Performance and $T_g$ of Room Temperature Vulcanized (RTV) Silicone Rubbers based Composites: Decabromodiphenyl Ethane /Sb$_2$O$_3$/RTV and Al (OH)$_3$/RTV

Juanjuan Wang*, Yaning Feng and Yule Yang

School of Materials Science and Engineering, Xi’an University of Technology, Xi’an, China

Abstract

Composites with high flame retardant behavior based on Room Temperature Vulcanizing silicone rubber (RTV), Al(OH)$_3$, and Decabromodiphenyl ethane (DBDPE)/Sb$_2$O$_3$ were fabricated employing reactive solution mixing process and three-roller milling. The effects of Al(OH)$_3$ and DBDPE/Sb$_2$O$_3$ on the performances of composites is systematically investigated. The composite structure was characterized by SEM. The hot performance of RTV-based composites was outlined by TG. The composite of DBDPE/Sb$_2$O$_3$/RTV shows better comprehensive performances than matrixes, which came to that 2.18MPa in tensile strength, 243.1% in elongation at break, 13.684kN/m in tear strength, 51.6HA in Shore hardness (A), 3.03×10$^{15}$ Ω•m in volume electric resistivity, FV-0 in the level of flame retardant property, 46 in oxygen indexes, and, the decomposition temperature between 300oC to 690oC the remain weight is 30.6%. These properties were acquired on the condition of DBDPE/Sb$_2$O$_3$ of 15-20 wt. % as complex additives for RTV matrix. DSC tests demonstrated that both of DBDPE/Sb$_2$O$_3$/RTV and Al(OH)$_3$/RTV composites were mainly of branch-chain crystal, and DBDPE/Sb$_2$O$_3$ showed some superiority in decreasing $T_g$ of RTV rubber than Al(OH)$_3$. New kinds of composite was acquired. It can be used in the field of flame retardant, anti-corrosion and voice absorbing.

Keywords: Hydrophobic property; Mechanical property; Flame retardant property; Thermal stability; Silicone rubbers

Introduction

Moisture-curable Room Temperature Vulcanized (RTV) Silicone Rubbers (SIR) play the important roles in a wide range of application for many years because of its innocuity, insulativity [1], hydrophobicity and hydrophobic transfer nature [2], resistance to elements [3], resistance to wear [4], cementability and conveniences and so on. As a result, great efforts have been devoted to the characterization and applications of RTV-based composites [5], both anti-contamination flashover coatings and high voltage insulating materials substation is the important example [5-6], which demand high strength, inflaming retarding, and insulativity imminently [7]. Many researches were aimed at mechanical or hot resistance properties separately up to present [8].

The study of mechanical property modification was concentrated on the system of CaCO$_3$/RTV, nano-CaCO$_3$/RTV, SiO$_2$/RTV [9-10] etc., and research for inflaming retarding and insulativity properties modifications were focused on Al(OH)$_3$, DBDPO and so on [11-13]. Researchers have been working on improving silicone rubber for insulators or engineering. In spite of the good properties of these, the unstabilizations and disunities restrict their practical applications [14]. In this paper, the composites of room temperature vulcanizing silicone rubber (RTV), Al(OH)$_3$, and (DBDPE)/Sb$_2$O$_3$ as a new kinds of fire retardant with high flame retardant behavior were fabricated by mixing the reactive solution and three-roller milling. The effects of Al(OH)$_3$, and DBDPE/Sb$_2$O$_3$, as a new kinds of flame retardant, on the hydrophobic natures, mechanical properties, fire properties, insulating performances and hot properties were investigated. The effects of doping on $T_g$ of composites were presented by the DSC method. Also, the ending properties were wholly reported in this paper.

Experimental

Raw Materials and Materials

The RTV matrixes with a brand name of number 107 Rubber were purchased from Chenguang Chemical Institute, Zigong city of Sichuan, China. And, Methyltris (methylmethyketoxime) silicone (D-30) as a cross-linking agent, dibutyl tin laurate (D-80) as a catalyst, KH550
as a resin acceptor, were provided by Xiantao Chemical Co., Xiantao city of Wuhan, China. The additives-Al(OH)₃, DBDPE and Sb₂O₃ were purchased from Wacker Co., Germany. Besides all of these, there were 102# gasoline as solvent, which were obtained from common market, China.

