

Preparation and Characteristics of High Voltage Liquid Silicone Rubber by Modified Cross-linking Agent

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There is a growing demand for a high voltage silicone rubber composite with high mechanical property and high electrical property. The effect of modified cross-linking agent on the mechanical, electrical properties, and short-circuit test performance of silicone rubber insulators have been investigated. To use base polymer, the various silicone polymers were prepared by the equilibrium polymerization. Aluminum trihydrate surface was treated by vinyl silane. Liquid silicone rubber nanocomposite was prepared from the compounding of VPMPs, HPDMS, catalyst, and alumina trihydrate modified with 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane. The mechanical property and electrical property for insulation materials were measured, indicating the high tensile strength and the good short-circuit property.

Keywords: High voltage insulator, Modified cross-linking agent, Short-circuit test, Liquid silicone rubber

1. INTRODUCTION

Silicone is the one of the most widely used polymer in insulation, coating, and rubber materials in the high voltage insulation. Because the silicone polymers used in preparing silicone rubber compositions include inorganic and organic portions, which each silicone chain atom has two organic groups attached to it. And these properties include excellent weather and thermal stability, oxidation resistance, good electrical properties, extreme low-temperature flexibility, and curability by a various methods at both elevated and ambient temperature[1-4].

As well as demand for power of our country grew rapidly in quantitative side since the 1980 subordinate personality centralism there in done tendency be. Therefore, to correspond to this accommodation KEPCO is propelling work that heightens power transmission, distribution voltage steadily. Therefore, insulation performance, important element that decides life of electric power device, is real condition that research and development of excellent insulating material is necessary. In the case of high voltage insulation insulator silicone rubber, to raise tracking characteristic alumina trihydrate (ATH) content more than 100 phr use must and mechanical properties fell greatly there by and mold flow-ability at injection molding work is fallen and have problem that when produce such as difficulty of removal of forms, workability is bad. Many researches of silicone rubber used for high voltage insulation were carried out[5-9].

Unfortunately, it is rare to see research on the effect of cross-linking agent on the mechanical, electrical properties, and insulation properties of liquid silicone rubber compound for high voltage insulator.

In this paper, the various silicone polymers, such as α , ω -vinyl poly(dimethyl-methylphenyl) siloxaneprepolymer (VPMPs) and α , ω -hydrogen poly(dimethylmethyl-hydrogen) siloxane prepolymer (HPDMS) were prepared by

the equilibrium polymerization. HVI liquid silicone rubber composite containing surface treated ATH modified by vinyl silane coupling agents was prepared by compounding VPMPs, surface treated ATH, and catalyst in high speed dissolver, and we have investigated the influence of modified cross-linking agent(HPDMS) on the mechanical and electrical properties, and insulate performance of silicone rubber insulator.

2. EXPERIMENTAL

2.1 Materials and reagents

1,3,5-trimethyl-1,3,5-triphenylcyclotri-siloxane ($D_3^{Me, Ph}$), octamethylcyclotetrasiloxane (D_4), 1,1,3,3-tetra-methyl-disiloxane (MS), 1,3,5-trimethylcyclotrisiloxane ($D_3^{Me,H}$), 1,1,3,3,-tetramethyl-1,3-divinyl-disiloxane (MVS), and 1,3-divinyltetramethyldisilazane (VMS) were supplied from Aldrich and Bayer Co. All materials were stored in a refrigerator and used without further purification. Tetramethylammoniumsiloxanolate (TMAS) used as initiator was prepared from the reaction of D_3 with tetramethylammonium-hydroxide (TMAH) purchased from Fluka Co. Nanosilica with 200 cm^3/g of surface area 100~150 nm diameter of particle and Pt were supplied from Degussa Co.

2.2 Preparation of VPMPs

VPMPs was prepared using equilibrium polymerization according to the reported method. For example, in a four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and nitrogen inlet tube, D_4 , $D_3^{Me, Ph}$ and MVS with a 14:4:1 mole ratio were added, respectively and reacted for 4 h at 90 °C, in the presence of 0.02 wt% of TMAS under nitrogen atmosphere. After completing the reaction, the reaction mixture was heated to 140 °C to decompose TMAS, and then vacuum stripped at 30 torr to remove oligomeric cyclic species and unreacted monomer (yield : 63 %)[10].

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Table 1. Formulation of LSR nanocomposite preparation.

