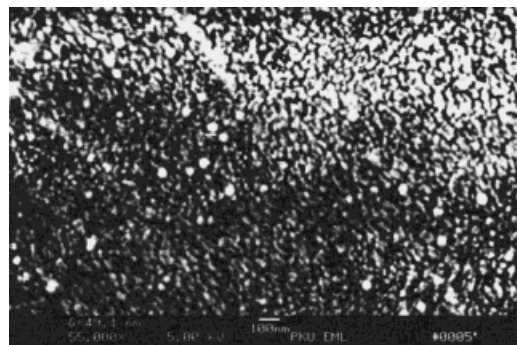

Figure 4 The magnified SEM micrograph of Figure 3.

separation in the hybrid system. Figure 5 is the plot of loss tangent over temperature of the pure SEBS elastomer and the SEBS/TiO_2–SiO_2 hybrid. Unlike the SEBS elastomer, the new broad damping peaks appear in the temperature regions from −70 to 70°C for the hybrid. This might arise from the interfacial effect of organic/inorganic phases.

The storage modulus data of the SEBS elastomer and the hybrids prepared in the presence of GOTMS are shown in Figure 6. The hybrids give higher modulus than the SEBS elastomer at low temperature due to the introduction of the inorganic component. However, at high temperature range from −25 to 100°C, the moduli of SEBS-G/TiO_2 and SEBS-G/SiO_2 hybrids are almost same as that of the SEBS elastomer. It is worth noting that, as literature reported,[19] the storage modulus of the hybrid material incorporating TEOS with the polymer is lower than that of the hybrid incorporating tetrabutyl titanate with the polymer. On
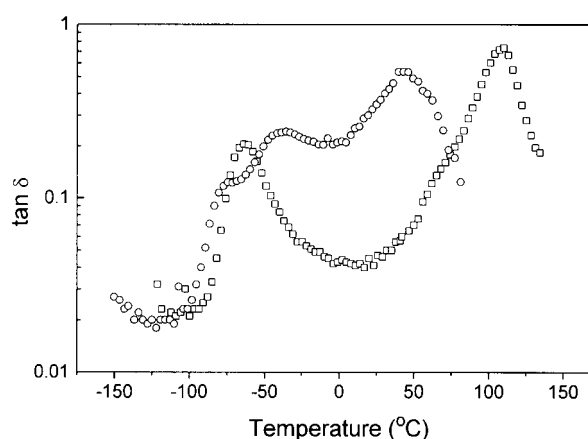

Figure 5 Loss tangent behaviors of (□) SEBS and (○) SEBS/TiO_2–SiO_2 hybrid.

the other hand, the amounts of SiO_2 content added to the SEBS-G/TiO_2 hybrid system would increase the storage modulus of the hybrid, but excessive SiO_2 content would decrease the modulus of the hybrid; for example, when the whole alkoxide content ($Ti(OC_4H_9)_4$ and $Si(OC_2H_5)_4$) does not change, the SEBS-G/TiO_2–SiO_2 hybrid material prepared at the condition of [Ti-$(OC_4H_9)_4$]:[$Si(OC_2H_5)_4$] = 2 : 1 has higher modulus than the hybrid prepared at the condition of [$Ti(OC_4H_9)_4$] : [$Si(OC_2H_5)_4$] = 1 : 2, and both hybrids have higher moduli than the SEBS-G/TiO_2 hybrid.

