Synthesis and Properties of High Voltage Silicone Rubber by Platinum-based Flame Retardant

Se-Young Jung[a] and Byung-Kyu Kim
Department of Polymer Science and Engineering, Pusan National University, Jangjeon 2-dong, Geumjeong-gu, Pusan 609-735, Korea

[a]E-mail : polyster@pusan.ac.kr

(Received August 29 2006, Accepted December 18 2006)

So that high-strength and electrical properties apply by excellent high voltage insulator electricity material, ATH content and platinum-based flame retardant that influence in flame retardant and tracking characteristic among composite of silicone rubber studied mechanical strength and influence getting to electrical properties. Composition of α, ω -vinyl poly (dimethyl-methylphenyl) siloxane(VPMPS) of a polymer quantity made doing mole of D4, $D3^{Me, Ph}$ and VMS by *1000*:15:0.2 mole ratio and uses basic catalyst *tetramethylammonium* silanolate(TMAS) and do opening equilibrium polymerization to be used to main polymer for high voltage insulation insulator. Control ATH content and content of platinum-based flame retardant and made high voltage insulation silicone rubber. Measured mechanical strength of making silicone rubber using UTM, and tracking characteristic according to standard of IEC 60587, flame retardant test studied effect that flame retardant characteristic gets in tracking characteristic, measuring according to UL94V method of test.

Keywords : High voltage insulator, Platinum-based flame retardant, Tracking characteristic, Silicone rubber, ATH(Alumina trihydrate)

1. INTRODUCTION

Siloxane(Si-O-Si) that silicone industry was begun commercialization[1,2] because E. G. Rochow succeeds in composition of methyl and phenylchlorosilane by direct method in 1941, and silicone atom and oxygen atom combine each other is middle of organic chemistry and inorganic chemistry by a polymer to staple. Therefore, the characteristic has heat resistance, cold resistance, stability of oxidation, weather resistance and electrical properties and water resistance, flame retardant, avirulent, gas permeability and tack etc. is excellent than other material. Specially, general insulating materials can not use at high temperature but silicone rubber has excellent insulation characteristic because there are little changes of insulation characteristic in wide range of temperature of -40 ~ 200 ℃. Because of this characteristic, researcher about application of field of electricity electron material of silicone rubber abuzz go, and electrical properties study to use by high tension insulation material is achieved much. 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 propeling work that heighten power transmission, distribution voltage steadily. Therefore, insulation performance, important element that decide 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 ATH content more than 80phr use must and mechanical properties fell greatly there by and mold flowability at injection molding work is fallen and have problem that when produce such as difficulty of removal of forms, workability is bad. Used ATH more than 90 phr to improve mechanical properties and wave that test electrical properties and tracking characteristic and flame retardant of silicone rubber for high voltage insulation insulator using from domestic and outside the country and hardness was made between 64~71. Also, B company product tensions strength displayed 35 kgf/㎠, percentage of elongation displayed very low value by 240 % and A company product tensions strength is displaying 60 kgf/㎠, percentage of elongation is displaying High properties of matter most by 270 % in occasion of physical properties, but do not reach greatly in characteristics of general silicon product.

Therefore, in this experiment used platinum-based flame retardant to maximize mechanical properties, electrical properties and workability minimizing ATH and studied mechanical, electrical properties and tracking characteristic by this.

2. EXPERIMENT

2. 1 Materials and reagents

1, 3-divinyl-1, 3 - tetramethyldisiloxane (VMS), 1, 3, 5 - triphenylmethylcyclotrisiloxane ($D_3^{Me,Ph}$) and octamethylcyclotetrasiloxane (D4) were supplied from Aldrich. Tetramethyl-.ammonium siloxanolate(TMAS) used as catalyst was prepared from reactions between hexamethylcyclotrisiloxane(D3) and tetramethylammonium hydroxide(TMAH) purchased from Fluka. Flame retardant HR-FS-3 was supplied from HaeRyong silicone. Nanosilica with 200 ㎡/g of surface and 80 ~ 100 nm of particle size was supplied from Degussa. ATH(SF-4)[table 1] was supplied from Smitomo Co. 2, 5-Dimethyl 2,5-t-butyl peroxy hexane(DMTBPH) used as cross-linking agent was supplied from Aldrich.

Table 1. Properties of ATH

Properties		SF-4
Chemical composition (%)	$Al(OH)_3$	99.7
	Na_2O	0.28
	SiO_2	0.02
Average particle size (㎛)		4
Water content (wt%)		0.34

2.2 α, ω-Vinyl Poly (dimethyl-methylphenyl) siloxane (VPMPS) cmposition

VPMPS was prepared using equilibrium polymerization according to McGrath method [3]. 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 VMS each 1000 : 15 : 0.2 mole ratio were added, respectively and reacted for 8 h at 90 ℃, in the presence of 0.02 wt%of TMAS under nitrogen atmosphere. After completing the reaction, the reaction mixture was heated to 150 ℃ to decompose TMAS, and then vacuum stripped at 30 torr to remove oligomeric cyclic spceies and unreacted monomer gets VPMPS of high viscosity that dimethyl and methylphenyl siloxane black unit is introduced to main chain after reaction is finished (yield : 72 %).

2.3 Compounding and test specimen

Extra-high voltage silicone rubber composition with optimum electrical properties and physical properties was prepared from compounding of prepolymer VPMPS, silica, ATH, and Flame retardant according to formulation shown in Table 2. using a kneading machine (Linden Co. Model KII 10) at 180 ℃ for 8 hours. Test specimen were prepared from compression mold with DMTBPH at 175 ℃ for 10 minutes under 15 MPa pressure.

