Research on the utilization of fly ash and rice husk silica as fillers for flame-retardant silicone rubber materials

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ABSTRACT

This paper investigates the effects of halogenated flame retardants (DBDPO, DBDPE, and Chloroparaffin), halogen-free fillers derived from industrial and agricultural waste (Fly Ash and Biosilico amorphous silica from rice husk), and the anti-structuring silanol agent ND-8 on the fire resistance of silicone rubber materials. The results demonstrate that incorporating 100 phr (parts per hundred rubber) of Fly Ash combined with Biosilico amorphous silica and silanol ND-8 into the silicone rubber compound facilitates the creation of a novel material with superior fire resistance. This improvement is attributed to the formation of a stable mullite and cristobalite ceramic surface layer, resulting in a residual ash content of 60% upon combustion. The material achieved a 5 VA rating (the highest level under the UL-94 standard), while simultaneously contributing to resource conservation and environmental pollution mitigation.

Keywords: Flame retardant materials; Fire retardant additives; Fly ash; Rice husk silica; Silicone rubber; Anti-structuring silanol agent.

1. INTRODUCTION

In contemporary research, various flame-retardant composite materials have been developed to address increasingly complex fire hazards. Electrical fires, often caused by short circuits and high-power electrical devices, pose significant risks to property and human safety, making the development of efficient flame-retardant materials increasingly important [1].

Silicone rubber is widely used in construction, transportation, electronics, automotive, and aerospace industries due to its excellent thermal stability, weather resistance, chemical inertness, electrical insulation, and low smoke emission during combustion [2]. However, the organic side groups attached to the silicone backbone, such as methyl and vinyl groups, make the material susceptible to ignition, limiting its use in fire-sensitive applications [3].

To improve its flame retardancy, two main approaches have been employed: chemical modification of the polymer structure and the incorporation of flame-retardant additives [4]. Common additives include halogenated compounds, phosphorus-, nitrogen-, and silicon-based flame retardants, inorganic fillers, intumescent systems, and nanomaterials. However, halogenated flame retardants release toxic and corrosive gases during combustion, raising environmental and health concerns [5].

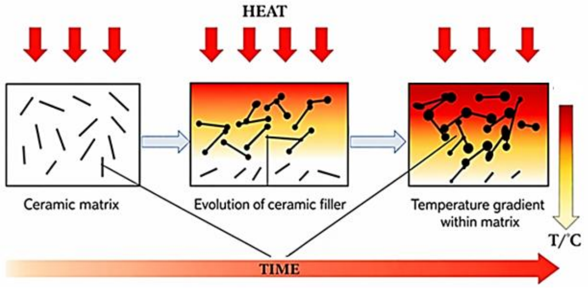

Figure 1. *Schematic representation of the surface ceramization process of flame-retardant silicone rubber materials [6].*

One of the most effective strategies for halogen-free silicone rubber is the synergistic use of inorganic fillers and silane or silanol coupling agents [6, 7]. These composites exhibit a surface ceramization effect above 600 °C (Figure 1), forming a stable ceramic layer that resists melting and dripping, maintains electrical integrity, and provides valuable time for firefighting and rescue operations [6].

Fly ash, an alumino-silicate primarily composed of quartz and mullite derived from coal combustion in thermal power plants, along with amorphous silica sourced from rice husk, is an abundant industrial and agricultural by-product in Vietnam. Modified fly ash as a flame-retardant material has received considerable attention recently, such as carbonate-coated fly ash as a flame-retardant filler for silicone rubber [8] and polyphenylene oxide-coated fly ash as a flame-retardant filler for EPDM rubber [9]. However, the utilization of fly ash and amorphous silica from rice husk as functional fillers specifically for flame-retardant silicone rubber remains largely unexplored. The successful application of these fillers in silicone rubber formulations would not only prevent resource waste but also significantly mitigate environmental pollution. Therefore, the search for effective halogen-free flame retardants and the development of eco-friendly elastomeric composites represent an urgent and essential task.

This study focuses on evaluating the influence of various flame retardants and fillers on the fire-resistant properties of silicone rubber materials.

