Thermal Stability and Mechanical Properties of Room Temperature Vulcanized Silicone Rubbers

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ABSTRACT: Based on much of the importance of RTV on the field of self-cleaning application for its nontoxic, tasteless, and thermal stability, the effects of D_4-SiO_2 on mechanical properties, $Al(OH)_3$ and decabromodiphenyl oxide ethyl(DBDPE) on flame retardant property of RTV matrix were investigated firstly. Then, a new kind of complex fire retardants was compounded. The morphology of additives and fracture appearance of composites were demonstrated by SEM. The hot property of RTV-based composites was outlined by TG. It is found that D_4-$SiO_2/Al(OH)_3$/DBDPE/Sb_2O_3/RTV composites were of better comprehensive performances in mechanical property, hot property, fire resistance property, and insulating property, which presented tear 26.73 kN/m of strength, 279.8% of elongation at break, 2.81 MPa of tensile strength, FV-0 at the level of flame retardant property, 46 of Oxygen index (OI) 3.03×10^{15} Ωm of Volume electric resistivity, the range of decomposition temperature was 370°C to 650°C, and the percentage of remain weight was 26.4%. Those properties was acquired on the condition of 11 wt % D_4-SiO_2 + 20 wt % $Al(OH)_3$ + 15 wt % DBDPE+ Sb_2O_3 at the amount of 3.0 wt % to 3.7 wt %. This investigation leads the authors to a conclusion that D_4-$SiO_2/Al(OH)_3$/DBDPE/Sb_2O_3 is a kind of better combination modifier than anyone kind of which in comprehensive properties for RTV. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 505–511, 2012

Key words: mechanical property; flame retardant property; volume electric resistivity; thermal stability; room temperature vulcanized silicone rubbers

INTRODUCTION

Silicone rubbers have taken an important role in a wide variety of application for almost 60 years. Much attention has been focused on the characteristics and applications of RTV-based composites. Among them the moisture-curable Room Temperature Vulcanized (RTV) Silicone Rubbers (SIR) have always represented one of the largest volumes and been of considerable commercial value for its innocuity, insulativity, resistance to elements, resistance to wear, cementability, excellent application property, and so on.[1–6] One of the important example is that was used as anticontamination flashover coatings in the insulator of high voltage substation, which required a property of high strength, inflaming retarding, and insulativity imminently. Maybe it was because of the difference in application field, most of the researches were aimed at mechanical or hot resistance properties separately up to present.[7–11]

The study of mechanical property modification was concentrated on the system of $CaCO_3$/RTV, nano-$CaCO_3$/RTV, SiO_2/RTV, etc., and research for inflaming retarding and insulativity properties modifications were focused on $Al(OH)_3$, Sb_2O_3, and so on.[12–15] In this article, a kind of new flame retardant was prepared to be used to inflaming retarding study for D_4-nano-SiO_2/RTV, and the ending properties, such as peel strength, tensile strength, elongation at break and volume electric resistivity, inflaming retarding level, hot resistance property were reported.

EXPERIMENTAL

Raw materials and materials

The selected RTV with a brand name of number 107 Rubber which act as matrix materials, was purchased from Chenguang Chemical Institute, Zigong city of Sichuan, China. Methyltris (methylethylketoxime) silicone (D-30) as a crosslinking agent, dibutyl tin laurate (D-80) as a catalyst, and KH550 as a coupling agent were provided by Xiantao Chemical Co., Xiantao city of Wuhan, China. One of additive—Nano-silicon dioxide was purchased from Wacker Co., Germany.

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TABLE I
Basic Proportion of RTV Matrix Composites

107 Rubber (g)	Solvent (g)	Crosslinking agent (g)	Acceptor (g)	Catalyst (g)	Others (g)
100	150	4	7	0.15	altering

Besides all of these, there were 102#gasoline as solvent, another two of additives Aluminums hydroxide and decabromodiphenyl oxide ethyl (DBDPE), donations trioxide as vice flame retardant, and so on. The latter three were obtained from common market, China.

