End Functionalization of Styrene–Butadiene Rubber with Poly(ethylene glycol)–poly(dimethylsiloxane) Terminator

Eunkyoung KIM,[†] Eunha LEE, Insun PARK,[*] and Taihyun CHANG[*]

*Advanced Materials Division, Laboratory 7, Korea Research Institute of Chemical Technology,
P. O. Box 107, Yusung, Taejeon 305–600, Korea*
[*]Department of Chemistry, Pohang Univerity of Science and Technology, Pohang 790–784, Korea

ABSTRACT: A polar polydimethylsiloxane terminator was prepared and reacted with living copolymer anion of styrene and butadiene, to synthesize end-functionalized styrene–butadiene rubber (SBR). As a polar functional terminator, poly(ethylene glycol)-poly(dimethylsiloxane) block copolymer (PEG-PDMS) containing a chlorosilyl moiety at one chain end (**1**) was synthesized by two-step hydrosilylation. End capping of poly(styrene–butadiene) living anion with PEG-PDMS terminator (**1**) afforded polymers with polar poly(dimethylsiloxane) end groups. PEG-PDMS terminated SBR, **SBR-1**, showed higher interaction with silica particles by microscophy and chromatography. Dynamic-mechanical analysis on silica composites of **SBR-1** strongly supports the assumption that the PEG-PDMS end groups behave as polar functional groups, showing increase of the glass transition temperature (T_g) and storage modulus in the composite of **SBR-1** with silica particles. The **SBR-1**/silica composite showed lower tan δ at 60°C and higher tan δ at 0°C as compared to SBR-Sn/silica composite.
KEY WORDS Styrene–Butadiene Rubber / End-Functionalization / Poly(dimethylsiloxane) Terminator / Silica Particles / Dynamic-mechanical Analysis /

Coupling reactions of living polymers with functional terminating agents are a challenging approach to the synthesis of chain-end functionalized polymers.[1—3] Particularly, end-functionalization using post-polymerization reactions of living polymers with electrophilic terminators have been developed to synthesize new functionalized polymers of narrow distribution in molecular weight. The terminators are 4-vinylbenzyl chloride, dihaloalkanes, halopropylstyrene, chlorosilane, alkyl chlorides bearing heteroatoms, carbon dioxide, ethylene oxide, poly(ethylene oxide) (PEO), tin (or silicon) tetrachloride, etc.[3—8] Such end-functionalization could be utilized to improve reactivity, hydrophilicity, solubility, and miscibility of the polymers.

End-functionalization of styrenic polymers has been important to develop polymers of higher interaction with inorganic fillers such as silica and carbon black.[7, 8] Interactions of tin coupled styrene–butadiene rubbers (**SBR-Sn**) are of particular interest in compounds incorporating carbon blacks, showing lower hysteresis than uncoupled SBR. Interactions of polymer with inorganic fillers seem important through the presence of hydrogen bonding or tin-carbon bonding. In this context introduction of polar functional group in the terminator is important to improve miscibility with inorganic fillers.

Shown here is an outline of the sysnthesis of end fucntionalization of **SBR**. This new methodology utilizes poly(ethylene glycol)-poly(dimethylsiloxane) block copolymer (PEG-PDMS), which contains an anion reactive chlorosilyl moiety at one chain end.
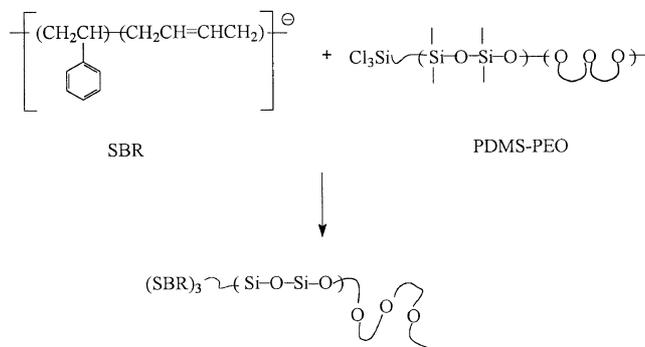
We selected the polysiloxane unit because interactions between PDMS and silanol groups of silica have been reported as a detectable degree.[9] Thus PDMS end-coupled SBR is expected to show stronger interaction with silica than uncoupled polymer. However, the siloxane unit only may not lead to large interaction with silica, since the hydrogen bonding interaction of dimethylsiloxane with silica is rather weak. Thus we attached a PEG unit on the terminator, to induce stronger hydrogen bonding between silica and the polymer. PEG end-functionalized polymers may exhibit polar characteristics originating from PEG units that have strong hydrogen-bonding abilities and hydrophilicities.[7] The incorporation of terminal PEG

[†]To whom correspondence should be addressed (Fax: +82-42-861-4151, E-mail: ekkim@krict.re.kr).

residues at polymer chain ends may possibly cause dramatic changes in their composite properties with silica. We present here a synthesis of end functionalized SBR using PEG-PDMS terminator (**1**) and dispersion characteristics of silica in the functionalized SBR.

