Well-balanced new solution styrene-butadiene rubber for the silica tire

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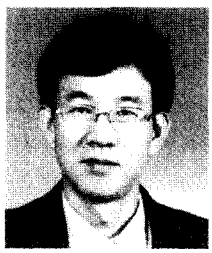
1. Introduction

The most widely used reinforcing fillers in tire industry are carbon black and silica. Recently the growing importance of silica is associated with the better tire performances, for instance in wet traction and rolling resistance, in silica-filled tire. In general solution styrene-butadiene rubber (S-SBR) is composed of non-polar monomers and therefore the resulting polymer should be non-polar. In contrary most frequently used reinforcing fillers in tire industry, such as carbon black and silica, have the polar groups on the surface. Especially silica has much more amounts of polar group, which is hydroxyl group and makes it difficult to be compatible with S-SBR in the rubber compounds. So there is little interaction between the rubber and filler leading to hysteresis loss between them. This hysteresis loss results in poor mechanical and dynamic properties in tire tread. Therefore it is required to develop the new elastomer that is more compatible with silica for lowering the hysteresis loss and making filler well dispersed through elastomer matrix. To overcome this incompatibility we need to polarize the living end of rubbers by functional groups.[1,2,3] In this paper, we present the new oligomeric coupling agent, α, ω-bis[2-(trichlorosilyl)ethyl]-polydimethylsiloxanes, synthesized by the hydrosilylation of trichlorovinylsilane by α, ω-dihydrido-poly-dimethylsiloxanes or α, ω-divinyl-polydimethyl-siloxanes by trichlorosilane in the presence of Pt(0)-divinyltetramethyl-disiloxane complex and its application for the synthesis of polydimethylsiloxane-modified radial S-SBR.

2. Experimental

2.1 Synthesis of α, ω-bis[2-(trichlorosilyl) ethyl]poly-dimethylsiloxane (I)

α, ω-bis[2-(trichlorosilyl)ethyl]polydimethylsiloxane (I) was synthesized by the hydrosilylation of trichlorovinylsilane by α, ω-dihydrido-poly- dimethylsiloxane in the presence of Pt(0)-divinyl-tetramethyl-disiloxane complex as Scheme (I). The synthesis was conducted as the following procedure. The 300 ml round-bottom flask was charged with 21 g of α, ω-dihydrido-polydimethylsiloxanes, 14.6 g of trichlorovinylsilane, 120 ml of toluene and catalytic amount of Pt(0)-divinyltetramethyl-disiloxane complex under inert atmosphere. The hydrosilylation was conducted at 60 ℃ for 3 hrs. (Scheme 1) And then the reaction mixture was passed through the an



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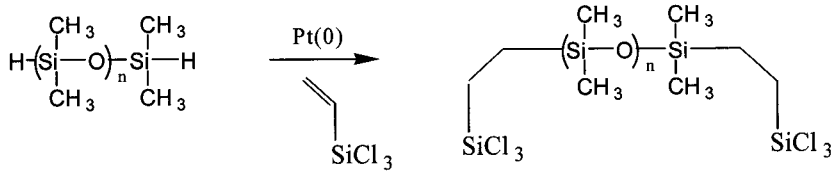


Scheme 1

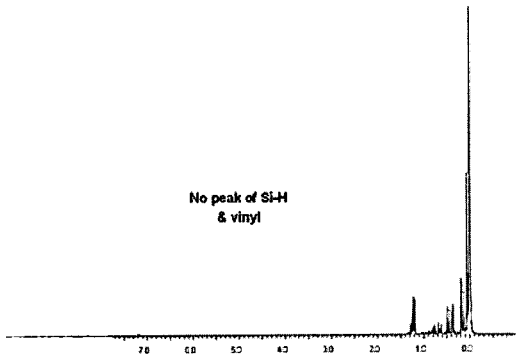


Figure 1

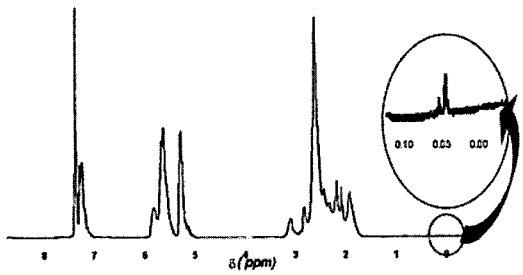


Figure 2

hydrous charcoal to remove residual platinum complex under inert atmosphere. The charcoal-treated solution was concentrated at 80 ℃ under reduced pressure to remove solvent and excess trichlorovinylsilane. The residual viscous liquid after concentration was confirmed as pure product after spectroscopic analyses in Figure 1. [H^1-NMR (ppm): 1.26 ($Si-CH_2$, m), 0.06($Si-CH_3$, m), IR (cm^{-1}): 2962, 1412, 1092, 1030 and 800]