2.4 Characterizations

2.4.1 Instrumental analysis.

FT-IR spectra were obtained from Perkin Elmer Spectrum GX FT-IR Spectrometer. ^{13}C-NMR and ^{1}H-NMR spectra were obtained from Variann EM-360 NMR for polymer solution in $CDCl_3$ solution. Tetramethylsilane(TMS) was used as an internal reference.

Thermal stability of HVSRC was evaluated by TG analysis (Seiko Company TG/DTA EXTRA 6000). TG graphs were obtained. Examination material puts 6~8 mg to aluminum pan and measured all examination ingredients at heating rate of 200 ℃/min in 40~800 ℃ extent under nitrogen air current and reference cell used vacant aluminum fan.

For quantity analysis of synthesis materials NIR spectra were obtained from NIR Flex N- 400 (Bushi company's NIR.

LSR Cross-linking density was measured at 110 ℃ using Monsanto Oscillation Disk Cure Meter(Model : ODR 100) according to ASTM D 2084.

Table 2. Formulation of compound acording to Flame Retardents Amount (unit : phr)

Samples / Ingredients	HVSR-0	HVSR-30	HVSR-60	HVSR-90
VPMPS	100	100	100	100
A-200	40	40	40	40
Process Oil	2	2	2	2
ATH	0	30	60	90
HR-FS-3	0, 5, 10, 15	0, 5, 10, 15	0, 5, 10, 15	0

Mechanical Properties were measured at room temperature using Instron Universal Testing Machine Model 4411 according to ASTM D 412 and 624.

Volume resistivity were measured using TOA Electronics company model SM-10E at 1 mm ㎜ thickness.

Dielectric strength of silicone rubber was measured according to ASTM D149[4-11].

Permittivity characteristic were measured at 35 ℃ ~ to 250 ℃, and 100,000 Hz to 1 Hz, using American TA Instruments company DEA (Dielectric Analyzer model 2970) .

2.4.2 Flame retardant test

Flame retardant was measured according to UL 94V method[12]. As it were, measured time that flame fire gets struck to be digested perfectly in test piece after remove while lightened flame for 10 seconds producing examination material that do compounding because ATH content does fluent by 20 phr unit to 20~100 phr to 2 mm x 12.5 mm x 125 mm relationship size. Displayed average value that test 10 times to heighten authoritativeness by result.

2.4.3 Tracking characteristic test

Tracking resistance was referred to IEC 60587 but the concentration of conductive material was twice of IEC standard in order to accelerate the tracking failure[13]. When the value of the current in the high voltage circuit through the specimen exceeded 60 mA over two seconds, the overcurrent device would break this circuit. The 60 Hz power supply can be varied up to about 6kV with a rated current not less than 0.1A for each specimen. The contaminant consists of 0.2 wt% NH_4Cl(twice of IEC 60587 standard) and 0.02 wt% isooctylphenoxy polyethoxy ethanol(Triton X-100 of nonionic) in de-ionized water.

Eight layers of filter-paper are clamped between the top electrode and the specimen to act as a reservoir for the contaminant. The contaminant is fed into this filler-paper pad so that a uniform flow between the top and the bottom electrodes occurs before voltage application. The rate of application of contaminant is 0.9 ml/min.

3. RESULT AND DISCUSSION

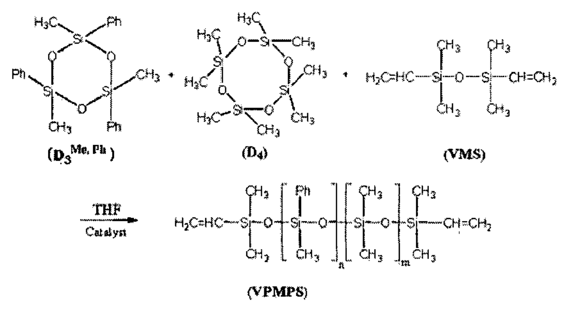
3.1 Synthesis of VPMPS

To be used to main polymer for high voltage insulation insulator composition of α, ω -vinyl poly (dimethyl-methylphenyl) siloxane(VPMPS) of a polymer quantity does mole rate of D4, $D3^{Me,\ Ph}$ and VMS by 1000:15:0.2 mole ratio doing nitrogen flow in 5 holes flask effector of 10 ℓ and made doing equilibrium polymerization after basic catalyst tetramethyl-ammonium silanolate(TMAS) adds 0.2 wt %. Used TMAH that is hydration fourth ammonium (quaternary ammoniumhydroxide) that display basicity by catalyst at this equilibrium polymerization reaction and the reason because TMAH at equilibrium polymerization reaction are low activation energy and temperature dependence than basic catalyst such as KOH and TBPS cyclosiloxane when make do opening, efficiency is very high and TMAH is deactivated in methanol and trimethylamine by heat at low temperature about 130 ℃ after reaction end with Scheme 1. and because thermal stability can compose excellent siloxane .

$$(CH_3)_4NOH \xrightarrow{\triangle} (CH_3)_3N + CH_3OH$$

Scheme 1. Decomposition of TMAS.

