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Investigation of the Effect of Huntit Filler on Flame Retardancy and Mechanical Properties of Silicone Rubber-based Materials in Cable Applications

[*1,2] Halil Can Uğraşkan 0009-0002-6410-4995, [1,2] Fatma Sevde Duman 0009-0007-5827-2120, [2] Serkan Emik 0000-0002-6005-9704

[11] 2M Kablo San. Tic. A.Ş., Department of R&D Center, Tekirdağ, Turkey.
[2] Istanbul University-Cerrahpaşa, Chemical Engineering Depart., Istanbul, Turkey.
[*] Corresponding author, e-mail: halilcanugraskan5@gmail.com

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Abstract

Silicone rubber is an organic/inorganic hybrid macromolecular polymer with properties such as fire resistance, strength, flexibility, chemical resistance, thermal stability, hydrophobicity, dielectric characteristics, resistance to environmental conditions, and biocompatibility. It is an elastomer and exhibits high-performance characteristics compared to most materials in its class. Its current properties and the relative ease of enhancing its characteristics have significantly increased the industrial utilization of silicone rubber. Due to its mineral structure, silicone rubber is frequently used as an insulating material to ensure circuit integrity in the production of fire-resistant cables. It exhibits low smoke zero halogen (LSZH) characteristics, with low level release of toxic gases as a result of combustion reactions. In this study, silicone rubber compounds including a natural mineral Huntite with improved fire-resistant properties compared to standard silicone materials suitable for cable production were prepared. After cable production the fire performance properties alongside the physico-mechanical characteristics of the final products were examined. To determine the flame retardancy of the material, limiting oxygen index (LOI%) and fire performance tests were performed according to the ISO 4589-2 and BS 6387 standards, respectively. The results show that Huntite is a suitable alternative material to improve silicone materials' flame resistance.

Keywords: Silicone rubber, Huntite-Hydromagnesite, Fire-retardant, Cable, Fire tests

Huntit Dolgusunun Silikon Kauçuk Üzerinde Alev Geciktirici ve Mekanik Özelliklerine Etkisinin Kablo Uygulamalarında İncelenmesi

Öz

Silikon kauçuk, yangına dayanıklılık, mekanik dayanıklılık, esneklik, kimyasal direnç, termal stabilite, hidrofobiklik, dielektrik karakteristikleri, çevresel koşullara karşı direnç ve biyolojik uyumluluk gibi özelliklere sahip organik/inorganik hibrid bir makromoleküler polimerdir. Elastomer sınıfındaki çoğu malzeme ile karşılaştırıldığında yüksek performans özellikleri sergiler. Sahip olduğu bu özellikler ve bu özelliklerin geliştirilmesinin göreceli kolay olması, silikon kauçuğun sanayide kullanımını önemli ölçüde artırmaktadır. Mineral yapısı nedeniyle silikon kauçuk yangına dayanıklı kabloların üretiminde devre bütünlüğünü sağlamak için bir yalıtkan malzeme olarak sıkça kullanılmaktadır. Yanma reaksiyonları sonucunda toksik gazların düşük seviyede salınımı ile düşük duman ve sıfır halojen (LSZH) özelliklerine sahiptir. Bu çalışmada, kablo üretimine uygun standart silikon malzemelere göre yangına dayanıklılık özellikleri geliştirilmiş, doğal bir mineral olan Huntit içeren silikon kauçuk bileşikleri hazırlanmıştır. Kablo üretiminden sonra nihai ürünün fiziko-mekanik özelliklerinin yanı sıra yangın performans özellikleri de incelenmiştir. Kabloların alev geciktirici özelliklerini belirlemek için ISO 4589-2 ve BS 6387 standartlarına göre sırasıyla sınırlı oksijen indeksi (LOI%) ve yangın performans testleri gerçekleştirilmiştir. Sonuçlar Huntitin silikon malzemelerin alev direncini arttırmak için uygun bir alternatif malzeme olduğunu göstermektedir.

Anahtar kelimeler: Silikon kauçuk, Huntit-Hidromagnezit, Alev geciktirici, Kablo, Alev testleri

[1] Corresponding author:
E-mail: halilcanugraskan5@gmail.com

1. Introduction

Silicone rubber (SR) is a semi-organic and semi-inorganic material with low heat release rate, low total heat release, and low fire index. [1-6] At the same time, SR has excellent thermal stability, which is transformed into a continuous, oxidation-resistant, insulating network-like silica ash covering the surface after burning, [7] effectively preventing further ablation. Its existing properties and the relative ease of property improvement significantly increase the use of silicone rubber in industry. Which is that silicone rubber is an excellent material to ensure the circuit integrity. However, its own flame retardancy performance is not enough to meet the requirements of products, such as fire door and fireproof cable material. [8,9]

In fire-resistant cable applications, the performance of SR material is insufficient to pass the tests required to meet standards such as BS 6387 protocols C, W, and Z. Therefore, in fire-resistant cable applications, the selection of materials and their compounding is crucial.