EXPERIMENTAL

Materials

Styrene was purified according to the usual procedures. Dodecylsilyl trichloride (**2**), hydride terminated polysiloxane (**3**, H–[Si(CH$_3$)$_2$–O]$_m$-Si(CH$_3$)$_2$–H, M_n = 580), platinum-divinyltetramethyl disiloxane complex in xylene, and triethyleneglycol monomethylallyl ether were purchased from Aldrich and used as received. Silica was purchased from Rhone–Poulenc Chimie (Zeosil 165). Silica was dried in a oven at 105°C for at least 24 h prior to use in order to remove the surface-bound water. *n*-Hexane and toluene were dried using sodium wire. THF was purified by benzophenone and dried before use. Tin coupled SBR (**SBR-Sn**) was synthesized by the reaction of poly(styrene–butadiene)anion with SnCl$_4$.[8]

Synthesis of CH$_3$O(CH$_2$CH$_2$O)$_3$(CH$_2$)$_3$–[Si(CH$_3$)$_2$–O]$_m$-Si(CH$_3$)$_2$–H (4)

Hydride terminated polysiloxane (**3**, 58 g) was dissolved in 400 mL toluene under a nitrogen atmosphere. To this solution was added 0.04 mL platinum-divinyltetramethyl disiloxane complex in xylene. Twelve grams of triethyleneglycol monomethylallyl ether slowly dropped into the solution and the reaction mixture was stirred at 60°C for 10 h. After the completion of the reaction, solvent was removed and the product was dried in a vacuum at 100°C for 2 h. The product mixture was dissolved in *n*-hexane and after passing through charcoal, *n*-hexane was removed under a vacuum oven, to yield 61.6 g of **4**: ^{1}H NMR (CDCl$_3$, ppm) δ 0.1–0.3 (Si–C$\underline{H}_3$), 0.4 (Si–C$\underline{H}_2$), 1.5 (C$\underline{H}_2$), 3.5 (C$\underline{H}_2$–O), 4.6(Si–$\underline{H}$); FT-IR (KBr, cm^{-1}) 1032–1090 (Si–O–Si), 1150 (–O–CH$_2$), 1260 (Si–CH$_2$), 2128 (Si–H).

Synthesis of Poly(ethylene glycol)-Poly(Dimethylsiloxane), Chlorosilyl-terminated, CH$_3$O(CH$_2$CH$_2$O)$_3$-(CH$_2$)$_3$–[Si(CH$_3$)$_2$–O]$_m$–Si(CH$_3$)$_2$–CH$_2$CH$_2$SiCl$_3$ (1)

The above polymer (**4**, 47 g) were dissolved in toluene under nitrogen atmosphere. To this solution was added 19.4 g vinyltrichlorosilane and 0.02 mL platinum-divinyltetramethyl disiloxane complex (in xylene). The reaction mixture was refluxed for 10 h. After completion of the reaction, solvent and volatile reactant were removed. The resulting material was dissolved in *n*-hexane and passed through charcoal to eliminate catalyst and impurities, to yield 62 g of **1**. ^{1}H NMR (CDCl$_3$, ppm) δ 0.07–0.3, 1.5, 3.3, 3.6. ^{29}Si NMR (CDCl$_3$, ppm) δ 8.2, -28. FT-IR(KBr, cm^{-1}) 804, 1027, 1261, 2876, 2962.

Synthesis of End-terminated SBR (**SBR-1**)

A nitrogen-filled autoclave charged with 2340 g cyclohexane and 5.4 g THF. Styrene (90 g) and butadiene (270 g) were added, followed by addition of 2.3 mL *n*-butyllithium (2 M solution in hexane). The reaction mixture was stirred for 1 h and then 7 g butadiene were added to the solution. After 30 min of stirring, an aliquot of the reaction mixture was quenched by methanol and analyzed by GPC. A solution of the terminator **1** (0.9 mmol) in cyclohexane was slowly added to the autoclave at 40°C. The mixture was stirred further for 30 min and then 10 mL MeOH was added to the mixture. Finally the end-functionalized polymer was isolated by steam stripping. ^{1}H NMR (CDCl$_3$, ppm) 6.3–7.3, 4.9–5.6, 3.4–3.8, 1.1–2.6, 0.04–0.09. FT-IR (KBr, cm^{-1}) 2850–3100, 1260 (Si–CH$_2$), 1032–1090 (Si–O–Si). T_g (DSC): −48°C. End termination of living SBR anion with **2** (dodecylsilyltrichloride) was similarly carried out, using the same molar ratio of styrene and butadiene. Styrene and vinyl were 25 wt% and 33 mol%, respectively, in all samples including SnCl$_4$ coupled SBR (**SBR-Sn**).

Preparation of Silica/SBR Composites

Compounds were mixed according to ASTM D3182 using a two-stage procedure in an internal mixer or a Brabender (Plastic coder) and sheeted off on a two roll mill. Polymer and one-half of silica in weight were added during the first stage of the internal mixing (1 min), while the remainder of silica was added during the second stage (1 min after the temperature of the mixture reached to 120°C).