That Vinyl group is substituted on end and TMAS that is basic catalyst to make dimethylsiloxane and prepolymer that have methylphenylsiloxane by block unit is formed first methylphenylsiloxane block unit because mountain fortress wall attacks first big $D3^{Me,Ph}$ more and dimethylsiloxane block unit is created and becomes end block by VMS because D4 is polymerized next know can. Displayed reaction vessel of VPMPS prepolymer manufacture to Scheme 2. Measured FT-IR and ^{13}C-NMR for structure confirmation about created VPMPS and result Appeared to Fig. 1 and 2. Figure 1 between 1020 and 1100 cm^{-1} by synthesis VPMPS FT-IR graph absorption by Si-O-Si bond absorption peak by methyl group that peak appear, and is combined to Si in 1243 cm^{-1} appeared, and also 1430, 1892, absorption peak by phenyl group combined to Si in 1961 cm^{-1} appears, and absorption peak by vinyl group combined to Si in 1613 cm^{-1} appeared. Figure 3. phenyl group carbon by Si-Ph appeared between 127.0~138.0 ppm if see ^{13}C-NMR on that display ^{13}C-NMR of VPMPS and ^{1}H-NMR spectra, and methyl carbon by Si-CH3 has appeared in 0.867 ppm and could confirm prepolymer structure that make seeing that proton by Si-vinyl group has appeared in 6 ppm in ^{1}H-NMR. Synthesis VPMPS prepolymer could know that wave and phenyl group content that do quantitative analysis using NIR and H-NMR prepolymer's block unit was not agreed according to mole ratio of reaction ratio because content of 1 mol/gr, vinyl group appears by 0.01 m mol/gr but the ratio is agreeing in general.



Scheme 2. Preparation of VPMPS.

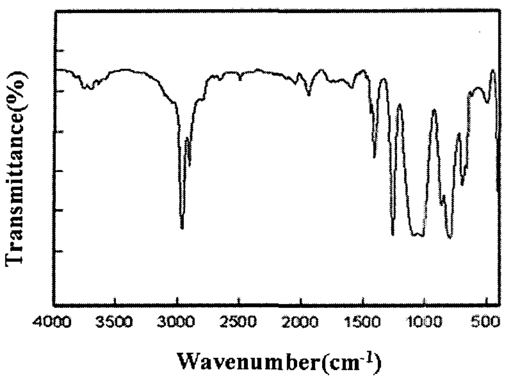


Fig. 1. FT-IR spectra for VPMPS.

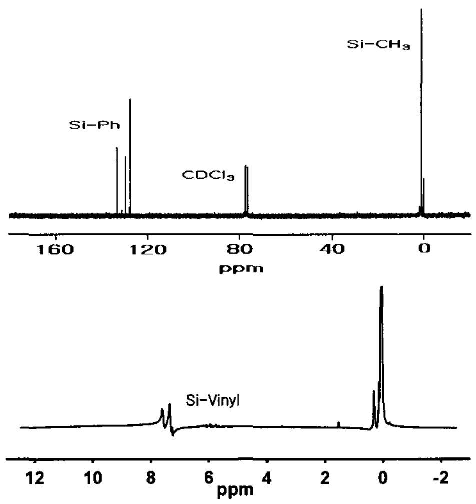


Fig. 2. ^{13}C-NMR and ^{1}H-NMR spectrum for VPMPS.

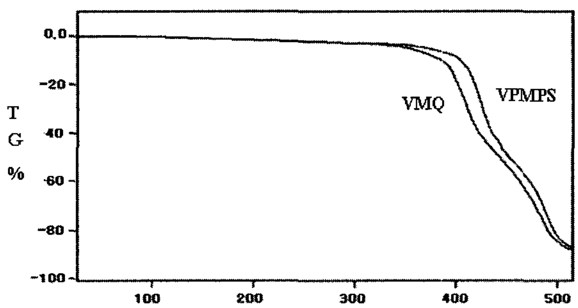


Fig. 3. Thermal properties of VPMPS and VMQ(α,w-vinyl polydimethyl siloxane).

Also, did TG Test to examine making polymer heat resistance and the result Appeared to Fig. 3. Silicone polymer that use usually to silicone rubber compound is begun to disintegrate in about 320 ℃ as VMQ that vinyl group is introduced, but VPMPS that make confirmed that heat resistance makes excellent silicone polymer seeing that is begun to disintegrate in 350 ℃ near.

3.2 Manufacture and characteristic of silicone rubber for high voltage insulator by use of platinum-based flame retardant

In the case of high voltage insulation insulator silicone rubber, to raise tracking characteristic ATH content more than 80 phr use must and mechanical properties fell greatly thereby and mold flowability at injection molding work is fallen and have problem that when produce such as difficulty of removal of forms, workability is bad. Used ATH more than 90 phr to improve mechanical properties and wave that test electrical properties and tracking characteristic and flame retardant of silicone rubber for high voltage insulation insulator using from domestic and outside the country and hardness was made between 64~71. Also, B company's product tensions strength displayed 35 kgf/㎠, percentage of elongation displayed very low

value by 240 % and A company's product tensions strength is displaying 60 kgf/㎠, percentage of elongation is displaying High properties of matter most by 270 % in occasion of physical characteristics, but do not reach greatly in characteristics of general silicone product. Therefore, in this experiment, used platinum-based flame retardant to maximize mechanical properties, electrical properties and workability minimizing ATH and studied mechanical, electrical properties and tracking characteristic by this.

As it were, displayed silicone rubber that make platinum-based flame retardant adding 0, 5, 10 and 15 phr after fill ATH 60 phr by HVSR-60-0, HVSR-60-5, HVSR-60-10 and HVSR-60-15 and ATH tested silicone rubber that make platinum-based flame retardant inputting 0, 5, 10 and 15 phr to 30 phr because do silicon rubber that input ATH 30 phr by HVSR-0-0, HVSR-0-5, HVSR-0-10 and HVSR-0-15 and does not use flame retardant by HVSR-90.