2. EXPERIMENTAL

2.1. Material

The primary raw materials utilized in this study consist of: High-molecular-weight synthetic rubber: Dimethyl methylvinyl siloxane (SKTV-1) - sourced from Russia; Fly ash: Provided by Song Da Cao Cuong Co., Ltd. (Vietnam), the material underwent particle size fractionation and surface treatment with an alkaline solution; Rice husk-derived silica (Biosilico) - Supplied by BSB Nanotechnology Joint Stock Company (Vietnam); Decabromodiphenyl oxide (DBDPO) - sourced from Russia; Decabromodiphenyl ethane (DBDPE) - sourced from China; Chloroparaffin (HP-70) - sourced from Russia; Anti-structuring agent: α,ω-dihydroxydimethylsiloxan (silanol ND-8) - sourced from Russia; Curing agent: Dicumyl peroxide - sourced from Russia.

2.2. Specimen preparation

Experimental samples were prepared according to the formulations listed in Tables 1 and 2. Silicone rubber compounds were mixed in a Haake PolyLab internal mixer (GmbH, Germany; chamber volume: 47 cm^3) at 35 - 45 °C. The rotor speed was initially set at 20 rpm and increased to 60 rpm after all ingredients, including the curing agent, were added.

The resulting compounds were then processed on a two-roll mill (at least 10 passes), followed by vulcanization in a hydraulic press at 150 °C and 20 MPa for 10–20 min, depending on the optimum cure time of each formulation. Finally, the vulcanized samples were post-cured in an oven at 200°C for 6 h to remove volatile impurities.

Table 1. *Formulations for comparing various flame retardants.*

Components	**Component content (phr)**			
	Sample groups			
	Sample groups 1	Sample groups 2	Sample groups 3	Sample groups 4
SKTV-1	100	100	100	100
Dicumyl peroxid	2	2	2	2
DBDPO	0 - 20	-	-	-
DBDPE	-	0 - 20	-	-
Cloroparafin	-	-	0 - 20	-
Fly ash	-	-	-	0 - 200

***Table 2.** Formulations for comparing different ratios of flame-retardant components.*

Components	**Component content (phr)**						
	Sample						
	M-1	M-2	M-3	M-4	M-5	M-6	M-7
SKTV-1	100	100	100	100	100	100	100
Dicumyl peroxid	2	2	2	2	2	2	2
Biosilico	-	25	25	-	25	25	25
Fly ash	-	-	-	100	100	100	80
Silanol ND-8	-	-	6	6	-	6	6

2.3. Analytical methods

Flame retardancy was evaluated according to OCT 1 90094-79 (equivalent to UL-94) using cylindrical specimens (Ø16 × 20 mm). Samples were exposed to a Bunsen burner flame (125 ± 10 mm) for 30 s at an angle of 60°, and the afterflame and afterglow times were recorded.

Mechanical properties were measured using a Gotech AI-3000 universal testing machine (Taiwan) according to GOST 270-75. Type 1 specimens were die-cut from vulcanized sheets (2.0 ± 0.2 mm thick).

The Limiting Oxygen Index (LOI) was determined using a Netzsch LOI 901 instrument (Germany) following GOST 21793-76. Materials with an LOI above 28% are considered self-extinguishing [10].

Volume resistivity was measured with a TomM-01 meter (Russia) according to GOST 6433.2-71 using square specimens (150 ± 3 mm, thickness 2.0 ± 0.2 mm).

Shore A hardness was determined in accordance with GOST 263-75.

Thermal decomposition behavior was investigated by simultaneous DSC–TGA (SDT Q600, TA Instruments, USA) under an air atmosphere. Approximately 20 mg of sample was heated from 30 to 1000 °C at a rate of 20 °C/min.

3. RESULTS AND DISCUSSION

3.1. Influence of various flame retardants on the flame retardancy of silicone rubber materials

To enhance the flame retardancy of silicone rubber materials, chlorine- and bromine-based flame retardants are commonly utilized. However, during combustion, silicone rubbers containing these additives release exceptionally toxic by-products, rendering them unsuitable for applications in enclosed spaces [5].

In order to develop flame-retardant materials free from halogenated compounds, two distinct groups of silicone rubber samples were prepared: a group containing widely available halogenated flame retardants (DBDPO, DBDPE, and Chloroparaffin) and a group utilizing fly ash fillers, as detailed in the formulations in Table 1. Based on these preparations, a comparative assessment of their flame-retardant performance was conducted, with the results presented in Table 3.

The results presented in Table 3 demonstrate that DBDPO and DBDPE provide effective flame-retardant performance when incorporated into the silicone rubber formulation at concentrations of 20 phr and 15 phr per 100 parts of SKTV-1 rubber, respectively. Chloroparaffin also demonstrates flame retardancy at a loading of 20 phr; however, it sustains an afterglow for an additional 34 seconds after the ignition source is removed.