**Preparation of Al(OH)₃/RTV and DBDPE/Sb₂O₃/RTV Composites**

All of Al(OH)₃ and DBDPE/Sb₂O₃ were parched under condition of 120 °C/10h also before this experiment. And, the 107 matrix rubber was heated and stirred for 5 hours at 200 °C to remove the moisture. Then, parched matrix rubber was mixed with Al(OH)₃ with various ratios (Table 1) at 185 °C/4h in the vacuum kneader. Mixers were diverted to a three-roller miller after a good soakage of powder. They were whetted for about 5 times to ensure an absolute mixing and soakage. Afterward, the mixture were put into a reaction kettle and coordinated with 120 # petrol as solvent. Then, the acceptor KH550, cross-linking agent D-30 and catalyst D-80 were put into reacting mixers according to the basic proportion (Table 1). After stirring for several hours, place the emulsion in an openness 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 above processes and proportion were repeated for DBDPE/Sb₂O₃/RTV composites and is merely for the instead of Al(OH)₃ with DBDPE/Sb₂O₃ on additives with the amount seen Table 1.

**Hydrophobic Tests**

Hydrophobic nature of samples was tested by the method of water spray grade according to literature [15,16]. Pre-cure adhesive samples were sprayed evenly on the surface of ceramics substrates (with dimensions of 3cm×6cm×0.2cm) at the thickness of 0.2 to 0.3mm, which was sprayed with water at a 45 degree angle after curing of sample adhesives.

**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: 500mm/min.

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

Shore Hardness of samples was measured with TH200 Shore durometer A, China.

**Fire resistance Property Tests**

The fire resistance property was surveyed and evaluated by the method of vertical burning. Testing temperature: (23±2) °C; instrument: Bunsen burner, calculagraph, China; shape of sample: (130±5)mm×(13.0±0.5)mm×(3.0±0.25)mm. The level of flame retardant property of rubbers by the method of Vertical Burning can be evaluated from Table 2 (a) according to literatures [17]. The flow chart is seen in Figure 1. The schema of test was demonstrated in Figure 2.

<table>
<thead>
<tr>
<th>107 (g)</th>
<th>Solvent (g)</th>
<th>D-30 (g)</th>
<th>KH550 (g)</th>
<th>D-80 (g)</th>
<th>additives (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>150</td>
<td>4</td>
<td>7</td>
<td>0.15</td>
<td>Al(OH)₃ (wt %)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10, 20, 30, 40, 50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5, 10, 15, 20, 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DBDPE/Sb₂O₃ (wt %)</td>
</tr>
</tbody>
</table>

**Table 1:** Basic proportion of RTV matrix and composites

OI was mensurated by GB /T 10707-2008, China.
Volume Electric Resistivity Tests

The Volume electric resistivity of composite was tested according to GB/T 1692 on megohm meter (ZC.36), China. Testing temperature: (23±2) ℃; relative humidity level: 60-70%; Shape of sample: square with length of side 100mm and thickness (1±0.2) mm; testing voltage: 1000V. Figure 3 is the sketch map of experimental electrode. The Volume electric resistivity was concluded from below:

\[
\rho_V = R_v \frac{s}{d}
\]

\(\rho_V\) — Volume electric resistivity, Ω•cm

\(R_v\) — volume resistance, Ω

\(d\) — thickness of sample, cm

\(s\) — active area of electrode, cm²

Characterization

The morphology of raw materials and the fracture surface of the composite were examined using a scanning electron micro-scope (SEM) (SEM, HITACHI-570). In the end, heat-resistant property of RTV was measured by TG (TG, Q600SDT). The transitions and \(T_s\) of RTV matrixes composites were investigated by DSC (Netzsch STA449F3). The IR spectra of raw materials and composites were performed with Fourier transform Infrared Spectrometer (EQUinox55).

Results and Discussion

Morphologies

Figure 3: Morphologies of raw materials and fractured surfaces of composites samples
Figure 4 displays the structure of raw materials and micro-photographs of the fractured surfaces of composites. It can be found that three of raw materials are of regular shape with dimensions in the range of 1 to 5 µm. The dimension of Al(OH)$_3$ is smaller but uneven and that of DBDPE and Sb$_2$O$_3$ is medium and maximal separately.