3.2.1 Mechanical properties

Appeared to Table 3. arranging mechanical properties of silicone rubber that do compounding differing content of ATH and flame retardant. In occasion of tension strength if sees in Table 3. ATH 90 phr when displayed 54 kfg/㎠, and is 60 phr when was filled values of 61 ~ 64 kfg/㎠, 30 phr when was filled value of 76 ~ 85 kfg/㎠ appear and displayed value more than 100 kfg/㎠ when ATH was not filled. Also, percentage of elongation ATH 60 phr when is added value more than 290 ~ 320 %, 30 phr occasion 515 ~ 570 % that do not use 395 ~ 510 %, ATH when is filled appear. In occasion of silicon rubber that Tear strength too, ATH 60 phr in case of was filled values of 13 ~ 15 kfg/㎝, ATH 30 phr in case of was filled 17 ~ 19 kfg/㎝ value appear, and does not use ATH values of 27 ~ 34 kfg/㎝ appear, confirmed that mechanical strength falls greatly according as therefore use ATH.

Table 3. Mechanical properties of high voltage silicone rubber according to experimental formulation.

Exp. No	Formulation			Tensile Strength (kgf/㎠)	Elongation (%)	Tear strength (kgf/㎝)	Hardness (Shore A)
	VPMPS	ATH	HR-FS-3				
HVSR-0-0	100	0	0	103	570	34	69
HVSR-0-5	100	0	5	108	590	31	71
HVSR-0-10	100	0	10	106	520	27	73
HVSR-0-15	100	0	15	101	515	27	73
HVSR-30-0	100	30	0	85	510	18	70
HVSR-30-5	100	30	5	76	465	19	71
HVSR-30-10	100	30	10	81	450	17	72
HVSR-30-15	100	30	15	79	395	18	74
HVSR-60-0	100	60	0	64	320	14	71
HVSR-60-5	100	60	5	64	300	13	71
HVSR-60-10	100	60	10	62	310	12	73
HVSR-60-15	100	60	15	61	290	12	75
HVSR-90-0	100	90	0	54	310	14	73

3.2.2 Thermal properties

Place that use high voltage insulation insulator is factor that weather resistance and heat resistance of insulation that is made according as low temperature area, wet shore area, mountains area and stain and damage is used in various place to serious industrial area in high temperature area are important. EPDM, EVA and Silicone rubber is known most to polymer insulation material used in domestic and abroad, and among them, silicone rubber only electrical properties that weather resistance, hydrophobicity and heat resistance is the most excellent many know . But, heat resistance is fallen by using much ATH to improve tracking characteristic. In the case of ATH, because dissolution temperature is disintegrated in 200℃ near, become factor that make heat resistance of silicone rubber low. Displayed pyrolysis characteristic by ATH content and content of flame retardant to Figure 4. and Figure 5. Was expose that amount of material that can know that the first dissolution amount in 200℃ near reduces according as ATH content decreases if see in Figure 4. and is resolved the first is proportional changelessly according to ATH content. The other side, is expose that pyrolysis in occasion 200℃ near that do not use entirely does not recapture ATH and could confirm that heat resistance stability is excellent. Therefore, to make insulation material that have excellent heat stabilization, is considered that ATH content should does by minimum. Figure 5. increases the first dissolution beginning temperature as content of flame retardant is increased in pyrolysis curve by content of flame retardant and decomposition velocity progressed slowly. This is considered by carbonization class is formed by platinum-based flame retardant and flame retardant and heat resistance were increased relatively.

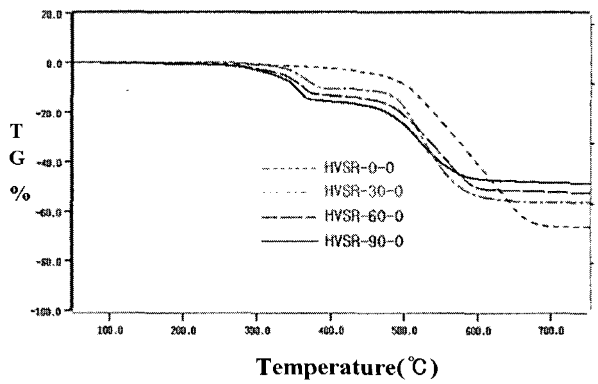


Fig. 4. Thermal gravity of HVSR according to the ATH contents.

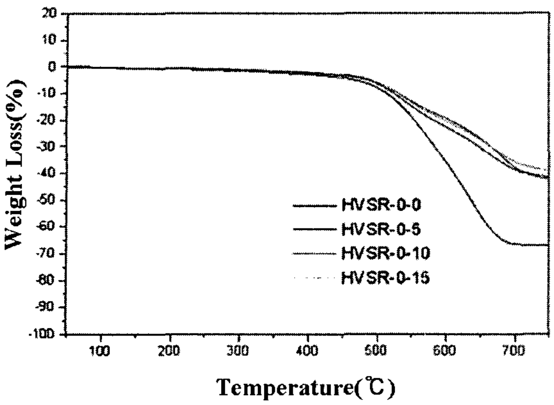


Fig. 5. Thermal gravity of HVSR according to the flame retardant contents.