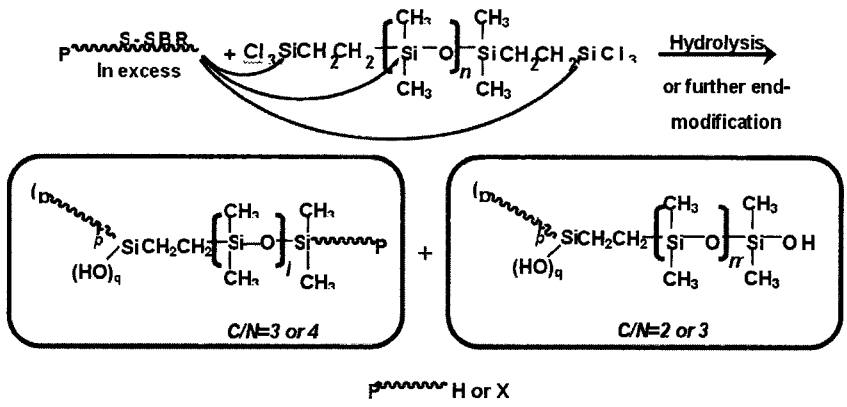
2.2 Polymerization

The target microstructure of the SBR was as follows: styrene content (34 wt%), vinyl content (48 %) in butadiene part, CE (Coupling Efficiency) ca. 55 and CN (Coupling Number) ca. 3.5. Polymerizations were carried out in 10 liter steel reactor equipped with magnetic drive impeller under inert atmosphere. 4,800 g of cyclohexane, 96 g of tetrahydrofuran, 272 g of styrene and 508 g of butadiene were introduced in the reactor, and the mixed solution was heated to 40 ℃. The initiator, 2 ml of n-BuLi (2 M solution in cyclohexane) was added to start polymerization. At the end of the polymerization 20 g of additional butadiene were added into the reactor to have butadienyl-terminal living polymer. After 20 minutes of reaction each of the coupling agents was introduced and the reaction was maintained under stirring for another 20 minutes. Finally the polymer solution was deactivated by adding 10 ml of butylated hydroxytoluene (BHT) in 1 M solution in cyclohexane. The polymer was characterized by GPC and H-NMR in Figure 2.

3. Results and discussion

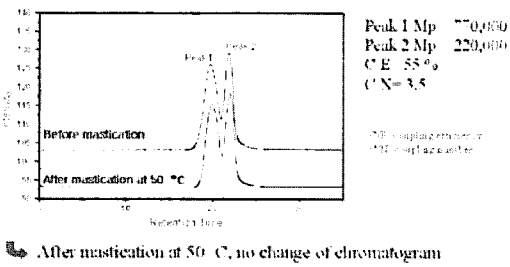
3.1 Reaction scheme (II) between the living anion of SBR and compound (I)

In the reaction of PSi86 with the living anion of SBR, the anions do the nucleophilic attack to the bond of the silicon halide in both sides and then the excess anions attack the bond of silicon oxide to break the oligomer chains. As a result we have two reaction products shown as C/N 4 product and C/N 3 product in reaction scheme 2.



C/N: Coupling Number, p = 2 or 3, q = 0 or 1 and p + q = 3; x = functional group

Scheme 2



After mastication at 50 °C, no change of chromatogram

Figure 3

3.2 GPC of polydimethylsiloxane-modified SSBR

This GPC Figure 3 shows one example of the end-modification reaction of the living polymer. It shows bimodal peak of the PSi86-coupled SSBR, which has C/N 3.5 and C/E 55 %. After mastication at 50 ℃, GPC shows the same chromatogram. That means the PSi86-coupled product is stable to compounding condition.

3.3 Density functional calculations on the hydrogen bonding energy between polysiloxane and silica

We employed DFT[4] methods to optimize the structure between dimethylsiloxane and silica in hydrogen bonding. Calculations were carried out using the program package, Gaussian94 (DFT) on Silicon Graphics (R10000 * 8 CPU Power Onyx) workstations in our laboratories. Two models, CN 4 polymer having dimethylsiloxane in mid-chain and CN 3 polymer having dimethylsiloxane and hydroxyl

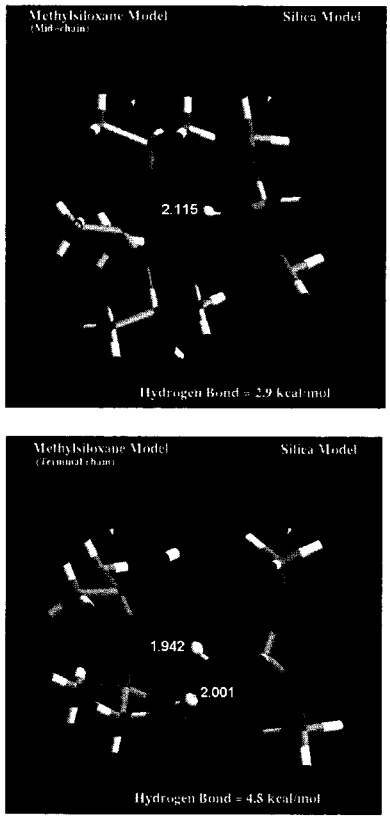


Figure 4

group in mid-chain, were compared in hydrogen bonding energy in Figure 4. CN 4 polymer shows 2.9 Kcal/mol of the hydrogen bond energy between the hydroxyl group on silica surface and dimethylsiloxane in mid-chain. CN 3 polymer shows higher hydrogen bond energy, 4.8 Kcal/mol, because it has two different hydrogen bonds possible of between hydroxyl group and dimethylsiloxane in polydimethyl-siloxane unit and hydroxyl group on silica surface. Typically, hydrogen bond energy ranges from 3 to 7 Kcal/mol. From the calculations, we could estimate that there are some extents of hydrogen bonding between polysiloxane chain in SBR and silica.