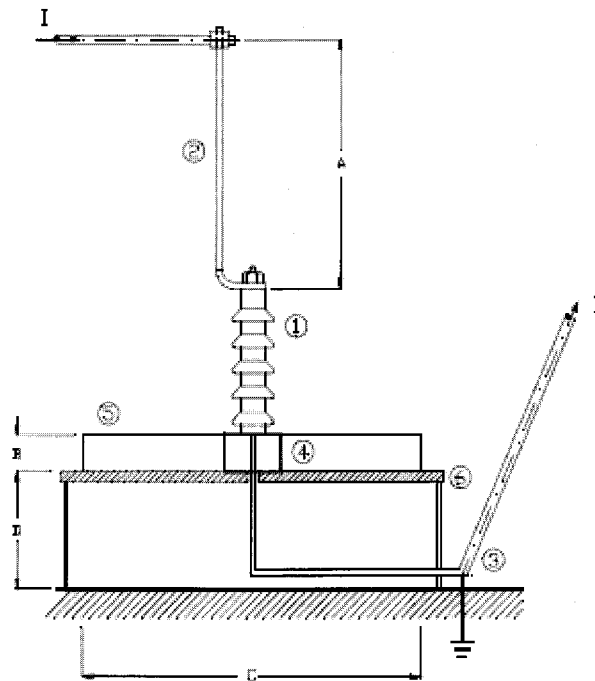
(Unit : phr)

Exp. No.	HVLSR-1		HVLSR-2		HVLSR-3		HVLSR-4	
	A	B	A	B	A	B	A	B
VPMPS	100	100	100	100	100	100	100	100
Silica	25	25	25	25	25	25	25	25
Aluminum trihydrate	100	100	100	100	100	100	100	100
Silane Couping Agent(VMS)	3	3	3	3	3	3	10	10
Pt (ppm)	50	0	50	0	50	0	50	0
Modified Cross-linker (HPDMS)	0	0	0	1	0	2	0	3
Cross-linker		3		3		3		3

2.3 Preparation of HPDMS

To use modified cross-linking agent, HPDMS was prepared with similar method of the preparation of VPMPS. D_4 , $D_3^{Me,H}$, and MS with 5:6.6:1 mole ratio, respectively, were

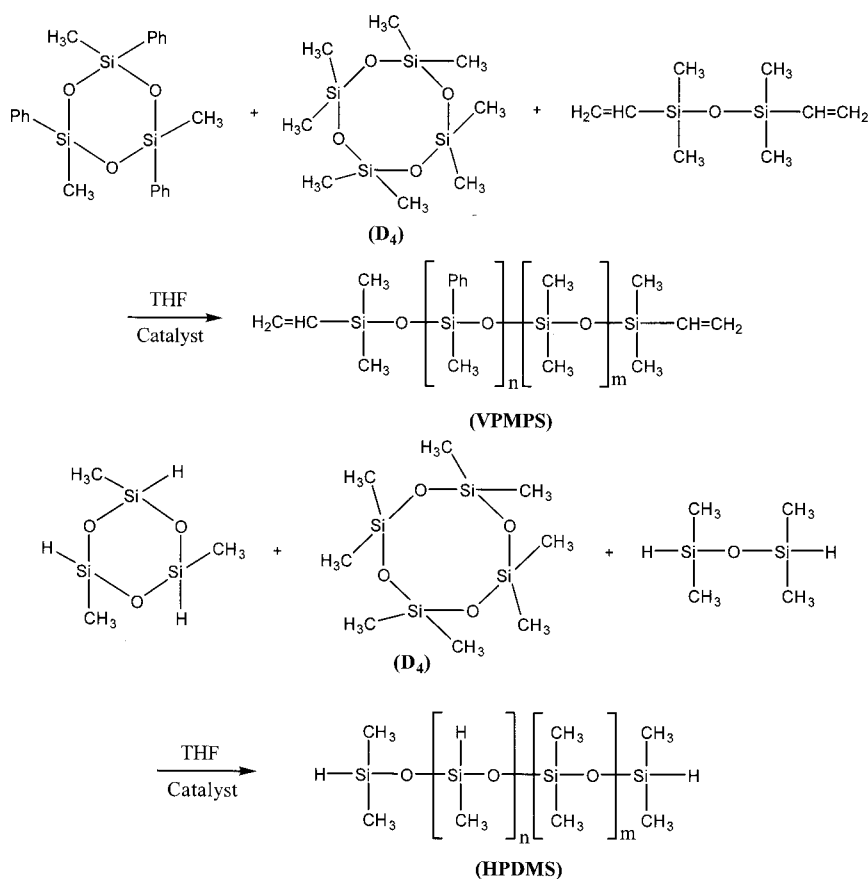
reacted at 90 °C for 4 h in the presence of 0.02 wt% TMAS under nitrogen atmosphere. After completing the reaction, the reaction mixture was heated to 140 °C to decompose TMAS, and then vacuum stripped at 30 torr to remove oligomer cyclic species and unreacted monomer (yield 64 %).