According to the SEM images of the fractured surfaces of RTV matrix composites, it is seen that particles of additives were different in dimension, but uniformly dispersed throughout the polymer matrix, suggesting that there was a better compatibility between the additives and RTV matrices. This finding revealed that the composites exhibited good miscibility with organic and inorganic phases, and, Sb$_2$O$_3$ can by no means weaken the combination of organic ingredient. It turned out to be that the combination of DBDPE/Sb$_2$O$_3$ /RTV is better than that of Al(OH)$_3$/RTV.

**Infrared Spectrum**

Figure 5 is the infrared spectrum of raw materials and composites. The peak in 3380 cm$^{-1}$ to 3620 cm$^{-1}$ and 914 cm$^{-1}$ to 1020 cm$^{-1}$ can be ascribed to the vibration of O-H, and the peak in 566 cm$^{-1}$ to 900 cm$^{-1}$ is related to the translatory peak of Al-OH-Al, which is the characteristic peak of Al(OH)$_3$ (Figure 4 (a)). The strong peak between 500 cm$^{-1}$ to 600 cm$^{-1}$ indicated the stretching absorption bands arising from different conformation of -Br, and absorption peak of -CH$_3$ and -CH$_2$ - are typified by peak in 750 cm$^{-1}$ and 1589.3 cm$^{-1}$ (Figure 4 (b)), which is the characteristic peak of DBDPE. The peak 1300 cm$^{-1}$ to 1500 cm$^{-1}$ in the characteristic peak of Sb$_2$O$_3$ (Figure 4 (c)). Figure 4 (d) demonstrated that no new phases were produced under the introductions of Al(OH)$_3$ and DBDPE/Sb$_2$O$_3$, showing a mainly physical action between the combinations inter phase.

**Hydrophobic Property**

Figure 5: Hydrophobic natures of composites
Figure 6 is the photos of hydrophobic of RTV matrix and composites. It can be found that neither Al (OH)$_3$ nor DBDPE/Sb$_2$O$_3$ can improve the hydrophobic property of RTV matrix in a desired outcome, which demonstrated that HC1-HC2 for both kinds of composites in hydrophobic level according to literature [15,16] by the method of water spray grade. It can be inferred that a lot of factors against hydrophobic came into being at the surface, for example hydrophilic byproduct (silanol), the increase of oxygen contents and structure change of part of backbone chain, which led to the loss or weakening of hydrophobic instantaneously under the introduction of Al (OH)$_3$ and DBDPE/Sb$_2$O$_3$.

Mechanical Property

Figure 7 shows the mechanical properties of composite with different additives. The tensile strength of DBDPE/Sb$_2$O$_3$/RTV and Al (OH)$_3$/RTV were demonstrated in Figure 7(a). It was found that there were ascending tendency from 0.42 MPa to 2.18 MPa in the range of 0-25 wt% in DBDPE/Sb$_2$O$_3$ for DBDPE/Sb$_2$O$_3$/RTV and 0.42 MPa to 1.932 MPa in the range of 0-70 wt% in Al (OH)$_3$ for Al(OH)$_3$/RTV, with the corresponding growth rate 419.1% and 360%, respectively.

The elongation at break reach its maximum value of 243.1% at the point of DBDPE/Sb$_2$O$_3$ 15 wt% for DBDPE/Sb$_2$O$_3$/RTV, and 96.4% for Al(OH)$_3$/RTV at the point of Al (OH)$_3$ 30 wt% seen from Figure 7 (b), and there were corresponding growth rate 209.3% and 22.6% for both the composites in comparison with the prior elongation at break 78.6%.

The tear strengths for both of RTV matrix composites for were demonstrated in Figure 7(c). It is found that the DBDPE/Sb$_2$O$_3$/RTV sample reached its maximum value of 13.684 kN/m at the point of DBDPE/Sb$_2$O$_3$ 15 wt%, and the maximum value of 7.242 kN/m for same property was obtained at the Al(OH)$_3$ amount of 40 wt% for the Al(OH)$_3$/RTV composite. Both of the increasing percentages to the tear strength of pure RTV 1.02 kN/m were 1241.6% and 610%, respectively.