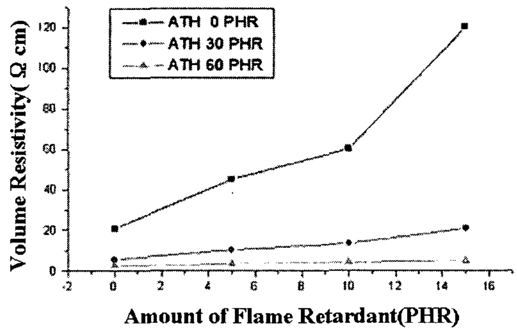


Fig. 6. Volume Resistivity of silicone rubber according to flame retardant & ATH contents.

3.2.3 Electrical properties

Measured dielectric breakdown strength and volume resistance to confirm electrical properties by ATH content and content of flame retardant and displayed the result to Fig. 6 and Fig. 7. Volume resistance fell greatly according as volume resistance value of silicon rubber that do not use ATH if see in Fig. 6. is appearing by 2×1015 Ω.cm, but ATH content increases. This is considered that volume resistance reduced according as polar substance such as H2O that exist to ATH increases.

Also, charge for the volume resistance by addition of flame retardant is low rate of increment when ATH uses 30 and 60 phr, according as flame retardant increases in occasion of HVSR-0 that do not use ATH, rate of increment of volume resistance appeared greatly.

Because this was increased Cross-linking density acting by catalyst that platinum that exist to platinum-based flame retardant causes silicone polymer's Hydrosilylation reaction, is considered that volume resistance increases

Fig. 7 is that display dielectric breakdown strength by ATH content, dielectric breakdown strength of HVSR-60 that ATH content uses 60 phr has cost of 24 ~ 26 kV/㎜, and dielectric breakdown strength of HVSR-30 that ATH content uses 30 phr is 27 ~ 32.5 kV/㎜, and displayed value of occasion 30 ~ 35 kV/㎜ that do not use ATH. Also, according as content of flame retardant increases, could know that dielectric breakdown strength increases. This crystal water combined to ATH according as ATH content increases increased and also void between ATH and silicon polymer increased after compounding and is considered that dielectric breakdown strength becomes low acting through fault to these.

3.2.4 Permittivity and Permeability

Figure 8, 9 and 10 ATH content measuring relation of permittivity by amount and frequency of flame retardant in extent of 250 ℃ in 50 ℃ to silicone rubber

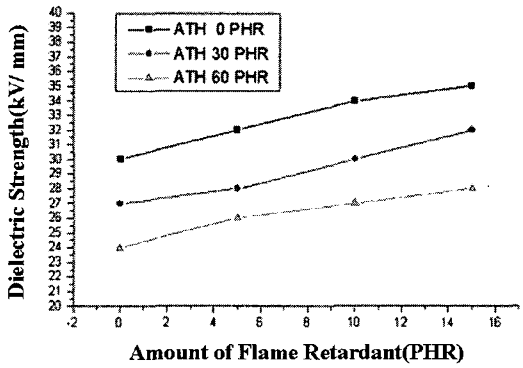


Fig. 7. Dielectric strengths of silicone rubber according to flame retardant contents.

that use 30 phr, 60 phr and 90 phr the result appear. Figure 9 displays result that measure relation of permittivity by frequency in range of temperature of 250 ℃ in 50 ℃ to silicon rubber that add ATH 30 phr. Present state that permittivity increases as temperature is increased in frequency of 1 Hz if see in picture appeared and present state that permittivity decreases as temperature increases in frequency more than 10 Hz appeared.

This is considered that permittivity is increased because water molecule activity increases as crystal water that exist to ATH actions of electric dipole orientation polarization is achieved smoothly in low frequency, and temperature increases. Figure 10 relation of permittivity by frequency of silicone rubber that ATH content is 60 phr, Fig. 10 result that test relation of permittivity by frequency of silicone rubber that ATH content is 90 phr appear. ATH 60 phr fill silicone rubber ATH that displaytendency similar to 30 phr add silicone rubber confirm can. Also, is displaying permittivity that is unstable according to temperature displaying value of best 5.25 near 230 ℃ because permittivity increases greatly in low frequency.

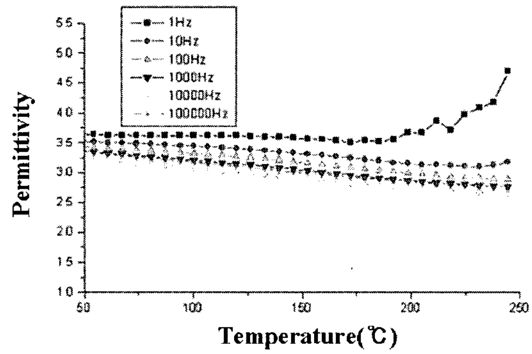


Fig. 8. Permittivity of HVSR-30-15 according to frequency.

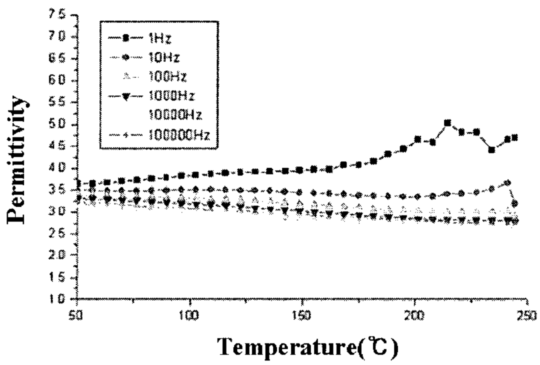


Fig. 9. Permittivity of HVSR-60-15 according to frequency.

