The effect of silane type on mechanical properties and fogging phenomenon of lamp socket rubber

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Abstract. Bis-(3-triethoxysilylpropyl) tetrasulphide (TESPT) and 3-mercaptopropyltrimethoxysilane (MTMO) were used as silane coupling agent for silica fume. The modified silica fume was used as reinforcing filler in ethylene propylene diene monomer (EPDM) for lamp socket rubber. The cure characteristics, rubber mechanical properties and fogging phenomenon of lamp socket rubber were investigated. Test results showed that the maximum torque (M_H) and differential torque (M_H-M_L) increased but the minimum torque (M_L), cure time at 10% and 90% decreased with the increasing of silane coupling agent loading. The comparison rubber mechanical properties of modified silica fume by TESPT and MTMO was also discussed. The TESPT showed the enhancement in rubber mechanical properties such as hardness, tensile strength and 300% modulus more than MTMO. The fogging test of lamp socket rubber by the gravimetric method used to control rubber products quality in automotive industry. The using of modified silica fume by TESPT showed the better result than MTMO due to less mass of condensable constituent.

1. Introduction

Silica fume or silicon dioxide (SiO_2) is a by-product from the production of ferrosilicon alloy that used as reinforcing filler in rubber industry. It is additionally utilized as carriers, anti-caking or free-flow agents in cosmetics and food applications. The silanol groups on the silica surface will affect to silica dispersion and rubber mechanical properties. This problem is solved by using the organosilanes or silane coupling agent, its providing the chemical bonding to the silica surface and resulting loss in hydrogen bonded. It can reduce the filler-filler interaction or increase rubber-filler interaction and also provides the potential for cross-linking to the rubber [1, 2]. The lamp socket rubber is a typical product that made from ethylene propylene diene monomer rubber (EPDM rubber) and uses silica as rubber filler due to good insulation and mechanical properties. A major problem in using silane coupling agent for improve rubber property in automotive industry is fogging phenomenon. It can evaporate and form as a film onto the surface of car lamp that causing a reduction in transparency. In the case of lamp socket rubber in automotive industry, the fogging problem has safety implications for drivers and passengers.

In the present, research is focused on the two types of silane coupling agent such as bis-(3-triethoxysilylpropyl) tetrasulphide (TESPT) and 3-mercaptopropyltrimethoxysilane (MTMO). The effect of silane coupling agent on the cure characteristics and mechanical properties in silica fume-filled EPDM rubber were investigated. Furthermore, the fogging test of lamp socket rubber filled modified silica fume by TESPT and MTMO was also discussed.

2. Experimental

2.1. Compounding and vulcanization of lamp socket rubber

Rubber formulations of lamp socket rubber were showed in table 1. The EPDM rubber, carbon black (N550), silica fume, oil, ZnO, stearic acid and silane were mixed in the kneader for 4 min. Then, chamber was cleaned and compound was mixed for 3 min. The accelerator such as ZDBC, TMTD and sulphur were added on a two roll mill. Finally, the specimens were prepared by compression molding at 165°C for 10 min.

2.2. Cure characteristics and mechanical properties of lamp socket rubber

Cure characteristics were measured by a Moving Die Rheometer (MDR2000) at 170°C for 10 min. The maximum torque (M_H), minimum torque (M_L), differential torque (M_H-M_L), cure time at 10% and 90% were determined, according to ISO 6502. A tensile testing machine (AG-IS, Shimadzu) was used for determining tensile strength, 300% modulus and elongation at break of the samples at 23$\pm$2°C, with an extension speed of 500 mm min^{-1}, according to ISO 37. The hardness test was performed using a hardness tester (Teclock) according to ISO 868 by a Shore A durometer.

2.3. Fogging test of lamp socket rubber

A lamp socket rubber was placed in beaker and then covered with an aluminum foil. For a period of sixteen hours the lamp socket rubber was heated to 100^{o}C, after that the aluminum foil was cooled to 21^{o}C, according to ISO 6452. The mass of the fog condensate collected during the test was calculated by the following equation (1):

$$m_F = m_2 - m_1 \quad (1)$$

where m_F is the mass of the fog condensate collected during the test (mg), m_1 is the initial mass of the aluminum foil (mg) and m_2 = the mass of the aluminum foil with the fogging condensate (mg).