Preparation of D_4-nano-SiO_2/RTV

All of raw materials and chemical agents were parched under condition of 120°C/10 h also before this experiment. The 107 matrix rubber were heated and stirred for 5 h at 200°C. Then, parched matrix rubber was mixed with D_4-nano-silicon dioxide with certain of ratio under condition of 185°C/4 h in the vacuum kneader. Mixers were diverted to a three-roller miller after a good soakage of powder. They were whetted for about five times to ensure an absolute mixing and soakage. In the end, mixers were put into a reaction kettle and coordinated with 120#petrol as solvent. Then, the acceptor KH550, crosslinking agent D-30, and catalyst D-80 were put into reacting mixers according to the basic proportion (Table I). After a reaction of hours under stirring, it is OK.

Preparation of D_4-nano-SiO_2/flame retardant/RTV composites

All of raw materials and chemical agents were parched under condition of 120°C/10 h also before this experiment. The same, the 107 matrix rubber were heated and stirred for 5 h at 200°C. Then, parched matrix rubber were mixed with nano-silicon dioxide and related flame retardant in a certain of ratio under condition of 185°C/4 h in the vacuum kneader. Mixers were diverted to a three-roller miller after a good soakage of powder. They were whetted for about five times to ensure an absolute mixing and soakage. In the end, mixers were put into a reaction kettle and coordinated with 120#petrol as solvent. Then, the acceptor KH550, crosslinking agent D-30, and catalyst D-80 were put into reacting mixers according to the basic proportion (Table I). After a stirring of hours, place the emulsion in an openess of vessel to get a room temperature curing at about the temperature of 25°C. It needs round about a couple of days, then, the final composite is OK. The latter experiments are repeated when flame retardants changes or its amount increasing.

Mechanical property tests

The peel strength of composite was examined according to GB/T530-81 on Wanneng electronic testing machine (WE-100). Testing temperature: (23 ± 2)°C; Shape of sample: right angle; speed of extension: 500 mm/min.

The tensile strength and elongation at break were performed according to GB/T 13022.91 with Wanneng electronic testing machine (WE-600). Testing temperature:(23 ± 2)°C; Shape of sample: Dumbbell; speed of extension: 500 mm/min.

Fire resistance property tests

OI was mensurated by GB/T 10707-2008. In addition, the fire resistance property was surveyed and evaluated by the method of vertical burning. Testing temperature: (23 ± 2)°C; instrument: Bunsen burner, calculagraph; shape of sample: (130 ± 5) mm × (13.0 ± 0.5) mm × (3.0 ± 0.25) mm. The schema of test was demonstrated in Figure 1.

Then, the performance rate of rubber by the method of vertical burning can be evaluated from Table II according to Ref. 16.

Volume electric resistivity tests

The Volume electric resistivity of composite was tested according to GB/T 1692 on megohm meter (ZC.36). Testing temperature: (23 ± 2)°C; relative humidity level: 60–70%; Shape of sample: square with length of side 100 mm and thickness (1 ± 0.2) mm; testing voltage: 1000 V. Figure 2 is the sketch map of experimental electrode. The volume electric resistivity was concluded from below:

$$\rho_V = R_V \frac{s}{d}$$

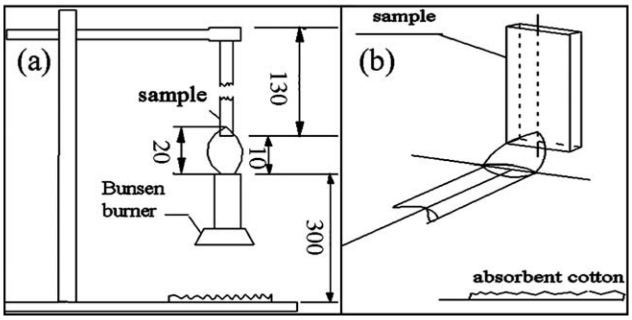

Figure 1 The demonstration of the method of vertical burning.

TABLE II
The Level of Flame Retardant Property and OI of Composites

The flaming and/or combustion hours	FV-0	FV-1	FV-2
	≤10	≤30	≤30
	≤50	≤250	≤250
	≤30	≤60	≤60

where ρ_V is the volume electric resistivity, Ω m; R_V is the volume resistance, Ω; d is the thickness of sample, cm; and s is the active area of electrode, cm^2.

Characterization

The morphology of the fracture surface of the composite was examined using a scanning electron microscope (SEM) (SEM, HITACHI-570) and a transmission electron microscope (TEM) (Hitachi, H-7500, Japan) was used to inspect the morphology of D_4-nano-SiO_2. Samples were cut at room temperature using a diamond knife in an Ultracut Uct microtome (Leica Company, Austria). In the end, heat-resistant property of RTV was demonstrated by TG (TG, Q600SDT).