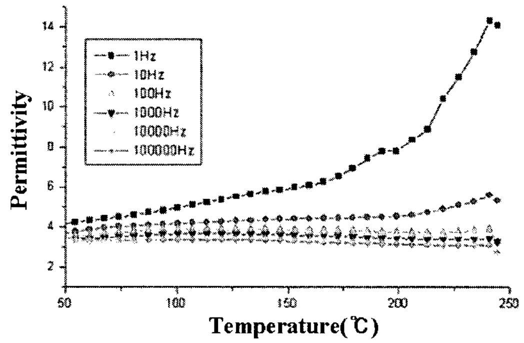


Fig. 10. Permittivity of HVSR-90-0 according to frequency.

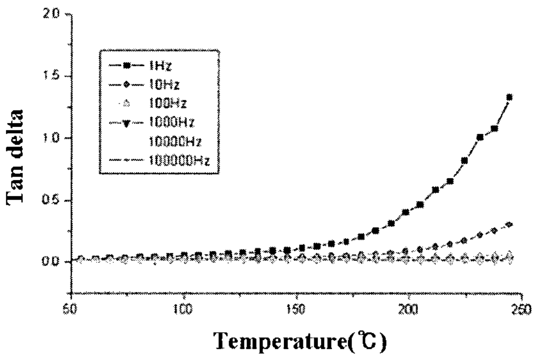


Fig. 11. Tangent delta of HVSR-30-15 according to frequency.

If synthesize effect that ATH and flame retardant get to permittivity, silicone rubber that use ATH is seen that is observed almost changelessly because when frequency is high, function of polarization is slowed and frequency achieves included free water, absorbed water and action of electric dipole orientation polarization of number of chemical combination smoothly to ATH in low occasion specific inductive capacity is increased and considered that permittivity rises according as ATH content increases because water molecule's activity increases as temperature increases.

The other side, because silicone rubber that do not use ATH does not exist material that cause polarizing action, is considered that do not suffer big impact in temperature and frequency. Also, was expose that difference of permittivity by content of flame retardant hardly exists. Therefore, was expose that is excellent insulation material that silicone rubber that use flame retardant without using ATH is stable in all frequencies and temperature.

Displayed dielectric loss about HVSR- 30-5 that ATH inputes flame retardant 5 phr to silicone rubber that input 30 phr to Fig. 11 and dielectric loss about HVSR- 30-15 that input flame retardant 15 phr to Fig. 12. ATH displayed dielectric loss change by frequency of HVSR-60-15 that input flame retardant 15 phr to silicone rubber that input 60 phr to Figure 13. dielectric loss increased according as temperature increases in low frequency fewer than dielectric loss 100 Hz about HVSR-90-0 that ATH inputes 90 phr, and High frequency more than 1000 Hz displayed fixed dielectric loss that hardly be influenced in change of temperature.

If synthesize these result, occasion temperature change and dielectric loss change by change of frequency that do not use ATH are little, appeared almost changelessly.

According as when use ATH, ATH content increases, width of dielectric loss change by change of frequency and change of temperature appeared greatly.

That is, dielectric loss increased according to temperature increase in case use ATH in low frequency fewer than 100 Hz, and 1000 Hz more than displayed almost fixed dielectric loss. Is considered that dielectric loss is increased because activity of water molecule that this exists to ATH as temperature increases is increased and therefore strength of polarization is increased, and polarization phenomenon is considered that is slowed and is not influenced by temperature increase in case frequency is high.

3.2.5 Tracking characteristic and flame retardant

Because High voltage insulation insulator is used in place that high voltage is always approved, suffer from

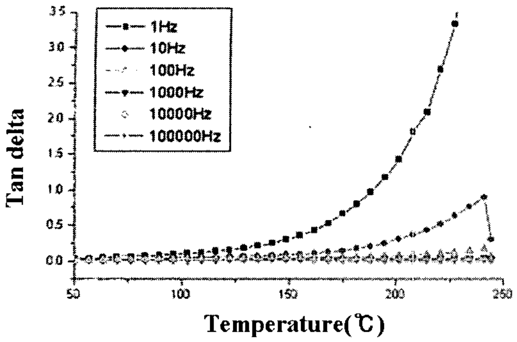


Fig. 12. Tangent delta of HVSR-60-15 according to frequency.

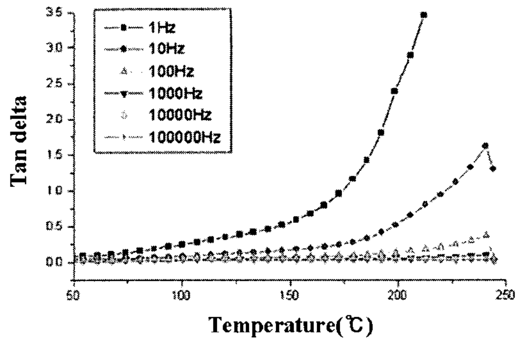
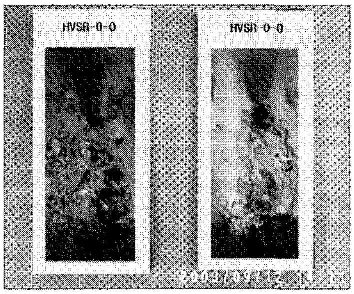


Fig. 13. Tangent delta of HVSR-90-0 according to frequency.

