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Investigation on the influence of silane coupling agent structure on the properties of nano-silica filled rubber compound

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Abstract: Silane coupling agent has long been used to enhance degree of reinforcement of silica in rubber matrix. Recently various types of these coupling agents have been developed and commercialized. In the present study, two new silane coupling agents were introduced as decyloxytriethylsilane and 5,11,17-Tritertbutyl-23-trimethylsilylethynyl-25,26,27,28-tetrapropoxy calix(4)aren to compare the effect of generating Van der waals interaction between filler and polymer matrix that was originated by decyloxytriethylsilane in comparison with π-π interactions that was due to 5,11,17-Tritertbutyl-23-trimethylsilylethynyl-25,26,27,28-tetrapropoxy calix(4)aren. Cure characteristics and physicomechanical properties of a nano-silica filled NR/SBR polymer based compounds using these two agents were investigated and compared with commercialized Si69. Distribution of the filler in the rubber matrix was considered by scanning electron microscopy. These two suggestions were presented coupling agent effects. Decyloxytriethylsilane was shown better results due to the reduction of curative absorption and van der waals interactions between filler and polymer matrix in comparison with π-π interactions that was originated by the other coupling agent.

Keywords: *Silane coupling agent, Nano-silica, NR/SBR, Van der waals interaction, π-π interaction*

Introduction

Silica is one of the most important fillers that used in rubber industries [1-3]. There are four major problems for applying it in rubber compounds. The first problem is the low affinity of silica towards most elastomers so it is difficult to incorporate it efficiently into rubber matrix. The second one is due to existence of hydroxyl groups on the silica surface. It results in strong filler-filler interactions and formation of hydrogen bonds [4,5]. This intermolecular hydrogen bonds make silica aggregates [6] and cause a poor dispersion of it in a rubber matrix. The third problem is the absorbtion of cure agents like zinc oxide on silica surface. It reduces the cure efficiency and cross link densities. The fourth problem is due to the acidic surface of silica that absorbs basic curing accelerator agents and causes the delay in the scorch time and reduction of the delta torque of a silica-filled rubber compound [7]. Nowadays there is a high concentration on applying nano-silica in rubber compounds to increase the reinforcing effects of silica by increasing

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the ratio of the surface to volume of the filler particles [8-10]. The smaller size and higher surface activity of the silica nanoparticles make the above mentioned problems more serious.

So far, the chemical treatment of the silica surface, has become the most successful method to improve rubber-filler interaction. Recently, much attention has been given to the use of silane coupling agents which serve, to some extent, to couple a filler to the rubber molecule on "like-to-like" basis. Silane coupling agent posses two active sites. One is capable of reacting with the silonal group on the silica surface whilst the other is compatible with rubber matrix. Silane coupling agent functions as a bridge between silica and rubber and enhances the rubber-silica interaction [11]. It improves the silica distribution and dispersion as well as to prevent adsorption of curatives on the silica surface. In general bis-(3-(triethoxisilyl)-propyl)-tetrasulfide (Si69) is used as silane coupling agent in rubber industry [12]. Nowadays the researches are focused on applying new type of silane coupling agents to achieve better performance [11,13].

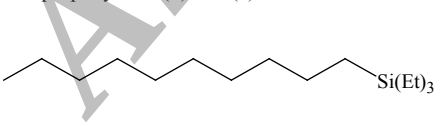
In the present work two new coupling agents were introduced. The first one was decyloxytriethylsilane (A) with a linear nonpolar hydrocarbon chain which could interacted with the elastomers by the van der waals forces. In addition it could interacted due to dipole-dipole forces with the silanol groups of the silica. The second agent was 5,11,17-Tritertbutyl-23-trimethylsilylethynyl-25,26,27,28-tetrapropoxy calix(4)aren (B). This material has contained the terthbutyl groups that interacted with polymer matrix and trimethylsilyl group that interacted with silica. In addition the existence of the aromatic groups in it's structure could caused the π-π interactions between these groups and the unsaturated parts of the elastomer structure. These two coupling agents were selected to compare the effects of van der waals and π-π interactions. Figure 1 is shown the structure of the mentioned agents in comparison with commercial Si69. The efforts have been made to investigate the effect of the coupling agents structure on cure characteristics, physicomechanical properties and dispersion of nano-silica in a NR/SBR polymer based compound to achieve a basic pattern for introducing new effective coupling agents.