- 1: Surge arrester
- 2: Flexible conductor
- 3: Rigid conductor
- 4: Support
- 5: Surrounding fence
- 6: Insulating wood platform

- A : 1,50 m
- B : 0,40 m
- C : 2,20
- D : 1,00 m

Fig. 1. Examination circuit diagram of IEC 60099 standards.



Scheme 1. Reaction scheme of the VPMS and HPDMS.

2.4 Preparation of polyorganosiloxane composite

High voltage liquid silicone rubber (HVLRSR) was prepared from the compounding of VPMS, HPDMS, catalyst, silica, and aluminum trihydrate modified with 1,3-divinyltetramethyldisilazane (VMS) according to composition rate shown in Table 1 using high speed dissolver(Linden Co. Model : K110) at 130 °C for 3 h under 100~500 rpm. Polyorganosiloxane composite which containing surface treated aluminium trihydrate was prepared from dispersing then to organosiloxane matrix.

2.5 Characterization

2.5.1 Instrumental analysis

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were obtained from Varian EM-360A NMR for polymer spectra were obtained from using Perkin Elmer Spectra GX FTIR spectrometer. Mechanical properties, strength and elongation were measured at room temperature using Instron Universal Testing Machine Model 4411 according to ASTM D412 and 624.

2.5.2 Tracking characteristic test

Tracking resistance was referred to IEC 61109. Test insulators with a creepage distance 520 were prepared by injection molding at 160 °C and 75 Kgf pressure[11].

2.5.3 Short circuit test

Short-circuit test was referred to IEC60099-4. Examination circuit diagram of IEC 60099 standards are shown Fig. 1. The test conditions are as follows,

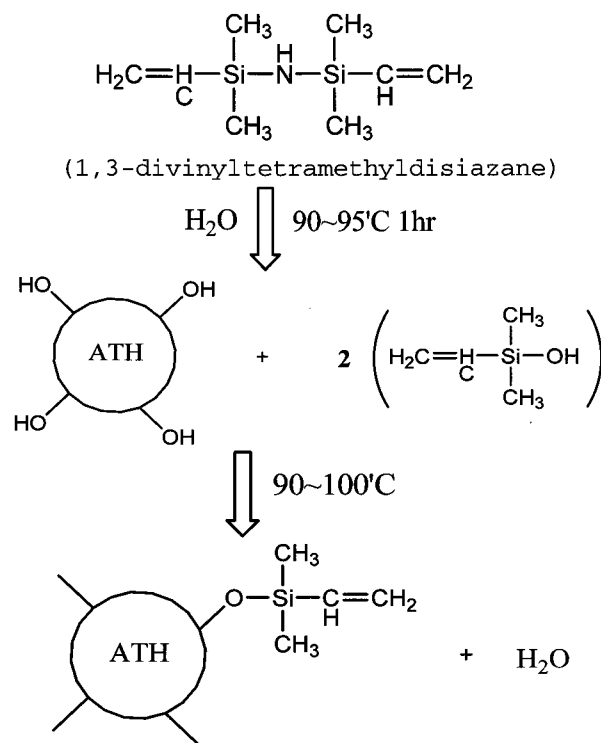
- 1) Rated short-circuit current I_S , 63 kA
- 2) Reduced short-circuit currents 25 kA, 12 kA
- 3) Short-circuit current with a duration of 1^s, 600 A

3. DISCUSSION AND RESULTS

3.1 Preparation of VPMS and HPDMS

In the synthesis of vinyl end-blocked prepolymer containing the block unit of dimethylsiloxane and methylphenylsiloxane, strong base, TMAS will attack first $\text{D}_3^{\text{Me,Ph}}$ with high ring strain, then dimethylsiloxanecyclictetramer D_4 , and finally terminated with MVS. Also, in the synthesis of prepolymer containing the block unit of dimethylsiloxane and hydrogenmethyl-siloxane block unit, TMAS, will attack $\text{D}_3^{\text{Me,H}}$ with high ring strain, then dimethylsiloxanecyclictetramer D_4 , and finally terminated with MS. It is expected that the basic TMAS initiator will attack $\text{D}_3^{\text{Me,ph}}$ or $\text{D}_3^{\text{Me,H}}$ with high ring strain first. The reaction mechanism for the preparation of VPMS and HPMHS is shown in Scheme 1[12-14].