Instruments

^{1}H NMR spectra were recorded on a BRUKER DPX spectrometer operating at 300 MHz. Gel permeation chromatography (GPC) was performed on Styragel columns (Waters Corp., Milford, MA) held at 35°C. Molecular weights were determined from a calibration curve of polystyrene standards. Polymer samples were prepared at 0.2% (w/w) solutions in THF and 100 μL sample solution were injected. The solvent delivery system was a Waters model 615 HPLC pump controlled by the Millennium software (Waters Corp.). For adsorption experiments, 10 mg silica were added to 1 g polymer solution in cyclohexane. Adsorption of the polymers on silica was measured at r.t. by monitoring
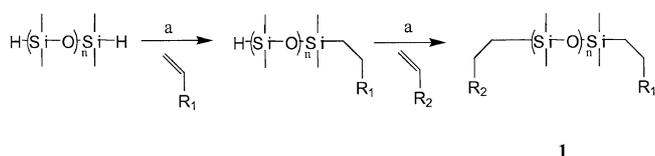
depletion of the polymers in the solution. Scanning electron microscopy (SEM) observation of cross section samples was made using a frozen sample and measured on a JEOL scanning electron microscope JSM-5800 LV model. Dynamic mechanical analysis was carried out in a TA instruments (DMA 2980) as a function of temperature between −150~150°C, with a rate of 5°C min^{-1} at an amplitude of 5. Rectangular specimens of $14 \times 12 \times 2.0$ mm^3 were clamped to the fixture in the chamber.

RESULTS AND DISCUSSION

Synthesis of a Polar Polysiloxane Terminator

Polar functional polysiloxane was obtained by introducing a poly(ethylene glycol) unit. For an effective coupling with living polymer anion, it was necessary to have a reactive group such as chlorosilane. Thus we designed poly(ethylene glycol)-poly(dimethylsiloxane) block copolymer containing an trichlorosilyl moiety at one chain end, $CH_3O(CH_2CH_2O)_nCH_2CH_2CH_2–Si(CH_3)_2–[O–Si(CH_3)_2–]_m–O–Si(CH_3)_2–CH_2CH_2Si-Cl_3$, where n and m are repeating numbers. The terminator was synthesized by hydrosilylation using hydride terminated polysiloxane (**3**) with vinyl substituted PEG, followed by hydrosilylation with vinyltrichlorosilane derivatives, in 90% yields, as summarized in Scheme 1. Key to the synthesis of **1** was control of half-hydrosilylation of **3**. Silylation was a stoichiometric reaction and afforded PEG-PDMS copolymer (**4**) in quantitative yield as determined by the area of the peak of characteristic vibration frequency of Si–H at 2128 cm^{-1} (Figure 1). Further hydrosilylation with vinyltrichlorosilane afforded a reactive terminator (**1**), of which IR spectrum indicated that the Si–H bond was completely reacted to give an end modified functional terminator. A similar result was obtained from the ^{1}H NMR spectra as estimated from the disappearance of a proton resonance for Si–H. Thus the intensity of the peak for proton resonance of Si–H at 4.6 ppm stoichiometrically decreased as silylation proceed.

Thermal stability of the polysiloxane terminators increased by introducing the PEG group (Figure 2)

and decomposition temperatures of the PEG modified polysiloxanes were above 210°C. Thus the PEG-PDMS terminator and polymer terminated with it could be utilized in a reaction requiring high temperature.

End coupling of SBR was carried out using living anions of poly(styrene–butadiene)s. Poly(styrene–butadiene)s with nearly uniform distribution of molecular weight was synthesized by anionic polymerization of styrene monomer and butadiene monomer in the presence of *n*-butyllithium. Polysiloxane terminated SBR was synthesized by coupling the living anion of poly(styrene–butadiene) copolymer with **1** or **2**. The initial average molecular weight (M_n) of SBR and coupling efficiency were targeted to ~150000 and 70%, respectively, for processing and mechanical properties. GPC chromatograms of the end-functionalized SBR with different terminators are summarized in Figure 3.

Coupling number of end terminator to the polymer was determined from the ratio of the peak molecular weight (M_p) for end-coupled and un-coupled polymer in GPC in Figure 3. Average coupling number for **SBR-1** and **SBR-2** were close to 3. This indicates that the entire trichloro group of the end terminator reacts with three SBR anions. Coupling efficiency of polymer could be determined from the ratio of the areas of two peaks (M_p) for end-coupled and un-coupled polymer in GPC. Coupling efficiency of **1** with SBR anion was
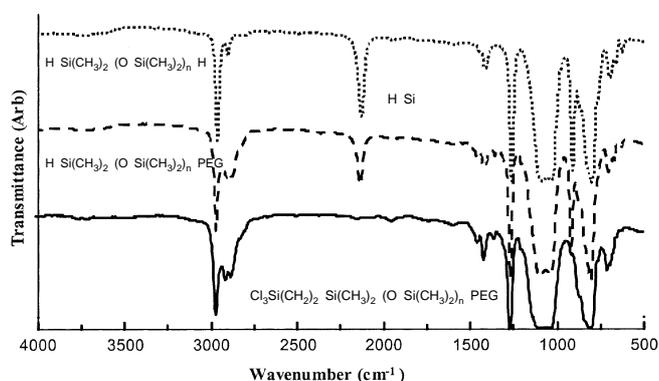
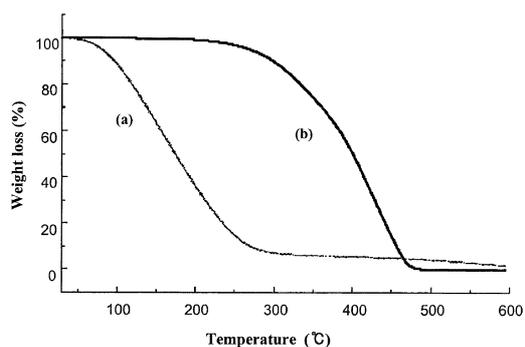**Figure 1.** FT-IR Spectra of PEG modified polysiloxane.