The loss tangent data of the hybrids are shown in Figure 7. Apparently, due to compatibility of the polymer chain and the inorganic network in the hybrid system, the hybrids prepared in the presence of GOTMS demonstrate much lower damping loss tangent value than the SEBS/TiO_2–SiO_2 (Fig. 5) in the range of −50 to 60°C but still much higher than the pure SEBS. The loss tangent transition, which locates at the temperature range of −76 to −74°C, is the glass transition of poly(ethylene-*co*-butylene) block segments which are not directly connected with metal oxide networks. All of the glass transition temperatures
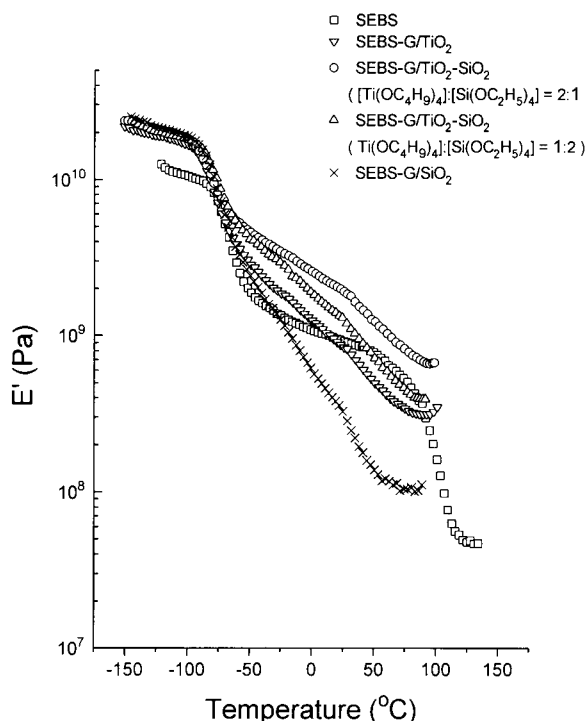
Figure 7 Loss tangent behaviors of (a) SEBS, (b) SEBS-G/TiO_2, (c) SEBS-G/TiO_2–SiO_2 ([$Ti(OC_4H_9)_4$] : [$Si(OC_2H_5)_4$] = 2 : 1), and (d) SEBS-G/TiO_2–SiO_2 ([$Ti(OC_4H_9)_4$] : [$Si(OC_2H_5)_4$] = 1 : 2). (Whole alkoxide content for all hybrids: 20 wt %.)

(T_gs) corresponding to poly(ethylene-*co*-butylene) segments are considerably lower than that of SEBS elastomer, 64°C. This can be attributed to the metal oxide networks' effect of making polystyrene and poly(ethylene-*co*-butylene) block segments completely immiscible, owing to the covalent connection of PSt segment with metal oxide networks. The hybrid samples broke when the temperature reached 80–100°C. This made further measurement impossible, and showed that the tensile strengths of the hybrids at temperatures near 100°C are not as good as pure SEBS.

CONCLUSIONS

A new hybrid material incorporating the functional SEBS elastomer (SEBS II) with tetrabutyl titanate and TEOS via the sol–gel process was successfully prepared. In order to form the chemical covalent bond between the polymer chain and the inorganic network to prevent the phase separation in the hybrid system, the coupling agent GOTMS was added to the reaction mixture. These hybrid materials were found to have good optical transparency over the pure SEBS elastomer.

In the SEBS/TiO_2–SiO_2 hybrid, the solvent extraction result shows that all the polymer chains are physically entrapped within the inorganic network and that the gel content is approximately equal to the actual inorganic oxide content. The

Figure 6 Storage modulus behaviors of SEBS and hybrids. (Whole alkoxide content: 20 wt %.)

percents of gel content in the SEBS-G/TiO$_2$–SiO$_2$ hybrids are much higher than the theoretical values because of formation of chemical covalent interaction between the organic polymer chain and the inorganic network.

The introduction of the coupling agent into the hybrids prevents the formation of inorganic oxide particles with large domain size. This results in a homogeneous material. The storage modulus of the SEBS-G/TiO$_2$ hybrid is higher than that of the SEBS-G/SiO$_2$ hybrid, and the addition of small amounts of SiO$_2$ to the SEBS-G/TiO$_2$ hybrid system increases the storage modulus of the hybrid. Due to incorporation of the inorganic network, the SEBS-G/TiO$_2$ and SEBS-G/TiO$_2$–SiO$_2$ hybrids are found to have higher damping loss tangent values than that of SEBS elastomer over the temperature range of two T_g transitions of SEBS.

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