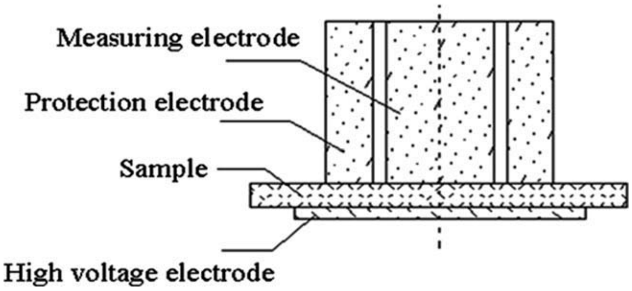

Figure 2 The sketch map of experimental electrode.

RESULTS AND DISCUSSION

Morphologies of raw materials and composites

The compatibility between the additives and RTV matrixes greatly affects the thermal, mechanical, and other properties of composites. The morphology of the additives was observed by TEM, and the SEM technique was utilized to elucidate the distribution

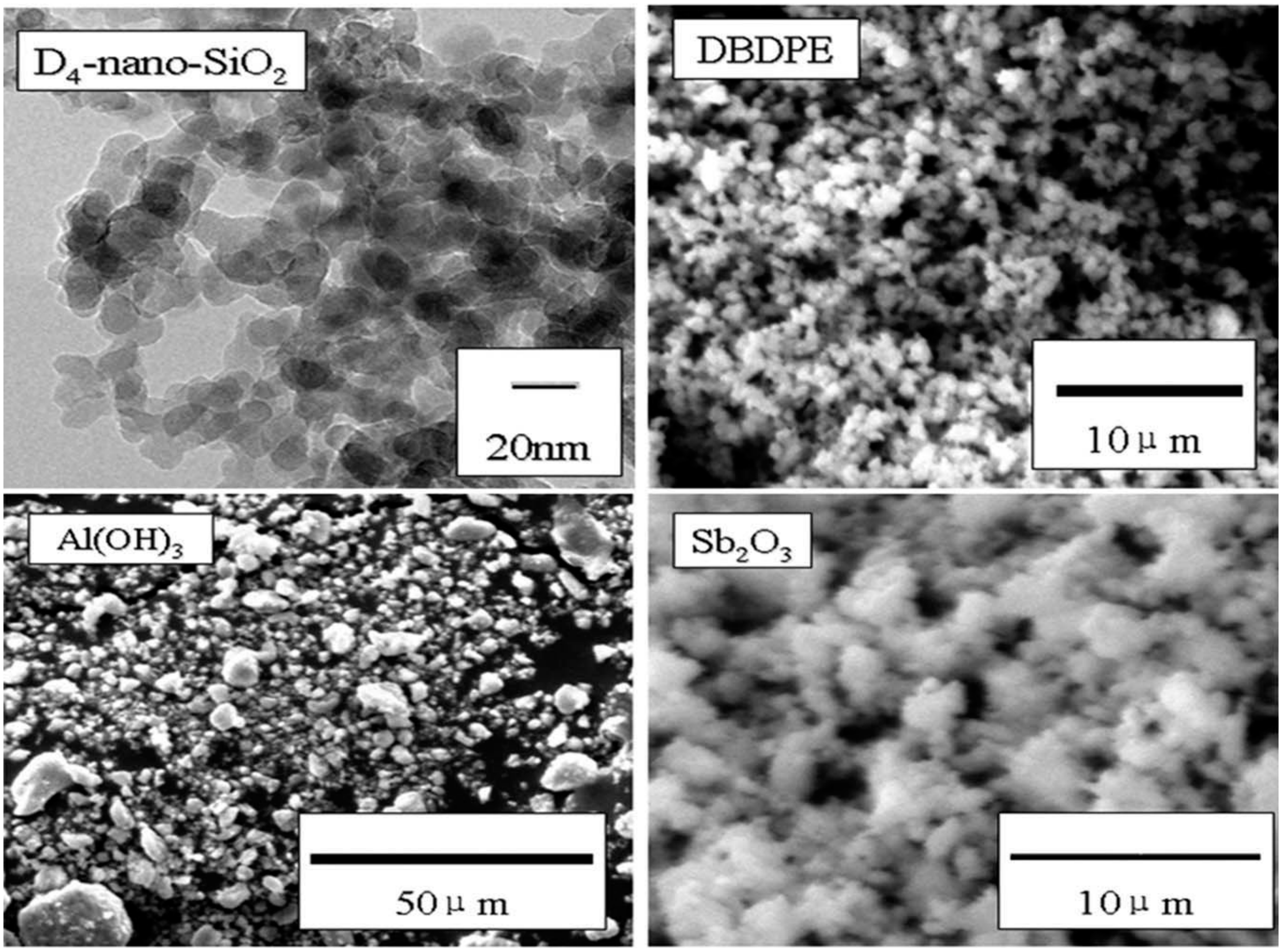

Figure 3 Morphologies of all raw materials.

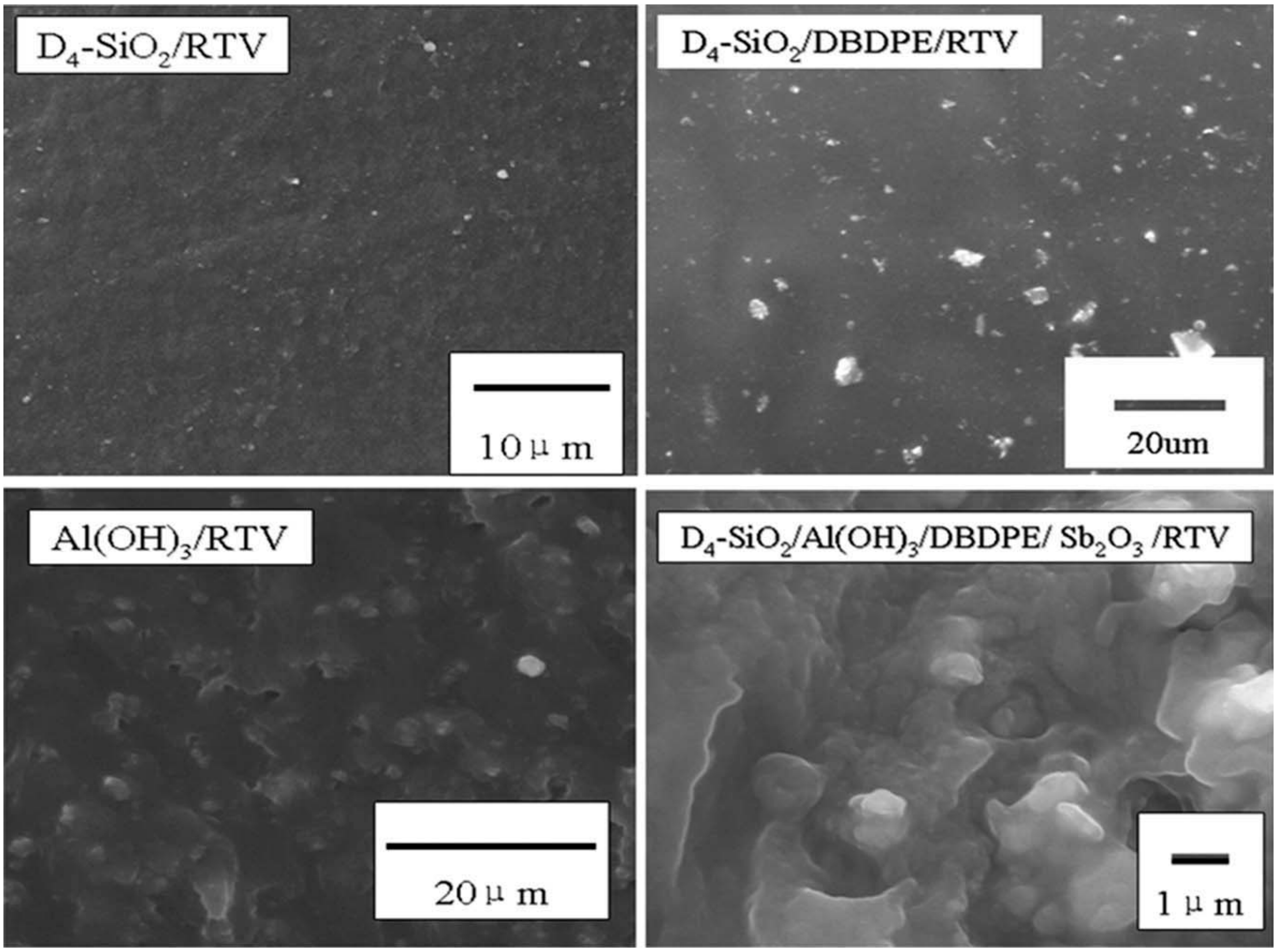

Figure 4 Morphologies of the fractured surfaces of composites.

of additives and the separation of the microphase in RTV matrixes.