Figure 2. Thermal stability of polysiloxane, (a) H–Si(CH$_3$)$_2$–(O–Si(CH$_3$)$_2$)$_n$–H, (b) H–Si(CH$_3$)$_2$–(O–Si(CH$_3$)$_2$)$_n$-PEG (**4**).

1

Scheme 1. Synthesis of polar polysiloxane terminators. a = Platinum-divinyltetramethyl-disiloxane complex in xylene, solvent = toluene; R$_1$ = CH$_2$O(CH$_2$CH$_2$O)$_3$CH$_3$, R$_2$ = SiCl$_3$.

Table I. GPC results of end terminated SBR

Sample code	End terminator	$M_n (\times 10^{-3})$ Initial M_w/M_n	$M_n (\times 10^{-3})$ End-coupled M_w/M_n^a	Coupling Number	Coupling efficiency %
SBR-1	**1**	166 (1.06)	525 (1.07)	2.8	65
SBR-2	**2**	135 (1.04)	427 (1.06)	2.9	68
SBR-Sn	SnCl$_4$	186 (1.04)	609 (1.07)	3.1	74

[a] M_w/M_n of the high M_w peak was determined by deconvolution of the bimodal peaks in GPC data using appropriate algorithms.
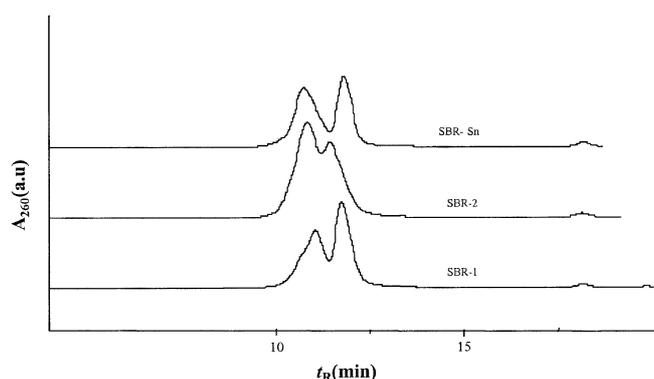
Figure 3. Analysis of SBR and end-coupled SBR by GPC.

determined as 65% in the equi-molar reaction (molar ratio between terminator to SBR anion = 1/3). Coupling efficiency of **2** was slightly higher under a similar condition. GPC results on end terminated SBR are summarized in Table I.

Interaction of End-functionalized SBR with Silica

Since silica has strong filler-filler interaction and adsorbs polar materials, a silica-filled rubber compound has poor dispersion of the filler and poor cure characteristics. To examine the effects of end–functionalization with PEG-PDMS group, we studied the interaction of end-functionalized SBR with silica particles, using a two component system, end-coupled SBR and silica, processed by a melt blending without vulcanizer additives.

A sheeted sample of silica composite of tin coupled SBR (**SBR-Sn**) was optically turbid, indicating phase separation of the organic and inorganic phases at a scale larger than the wavelength of visible light. Similarly a sheeted sample from **SBR-2**/silica composite showed inhomogeneity. When **SBR-1** was melt processed with silica particles, the homogeneity of the sample was much improved and the sample became translucent. Thus organic (SBR) and inorganic phases (silica) in **SBR-1**/silica composite were mixed at a nano level smaller than the wavelength of visible light. Figure 4 shows SEM micrographs of the cross section of melt blended composite sample. The samples prepared from **SBR-Sn**/silica and **SBR-2**/silica composite showed phase separation between the silica and poly-

mer. The micrographs show that the particles are approximately spherical in shape and cluster into irregularly shaped aggregates of various sizes and spacing.

Bright spots indicate silica, from which the size of silica domain was estimated to be around 1.2 μm at largest. The sample prepared from **SBR-1**/silica composite showed much smaller bright spots (Figure 4c) and filler particles were more uniformly dispersed. The silica domain was much less than 0.2 μm at most, even with addition of 20 phr silica particles. (Figure 4d) These results demonstrate improvement of the homogeneity with the introduction of the polar group to the polymer. Improvement of the dispersion of the silica particles in **SBR-1** was supposedly caused by increase in interactions at the interfaces. Interactions between poly(dimethylsiloxane) (PDMS) and silica have been extensively studied because silica is widely used as a reinforcing material for PDMS.[9] Thus PDMS end-coupled SBR is expected to show stronger interaction with silica than uncoupled polymer. Copolymers made up of dimethylsiloxane segments (DMS) of different length, regularly separated by one bisphenol A unit (BPA) showed two types of hydrogen bonding interactions: weak interacions between DMS segments and silanol groups, and strong intractions between the phenol functions of the copolymers and silanol groups of the silica.[9] Moreover, it was reported that the interaction of ethylene oxy group with silica is very strong, due to specific hydrogen bonding.[7, 10] Previous studies gave insight into the role of the relative strengths of the different interactions, suggesting that ethylene oxy blocks (PEG) interact more strongly with silica than PDMS blocks. In Scheme 2, the interaction of silica surface with polar ethyleneoxy group of the polymer end is described.

