JOURNAL OF Applied Polymer SCIENCE

Effect of borax on the thermal and mechanical properties of ethylene-propylene-diene terpolymer rubber-based heat insulator

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ABSTRACT: The effect of Borax on the mechanical and ablation properties of three different ethylene-propylene-diene terpolymer (EPDM) compounds containing 20 phr carbon fiber, 20 phr Kevlar or 10 phr/ 10 phr carbon fiber/ Kevlar was investigated. All formulations contained 30 phr fumed silica powder and 10 phr paraffinic oil. It was found that adding Borax to the composite samples containing carbon fiber or Kevlar fiber or their mixture with an equal ratio can increase the tensile strength, elastic modulus and hardness with a slightly decrease in the elongation at break of the rubber samples. The results of thermogravimetry analysis (TGA) on the various samples showed significant increase in the char yield at 670°C by adding Borax to the rubber compounds. Moreover, ablation resistance of samples was also improved by increasing Borax content. Meanwhile, density and thermal conductivity of the insulator were also reduced up to about 10% when the carbon fiber was replaced with the Borax. The results indicated that composites containing Kevlar have high storage modulus and produce compact and stable char. EPDM rubber composite containing Borax (20 phr), carbon fiber (10 phr), and Kevlar (10 phr) showed thermal and ablative properties comparable with those of the asbestos-filled EPDM. The thermal conductivity and ablation rate of the above- mentioned sample were 0.287 W/m/K and 0.13 mm/s respectively. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41936.

KEYWORDS: composites; degradation; flame retardance; rubber; thermal properties

Received 11 August 2014; accepted 3 January 2015
DOI: 10.1002/app.41936

INTRODUCTION

To fabricate and design solid rocket motors, an elastomeric insulator is located between the solid propellant and the motor chamber. This elastomeric layer has two important functions. Firstly, it absorbs the mechanical stresses induced to the rocket motor during the propellant casting, storage, transportation, and flight; Secondly, it protects the motor case from high-temperature gases and particle streams generated by the propellant combustion. On the other hand, the insulator should has elastomeric properties and resists against the high temperature and ablative function of the combustion product. Ablation is an erosive phenomenon with a removal of material by a combination of thermo-mechanical, thermo-chemical, and thermo-physical factors from high temperature, pressure, and velocity of combustion flame in the solid rocket motor.[1,2]

Ethylene-propylene diene terpolymer (EPDM) rubber is a terpolymer of ethylene, propylene, and a non-conjugated diene. It has thermal conductivity and glass transition temperature of about 0.25 W/m/K and -50°C, respectively, which can introduce it as a suitable heat insulator binder.[3–6] Long shelf life and excellent low-temperature properties are also two important properties of EPDM. Meanwhile, the char yield and ablation resistance of EPDM is relatively low that need to be reinforced with fillers.[3,5,6]

Carbon black and silica, including fumed and precipitated silica, are two main fillers to improve mechanical and ablative properties of the elastomeric insulators. Fumed silica such as Aerosil shows a higher reinforcing effect in comparison with the precipitated silica because it has finer particle size and a higher specific surface area. In comparison with the precipitated silica, lower density and thermal conductivity can be obtained with the fumed silica.[7] However; fibrous fillers play an important role in the improvement of thermal and ablative properties of insulators.[1]

Although not so long ago, asbestos was the best reinforcement for solid rocket insulation due to outstanding performance in mechanical, thermal and ablative[8]; however, asbestos has been discarded because of its environmental pollution. Therefore, the

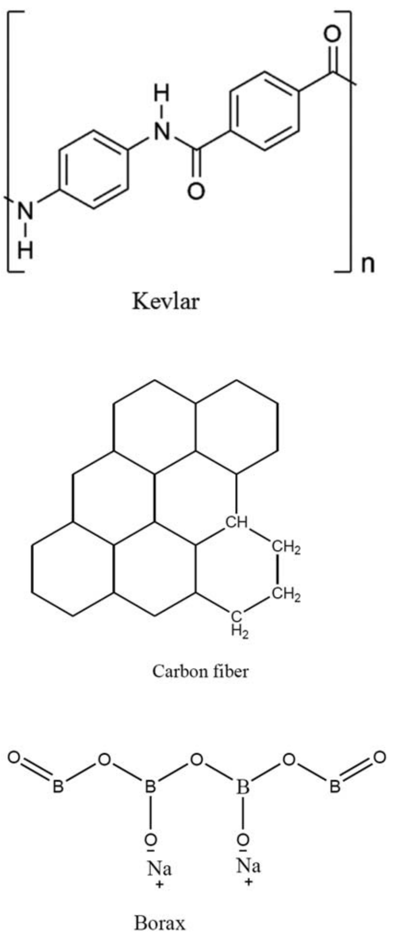

Figure 1. Chemical structures of the Kevlar, carbon fiber, and (anhydrous) Borax.