Figure 3 is the appearances of all raw materials. We can find that the dimension of SiO_2 is in the range of 10 nm to 5 nm, and that of DBDPE, $Al(OH)_3$, and Sb_2O_3 are of 1 to 2 μm, 1 to 4 μm, 2 to 6 μm, respectively.

Figure 4 displays the SEM microphotographs of the fractured surfaces of composites. According to the SEM micrographs, particles of additive were different in dimension but uniformly dispersed throughout the polymer matrix, showing that there was a better compatibility between the additives and RTV matrixes. This finding indicated that the composites exhibited good miscibility of organic and inorganic phases.

The mechanical properties of composites

Figure 5 shows the mechanical properties of composite with different additives. The tear strength, tensile strength, and elongation at break of D_4-SiO_2/RTV were demonstrated in Figure 5(a). It was found that tensile strength and elongation at break rose from 1.1 MPa to 3.05 MPa and 140% to 332.5% separately during the range of D_4-SiO_2 0–13 wt %, and the tear strength got its maximum of 25.6 kN/m at the point of D_4-SiO_2 11 wt %, but that of minimum is 1.02 kN/m at the point of D_4-SiO_2 0 wt %. So, the most augmenter of tear strength, tensile strength, and elongation at break of D_4-SiO_2/RTV were 2460.6%, 186.4%, and 137.5% separately.

The tear strength of $Al(OH)_3$/RTV with the amount of $Al(OH)_3$ from 0 to 40% and DBDPE/RTV with the amount of DBDPE from 0 to 25% were demonstrated in Figure 5(b,c) separately. It was found that the $Al(OH)_3$/RTV sample achieved its maximum value of 6.863 kN/m in tear strength at the point of $Al(OH)_3$ 20 wt %, and the maximum value of 13.684 kN/m for same property was acquired at the DBDPE amount of 15 wt % for the DBDPE/RTV composite. Both of the increasing percentages to the tear strength of pure RTV 1.02 kN/m were 770.89% and 1243.53% separately. So, the results all above indicated that D_4-SiO_2, $Al(OH)_3$, and DBDPE can give a big advance in mechanical properties for RTV matrix composites, and D_4-SiO_2