Hydrogen bonding interactions are assumed to be strong enough to tie the polymer to silica during the melt process. Therefore, hydrogen bonding interactions are supposed to function as linkers between an organic polymer and silica particles. As a consequence of increased interaction between the interfaces of two elements, the silica would be integrated homogeneously to the polysiloxane terminated SBR. Distribution of the two phases may be discussed more specifically from
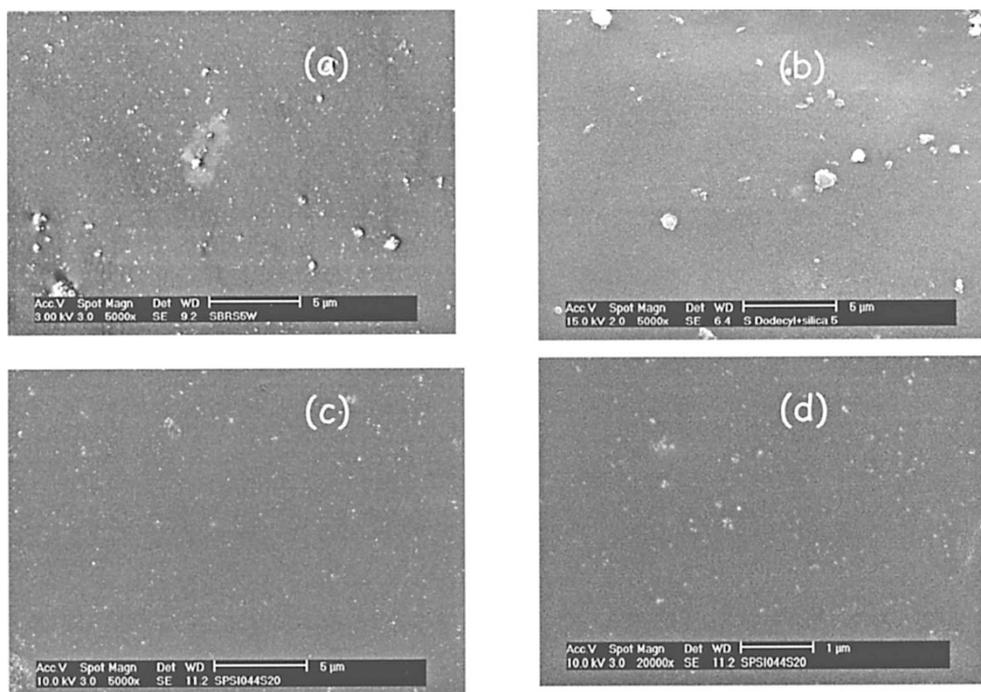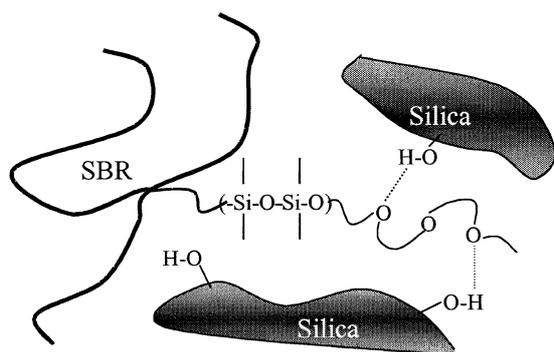
Figure 4. SEM micrographs of dispersions of silica in end functionalized SBRs, (a) **SBR-Sn** with 5 phr of silica, (b) **SBR-2** with 5 phr of silica, (c) **SBR-1** with 5 phr of silica, (d) **SBR-1** with 20 phr of silica.


Scheme 2. Interaction between polymer and silica.

adsorption of polymer on silica particles, determined by GPC.

Distribution of Organic and Inorganic Phases

Both polystyrene segment and PEG end groups may interact with surface hydroxy groups of silica particles. Since a PEG group has a stronger hydrogen-bonding with the hydroxy group, **SBR-1** could show stronger tendency to be adsorbed on silica than **SBR-Sn** or **SBR-2**. To determine the polymer adsorption on silica we determine the adsorption of polymer on silica. If we assume that the silica surface is not saturated with the adsorbed polymers when the silica particle is in a dilute polymer solution, adsorption can be represented as:

$$\text{Polymer/solvent} + \text{silica} \longrightarrow \text{solvent} + \text{polymer/silica}$$

$$(1)$$
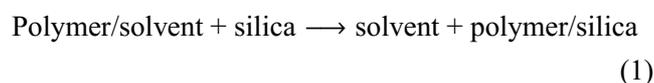
A polymer adsorption isotherm was obtained from the polymer/cyclohexane solution in contact with silica under stirring. The proportion of polymer, silica, and solvent was kept constant. An aliquot of the supernatant solution after certain periods of contact time was analysed by GPC to determine the amount of the polymer left in the solution. Figure 5 shows the GPC chromatograms of the end-modified polymers dissolved in cyclohexane at different contact times. **SBR-1** showed two major peaks, one of which in the high molecular weight region could be assigned as the end-coupled **SBR-1**, in which ~3 SBR living polymers are coupled to the terminator **1**. The peak at low molecular weight region could be assigned as uncoupled products of the starting living polymers.