The neat silicone rubber sample and the sample group containing only fly ash failed to demonstrate flame-retardant properties, as these compositions had no significant impact on the afterflame and afterglow durations of the silicone elastomers. This indicates that the independent use of fly ash filler in silicone rubber formulations is insufficient to induce a flame-retardant effect. Consequently, the synergistic combination of fly ash with other fillers and additives will be investigated in the subsequent sections.

Table 3. *Flame retardancy test results for silicone rubber compounds.*

Sample groups	Flame retardant content	Ignition time (s)	Afterflame time (s)	Afterglow time (s)
Flame-retardant-free	0	30	46	55
Sample groups 1	5	30	40	43
	10		32	No afterglow
	15		31	
	20		No flaming and no afterglow	
Sample groups 2	5	30	36	41
	10		35	41
	15		No flaming and no afterglow	
	20		No flaming and no afterglow	
Sample groups 3	5	30	50	57
	10		38	41
	15		37	40
	20		No flaming	34
Sample groups 4	20	30	38	45
	50		38	47
	100		39	47
	150		37	45
	200		36	44

Furthermore, the data presented in Table 4 reveal that halogenated flame retardants do not significantly affect the mechanical strength of silicone rubber. While the mechanical properties of fly ash-filled rubber are superior to those of samples containing halogenated additives, they remain considerably lower than those of standard commercial silicone rubber materials.

Table 4. *Mechanical properties of selected vulcanized silicone rubber samples.*

Parameters	Sample		
	DBDFO 20 phr	DBDFE 20 phr	Fly ash 100 phr
Tensile strength, MPa	0,29	0,32	2,6
Elongation at break, %	67	70	253

3.2. Investigation of the influence of fillers on the flame retardancy of silicone rubber materials

Since fly ash filler alone did not demonstrate either flame retardancy or reinforcement efficiency in the basic silicone rubber formulations investigated above, the authors conducted experiments combining fly ash with reinforcing silica and the anti-structuring silanol agent ND-8. This approach mirrors the compositions commonly found in commercial silicone rubber grades, as detailed in Table 2, to further evaluate their flame-retardant performance.

It is well-established that various types of silica fillers, such as Aerosil 200, Aerosil 300, Zeosil, or mica powder, can be selected to reinforce silicone rubber compounds. In this study, as previously mentioned, Biosilico amorphous silica (derived from rice husk, with properties nearly equivalent to Aerosil 300) was selected. It should be noted that silica is primarily a reinforcing filler and not an inherent flame retardant.

The influence of fly ash on the flame retardancy of silicone rubber when integrated with different fillers was systematically studied. The flame retardancy results for the vulcanized silicone rubber samples are presented in Table 5.

Table 5. *Flame retardancy test results of vulcanized silicone elastomer samples.*

Sample	Ignition time (s)	Afterflame time (s)	Afterglow time (s)
M-1	30	46	55
M-2		55	65
M-3		45	60
M-4		48	51
M-5		37	42
M-6		No flaming and no afterglow	
M-7		41	52

The experimental results in Table 5 indicate that Biosilico amorphous silica does not affect the flame-retardant properties of the silicone rubber; instead, it serves as a reinforcing filler. Furthermore, the ND-8 anti-structuring silanol agent only acts as a dispersing aid and reduces the activity of the silica filler to prevent premature vulcanization during storage. However, the combination of 100 phr of fly ash with Biosilico amorphous silica and ND-8 silanol results in a silicone rubber material with high flame retardancy.

As reported in [6], when temperatures exceed 600 °C, silicone rubber containing aluminosilicate fillers begins to form a cristobalite ceramic surface layer. Above 1200 °C, a mullite-cristobalite ceramic layer is formed through eutectic reactions and the condensation of active -Si-OH and -Al-OH groups from the decomposition products within the compound. These products include SiO_2 from the polysiloxane chain degradation (> 500 °C), combined with Biosilico amorphous silica, ND-8 silanol, and fly ash. This ceramic layer possesses a highly stable three-dimensional structure that can withstand extreme temperatures (up to 1800 °C) and acts as a thermal barrier, protecting the inner layers and enhancing the material's flame retardancy.