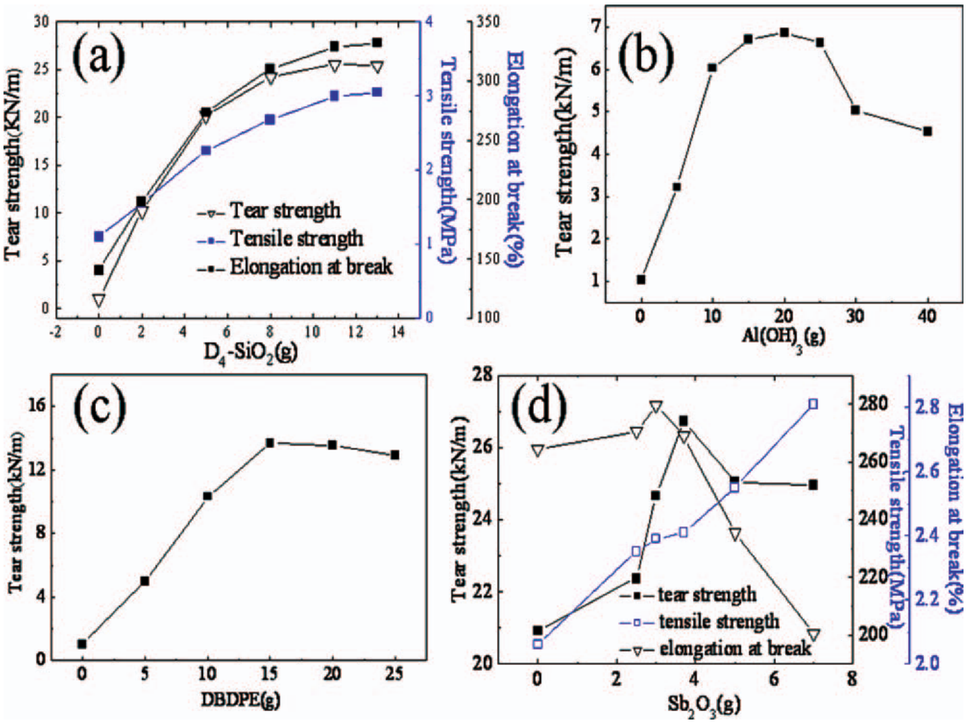

Figure 5 Mechanical performances of composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is the just excellent one among three. The latter two are often used to property modification about fire resistance. So, there will be a chance of improving in comprehensive properties by three of these additives.

Sb_2O_3 is a kind of excellent flame-retardant synergists. The final mechanical properties of RTV composite matrix composed with 11 wt % D_4-SiO_2 + 20 wt % $Al(OH)_3$ + 15 wt % DBDPE to the amount of Sb_2O_3 was demonstrated in the Figure 5(d). It seems

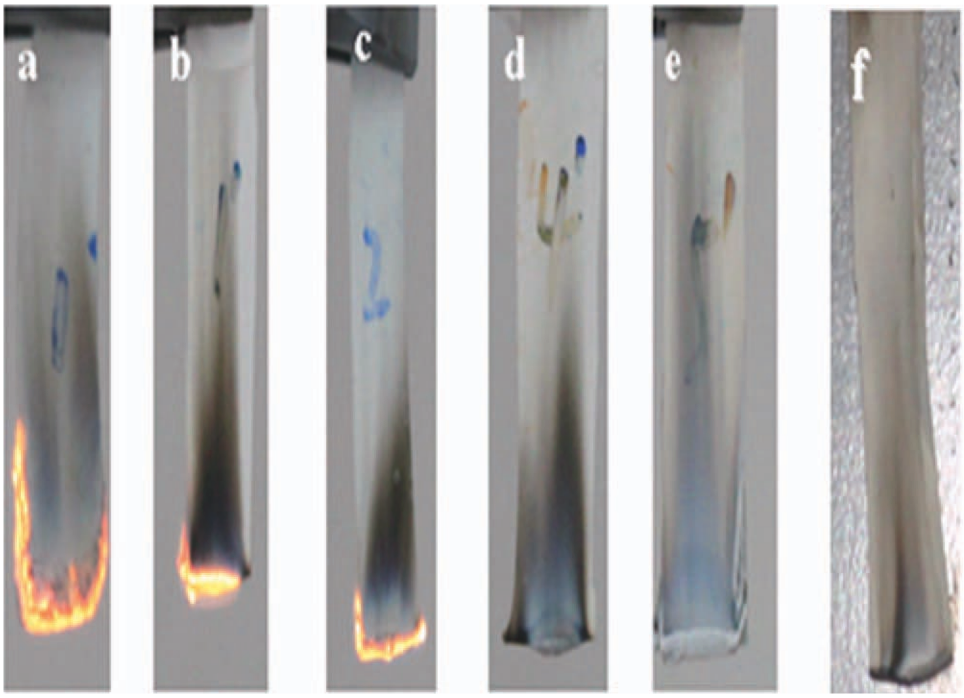

Figure 6 Schematic captures of fire resistance property test for composites with different amount of Sb_2O_3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
The Level of OI of Composites

Contents of Sb_2O_3/wt %	Level of vertical burning	Flaming times of clear heat/s	OI
0	FV-2	<30	22
2.5	FV-0	8	25
3	FV-0	2–5	38
3.7	FV-0	0	46
5	FV-0	0	48
7	FV-0	0	48

to authors that there had different variation trends for tear strength, tensile strength, and elongation at break to the amount of Sb_2O_3. The tear strength and elongation at break rose from 20.91 kN/m to 26.73 kN/m at the point of Sb_2O_3 3.7% and 264.3% to 279.8% at the point of Sb_2O_3 3.0% separately with the amount of Sb_2O_3 0 wt % to 7 wt %, but the tensile strength rose straight upward from 2.06 MPa to 2.81 MPa during the range of same. The increasing percentages were 27.8%, 5.9%, and 36.4% separately. It has been thought that the difference variation trends between D_4-SiO_2/$Al(OH)_3$/DBDPE/Sb_2O_3/RTV composite and the first three samples derived of the difference in two-phase cooperation.