Addition of silica particles under stirring resulted in significant decrease in the intensity of the two peaks. Within 1 h of stirring the peaks for **SBR-1** was disappeared indicating the complete depletion of the polymers due to the adsorption, whereas ~70% of peak was left in the solution of **SBR-2** even after 2 h. Time dependence of specific polymer absorption was monitored based on change in intensity of the elution peak for the end coupled SBR eluted at the retention time of 12.3 min. (Figure 6).

Polymer adsorption is thought to involve diffusion of polymer chains to the interface, attachment, and interfacial reconfigurations.[11, 12] The first step is the mass transfer to the surface, dictated by the polymer diffusion rate. The first step is the slow rate-determining step under static conditions. The next step is attachment of
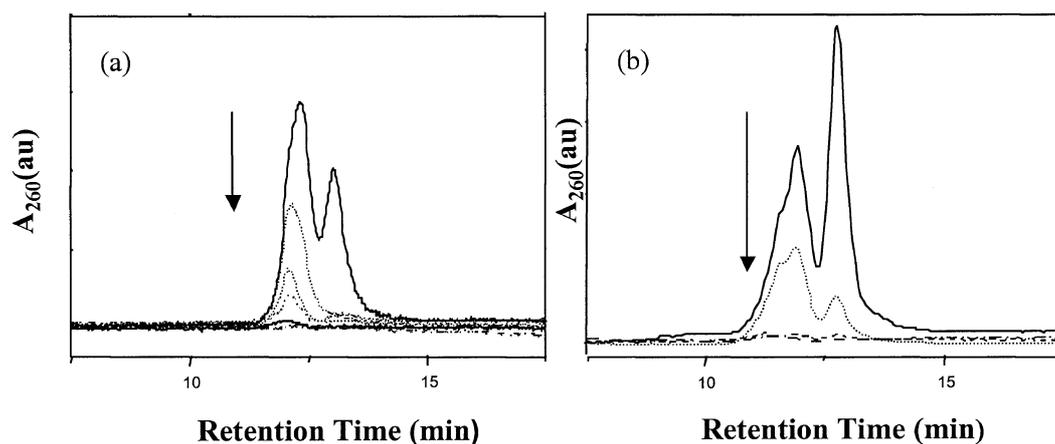
Figure 5. Adsorption dynamics of end terminated SBR on silica in cyclohexane, by GPC, (a) **SBR-2** (top to bottom: 0, 2, 4.4, 6.7, 8.5, 23.8 h), (b) **SBR-1** (top to bottom: 0, 0.16, 0.58, 1 h).
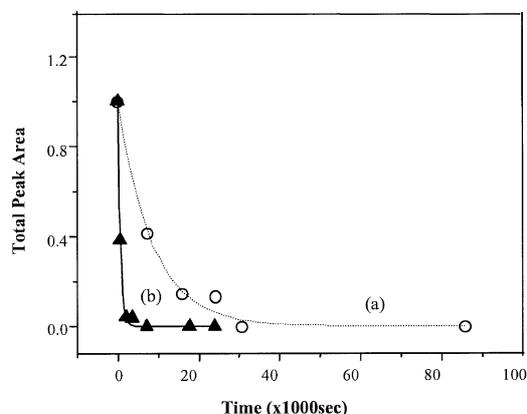

Figure 6. Rate of polymer adsorption on silica bed in cyclohexane, (a) **SBR-2**, (b) **SBR-1**.

polymer to the surface if the energetics are favorable. In the final step polymers rearrange slowly to adopt a more energetically favorable conformation. In this experiment the suspension was constantly stirred and thus diffusion of polymer to the surface of silica may have not been slow. The difference in the rate of adsorption in Figure 6 may arise from the second step. This step is considered to be strongly affected by the interaction between the polymer and silica. Since **SBR-1** has polar PEG-PDMS groups, the interaction between **SBR-1** and silica would be stronger than **SBR-2** or **SBR-Sn**. If so, the difference in the rate of adsorption in Figure 6 could be explained by effects of the polar functional group.

Dynamic Mechanical Properties of SBR Silica Hybrid Materials

Dynamic mechanical properties were studied to estimate storage modulus (E'), loss modulus (E''), and tan δ of polymer composites. Figure 7 shows storage modulus and tan δ peak magnitude of SBR composites. The temperature dependence of dynamic mechan-

ical properties of the **SBR-Sn**/silica hybrids containing different amounts of silica is shown in Figure 7 (a). In the sample without silica, the storage modulus clearly decreased in the glass transition region (T_g) and was low in the rubbery region. A decrease in the modulus in the T_g region is due to the micro-Brownian motion of the network chains.[13] However, in the composite, the modulus in the rubbery region increased with silica content and thus the glass transition behavior became indistinct. This shows that the micro-Brownian motion of SBR is strongly restricted by the composition with silica. The storage modulus of the hybrid systems with over 10 wt% silica showed no decrement in the glass transition region and remained high even in the high temperature region over 150°C. This means that the heat resistance of the composite is significantly improved by the composition with a silica. The data show that storage modulus, tan δ peak magnitude and T_g are sensitive to silica content. The composition-dependent single glass transition of the melt-processed samples clearly indicates that the system is miscible at all compositions (Figure 7 (b)). As hard silica content increases, the glass-transition temperature increases. This is consistent with polymers that have increasing crystallinity.[14] The increasing silica content results in larger and harder microcrystalline domains that restrict the molecular motion of the soft segment, thereby increasing the glass-transition temperature. The height of the tan δ peak is related to the amount of the amorphous material present.[15] As silica content increases, tan δ peak magnitude decreases as a result of reduced rotational freedom of the SBR chain.