Nowadays, the most widely used groups of mineral fire retardants are metal hydroxides such as Aluminum hydroxide (ATH) and Magnesium Hydroxide (MDH). In addition, silicone dioxide and calcium carbonate are the most widely used groups of cost-effective mineral fillers in industrial applications.

In silicone rubber compounding, inorganic reinforcement agents, especially silicon dioxide, are commonly used to modify mechanical properties such as tensile strength, elongation, and hardness according to the filler's particle size. Since these fillers has inorganic structure, they also improve the char forming properties, resulting in improved flame-retardant properties. But the main utilization of reinforcement agents is cost reduction.

Metal hydroxides act as fire retardants by releasing water vapor through endothermic decomposition leaving a thermally stable inorganic residue. When used as a filler in polymer composites, they dilute the combustible polymer decomposition products with water, cooling the condensed phase through the endothermic dehydration.

Nowadays, the use of mineral rocks as flame retardant fillers in industrial applications is becoming widespread. Considering the literature studies, grinding them to appropriate sizes, causes both flame retardancy as well as cost reduction. There are studies in the literature on the utilization of Huntite-Hydromagnesite among these filler materials such as Aluminum hydroxide (ATH) , Magnesium hydroxide (MH), Zinc Borate (ZB), Colemanite (C). [10-14]

Huntite, with the formula $Mg_3Ca(CO_3)_4$, is a rock-type carbonate compound found mixed with Hydromagnesite in nature and can be produced in desired particle sizes with modern grinding technology. It decomposes by an endothermic reaction similar to ATH and MDH. Decomposition begins with the separation of chemically bound H_2O at temperatures above 240°C, and forms char in the physically stable Mg and Ca oxide structure with the separation of CO_2 at high temperatures (450-800°C) [15].

Since the discovery of natural Huntite-Hydromagnesite deposits in late 1980's, there has been considerable number of works published regarding the structure [16-21] and thermal decomposition [22-37] of Huntite-Hydromagnesite materials. Due to its two-stage decomposition using Huntite-Hydromagnesite mineral instead of Quartz in silicone rubber compound is promising for fire retardancy applications.

In this study, it was aimed to examine the use of natural mineral filler Huntite instead of quartz, which is widely used in silicone rubber compositions, in terms of both mechanical and fireproof properties. For this purpose, mechanical and fire-retardant properties of Silicone Rubber/Huntite

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composites were investigated by comparing them with a standard Silicone/Quartz composite. By subjecting the cables produced by the standard extrusion method to the relevant international fire tests, the effect of Huntite mineral as a fire-retardant material for silicone compounds for cable production applications has been scientifically investigated.

2. Materials and Methods

2.1. Materials

Two different peroxide curable high-consistency rubber (HCR) silicone rubber, commercial name Elastosil R 401/55 S and Elastosil R 500/60 OH was purchased from Wacker Chemie AG, (Munich, Germany). Natural Huntite-Hydromagnesite mineral was purchased from Minelco Ltd., (İzmir, Turkey). The curing agent, di(2,4-dichlorobenzoyl) peroxide was purchased from Akzo Nobel GmbH, (Amsterdam, The Netherlands) and the coloring blue pigment was purchased from Rockwood Pigments (Kidsgrove, England). All materials were used as received.

2.2. Sample Preparation

Silicone rubber composites were prepared using two roll-mill operating at room temperature according to formulations given in Table 1. The silicone rubbers were initially softened, after Huntite-Hydromagnesite mineral were introduced as fillers. The Rubber and filler thoroughly mixed until a visually homogeneous mixture was achieved. After 25 minutes of mixing, a curing agent, DCBP, was added to the system. The total mixing time extended to approximately 30 minutes. Following the compounding process, the silicone rubbers were allowed to condition for 16 hours. Subsequently, the silicone rubber formulations were extruded onto copper wire with a 1.5 mm² surface area using an extruder with 90 mm screw diameter to form the cores of the selected LIHH 2x1.5mm² control cable for this study. For a reference sample SR/Quartz composite has been chosen. All of these production steps applied as same for the sample 2M30.