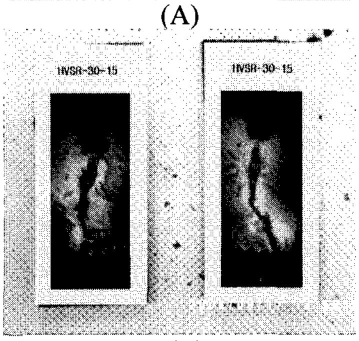
electrical stress of appearance, corrosion etc.. of arc by high voltage and insulation material is aged and loses function accordingly. Therefore, because is resistant to high voltage insulator insulation material about high voltage, it is important characteristic and test is essential in reply. There is tracking test method to method that this does test. Tracking method of examination spills solution that is polluted on surface of inclined examination material and there are IEC 60587, method of ASTM D 2303 and several methods such as RWDT (Rotate Wheel Dip Test) method[14] that use a rotate wheel that approve voltage, and this experiment selected method of IEC 60587 that this among worldwide most widely use. Test result arranged to Table 4 and Fig. 14. ATH silicone rubber that make flame retardant inputting 15 phr to 30 phr, 60 phr use add silicone rubber HVSR-0-0 and 5 phr add HVSR-0-5 that flame retardant is not added as the picture that take state of test piece after test tracking by arc that silicone rubber is charged extensively because is burnt see can. Also, flame happened much while silicone rubber is burnt by arc. But, track of flame retardant was formed very narrowly in occasion of 15 phr add HVSR-

Table 4. Tracking Properties and Flame Retardants of high Voltage silicone rubber according to experimental formulation.

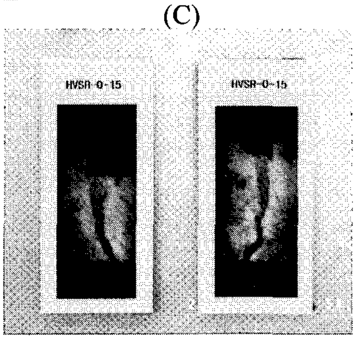
Exp. No	Formulation			Tracking Test Results (Min.)	Flame Retardants (Sec.)
	VPMPS	ATH	HR-FS-3		
HVSR-0-0	100	0	0	21	∞
HVSR-0-5	100	0	5	126	136
HVSR-0-10	100	0	10	186	94
HVSR-0-15	100	0	15	285	36
HVSR-30-0	100	30	0	54	∞
HVSR-30-5	100	30	5	183	116
HVSR-30-10	100	30	10	296	59
HVSR-30-15	100	30	15	380	21
HVSR-60-0	100	60	0	160	340
HVSR-60-5	100	60	5	234	95
HVSR-60-10	100	60	10	347	28
HVSR-60-15	100	60	15	480	8.6
HVSR-90-0	100	90	0	350	230



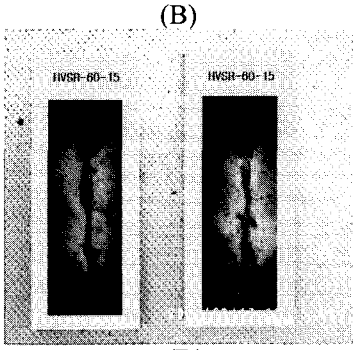
(A)



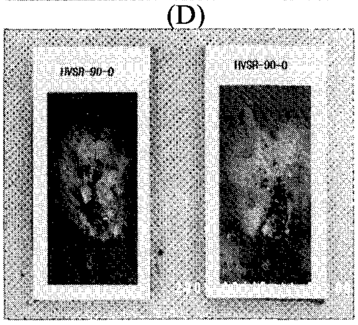
(C)



(B)



(D)



(E)

Fig. 14. Photographs of Specimen after tracking test A:HVSR-0-0, B:HVSR-0-15, C:HVSR-30-15, D:HVSR-60-15, E:HVSR-90-0.

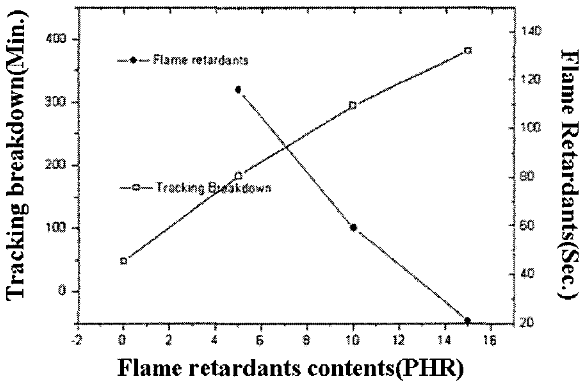


Fig. 15. Tracking test results and flame retardants according to the flame retardants contents (at ATH of 30 PHR).

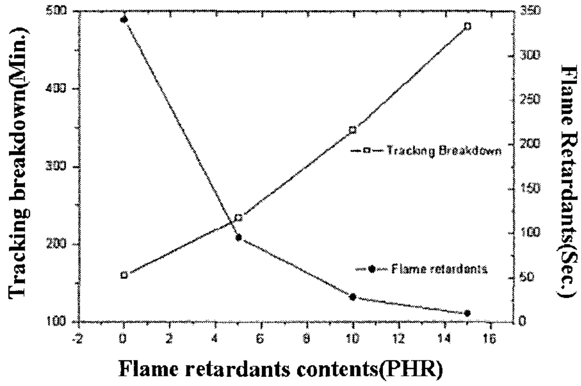


Fig. 16. Tracking test results and flame retardants according to the flame retardants contents (at ATH of 60 PHR).

0-15 because charged dimension decreased as amount of flame retardant is increased and tracking characteristic is improved. Also, when flame retardant is empled 15 phr, HVSR-0-15 and HVSR-30-15 that ATH uses 30 phr and ATH track formation state after tracking examination of 60 phr add HVSR-60-15 that ATH is not used appeared similarly. Because this was increased flame retardant of silicone rubber according as amount of platinum-based flame retardant is increased the quantity that tracking mechanism uses ATH flame retardant, is considered that ATH amount does not affect in tracking characteristic.