Experimental

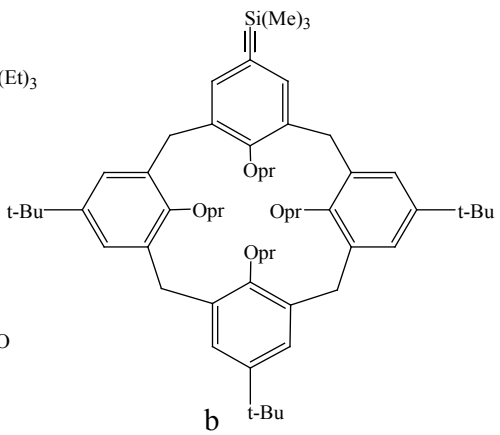
Materials

SMR 20 (NR) with mooney viscosity ML(1+4) at100 °C of 52.5. SBR 1500 containing 23% styrene with mooney viscosity ML(1+4) at100 °C of 52 was obtained from Bandar Imam Petrochemical Company, Iran. ZnO 91.2% was prepared from Pars Ox-

Figure 1 (a) Decyloxytriethysilane (b) 5,11,17 Tritertbutyl- 23-trimethylsilylethynyl-25,26,27,28-tetrapropoxy calix(4)aren (c) Si69



a



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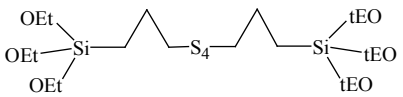


C

ide Parto Iran. Rubber process aromatic oil no. 290 was obtained from Behran Oil Company, Iran. Sulfur 99.7% was supplied by Tesdak Company, Iran. CBS Vulkasit CZ/C 98.5% was obtained from Lanxess. Dusantox 6PPD was provided from Duslo with minimum 97% active substance content. Flectol TMQ-PST was obtained from Flexsys. Antilux 654 was supplied by Rheinchimie. Stearic acid 95% was provided from Palmoleo Sdn. Bhd. Carbon black N-375 was obtained from Iran Carbon Company with N_2 surface area 95-105 m^2/g. Nanosilica was supplied by Degussa with N2 surface area 178 m^2/g and average particle size 19/3 nm. Si69 was obtained from Degussa. Decyloxytriethylsilane and 5,11,17-Tritertbutyl-23-trimethylsilylethynyl-25,26,27,28-tetrapropoxy calix(4)aren was prepared before [14].

Instruments

The cure characteristics of different compounds were measured at 160 °C with MDR 900, HIWA Company, Iran. The compounds were cured in a laboratory press PTP 600, PGH Company at 160 °C and 220 KN. Hardness was measured with a Bareiss 49038 Hardness-meter Shore A Type, according to ASTM D2240. Abrasion was measured by Bareiss 2243 according to ASTM D5963. Fatigue tests have done by HIWA 600, HIWA Company according to ISO 6943. Tensile tests were carried out on dumbbell shaped specimens by M-350-5019, Testometric Company, according to ASTM D412. SEM images were prepared by MV2300 Obducat Company from cryofractured samples that coated by gold with Auto Sputter Coater-E 5200, Quorumtech Company.

Mixing Recipe

Table 1 is shown the compounds Formulation. They were prepared in 60 minute on a laboratory two roll mill (Wellshayang, 6" * 18"). Components were added as follows in addition times:

- 0 min: NR (mastication)
- 3 min: SBR (blending of NR and SBR)
- 6 min: carbon black, silica, silane coupling agent and other chemicals.
- 40 min: oil
- 50 min: sulfur and CBS
- 60 min: discharge

Table 1 Compounds formulation

Compound	NS1 (phr)	NS2 (phr)	NS3 (phr)	NS4 (phr)
NR	75	75	75	75
SBR	25	25	25	25
Carbon black	25	25	25	25
Nano-silica	25	25	25	25
Si69	0	0.8	0	0
Decyloxy	0	0	0.8	0
Calix(4)aren	0	0	0	0.8
Aromatic oil	10	10	10	10
S	1.5	1.5	1.5	1.5
CBS	0.75	0.75	0.75	0.75
6PPD	1.5	1.5	1.5	1.5
TMQ	1	1	1	1
Antilux 654	2	2	2	2
Srearic acid	2	2	2	2
ZnO	4	4	4	4

Results and discussion

Compound NS1 that has no coupling agent in its formulation was adhered to the mold and could not passed the exams. Figure 2 is presented the rheometric curves of the prepared compounds. In comparison of different coupling agents, the compound that was

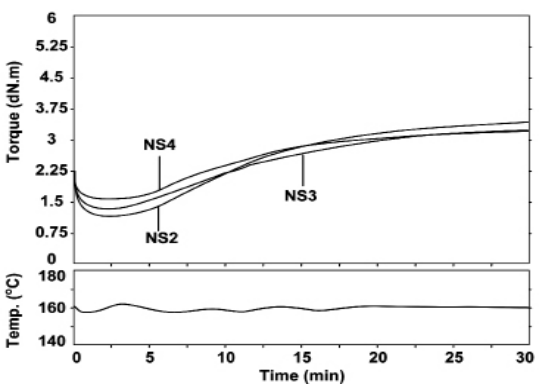


Figure 2 The rheometry curves of the compounds

contained Si69 shown the higher MH (the maximum torque in a cure curve) and crosslink densities. It may due to the existence of sulfur in its structure which was helped the cure system. The two other coupling agents were shown nearly the same MH.