Table 1. Formulations of Silicone rubber composites

Composition (phr)	**Compound Code**			
	2M204	**2M205**	**2M206**	**2M30**
Silicone Rubber /1	50,00	50,00	50,00	50,00
Silicone Rubber /2	50,00	50,00	50,00	50,00
Huntite-Hydromagnesite	20,00	25,00	30,00	-
Quartz	-	-	-	30,00
Curing agent	1,35	1,35	1,35	1,35
Coloring pigment	0,35	0,35	0,35	0,35

The general schematic view of the continuous extrusion process used in the study, which includes (i) extruding SR on wire, (ii) passing the covered wire through the heat-shocking units located downstream of the extrusion line, (iii) the vulcanization process by passing through a hot air-flowing heat tunnel is given in Figure 1.

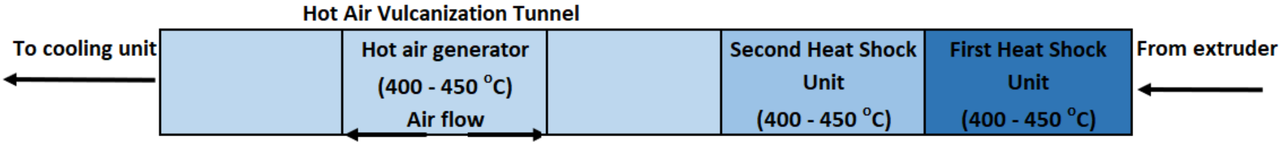

Figure 1: General schematic view of the extrusion process

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As seen in Figure 2, the selected LIHH type cable's structure consists of multiple layers: While stranding the cable cores (produced by SR extrusion process) to form the appropriate structure, they are stranded with a layer of fiberglass tape. Finally, to give the cable its final form, a HFFR material is extruded as outer sheath.

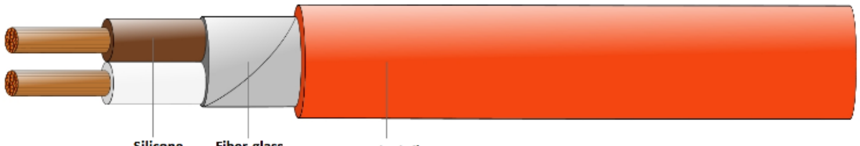

Figure 2: LIHH type cable's structure

2.3. Characterization Methods

Rheological analysis performed by a moving die rheometer MDR (Gotech M-3999AU). Analysis carried out at 120°C for 5 min. The torque value was monitored as a function of time. In rheological analysis, standard curing parameters:

ML, minimum torque – A measure of the viscosity of the uncured compound.

MH, maximum torque – A measure of cure state. With some compounds, maximum torque can be related to vulcanizate modulus and hardness.

ts2 – time for torque to increase 0.2N.m or above ML –a measure of scorch time or processing safety.

t10, t50, t90 – time to reach 50% or 90% of maximum torque development, calculated as time to 0.5 MH or 0.9 MH – a measure of cure rate or an estimate of cure time at the test temperature.

were investigated.

Tensile strength and elongation measurements were performed using Universal Testing Machine (Zwick model Z005) at room temperature. Tensile tests conducted on dumbbell shaped samples (125x75x3.0 mm^3) at a speed of 50 mm/min according to the standard IEC/EN 60801. Tensile strength, percentage elongation at break and modulus values were recorded. All the results were calculated with an average value of five samples with standard deviations.

The material's hardness was determined utilizing a digital Shore A durometer (ZwickRoell 3130). For this purpose, test plates with dimensions of 10x10x0.3 cm^3 were prepared using a hot press (Marestek M-gps-01) at 180°C for 6 minutes under a pressure of 150 MPa with SR materials.

LOI values were measured by Oxygen Index analyzer (Mares) on test bars of size 130x6.5x3.2 mm^3, according to the ISO4589-2 determination of oxygen index test standard.

The fire performance of silicone materials was evaluated on the final product through the application of C-W and Z tests in accordance with the BS 6387 standard, PH120 test according to EN 50200 standard and FE 180 test according to IEC 60331-21/23. One of the important applications of these composites is their behavior in fire simulation. Protocol C test involves the application of only flame onto the cable, while Protocol W test simulates the scenario where fire extinguishing systems apply water jets onto the cable while flames are present during a fire. On the other hand, Protocol Z test is designed to assess the impact of falling objects onto the cable or the system containing the cable during a fire. PH 120 test involves mounting the cable in a U-shape on a vertical wall and applying force during the free-fall motion of a cylindrical rod with a mass of 25 kg onto the wall where the cable is mounted, under the flame at a temperature of 830°C, to assess the circuit integrity. In the FE 180 test, the cable must operate without compromising circuit integrity for a minimum of

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180 minutes under a flame at a temperature of at least 750°C. These fire tests aim to assess situations that could compromise circuit integrity in a real fire scenario.