Figure 15 and 16 show the relation with tracking characteristic and flame retardancy by content of flame retardant.

As shown in Fig. 15 in case of HVSR-30 containing 30 phr ATH, flame retardant and tracking characteristic was improved by using more than 10 phr platinum-based flame retardant, HVSR-30-15 filled with 30 phr ATH and 15 phr platinum-based flame retardant satisfied IEC 60587 standard for tracking characteristics. Figure 16 shows tracking properties and flame retardants according to the flame retardants contents of HVSR-60 containing 60 phr ATH, HVSR-60-10 filled with 60 phr ATH and 10 phr platinum-based flame retardant satisfied IEC 60587 standard for tracking characteristics.

Therefore, tracking characteristic was influenced by flame retardant, and it confirmed that tracking characteristic is improved using platinum-based flame retardant.

4. CONCLUSION

For improving tensile strength and electrical properties, α,w-Vinyl poly(dimethyl-methylphenyl)siloxane pre-polymer (VPMPS) containing methylphenyl siloxane was prepared by the equilibrium polymerization. And also, high voltage silicone rubber composite were prepared from VPMPS, ATH, and platinum-based flame retardant in high speed kneader.

The influence of platinum-based flame retardant on the mechanical properties, electrical properties, flame retardant, and tracking performance of silicone rubber for high voltage insulator and the following have investigated and the followings are concluded.

1. As main polymer for high voltage insulation insulator, α, ω -vinyl poly (dimethyl-methylphenyl) siloxane(VPMPS) with high temperature stability was successfully prepared by the equilibrium polymerization using basic catalyst tetramethylammonium silanolate (TMAS). Also, high voltage silicone rubber composites were prepared from VPMPS, ATH, and platinum-based flame retardant in high speed kneader.

2. The mechanical properties of high voltage insulation silicone rubber were improved by reducing ATH content and using platinum-based flame retardant. In occasion of silicone rubber without ATH, mechanical strength is more than 100 kfg/㎠ more elongation is 515 ~ 570 %.

3. By reducing ATH content and using platinum-based flame retardant, in near 200 ℃ weight loss was decreased, also, in case of HVSR-0 without ATH thermal decomposition was not appeared. So, thermal stability of high voltage insulation silicone rubber was improved by reduce ATH content and makes using platinum-based flame retardant.

4. By reducing ATH content, breakdown strength, volume resistance, and permittivity were improved, and by increasing platinum-based flame retardant, electrically properties, flame retardant property, and tracking performance were improved. Therefore, tracking characteristic was influenced by flame retardant, and it confirmed that tracking characteristic is improved using platinum-based flame retardant.

The mechanical strength, dielectric strength, heat stability, flame retardant, and tracking characteristic of HVSR-30-15 filled 30 phr ATH and 15 phr platinum-based flame retardant was by far best.

By minimizing the ATH content and using the platinum-based flame retardant, high voltage silicone rubber having high strength, good tracking properties , and good electrical properties was prepared.

REFERENCES

[1] J. M. Zeigler and F. W. Gordon Fearon, “Silicone-Based Polymer Science A Comprehensive Resource”, American Chemical Society, Washington, p. 47, 1990.

[2] M. F. Lewis, "The science and technology of silicone rubber", Rubber Chemistry and Technology, Vol. XXXV, p. 5, 1962.

[3] J. E. McGrath, J. S. Riffle, L. Yilger, and A. K. Banthia, ACS. Symp. Ser., No. 211, Chap. 2, 1983.

[4] ASTM D 149, "Standard Test Methods for Dielectric breakdown Voltage and Dielectric Strength of Solide Electrical Insulating Materials at Commerical Power Frequencies", 1987.

[5] ASTM Stardard D 149, Section 9, Vol. 09, p. 17, 1989

[6] W. Reddish, "The dielectric properties of poly-ethylene terephthalate", Trans. Faraday. Soc., Vol. 46, p. 495, 1950.

[7] A. Toureile and J. P. Reboul, "High-field conduction phenomena in polymers", Ann. Soc. Sci., Bruxelles, Vol. 89, p. 190, 1975.

[8] K. S. Cole and R. H. Cole, "Dispersion and absorption in dielectrics", J. Chem. Phys., Vol. 9, p. 341, 1941.

[9] T. Umemura. T. Kashiwaxaki, and T. Suzuki, "Impurity effect on dielectric properties of polypropylene", Jpn. J. Appl. Phys., Vol. 194, p. 769, 1980.

[10] P. Paul and C. N. Reddy, "Braekdown characteristics of solid dielectrics immersed in high pressure gaseous media and subjected to direct voltage with ripple", IEEE Trans. on Electrical Insulation, Vol. EI-15, p. 43, 1980.

[11] Callens, "Debye relacation equations for a standard linear solid with high relaxation strength", J. Mat. Sch., Vol. 12, p. 251, 1977.

[12] UL Standard 94, "Test for Flammability of Plastic Materials for Parts in Devices and Appliances", 4'nd edition, 1984.

[13] IEC 60587, "Test Methods for Evaluating Resistance to Tracking and Erosion of Electrical Insulating Materials used Severe Ambient Condotions", 1984.

[14] IEC 61302, "Electrical Insulating Materials-Method to Evaluate the Resistance to Tracking and Erosion-Rotating Wheel Dip Test", 1995.