SBR resin clearly shows a large tan δ peak in the glass transition region. In this study, the **SBR-Sn** sample showed a large tan δ peak in the glass transition region. The area of the tan δ peak slightly decreased with more silica added into SBR. The motion of **SBR-Sn**
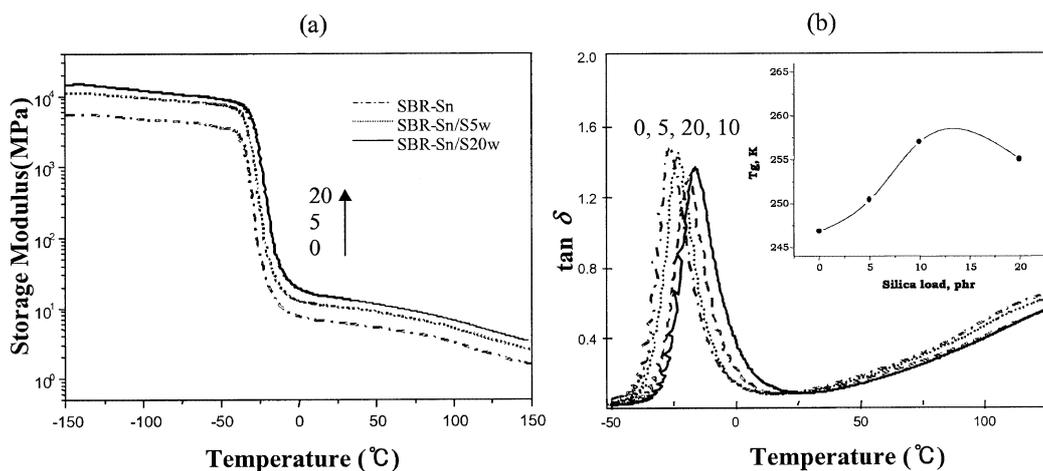
(a)

(b)

Figure 7. DMA of melt processed film of SBR/Silica composites, (a) storage modulus, (b) tan δ. The number indicates silica content (phr). Insert shows T_g determined from tan δ.
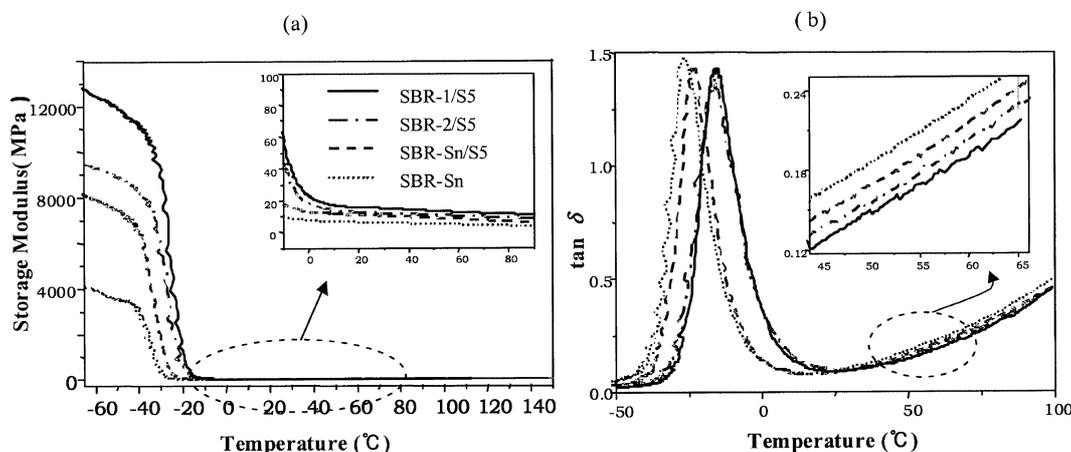
(a)

(b)

Figure 8. Storage modulus of functionalized SBR/Silica composite, (a) storage modulus and (b) tan δ.

chains is thus not much restricted in the silica composites and silica interaction with **SBR-Sn** should be considered to be at a micro or bulk level, not at a molecular level.

As expected from the contribution by the inorganic silica particles, the **SBR-Sn**/silica composite shows improved mechanical properties, as determined by DMA techniques. Thus T_g of **SBR-Sn** at $-26°C$ was raised to $-16°C$ upon composition with 10 phr of silica as shown in Figure 7 (b). Further addition, however resulted in lowering of T_g, possibly due to phase separation between the silica and SBR as silica content increased.

Addition of silica particles to the end-functionalized SBRs increased the storage modulus in the rubbery region and T_g, as determined from the DMA data shown in Figure 8. Increase was much more significant in the **SBR-1**/silica composite than in the **SBR-2**/silica. This strongly indicates that the micro-Brownian motion of the PEG-terminated SBR is strongly restricted by compounding with silica, due to stronger interaction between the silica and PEG-polysiloxane group.