So, the investigation leads the author to a conclusion that D_4-SiO_2/$Al(OH)_3$/DBDPE/Sb_2O_3/RTV can give a better comprehensive properties for RTV matrix, among then the best constitution is 11 wt % D_4-SiO_2 + 20 wt % $Al(OH)_3$ + 15 wt % DBDPE+ Sb_2O_3 with the amount of 3.0 wt % to 3.7 wt %.

Fire resistance property of D_4-nano-SiO_2/$Al(OH)_3$/DBDPE/Sb_2O_3/RTV

The method of vertical burning was used to mensurate the fire resistance property of D_4-nano-SiO_2/$Al(OH)_3$/DBDPE/Sb_2O_3/RTV. The burning picture and burning time of samples about different Sb_2O_3 amount was shown in Figure 6 and Table II. From Figure 6, it was found that the fire resistance property of composites can be improved greatly with Sb_2O_3, which can be more and more excellent with the increasing of Sb_2O_3 amount. Referring to the Tables II and III, researches enable us to conclude that the scale of flame retardant property for D_4-nano-SiO_2/$Al(OH)_3$/DBDPE/Sb_2O_3/RTV could be FV-0, and its LOI could be 46–48 in the range of 3.7 wt % to 7 wt % for Sb_2O_3.

Volume electric resistivity

From the tendency in Figure 7(a–c). It can be clearly observed that Volume electric resistivities of RTV with the different additives were closely related to the amount of additives, and there were almost the same variation trends in Volume electric resistivities—the amount of additives for different RTV matrix composites. It were found that there were a dramatic decreasing in Volume electric resistivity during a low oxalate of additives (SiO_2% < 2 wt %, $Al(OH)_3$% < 10 wt %, and DBDPE% < 5 wt %), whilst a little variation in Volume electric resistivity after that amount. The Volume electric resistivities

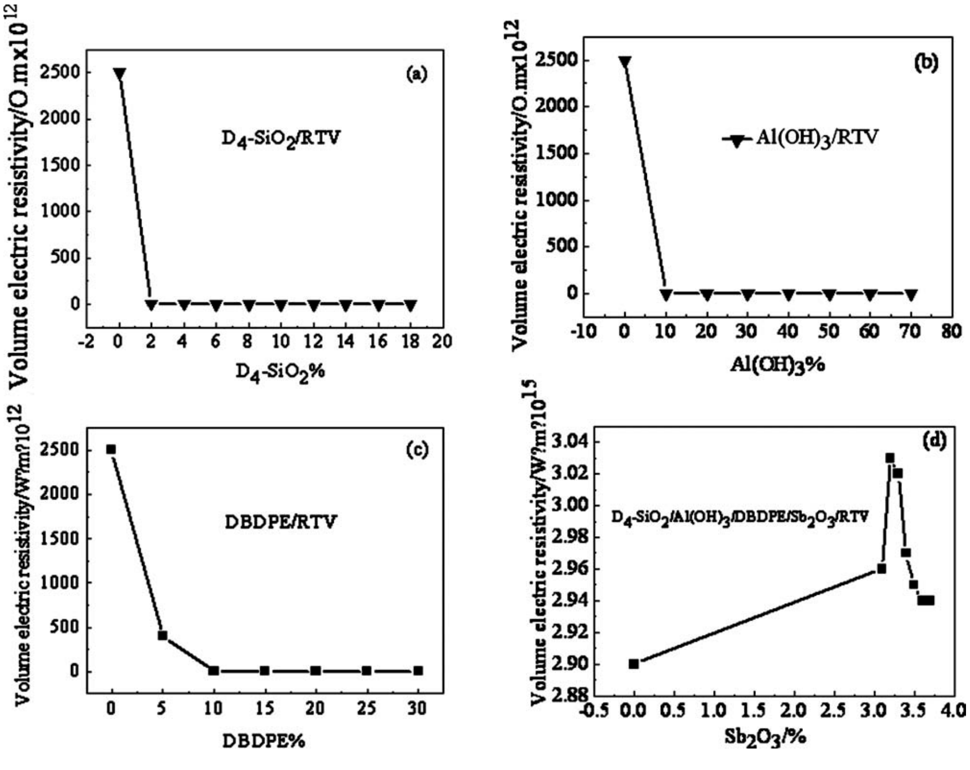

Figure 7 Volume electric resistivities of RTV matrix composites.