3.4 Comparisons of mechanical properties and dynamic properties

Three differently synthesized S-SBR samples, polydimethylsiloxane-modified S-SBR (ST 6350S), VSL-5025(Lanxess) and T-3335(Asahi), were compared in mechanical properties and dynamic properties in silica-filled vulcanizates. Each of SBR samples was mixed according to the compound recipe given in Table 1.

After vulcanization, each sample was analyzed by tensiometer and DMTA. The result was shown in Table 2. All samples have similar raw material tgs but compound tgs were different from one another. In the case of ST 6350S, compound tg is remarkably increased compared to the others. This would be one of the evidences that ST 6350S is more interactive to silica and so the chain end of polymer lose its free rotation ability. Mechanical properties of ST 6350S were best among the tested samples in Table 2. This could be explained that the polydimethylsiloxane chain in the polymer would act as a wetting agent of silica that would make silica disperse better through rubber matrix. In dynamic properties ST 6350S showed excellent improvement both rolling resistance index and wet traction index, while two index are usually laid down in trade-off relation.

Table 1

S-SBR	137.5
Silica	80
Si-69	6.4
ZnO	2.5
Stearic acid	1.5
A/O*	1.9
Sulfur	1.1

* N-phenyl-N'-isopropyl-p-phenylenediamine

Table 2

Test grade	ST-6350S	VSL-5025	T-3335
Raw MV (ML)	53	62	62
Styrene (wt%)	34	25	36
Vinyl (mol%)	48	56	40
Oil (phr)	37.5	37.5	37.5
Tg (℃)	-27	-26	-29
Comp. MV (100 ℃)	122	123	123
Hd's (shore A)	72	70	71
M 100%	32.9	28.4	26.8
M 200%	80.7	67	62.7
M 300%	140	118	108
Tb	256	225	214
Elong. (%)	490	500	530
Compound Tg	-2.3	-8.2	-7.7
Tan δ at Tg	0.7814	0.6645	0.8207
Tan δ at 10 ℃	0.4377	0.3192	0.3149
Tan δ at 60 ℃	0.0972	0.1244	0.1112

4. Conclusion

α, ω-bis[2-(trichlorosilyl)ethyl]polydimethylsiloxane, which was newly synthesized from the hydrosilylation of trichlorovinylsilane by α, ω-dihydridopolydimethylsiloxane in the presence of Pt(0)- divinyltetramethyl-disiloxane complex, was successfully applied as a multi-reactive coupling agent for the synthesis of the well-balanced new solution styrene-butadiene rubber (S-SBR). The living end of anionically polymerized styrene-butadiene rubber(SBR) was easily reacted and coupled with α, ω -bis[2-(trichlorosilyl)ethyl]-polydimethylsiloxane to

give polydimethylsiloxane-modified SBR. GPC and H-NMR analyses showed that the product was the mixture of polydimethylsiloxane- modified 3- and 4-coupled S-SBRs. This S-SBR was compared with the competitor's ones in silica-filled vulcanizate. Its silica-filled vulcanizate properties showed significant improvements in both mechanical and dynamic properties among the tested S-SBRs. These simultaneous improvements could be attributed to a better interaction between silica fillers and polydimethylsiloxane-modified SBR by hydrogen bonding.

References

1. (a) William L. Hergenrother; Richard A. Schwarz; Richard J. Ambrose USP 4,239,860, 1980 (b) Shizuo Kitahara; Toshihiro Fujii; Nagatoshi Sugi USP 4,424,306, 1984 (c) Hiroyuki Watanabe; Kohkichi Noguchi; Toshio Kase USP 4,614,771, 1986 (d) Mitsuyoshi Aonuma; Hiroyuki Watanabe; Haruki Kawada; Kohkichi Noguchi; Akio Ueda; Shuichi Akita; Tetsuo Ohyama; Toshio Kase USP 4,647,625, 1987 (e) Young. H. Ko; Eun.K. Kim; Hyung.S. Cho USP 6,566,480 B2 2003
2. Yasuhito Ijichi, Takeji Hashimoto, Lewis J. Fetters *Macromolecules* 1989, **22**(6); 2817-2824.
3. J. Chan, S. Fox, D. Kiserow, C. Ramireddy, P. Munk, S. E. Webber *Macromolecules*; **26**(25); 1993, 7016-7023.
4. (a) Hohenberg, H.; Kohn, W. *Phys. Rev.* 1964, B 136, 864. (b) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*, Oxford University: New York, 1989. (c) Ziegler, T. *Chem. Rev.* 1991, 95, 7401. (d) Labanowski, J. K.; Andzelm, J. W., Eds. *Density Functional Methods in Chemistry*, Springer-Verlag: New York, 1991.