According to the BS 6387 standard, in these tests, the cable is installed on the test apparatus, and the declared voltage is applied to the conductors. The cable is then subjected to a flame at 950 ± 40°C for Protocol C, 650 ± 40°C for Protocol W, and 950 ± 40°C for Protocol Z. In all these tests cable must maintain its electrical continuity.

According to BS 6387 standard, in C fire test protocol, flame at a temperature of 950 ± 40°C is applied to the cable, which is mounted parallel to the flame source burner with a distance of 75 mm. The cable tested for 180 minutes must maintain its electrical continuity.

According to BS 6387 standard, the W fire test protocol involves a total duration of 30 minutes. Starting from the 15th minute of the test, the cable is subjected to water spray with a rate of 0.25 L/m^2/s. The cable must maintain its electrical continuity for an additional 30 minutes under the water spray. In accordance with the BS 6387 standard, the Z protocol apparatus incorporates a rod weighing 25 kg. At 30-second intervals, this rod undergoes free fall motion, inducing vibrations on the wall to which the cable is affixed.

Aging tests were conducted on the insulation part of the cores. The copper wire separated from the silicone insulation without causing damage to the material. The test was carried out inside an oven at a temperature of 200°C for a duration of 10 days. Tensile measurements were performed after 16 hours of conditioning, and the percentage changes were recorded.

3. Results and Discussions

3.1. Rheological Behavior of Composites

The Elastosil R 401/55 S and Elastosil R 500/60 OH HCRs are noted for their easy pigmentation, good flexibility, good processing characteristics, and mechanical properties. After preparing the silicon rubber compounds, firstly, the curing characteristics of these compounds were investigated. For this purpose, the torque versus time curves were obtained in a moving die rheometer for 5 minutes at 120°C under 1.67 hz±0.01 oscillating frequency. As seen in Table 2 and Figure 3, while the addition of filler did not affect the T_{s2}, T_{10}, and T_{50} and slightly increased T_{90} values (that is, it did not cause any significant change in the vulcanization process), it caused an expected increase in the measured maximum torque value. The results indicated that the all-silicone rubber compounds have good processability, and can be easily cured by extrusion process.

Table 2: Vulcanization parameters of the composites

	MH (dN-m)	ML (dN-m)	T_{s2} (m:s)	T_{10} (m:s)	T_{50} (m:s)	T_{90} (m:s)
2M204	15,889	4,521	00:22	00:21	00:28	00:49
2M205	15,027	3,66	00:22	00:21	00:28	00:47
2M206	16,821	4,716	00:22	00:21	00:28	00:50
2M30	18,924	6,314	00:22	00:21	00:28	00:53

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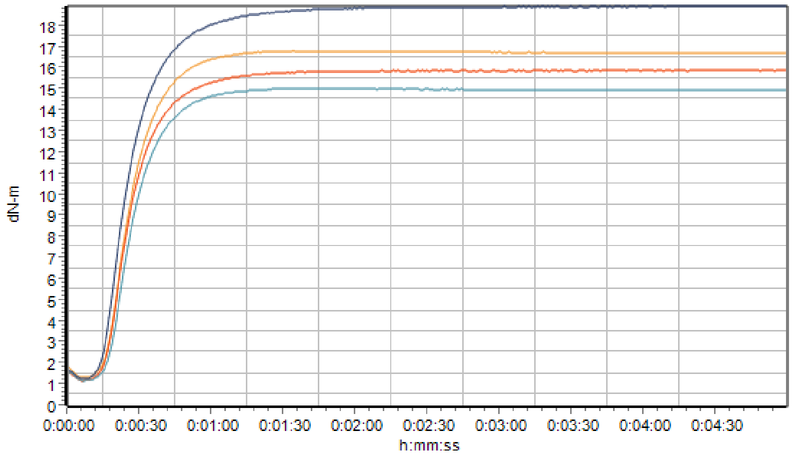

Figure 3: Rheological analysis of the composites

3.2. Mechanical Properties

The values of all mechanical parameters did not change significantly (Table 3) compared to 2M30 sample. This indicates that the Huntite-Hydromagnesite mineral allows the use of this compound as insulation for a wire, which is a crucial parameter for cable standards. Conversely, addition of mineral filler has resulted in an improvement in the Shore A hardness value (Table 4).