The structure of VPMS and HPDMS prepolymer were confirmed by the measurement of FT-IR and $^{13}\text{C-NMR}$. The



Scheme 2. Reaction scheme for aluminum trihydrate surface treated with VMS silane coupling agent.

FT-TR spectra of VPMPs and HPDMS exhibited strong absorption peak at 1100 to 1020 cm^{-1} due to the Si - O - Si stretching vibration at 1343, 1613 cm^{-1} , due to Si-vinyl respectively. And the peaks due to Si-Ph appeared at 1430, 1892, 1961 cm^{-1} , the peak due to Si-H appeared at 2160 cm^{-1} . In the ^{13}C -NMR spectrum of VPMPs the peaks due to Si-Ph appeared at 127.0~138.0 ppm and at 0.867 ppm due to Si- CH_3 .

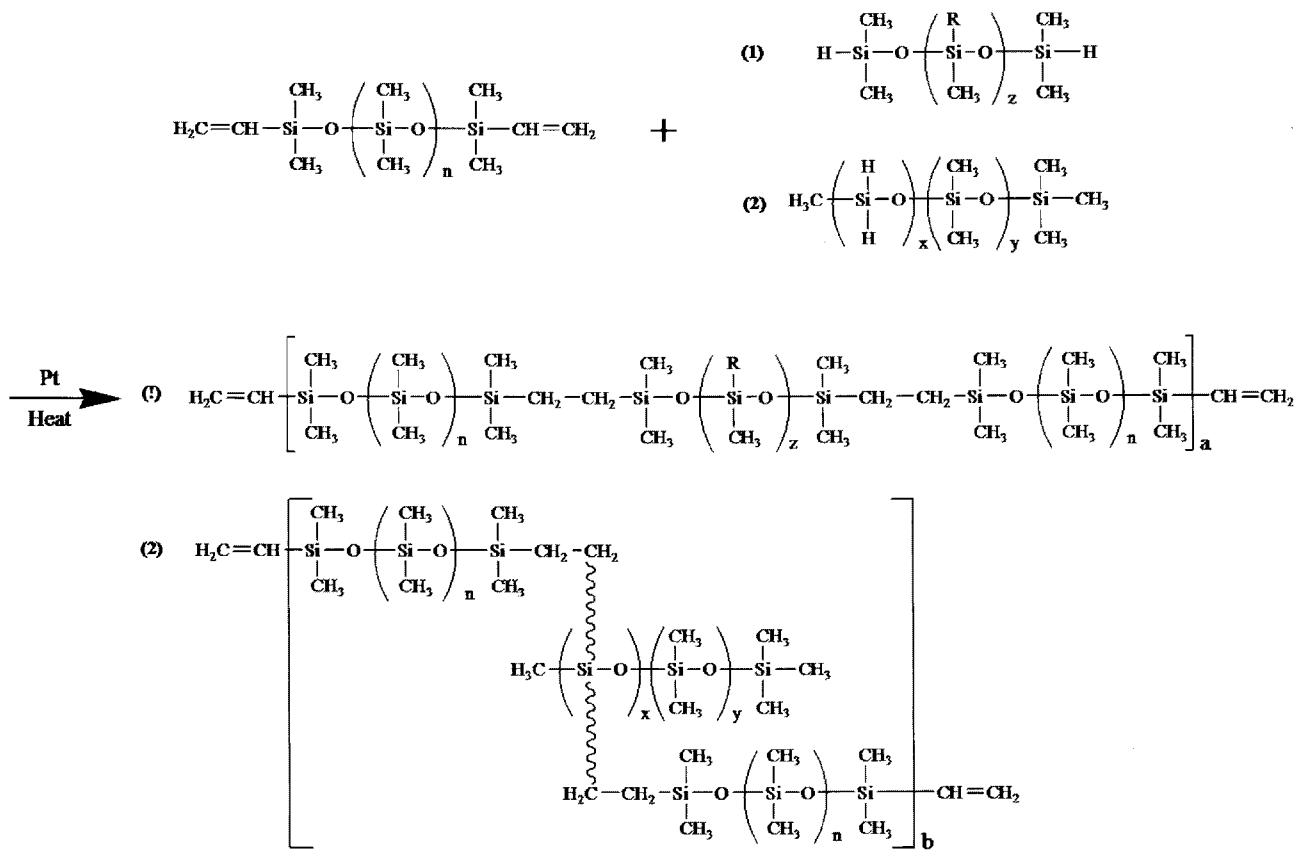
3.2 Preparation of polyorganosiloxane composite