Nevertheless, to achieve effective flame retardancy, the ceramic framework density after combustion must be sufficiently high. This requires a high concentration of fly ash filler in the rubber matrix to effectively dilute the polymer. As shown in Table 5, a fly ash content of 100 phr (sample M-6) yields high flame-retardant efficiency, whereas a content of 80 phr (sample M-7) fails to provide flame retardancy.

The vulcanized silicone rubber sample M-6, after the flame retardancy evaluation, was prepared for further testing of other technical specifications, as presented in Table 6.

Table 6. *Technical specifications of the vulcanized silicone rubber sample.*

Properties	Results	
	M-6	IRP-1338
Density, g/cm^3	1,21	-
Tensile strength at break, MPa	6,8	$\geq 6,4$
Elongation at break, %	356	≥ 330
Shore A hardness	69	58 ÷ 70
Limiting Oxygen Index,%	42	-
Volume resistivity, Ω·m	$2,5.10^{13}$	-
Operating temperature, ^{0}C	- 60 ÷ 250	- 60 ÷ 250
Flame retardancy under single exposure to an open flame	Yes	Yes

The evaluation results of several technical specifications for the M-6 silicone rubber material are consistent with and meet the fundamental technical requirements for heat-resistant and flame-retardant silicone rubbers. Specifically, they are comparable to the Russian IRP-1338 grade-a flame-retardant, heat-resistant material based on silicone rubber and mineral silica fillers used in aerospace applications [11].

3.3. Thermal analysis of vulcanized silicone rubber samples

The thermogravimetric analysis (TGA) curves, which illustrate mass changes, mass loss rates, and heat flow variations for the vulcanized silicone rubber samples (M-1 to M-6, Table 2), are presented in Figure 2.

The thermal curves in Figure 2a show that the sample group without fly ash (M-1, M-2, M-3) experienced a mass loss of over 60%, whereas the group containing fly ash (M-4, M-5, M-6) exhibited a lower mass loss of approximately 40%. A significant mass loss was observed for all samples within the temperature range of 400 °C to 600 °C. This observation is entirely consistent with the initiation of the surface ceramic layer formation process previously discussed in Section 3.2.

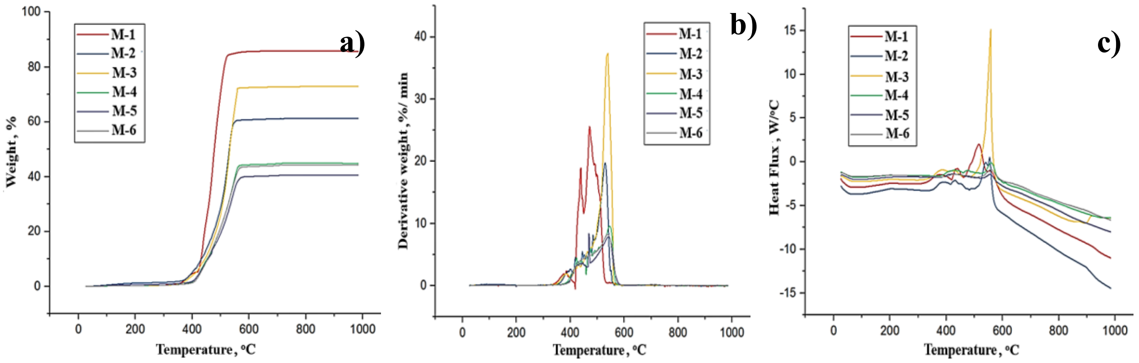

Figure 2. *The thermogravimetric analysis (TGA) curves:*
a) Mass changes; b) Mass loss rates; c) Heat flow variations.

The analysis of the thermal curves in Figure 2b shows that the nature of the mass loss rate curves is similar for all vulcanized silicone rubber samples. Each exhibits a primary peak within the temperature range of 500 - 550 °C, with a maximum mass loss rate exceeding 10%/min. An exception is observed for sample M-1 (unfilled), which displays two nearly equal mass loss rate peaks; this could be attributed to the decomposition of different components within the silicone rubber matrix.

Exothermic reactions for all samples were also observed within the same temperature range of 400 - 600 °C through the heat flow analysis results (Figure 2c). Sample M-3 exhibited the highest peak heat flow value in this range, corresponding to its maximum mass loss rate and the lowest ash content among the filled samples. This indicates the simultaneous and intense decomposition of the silicone rubber, Biosilico amorphous silica and the ND-8 anti-structuring silanol agent.