Table 1. Formulations of the lamp socket rubber.

Materials	No silane	MTMO-2.5phr	MTMO-3.5phr	TESPT-2.5phr	TESPT-3.5phr
EPDM rubber	100	100	100	100	100
Carbon black N-550	20	20	20	20	20
Silica fume	50	50	50	50	50
Oil	30	30	30	30	30
ZnO	5	5	5	5	5
Stearic acid	1	1	1	1	1
MTMO	-	2.5	3.5	-	-
TESPT	-	-	-	2.5	3.5
Sulphur	0.5	0.5	0.5	0.5	0.5
TMTD	1.5	1.5	1.5	1.5	1.5
ZDBC	1	1	1	1	1

3. Results and discussion

3.1. Cure characteristics and mechanical properties of lamp socket rubber

The effect of silane coupling agent, i.e., bis-(3-triethoxysilylpropyl) tetrasulphide (TESPT) and 3-mercaptopropyltrimethoxysilane (MTMO) on the cure characteristics were showed in table 2. It can be seen that the differential torque (M_H-M_L) and the maximum torque (M_H) increased with the addition of TESPT and MTMO. The both of silane coupling agent showed results higher than without silane coupling agent. It was due to increase concentration of crosslinking in the rubber chain [3]. It is well-known that the addition of silane coupling agent enhances the rubber crosslink density [4], especially for TESPT because of it can provide sulphur atom to link in the rubber chain (sulphur donor) [5]. In consideration of the minimum torque (M_L), it was clearly seen that the addition of silane coupling agent (both of them) reduced the minimum torque (M_L) more than without silane coupling agent. This was attributed to the silane effect that reduced filler-filler interaction in rubber compound because silane coupling agent reacted with silanol groups on the surface of silica fume and reduced hydrogen bonding. This was also believed that silane coupling agent improved filler dispersion in rubber compound and rubber mechanical properties; as explained later. According to the results of cure time at 10% and 90%, the curing time of addition of silane coupling agent showed faster than without silane coupling agent [6]. It was due to reduction of silanol groups on silica fume surface and less absorption of rubber accelerator. Therefore, the silane coupling agent contributed to enhancing cure state in the rubber compound.

Table 2. Cure characteristics of the lamp socket rubber.

Properties	No silane	MTMO-2.5phr	MTMO-3.5phr	TESPT-2.5phr	TESPT-3.5phr
M_H (lb-in)	6.05	6.77	7.20	6.92	7.35
M_L (lb-in)	0.83	0.79	0.75	0.77	0.73
M_H-M_L (lb-in)	5.22	5.98	6.45	6.15	6.62
T_{10} (min)	0.96	0.83	0.72	0.79	0.68
T_{90} (min)	4.31	3.81	3.52	3.73	3.41

Table 3 shows the effect of silane coupling agent on mechanical properties. It was found that the hardness of all compounds filled with modified silica fume increased with the increasing of silane coupling agent loading. The compound filled with the modified silica fume by TESPT showed the higher value than the modified silica fume by MTMO and without silane coupling agent, respectively. This corresponded with the differential torque (M_H-M_L); as the above. The higher of differential torque (M_H-M_L) value not only enhancing the crosslink density but also compound stiffness [7]. It is well known that the compound stiffness is directly proportional to compound hardness. The tensile strength and 300% modulus were also showed in table 3. The test results showed that tensile strength and 300% modulus increased with the increasing of silane coupling agent loading. This was due to concentration of crosslink density. Comparing the type of silane coupling agent, TESPT showed the tensile strength and 300% modulus more than MTMO. This may be attributed to the influence of sulphur atom in TESPT which could split off and reacted to rubber chain during vulcanization. Moreover, the elongation value of the presence of silane coupling agent was lower than without silane coupling agent due to crosslink density in rubber chain and affected to hardly extension. Thus, the modified silica fume by TESPT was superior to MTMO.

Table 3. The mechanical properties of the lamp socket rubber.