other fibrous fillers such as the carbon and Kevlar have been replaced due to the higher ablative resistance and char yield.[9,10] It should be mentioned that Kevlar is the trade name of aramid fiber where aramid is polyamide containing amid bonds connected to the two aromatic rings (Figure 1). In general, the char layer strength can be improved by increasing the fibrous heat resistance and mechanical strength. The char layer is a light and porous cover with a low thermal conductivity that acts as a protective insulator against the penetration of flame and oxygen to the sub-layers.[10,11]

Kevlar is used in the various applications, for example in conveyor belt and circuit boards, due to the valuable properties such as the high strength, high modulus and high heat resistance.[12] On the other hand, carbon fiber- reinforced insulators have some advantages such as better ablation resistance. High thermal conductivity and breakage during compounding are two main disadvantages of the carbon fiber. Meanwhile, Kevlar has low density and low thermal conductivity.[13] The other fibrous fillers such as poly(p-phenylene benzobisoxazole) (PBO),[2] polysulfonamide,[14] and melamine fibers[15] have also been used instead of the carbon fiber and Kevlar in some cases. These fibers have ablative resistance better than the Kevlar and carbon fiber in the laboratory tests but their ablative and thermal properties have not been evaluated in the industrial and operational tests. Furthermore, Kevlar and carbon fiber-reinforced insulators do not have the ablative performance comparable with the asbestos-reinforced insulators. To improve the ablative performance, fibrous fillers have been used with the other supplemental materials such as flame retardant or char former.[16–22] Among different supplementary materials, several appropriate compounds are: (1) thermoplastic polyamide compounds,[18] (2) mixed ammonium sulfate and antimony oxide as a hybrid flame retardant,[19] (3) chlorinated paraffinic compound with zinc hydroxystannate,[20] and (4) organic fillers with low-density and low thermal conductivity such as polyvinyl chloride. In the recent years, ammonium polyphosphate has also been used as char former and flame retardant to decrease regression rate of the flame.[22]

As mentioned earlier, ablation resistance and char yield of Kevlar are weaker than those of carbon fiber. Hence, it is necessary to use the other supplementary material with low thermal conductivity and high char yield properties such as Borax.[22–24] It has been reported that ablation properties of the various polymeric resin composites including phenolic, epoxy and polyester resins can be improved by adding Borax.[22–24] Formation of stable char and suitable thermal and ablative properties are main factors in designing of the heat insulator. Because of its low thermal conductivity and high char yield, Borax is a suitable supplement material to be used for designing a heat insulator for the solid propellant. To our knowledge, there is no report on using Borax as an additive in the rubber-based heat insulators. Therefore, as a new experience, possibility of using Borax along with the carbon fiber and Kevlar to improve thermal and ablation resistance of the EPDM rubber-based non-asbestoses insulator containing 30 phr fumed silica powder and 10 phr paraffinic oil is investigated in the present work. Mechanical, thermal and ablative properties of EPDM-based insulator reinforced with chopped Kevlar, carbon fiber and Borax are studied with more details. Insulator properties of the samples are compared with those of sample reinforced with the asbestos as a control sample. Suitable formulation is then introduced on the basis of obtained results.

EXPERIMENTAL

Materials and Specimen Preparation

The material specifications and suppliers are given in Table I. Chemical structure of the Borax, Kevlar and carbon fiber are also given in Figure 1. Formulations given in Table II were mixed by using a laboratory Banbury mixer. All formulations contained 30 phr fumed silica powder and 10 phr paraffinic oil. The mixing of insulator ingredients was done by using C.W. Brabender Banbury mixer (model: BR1600, capacity: 1.5 lit, Farrel Co.). At first, the given amount of EPDM was masticated in the Banbury mixer at about 95°C for 10 min. In the second stage, fibrous and particulate fillers along with the processing aid oil were added into the masticated EPDM and then mixed for 15 min at 80°C. Finally, the prepared master batch was mixed with a given amount of the peroxide crosslinking agent for 5 min at 80°C. All formulations were cured with the 1.5 phr dicumyl peroxide system under press for 15 minutes at 140°C.