A most important result was the increase of tan δ at

$0°C$ and decrease of it at $60°C$. Tan δ at $0°C$ represents wet skid resistance while at $50–80°C$ represents rolling resistance (of tire for example).[8, 16] The **SBR-1**/silica composite shows lower tan δ at $60°C$ by about 11% than **SBR-Sn** or **SBR-2**. Tan δ at $0°C$ for **SBR-1**/silica composite increased more than 160% as compared to that for **SBR-Sn**/Silica composite. Therefore **SBR-1** is expected to reduce rolling resistance and to show better wet skid resistance when applied to tires. Thermo-mechanical properties of the silica-SBR compositions are summarized in Table II. Further studies on the structure and properties of end-terminated SBRs are in progress to improve processing conditions and the mechanical properties of anionically synthesized polymers.

CONCLUSION

A poly(ethylene glycol)–poly(dimethylsiloxane) (PEG-PDMS) block copolymer containing an trichlorosilyl moiety at one chain end was prepared from allyl-PEG by hydrosilylation with

Table II. DMA of SBR/silica composites

Sample	Silica content	Storage modulus	T_g (°C)	tan δ at 60°C	tan δ at 0°C
	phr	($\times 10^3$ Mpa) at 60°C		Increase*	Increase*
SBR-1/S5	5	12.5	−15	0.191 (−0.024)	0.378 (0.236)
SBR-2/S5	5	9.3	−17	0.203 (−0.012)	0.365 (0.223)
SBR-Sn/S0	0	4.0	−26	0.233 (0.018)	0.138 (−0.004)
SBR-Sn/S5	5	7.9	−23	0.215 (0)	0.142 (0)

*As a reference to **SBR-Sn**/S5.

dimethylethoxysilane, followed by further hydrosilylation with trichloro-vinylsilane. End-functionalized poly(styrene–butadine)s with PEG-PDMS residues were synthesized by the termination reactions of the anionic living polymer of styrene and butadienes with PEG-PDMS containing an trichlorosilyl moiety. The composite of PEG-PDMS terminated SBR (**SBR-1**) with silica showed better dispersion of silica particles as compared to a dodecylsilyl or tin terminated SBR/Silica composites. Furthermore, the **SBR-1**/silica composite showed improved thermo-mechanical properties.

REFERENCES

1. "Anionic Polymerization, Principles and Practical Applications", H. L. Hsieh and R. P. Quirk, Ed., Marcel Dekker, Inc., New York, N.Y., 1996.

2. a) K. Ueda, A. Hirao, and S. Nakahama, *Macromolecules*, **23**, 939 (1990).
   b) A. Hirao, H. Nagahama, T. Ishizone, and S. Nakahama, *Macromolecules*, **26**, 2145 (1993).

3. a) A. Hirao, M. Hayashi, and S. Nakahama, *Macromolecules*, **29**, 3353 (1996).
   b) A. Hirao, M. Tohoyama, and S. Nakahama, *Macromolecules*, **30**, 3484 (1997).
   c) M. Hayashi, S. Nakahama, and A. Hirao, *Macromolecules*, **32**, 1325 (1999).

4. a) M. A. Peters, A. M. Belu, R. W. Linton, L. Dupray, T. J. Meyer, and J. M. Desimone, *J. Am. Chem. Soc.*, **117**, 3380 (1995).
   b) M. O. Hunt, A. M. Belu, R. W. Linton, and J. M. DeSimone, *Macromolecules*, **26**, 4854 (1993).

5. M. P. Labeau, H. Cramail, and A. Deffieux, *Polym. Int.*, **41**, 453 (1991).

6. a) R. P. Quirk, J. Yin, and L. J. Fetters, *Macromolecules*, **22**, 85 (1989).
   b) R. P. Quirk and J.-J. Ma, *J. Polym. Sci., Part A: Polym. Chem.*, **26**, 2031 (1998).

7. C. P. Tripp and M. L. Hair, *Langmuir*, **12**, 3952 (1996).

8. V. R.-S. Quiteria, C. A. Sierra, and J. M. Gomez-Fatou, *Die Angewandte Makromolekulare Chemie*, **246**, 85 (1997).

9. F. Tronc, L. Lestel, C. Amiel, and S. Boileau, *Langmuir*, **15**, 7080 (1999).

10. a) C. G. P. H. Schroen, M. A. Cohen-Stuart, K. van der voort Maarschalk, A. van der Padt, and K. van't Riet, *Langmuir*, **11**, 3068 (1995).
    b) J. A. Shar, T. M. Obey, and T. Cosgrove, *Colloids Surf.*, **150**, 23 (1999).

11. "Colloid-Polymer Interactions: From Fundamentals to Practice", R. S. Farinato, P. L. Dubin, Ed., John Wiley & Sons, Inc., New York, N.Y., 1999.

12. A. Elaissari, A. Haouam, C. Huguenard, and E. Pefferkorn, *J. Colloid Interface Sci.*, **149**, 68 (1992).

13. "Rubber Engineering", Indian Rubber Institute, MacGraw-Hill, Columbus, OH, 2000.

14. a) Q. Hu and E. Marand, *Polymer*, **40**, 4833 (1999).
    b) Z. Ahmad, M. I. Sarwar, S. Wang, and J. E. Mark, *Polymer*, **38**, 4523 (1997).

15. "Dynamic Analysis of Polymeric Material", T. Murayama Ed., Elsevier Scientific, New York, N.Y., 1978.

16. a) F. Tsutsumi, M. Sakakihara, and N. Oshima, *Rubber Chem. Technol.*, **63**, 8 (1990).
    b) F. Cataldo, *Die Angewandte Makromolekulare Chemie*, **270**, 81 (1999).