Shore Hardness of composites was measured and the results are shown in Fig.7 (d). It can be found that there was an increasing tendency at the Shore hardness for both of composites in the range of DBDPE/Sb$_2$O$_3$ 0-25 wt% and Al(OH)$_3$, 0-70 wt%, and the final Shore hardness was of 51.6HA at the point of DBDPE/Sb$_2$O$_3$, 25% for DBDPE/Sb$_2$O$_3$/RTV and reaching to 57.2HA at the point of Al(OH)$_3$ content above 60% for Al(OH)$_3$/RTV. The ending increasing rates were 106.4% and 128.6% separately.
The above results demonstrate the fact that both of Al(OH)$_3$ and DBDPE/Sb$_2$O$_3$ can significantly improve the mechanical properties for RTV matrix composites, and DBDPE is the just excellent one among two with the synergistic effect of Sb$_2$O$_3$. There will be a chance of improving in comprehensive properties by DBDPE/Sb$_2$O$_3$/RTV.

**Fire Resistance Property**

The burning time and fire properties of samples about different additives and its amount were shown in Table 2. It was found that the fire resistance property of composites can be improved greatly with the addition of DBDPE/Sb$_2$O$_3$ and Al(OH)$_3$, which can be more and more excellent with the increasing of additives amount for both kinds of samples. As can be seen from Table 2, we can concluded that the scale of flame retardant property for DBDPE/Sb$_2$O$_3$/RTV was FV-0, and Al(OH)$_3$/RTV the same level. There also can be found from Table 2 (a) and (b) that DBDPE/Sb$_2$O$_3$/RTV are of better general burning performance with 46 in OI at the range of additive amount 20 wt% above than that of Al(OH)$_3$/RTV with 42 in OI at the range of Al(OH)$_3$ 60 wt% above. Therefore, the DBDPE/Sb$_2$O$_3$/RTV shows better fire properties than Al(OH)$_3$/RTV.

<table>
<thead>
<tr>
<th>Contents of DBDPE/Sb$_2$O$_3$/ wt%</th>
<th>Level of vertical burning</th>
<th>Flaming times of clear heat/s</th>
<th>OI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>FV-2</td>
<td>&lt;30</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>FV-2</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>10</td>
<td>FV-0</td>
<td>10</td>
<td>38</td>
</tr>
<tr>
<td>15</td>
<td>FV-0</td>
<td>3.5</td>
<td>44</td>
</tr>
<tr>
<td>20</td>
<td>FV-0</td>
<td>0</td>
<td>46</td>
</tr>
<tr>
<td>25</td>
<td>FV-0</td>
<td>0</td>
<td>46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Contents of Al(OH)$_3$/ wt%</th>
<th>Level of vertical burning</th>
<th>Flaming times of clear heat/s</th>
<th>OI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>FV-2</td>
<td>&lt;30</td>
<td>18</td>
</tr>
<tr>
<td>10</td>
<td>FV-2</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td>20</td>
<td>FV-2</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>30</td>
<td>FV-1</td>
<td>10</td>
<td>32</td>
</tr>
<tr>
<td>40</td>
<td>FV-1</td>
<td>5</td>
<td>38</td>
</tr>
<tr>
<td>50</td>
<td>FV-0</td>
<td>3.5</td>
<td>38</td>
</tr>
<tr>
<td>60</td>
<td>FV-0</td>
<td>0</td>
<td>42</td>
</tr>
<tr>
<td>70</td>
<td>FV-0</td>
<td>0</td>
<td>42</td>
</tr>
</tbody>
</table>

Table 2: Fire Performances and OI numbers of composites

**Volume Electric Resistivity**

![Figure 7: Volume electric resistivities of RTV matrix composites](Image)
The thermal decomposition characteristics of pure RTV matrix and composites were shown in Figure 9. It is seen that there were different weight loss events for different composites in the temperature range of 20 to 1000 °C, and the decomposition of the composites was influenced largely by the introduction of additives but first decomposition temperature, which declared that there were about the same beginning decomposition temperature (300 °C) and the different ending decomposition temperature for pure RTV (640 °C), DBDPE/Sb₂O₃/RTV (690 °C) and Al(OH)₃/RTV (530 °C) composites. The residual were 2.08% for pure RTV, 30.6% for DBDPE/Sb₂O₃/RTV and 43.2% for Al(OH)₃/RTV, respectively. So, Measurements show that both of Al(OH)₃ and DBDPE/Sb₂O₃ can improve the performance of heat decomposition for RTV matrix and the comprehensive case are same basically.