Table I. Specifications, Trade Name, and Supplier of the Raw Materials Used in Formulation of EPDM-Based Heat Insulator

Material	Specifications	Trade name	Supplier
EPDM	Ethylene content: 57 wt %	Kep270	Kumho Polychem Co., Ltd., Korea
	Moony viscosity [ML1+4], 125°C: 71		
	Ethylidene norbornene (ENB) content: 4.5 wt %		
	M_w =1.60 × 10^5 g/mol		
Carbon fiber	Chopped,10 mm	CC200	Seal Co., Italy
	Density: 1.9 g/cm^3		
	Tensile strength: 2.5 (GPa)		
	Elongation at break: 1(%)		
	Modulus: 200 (GPa)		
	LOI index: 55 (Vol %)		
Kevlar	Chopped,10 mm	Twaron-1001	Akzo Co. Ltd., Holland
	Density:1.4 g/cm^3		
	Tensile strength: 3 (GPa)		
	Elongation at break: 2.3 (%)		
	Modulus: 125 (GPa)		
	LOI index: 29 (Vol %)		
Borax ($Na_2B_4O_7.5H_2O$)	Density: 1.73 g/cm^3	Borax powder	Etimaden, Turkey
	Melting point: 743°C		
Fumed silica	Surface area: 200 m^2/g	Aerosil	Degussa, Germany
Asbestos	Chopped, 6 mm	-	Lijian Composite Materials, China
	Density: 2.5 g/cm^3		
Curing agent	DCP, Assay = 99%	Dicumylperoxide	Liuyang Sanji Chem. Co., China
C_5 hydrocarbon Petroleum resin	Laboratory grade	PR1-100	Shandong Landum Petroleum Resins Co. Ltd., China
	Softening point (°C): ~ 90		
	Purity: 99%		
	Ash content (%): 0.1		

Determination of Physical and Mechanical Properties

Tensile strength, elongation at break and modulus were measured according to ASTM D412-98a (Reapproved 2002) by using an Instron machine (Model: Inspekt 50) with the tensile speed of 100 mm/min and the gauge length of 25 mm. According to this standard, for materials having a yield point at an elongation less than 20% when tested at 500 mm/min, the rate of elongation can be reduced to lower speed. In our samples, the Kevlar filled composites have a yield point at the elongation less than 20% (at 500 mm/min), so tensile properties of all samples were measured with the tensile speed of 100 mm/min.

The crosslinking density of EPDM samples was evaluated by swelling the rubber samples in the xylene as a solvent. The vulcanized samples of 20×20 mm^2 size were cut from a 2 mm thickness sheet and immersed in 100 mL of the xylene at the room temperature for 72 h.[25] The swelling ratio was determined gravimetrically by weighing the polymer sample prior to immersion in xylene (W_i) and after equilibration in the solvent (W_f). Swelling index was then calculated by using the following equation:

$$\text{Swelling index} = \text{final mass}/\text{initial mass} = W_f/W_i$$

REX 1600 shore A hardness was used to measure hardness of the rubber. Theoretical density of solid rubber sheets was calculated by using the rule of mixture.[26]

Determination of Thermal Properties

The char yield and decomposition temperature of samples were determined according to DIN51006 standard by using thermogravimetry analysis (TGA/DTA, LINSEIS STA Model PT1600) with the heating rate of 10°C/min under nitrogen atmosphere from ambient temperature to 700°C. Samples had the same weight of 30 mg. Most of the phenomena related to weight changes such as the decomposition, dehydration and oxidation were occurred up to maximum temperature of 670°C and above this temperature no significant weight changes was observed. So, the char yield of samples was calculated at 670°C.

Table II. Amounts (as Part Per Hundred Rubber, phr) of Carbon Fiber, Kevlar, and Borax Used in the Formulation of Various Samples

Sample code	Carbon fiber (phr)	Kevlar (phr)	Borax (phr)
CF20	20	0	0
CF20BX5	20	0	5
CF20BX10	20	0	10
CF20BX15	20	0	15
CF20BX20	20	0	20
Kev20	0	20	0
Kev20BX5	0	20	5
Kev20BX10	0	20	10
Kev20BX15	0	20	15
Kev20BX20	0	20	20
CF10Kev10	10	10	0
CF10Kev10BX5	10	10	5
CF10Kev10BX10	10	10	10
CF10Kev10BX15	10	10	15
CF10Kev10BX20	10	10	20
As20	EPDM reinforced with 20 phr Asbestos		

Dynamic mechanical thermal analysis (DMTA) was also carried out for cured EPDM samples by a dynamic mechanical thermal analyzer (DMA-Triton, Tritec2000) according to ASTM E1640-04[27] with a programmed heating rate of 10°C/min.