4. CONCLUSIONS

The study demonstrates that incorporating fly ash into halogen-free silicone rubber formulations at a loading of 100 phr (parts per hundred rubber), in combination with Biosilico (amorphous silica derived from rice husk) and ND-8 anti-structuring silanol agent, facilitates the formation of a stable surface ceramic layer during combustion. This process results in a residual ash content (ceramic framework) of approximately 60% by mass. The formation of this protective ceramic layer imparts high flame retardancy to the silicone rubber material, which can be evaluated as equivalent to the highest 5 VA rating according to UL-94 standards. This material shows significant potential for applications similar to the Russian IRP-1338 flame-retardant and heat-resistant grade used in the aerospace industry.

REFERENCES

[1]. Hongyu Niu et al., *"Recent progress on thermally conductive and electrical insulating rubber composites: Design, processing and applications"*, Composites Communications, Vol. 22, pp. 100430, (2020).

[2]. Wu Y.-Y. et al., *"Large-scale and facile fabrication of phenyl-containing silicone foam materials with lightweight, wide-temperature flexibility and tunable pore structure for exceptional thermal insulation"*, Chemical Engineering Journal, Vol. 492, pp. 152183, (2024).

[3]. Chen H.Y. et al., *"Self-Adhesive Polydimethylsiloxane Foam Materials Decorated with MXene/Cellulose Nanofiber Interconnected Network for Versatile Functionalities"*, Advanced Functional Materials, Vol. 33, No. 48, pp. 2304927, (2023).

[4]. Yi-Hao Tang et al., *"Recent Advances in Fire-Retardant Silicone Rubber Composites"*, Polymers, Vol. 16, No. 17, pp. 2442, (2024).

[5]. Shui-Yu Lu and Ian Hamerton, *"Recent developments in the chemistry of halogen-free flame retardant polymers"*, Progress in Polymer Science, Vol. 27, No. 8, pp. 1661–1712, (2002).

[6]. Jianhua Li, *"Research status and development trend of ceramifiable silicone rubber composites: a brief review"*, Materials Research Express, Vol. 9, pp. 012001, (2022).

[7]. Zbigniew Pędzich et al., *"Optimisation of the Ceramic Phase for Ceramizable Silicone Rubber Based Composites"*, Advances in Science and Technology, Vol. 18, pp. 202027, (2011).

[8]. Yongha Kim et al., *"Valorization of fly ash as a harmless flame retardant via carbonation treatment for enhanced fire-proofing performance and mechanical properties of silicone composites"*, Journal of Hazardous Materials, Vol. 404, pp. 124202, (2021).

[9]. Патент RU2750160C1, *"Теплозащитный материал"*, Бюл. № 18, (2021).

[10]. M. I. Nelson et al., *"A dynamical systems model of the limiting oxygen index test"*, ANZIAM Journal, Vol. 43, No. 1, pp. 105–117, (2001).

[11]. *"Смеси резиновые для резинотехнических изделий авиационной техники"*, ТУ 38 0051166-2015, (2015).

TÓM TẮT

Nghiên cứu sử dụng tro bay và silica từ tro trấu làm chất độn cho vật liệu cao su silicon chống cháy

Trong bài báo này, ảnh hưởng của các chất chống cháy có chứa halogen (DBDPO, DBDPE và Cloroparafin), chất độn từ phế thải công nghiệp, nông nghiệp không chứa halogen (Tro bay, Silica vô định hình từ tro trấu Biosilico) và chất chống cấu trúc silanol ND-8 đến khả năng chống cháy của vật liệu cao su silicon đã được nghiên cứu. Việc kết hợp 100 pkl chất độn Tro bay với silica vô định hình từ tro trấu Biosilico và chất chống cấu trúc silanol ND-8 trong thành phần hỗn hợp cao su silicon giúp tạo ra vật liệu mới có khả năng chống cháy cao nhờ hình thành lớp gốm bề mặt mullit, cristobalit bền vững với hàm lượng tro 60% khi cháy, tương đương với mức chống cháy cao nhất 5 VA theo tiêu chuẩn UL-94, đồng thời giúp ngăn ngừa lãng phí tài nguyên và giảm thiểu ô nhiễm môi trường.

Từ khoá: Vật liệu chống cháy; Phụ gia chống cháy; Tro bay; Silica từ tro trấu; Cao su silicon; Chất chống cấu trúc silanol.