Table 2 is presented the physicomechanical properties of the compounds. Abrasion was highly increased in the compound contained (B). It was due to the special structure of this agent that could absorbed the zinc ions and reduced the cure efficiency. In addition it could concluded that the π-π interactions was less effective than van der waals interactions which was presented between (A) and polymer matrix. It might caused the poor distribution of the reinforcing agent and increased abrasion. Fatigue test was suitable for the three compounds. Tensile strength, modulus 100% and modulus 300% were shown better results by applying the (A) coupling agent in comparison with (B). They were confirmed again on these facts that the curing agents were more effective in the presence of a linear hydrocarbon due to it's lower interaction with zinc ions, distribution of the filler was better and stronger filler-coupling agent and polymer-coupling agent interactions were existed. The higher amount for elongation at break by applying (A) in comparison with two other coupling agents was shown it's higher tendency to got rubberized. Si69 was shown better results for hardness, abrasion, tensile strength, modulus 100% and modulus 300%. The (A) agent could simply synthesized by the followed reaction:

$$C_{10}H_{21}OH + ClSi(C_2H_5)_3 \rightarrow C_{10}H_{21}OSi(C_2H_5)_3 + HCl$$

It was produced more simply and cheep than Si69 and could be a good choice as a coupling agent after optimization of its amount in the compound formulation.

Figure 3 is presented the nano-silica distribution in rubber matrix. In comparison of the compounds NS4 and NS5, (A) was caused the better distribution of nano-silica in the rubber matrix.

Table 2 Physic mechanical properties of the Compounds

Compound	NS2 (phr)	NS3 (phr)	NS4 (phr)
Hardness (Shore A)	40	34	33
Abrasion (mm^3)	110	150	280
Fatigue (KC)	>300	>300	>300
Tensile strength (MPa)	14.4	8.7	5.8
Modulus 100% (MPa)	1.05	0.59	0.59
Modulus 300% (MPa)	3.91	1.78	1.58
Elongation at break (%)	634	707	636

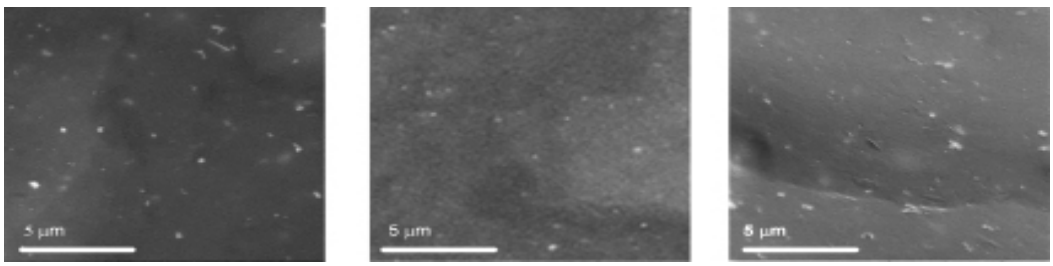
Conclusion

Two new suggested materials were shown coupling agent effects. The results were presented that in comparison of two linear and unsaturated structure for silane coupling agents, lower curative absorption was seen for (A). The van der waals interactions between (A) and the polymer was more effective than the π-π interactions between (B) and the polymer matrix. (A) was caused the better distribution of nano-silica in the rubber matrix.

References

[1] Wolff, S.; Wang, M. J.; Rubber Chem. Technol.; 65, 329-

Figure 3 SEM images of the compounds



NS2 NS3 NS4

343; 1992.

[2] Boonstra, B. B.; Cochrane, H.; Dannenberg, E. M.; Rubber Chem.Technol.; 48, 558-577; 1975.

[3] Voet, A.; Morawski, J. C.; Donnet, J. B.; Rubber Chem. Technol.; 50, 342-356; 1977.

[4] Ou, Y. C.; Yu, Z. Z.; Vidal, A.; Donnet, J. B.; Rubber Chem. Technol.; 67, 834-845; 1994.

[5] Byers, J. T.; Rubber World; 218(6), 38-47; 1998.

[6] Li, Y.; Wang, M. J.; Zhang, T.; Zhang, F.; Fu, X.; Rubber Chem.Technol.; 67, 693-700; 1994.

[7] Choi, S. S.; Choi, S. J.; Bull. Korean Chem. Soc.; 27(9),