To evaluate ablation resistant properties of the EPDM samples, an oxyacetylene flame test was carried out according to ASTM E285-80 by using solid rubber sheets with dimensions of $80\times80\times5$ mm^3 according to the ASTM E285-80 standard test.[28] A hot gas flow with a temperature of 3000°C would be created in this test. The velocity of the hot combustion gas was controlled by the flow rate of acetylene and oxygen. The rubbery samples were set with the distance of 20 mm and angle of 90° from high temperature torch. Then the ablation rate of the samples was determined. The erosion rate is defined as a thickness of sample that pieced due to the ablation per second.

The thermal conductivity of solid composite insulator is defined as a time rate of steady heat flow through unit thickness of a disk shape sample with a 1 cm in diameter and a 1 mm in thickness. Laser flash thermal diffusivity method (LFTD) [29] at 25°C was used to evaluate thermal conductivity. According to this method, a short-duration and high intensity heat pulse is applied onto one face of the test sample and temperature rising on the opposite face as a function of time is recorded. The thermal diffusivity of the sample (α) is then calculated according to ASTM E 1461 by using eq. (1).

$$A=0.139L^2/t_{1/2} \quad (1)$$

where L is the thickness of the sample and $t_{1/2}$ is the time from the initiation of the pulse until temperature of the opposite face of the sample reaches to one-half of its maximum. The specific heat capacity of the sample was also measured using this method as well as by differential scanning calorimeter (Perkin-Elmer DSC 8000) according to ASTM E1269-95. Then, the thermal conductivity of the sample (k) was determined via eq. (2).[10]

$$K=\alpha\rho C_p \quad (2)$$

where C_p is the specific heat capacity and ρ is density of the sample.

It should be mentioned that at least three specimens from each sample were subjected to the thermal and mechanical analyses. A good reproducibility was observed for obtained results (see error bars given in the Results section).

RESULTS AND DISCUSSION

Mechanical and Physical Properties

During the storage, transportation, and flight, the motor chamber undergoes a large thermal deformation as well as a high thermal stress.[2] Therefore, it is necessary to optimize tensile strength and elongation at break of insulators used in the rocket motor. It should be mentioned that materials such as DCP, oil and fumed silica have been used with same amounts in all of the composite samples. So addition of them has the same effect on the composite properties in all samples. In addition, these materials don't have any interaction with borax.

The aim of this work is to design Borax-loaded EPDM heat insulator with various properties close to those of Asbestos-based EPDM insulator. Hence, in the present work, EPDM reinforced with 20 phr Asbestos as well as the Borax- free EDPM compounds were considered to be control samples. Then, properties of other samples were compared with the above-mentioned samples. The effect of Borax content on the mechanical and physical properties of the composites is shown in Table III. The introduction of Borax to the CF20, Kev20 and CF10Kev10 composites leads to increase in the tensile strength, elastic modulus and hardness. Meanwhile, elongation at break of the samples decreases marginally by increasing the Borax content. Alkaline or acidic nature of the fillers can influence the curing rate of sulphur- and peroxide-vulcanized rubber. Under similar curing conditions used in the present study, observed mechanical properties can be attributed to increased chemical crosslinking density in the presence of Borax because Borax particles as an alkaline filler can accelerate vulcanization of the EPDM by producing more radicals from dicumyl peroxide (DCP).[30] Swelling index is an indirect measure of crosslinking density: the higher the swelling index, the less chemical and physical crosslinks exist. The swelling index decreased by increasing borax content (Table III), indicating that chemical crosslinking density increases by increasing borax content.

As shown in Table IV, the density of Borax is less than carbon fiber, so using it instead of or along with the carbon fiber reduces the density and weight of insulator. Low density thermal insulator in space applications, for thrust control and upper stage motors, is necessary. Figure 2 shows that density of the CF20 composite is reduced initially by adding Borax to the formulation because of the lower density of Borax in comparison with the carbon fiber. Density is then increased gradually by further increasing the Borax weight percent in the compound.