The ATH was incorporated with VPMPs on a high speed dissolver at room temperature. The quantity of ATH was 100 phr based on 100 phr of VPMPs. And 10 phr of VMS

as surface treating agents and 50 ppm of platinum catalyst were added. An uncured LSR composite was prepared by compounding for 4h at 90 ~ 120 $^\circ\text{C}$ according to the formulation shown in Table 1 using for 2 hr at 150 $^\circ\text{C}$ on high speed dissolver. Modification of ATH with vinylsilanol was investigated by measurement of FT-IR. FT-IR spectrum of ATH before modification with VMS show strong absorption peak due to silanol group at 3400 cm^{-1} , but after modification the absorption peak due to silanol group disappeared. The OH groups are introduced on the surface of ATH, and then by the reaction of silanol group on ATH surface with VMS, functional groups are introduced on the surface ATH. The reaction mechanism of surface treatment is shown in Scheme 2[15].

Table 2. Properties of HVLSR according to modified cross-linking agent.

Properties	HVLSR-1	HVLSR-2	HVLSR-3	HVLSR-4	Units
Specific gravity					g / cm^3
Hardness	65	64	61	56	Shore A
Tensile Strength	44	58	62	66	Kgf / cm^2
Elongation at break	180	260	320	460	%
Tear Strength	11	16	21	28	Kgf / cm
Dielectrically Strength	25	26	24	25	kV / mm
Volume Resistivity	1.2×10^{14}	1.0×10^{14}	0.8×10^{14}	1.1×10^{14}	$\Omega \cdot \text{cm}$



Scheme 3. Reaction scheme for cross-linking agent.

3.3 Properties of HVLSR composite containing modified cross-linking agent

3.3.1 Mechanical properties

Mechanical and electrical properties of HVLSR according to modified cross-linking agent were measured and the results are shown in Table 2.

As shown in Table 2, the tensile strength and elongation of HVLSR-1 without modified cross-linking agent are 44 Kgf / cm² and 180 %, HVLSR-4 containing 3 phr of modified cross-linking agent are 66 Kgf / cm² and 460 %.

According to increasing the content of modified cross-linking agent, tensile strength and elongation are increased. The reaction mechanism of cross-linking of LSR is shown in Scheme 3. These results indicate that the modified cross-linking agent act as chain extender, and bring about increasing of molecular weight of VPMS and mechanical properties.

3.3.2 Tracking properties

Figure 2 and Fig. 3 show tracking characteristic and short circuit test of HVLSR according to modified cross-linking agent and ATH surface treatment.

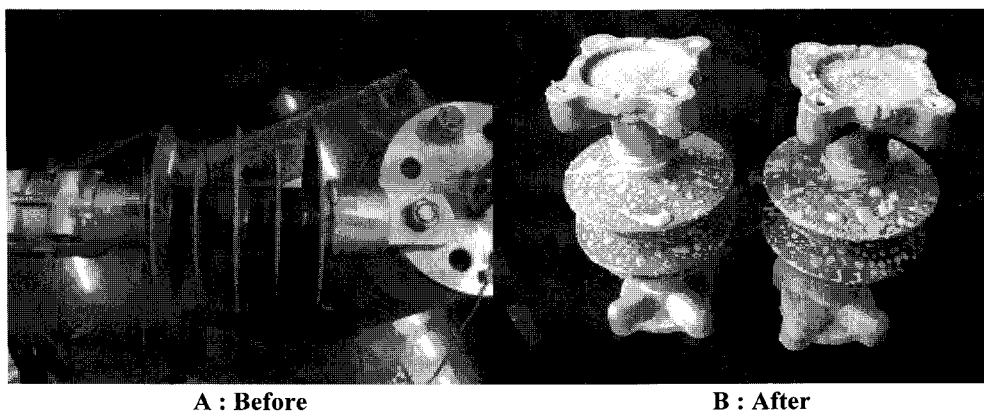


Fig. 2. The specimen of tracking test(A: Before the tracking test, B: After the tracking test).