Table 3: Mechanical test results according to IEC/EN 60801

Tensile Strength	Sample designation			
Composition (phr)	2M 204	2M205	2M206	2M30
Dumbbell	7,72	8,51	7,34	8,45
Standard Deviation	0,30	0,39	0,14	0,45
Core insulation	6,44	7,42	7,78	8,18
Standard Deviation	0,26	0,30	0,17	0,21

Elongation	Sample designation			
Composition (phr)	2M 204	2M205	2M206	2M30
Dumbbell	380,90	443,13	380,21	384,92
Standard Deviation	22,40	45,91	19,50	23,73
Core insulation	459,50	344,60	368,71	346,90
Standard Deviation	36,54	38,22	26,90	32,48

3.3. Aging Properties

Cables are electrical equipment that need to be used for a long time, therefore, it is necessary to examine the aging characteristics of cable insulation materials through thermal aging tests. The compliance of cables with the IEC/EN 60811-401 and IEC/EN 60811-501 standards has been assessed through thermal aging tests, and the effect of Huntit-Hydromagnesite mineral on thermal aging has been investigated. As seen in Table 4, the use of filling material at a rate of 30 phr indicates that the material does not meet the specified standards. It has been determined that the most optimal level for the usage rate of the filling material, based on aging characteristics, is 25 phr.

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Table 4: Thermal aging test results according to IEC/EN 60811-401 and IEC/EN 60811-501

Compound	**Tensile strength* (N/mm²)**	**Elongation* (%)**
2M204	4,58	166,254
2M205	4,49	140,42
2M206	2,16	104,37
2M30	5,68	147,7

*: Standard values for Tensile Strength= 4 N/mm^2 and Elongation= 120%

3.4. Flame Retardancy Properties

Table 5 and 6 present the results of BS 6387, EN50200 and IEC 60331-21/23 fire tests and LOI test.

Table 5: Results of Flame Tests

Insulation Material	FE 180	PH 30	BS 6387 C	BS 6387 W	BS 6387 Z
2M204	✓	✓	✓	*X*	✓
2M205	✓	✓	✓	*X*	✓
2M206	✓	✓	✓	*X*	✓
2M30	✓	✓	✓	*X*	✓

Table 6: Results of LOI Test

Compound	2M204	2M205	2M206	2M30
LOI (%)	28	29	30	29

As seen in the table 5 and table 6, all samples exhibit exceptional fire resistance. Addition of Huntite-Hydromagnesite at 20, 25 and 30 phr also improved char formation significantly.

The two-stage degradation mechanism of Huntite-Hydromagnesite mineral delays the spread of flames, while the resulting fused silica structure, along with the ash-retaining effect of the fiberglass tape, forms a protective layer on the copper surface. This condition ensures the circuit integrity of the cable even under the most challenging conditions. This char formation helps the cable structure pass fire tests except BS 6387 W. It is concluded that the main reason why no formulation can pass the BS 6387 W test is that the water spray in this test is a sign that the char formed as a result of combustion has a porous structure. CO_2 and water formed during the thermal decomposition of huntite cause the resulting char to become porous. It is thought that with the extra additives added to the formulations, products that can successfully pass the BS 6387 W test can be produced due to a less porous and more durable char formation, in other words ceramified char structures. Nevertheless, since all cable structures have high LOI values and pass fire tests except BS 6387 W, it can be easily said that huntite is a highly effective mineral filler in the production of fire-resistant silicone cables.

4. Conclusions

Despite obtaining positive results in fire tests conducted according to specified standards for all samples, the sample incorporating 30 phr Huntite filler yielded unfavorable outcomes in aging tests conducted within the ambit of IEC/EN 60811-401 and IEC/EN 60811-501.

Notwithstanding the affirmative outcomes in BS 6387 C-Z tests and IEC 60331-21/23 FE 180 tests for all tested compounds, the fire test performance of the compounds fell short of meeting the terms of BS 6387 W. It is discerned that the final products lack resistance to the water factor in the BS 6387 W test.

In light of these findings, the optimal ratio of Huntite-Hydromagnesite filler for cable applications appears to be 25 phr. The cost-effectiveness relative to the base compound has facilitated

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the simultaneous enhancement of both properties and cost in the final product by augmenting the quantity of Huntite material.

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