Properties	No silane	MTMO-2.5phr	MTMO-3.5phr	TESPT-2.5phr	TESPT-3.5phr
Hardness (Shore A)	58$\pm$1	60$\pm$1	62$\pm$0.5	61$\pm$1	63$\pm$1
Tensile strength (MPa)	15$\pm$0.4	15.8$\pm$0.5	16.9$\pm$0.3	16.1$\pm$0.5	17.2$\pm$0.4
Elongation (%)	750$\pm$40	730$\pm$50	700$\pm$40	720$\pm$50	680$\pm$50
300% modulus (MPa)	3.98$\pm$0.05	4.21$\pm$0.04	4.58$\pm$0.05	4.39$\pm$0.04	4.79$\pm$0.04

3.2. Fogging test of lamp socket rubber

The purpose of fogging test was developed rubber products which was low volatile substance. Therefore, results can be used to control the quality of rubber products. This experiment was complied with the gravimetric method (ISO 6452) which was weighed the sample to determining the mass of condensable constituent. Figure 1 shows the influence of silane coupling agent on fogging test. It can be observed that the mass of condensable constituent increased with the increasing of silane coupling agent loading. It can be clearly seen that the mass of condensable constituent of lamp socket rubber was modified by MTMO higher than that of TESPT. It was due to the molecular weights of MTMO lower than TESPT and contributed to highly weight evaporation. Although the addition of silane coupling agent affected to fogging phenomenon but it enhanced the rubber mechanical properties such as tensile strength, 300% modulus, etc. Thus, the usage of modified silica fume by TESPT was first priority that the rubber manufacturer should be used to it in lamp socket rubber.

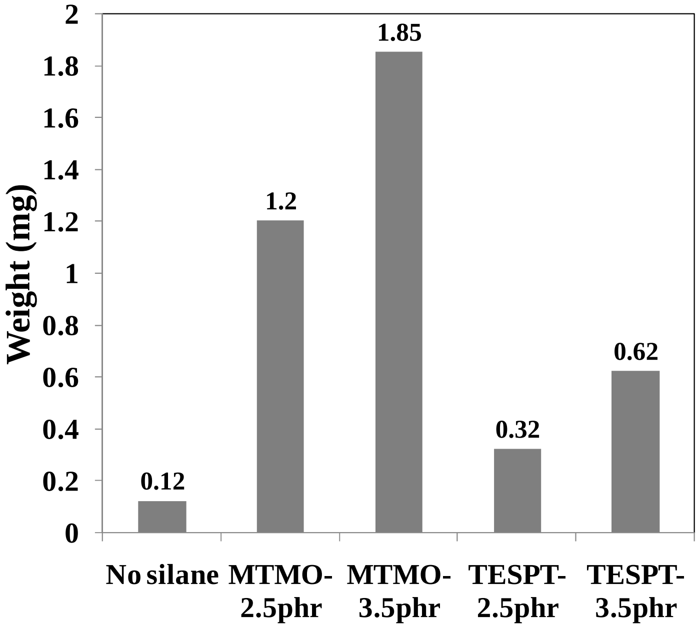

Figure 1. The influence of silane coupling agent on fogging test.

4. Conclusions

The presence of silane coupling agent such as bis-(3-triethoxysilylpropyl) tetrasulphide (TESPT) and 3-mercaptopropyltrimethoxysilane (MTMO) for surface modification of silica fume in lamp socket rubber were investigated. It has significantly improved the cure characteristics and rubber mechanical properties, especially in case of modified by TESPT because of sulphur donor effect. The increment of silane coupling agent contents and crosslink density in rubber chains affected increasing of the state of cure. Therefore, TESPT promoted better fogging phenomenon than MTMO due to the higher molecular weight.

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References

[1] Sae-oui P, Sirisinha C, Thepsuwan U and Hatthapanit K 2006 *Eur. Polym. J.* **42** 479

[2] Siriwong C, Sae-oui P and Sirisinha C 2014 *Polym. Test. 38* 64

[3] Zhang H, Gao Y, Li F, Zhang Z, Liu Y and Zhao G 2016 *Plast. Rubber Compos.* **45** 9

[4] Wiphawadee P, Nakason C, Kummerlöwe C and Vennemann N 2015 *J. Chem.* **117** 1535

[5] Ismail H, Mahir N A and Ahmad Z 2011 *Polym-Plast. Technol.* **50** 893

[6] Yan H, Sun K, Zhang Y, Zhang Y and Fan Y 2004 *J. Appl. Polym. Sci.* **94** 1511

[7] Suntako R 2017 *J. Polym. Res.* **24** 131