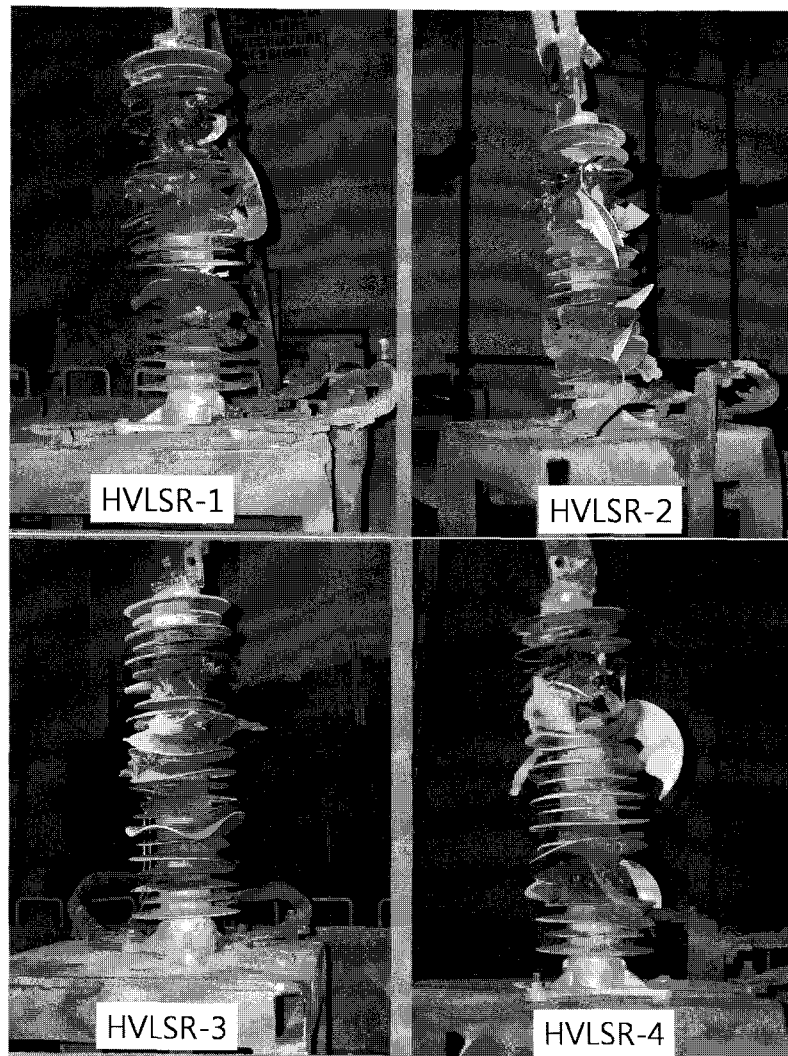


Fig. 3. Short circuit test of HVLSR according to modified cross-linking agent.

On increasing the content of modified cross-linking agent, short circuit test property is improved. When all compounds were filled with 100 phr of ATH, All insulator satisfied IEC 61109 standard for tracking characteristics. But HVLSR-1 and HVLSR-2 without and 1phr of modified cross-linking agent were failed at short-circuit test, because the broken piece of HVLSR-1 and HVLSR-2 fallen over surrounding fence are 35 gr and 22 gr. But HVLSR-3 and HVLSR4 that were filled with 3 and 4 phr of modified cross-linking agent satisfied IEC60099-4 standard for circuit test. On increasing the content of modified cross-linking agent, tensile strength, elongation, and tear strength of silicone rubber are increased[16]. So that short circuit test property is improved. These results indicate that the elongation of high voltage silicone insulator is one of the most important factor in short-circuit test. And by using modified cross-linking agent, elongation can be improved to satisfy IEC60099-4.

4. CONCLUSION

VPMS containing the block unit of dimethyl siloxane and methylphenyl siloxane was prepared by the equilibrium polymerization. Also, HPDMS containing the

dimethylsiloxane and hydrogen methylsiloxane can be prepared. And high voltage liquid silicone rubber compound which containing surface treated ATH and modified cross-linking agent was prepared from dispersing then to organosiloxane matrix. The HVLSR insulator with 3 phr of modified cross-linking agent has high mechanical property and satisfy IEC 60099-4 standard for circuit test and IEC 61109 standard for tracking characteristics .

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