**Thermal Property**

The thermal decomposition characteristics of pure RTV matrix and composites were shown in Figure 9. It is seen that there were different weight loss events for different composites in the temperature range of 20 to 1000 °C, and the decomposition of the composites was influenced largely by the introduction of additives but first decomposition temperature, which declared that there were about the same beginning decomposition temperature (300 °C) and the different ending decomposition temperature for pure RTV (640 °C), DBDPE/Sb₂O₃/RTV (690 °C) and Al(OH)₃/RTV (530 °C) composites. The residual were 2.08% for pure RTV, 30.6% for DBDPE/Sb₂O₃/RTV and 43.2% for Al(OH)₃/RTV, respectively. So, Measurements show that both of Al(OH)₃ and DBDPE/Sb₂O₃ can improve the performance of heat decomposition for RTV matrix and the comprehensive case are same basically.

**DSC and Tᵢ**

The DSC curve of Al(OH)₃/RTV composites and RTV matrix is shown in Figure 10. It can be found that RTV matrix shows one endothermic peak at about 720 °C (about 590 °C), which means parts of crystallization for RTV. And, for Al(OH)₃/RTV composites, the DSC curve showed that besides two small endothermic peaks at about 410 °C and 490 °C, one big endothermic peak appeared at about 600 °C, and the peak temperature of transformation was about 510 °C (the first Tᵢ about 380 °C), which indicated that the doping of Al(OH)₃ in RTV can decrease the Tᵢ of 35.6% than pure RTV, and, the structure of the tested sample was mainly of branch-chain crystal.
Figure 10 shows the DSC of DBDPE/Sb$_2$O$_3$/RTV composites and RTV matrix. DBDPE/Sb$_2$O$_3$/RTV composites shows three endothermic peaks, and, all the peaks moves to the left within the range between 5wt. % and 25wt.% . Moreover, the level of left shift increased with the increase of the DBDPE/Sb$_2$O$_3$ content. Samples of 5wt.% DBDPE/Sb$_2$O$_3$/RTV (the first $T_g$ about 320 °C) shows a decrease of 45.8% than RTV (the first $T_g$ about 590 °C) in $T_g$.

The results lead to a conclusion that DBDPE/Sb$_2$O$_3$ showed some superiority in decreasing $T_g$ of RTV rubber than Al(OH)$_3$, and, both of DBDPE/Sb$_2$O$_3$/RTV and Al(OH)$_3$/RTV composites were mainly of branch-chain crystal.

Conclusions

The research concludes that the overall properties of RTV matrix can be significantly improved by incorporating Al(OH)$_3$ and DBDPE/Sb$_2$O$_3$, whilst DBDPE/Sb$_2$O$_3$/RTV was more than Al(OH)$_3$/RTV. The final performance and corresponding proportion were reported as Table 3. There is reason to believe that the date was critical to relative engineering research. Therefore, Al(OH)$_3$ and DBDPE/Sb$_2$O$_3$ are good modifiers for RTV matrices. As for the compositers, we hope for a kind of compositers with excellent flame retardant, anti-corrosion and damping-absorption functions.

<table>
<thead>
<tr>
<th>Proportion</th>
<th>15-20 wt.% DBDPE/Sb$_2$O$_3$/RTV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
<td></td>
</tr>
<tr>
<td>Tensile strength</td>
<td>2.18 MPa</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>243.1%</td>
</tr>
<tr>
<td>Tear strength</td>
<td>13.684 kN/m</td>
</tr>
<tr>
<td>Shore Hardness A</td>
<td>51.6 HA</td>
</tr>
<tr>
<td>The level of flame retardant</td>
<td>FV-0</td>
</tr>
<tr>
<td>OI</td>
<td>46</td>
</tr>
<tr>
<td>Volume electric resistivity</td>
<td>7.1×10$^{14}$ Ω • m</td>
</tr>
<tr>
<td>The range of decomposition temperature</td>
<td>300 °C to 690 °C</td>
</tr>
<tr>
<td>The ending percentage of remain weight</td>
<td>30.6%</td>
</tr>
</tbody>
</table>

Table 3: The ending performances of DBDPE/Sb$_2$O$_3$/RTV composites

Acknowledgement

This work is financially supported by National Natural Science Foundation of China (No. 51707153), the Shaanxi Province Key Laboratory of Science and Technology Innovation Project (2014SZS09-K04, 2014SZS09-Z01), the Natural Science, and Special fund of Education Department Foundation of Shaanxi Province of China (101-221206, 101-43116033), the natural science foundation of Shaanxi province (No.2019JM-166) and Science Foundation of Xi’an University of Technology in China (2015TS002, 101-2560816012).

References