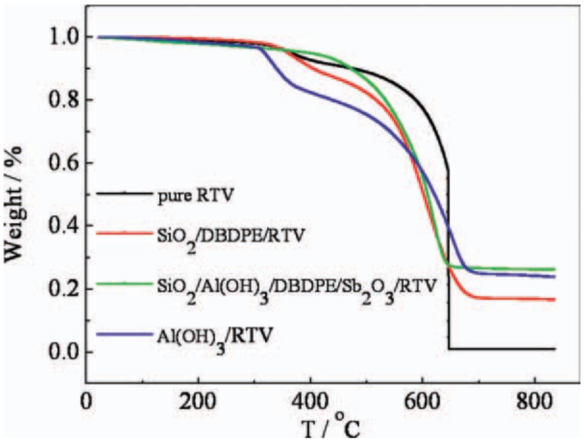

Figure 8 Thermal properties of RTV matrix composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of three samples were decreased from 2.5×10^{15} Ωm to 1.8×10^{9} Ωm, 2.0×10^{9} Ωm, and 1.9×10^{10} Ωm for SiO_2/RTV, $Al(OH)_3$/RTV, and DBDPE/RTV separately during the range of SiO_2 from 0 wt % to 18 wt %, $Al(OH)_3$ from 0 wt % to 70 wt %, and DBDPE from 0 wt % to 30 wt %. It maybe inferred that the peculiar currents of change of Volume electric resistivity of RTV composite matrixes is due to a conductive path, which can be formed by lots of particles on the condition that large amount of additives, whilst there were not just the same path except for little connections of single particles each other when the amount of supplements was less relatively.

Figure 7(d) indicated that Volume electric resistivity of $SiO_2/Al(OH)_3$/DBDPE/RTV was 2.9×10^{15} Ωm, and Sb_2O_3 imposed a slightly effect on composites. There was a maximum of 3.03×10^{15} Ωm at the point of Sb_2O_3 3.2% for composites.

The thermal properties of RTV matrix composites

Figure 8 shows TG curves of RTV composites. It is inferred from this curve that there were different weight loss procedure for different composites during the range of 20°C to 850°C. There were the same beginning decomposition temperature for pure RTV, SiO_2/DBDPE/RTV, and $SiO_2/Al(OH)_3$/DBDPE/Sb_2O_3/RTV composites at 370°C, and the same ending decomposition temperature for the same three samples at 650°C, $Al(OH)_3$/RTV composite had a different beginning decomposition temperature at 320°C, and a different ending decomposition temperature at 680°C. The ending percentage of remain weight were 0.98% for pure RTV, 16.4% for SiO_2/DBDPE/RTV, 26.4% for $SiO_2/Al(OH)_3$/DBDPE/Sb_2O_3/RTV, and 23.5% for $Al(OH)_3$/RTV, respectively. So, it can be concluded that a high temperature performance can be attained with $Al(OH)_3$ doping and comprehensive effect by $SiO_2/Al(OH)_3$/DBDPE/Sb_2O_3 could attach RTV matrix a good high and low temperature resistance property.

TABLE IV
The Ending Performance Parameters of RTV Matrix Composites

Proportion	11 wt % D_4-SiO_2 + 20 wt % $Al(OH)_3$ + 15 wt % DBDPE + Sb_2O_3(3.0 wt % to 3.7 wt %)	
Properties	tear strength	26.73 kN/m
	elongation at break	279.8%
	tensile strength	2.81 MPa
	he level of flame retardant	FV-0
	OI	46
	Volume electric resistivity	3.03×10^{15} Ωm
	the range of decomposition temperature	370°C–650°C
	the ending percentage of remain weight	26.4%

CONCLUSIONS

The article concludes that RTV matrix was endowed an excellent mechanical by D_4-nano-SiO_2, a good high temperature resistance performance by $Al(OH)_3$ doping and a better comprehensive properties by the joint action of D_4-$SiO_2/Al(OH)_3$/DBDPE/Sb_2O_3. The best performance parameters could be reported as Table IV. These results will be significant for engineering materials typified by RTV.

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