Table III. Effect of Carbon Fiber (CF), Kevlar (Kev), and Borax (BX) on the Mechanical and Physical Properties of EPDM-Based Insulators

Sample code	Tensile strength (MPa)	Elongation (%)	Modulus (MPa)	Hardness (shore A)	Density (g/cm^3)	Swelling index
CF20	6.03 ± 0.08	655 ± 6	22.1	79	1.220	5.7
CF20BX5	6.25 ± 0.09	560 ± 5	23.1	80	1.210	–
CF20BX10	6.66 ± 0.09	497 ± 4.5	25.2	82	1.212	5.2
CF20BX15	7.10 ± 0.10	471 ± 4.5	26.5	83	1.213	4.5
CF20BX20	7.20 ± 0.10	430 ± 4	27.3	84	1.217	3.3
Kev20	8.22 ± 0.12	65 ± 1	94.0	88	1.162	5.2
Kev20BX5	8.83 ± 0.12	60 ± 1	112.0	89	1.169	–
Kev20BX10	9.10 ± 0.12	61 ± 1	120.3	91	1.173	4.6
Kev20BX15	9.50 ± 0.12	57 ± 1	138.0	91	1.177	4.1
Kev20BX20	9.75 ± 0.13	50 ± 1	147.2	95	1.181	3.1
CF10Kev10	7.10 ± 0.13	75 ± 1	58.8	92	1.191	–
CF10Kev10BX5	7.40 ± 0.10	66 ± 1	62.0	93	1.193	–
CF10Kev10BX10	7.60 ± 0.10	60 ± 1	67.0	94	1.195	–
CF10Kev10BX15	7.80 ± 0.10	54 ± 1	72.0	95	1.198	–
CF10Kev10BX20	8.10 ± 0.11	50 ± 1	75.0	95	1.200	–
As20	7.40 ± 0.10	122 ± 1	24.2	96	1.210	–

The sample containing 20 phr Kevlar has shown low density and high tensile strength, which is suitable for space applications. However, addition of Kevlar leads to a tangible loss in sample elongation.

Brittleness of carbon fiber under shear force of mixing has been reported and breaking of the carbon fiber has also been observed in practically prepared samples.[1] On the other hand, as shown in Table I, elongation at break for carbon fiber is half amount of those of Kevlar fiber. So, it seems that flexibility of the Kevlar fiber is higher than that of the carbon fiber. Hence, due to the high strength and flexibility of Kevlar, breaking of its fibers during compounding could not be possible. However, the twisted network of fibers in the polymer matrix, high aromatic and rigid structure of Kevlar decreases elongation and increase the tensile strength and elastic module.[7] Moreover, adding Borax as rigid and stiff inorganic particulate filler to the rubber composite can decrease elongation at break of the EPDM rubber composite. It is then necessary to use chopped fibers with a length of less than 10 mm to increase the flexibility of Kevlar-reinforced insulators. The sample containing carbon fiber in the presence of various amounts of Borax has lower tensile strength and higher elongation at break with respect to the 20 phr asbestos-reinforced EPDM sample. It can be attributed to brittleness of the carbon fibers where shorter lengths of the carbon fibers can be formed when they are exposed to the shear force of the compounding process.[1]

Char Yield and Decomposition Temperature

Ablation of insulator compound in the ablative environment can produce the stable and porous char layer which acts as protective boundary layers for ablation in this situation. TGA was used to evaluate decomposition temperature and char yield of the fillers used in the EPDM- based composites. Figures 3 and 4 show the TGA and DTG curves of Kevlar, carbon fiber, and Borax, respectively. Figure 3 indicates that the char yield of carbon fiber is more than that of Kevlar. The carbon fibers tend to release the higher amount of carbonaceous product. On the other hand, the existence of oxygen atom in the structure of Kevlar can help to oxidation of carbon atoms and release of CO and CO_2, decreasing the char yield and causing delamination of the char layers. So, each factor that prevents carbon atoms from oxidation can help to form more char.[31,32]

DTG curve of Kevlar shows a maximum mass loss at 525°C, whereas that of carbon fiber indicates a maximum mass loss at

Table IV. Physical and Thermal Properties of Kevlar, Carbon Fiber, and Borax

Sample name	Decomposition temperature (TGA, °C)	Char yield (TGA, %)	Density (g/cm^3)	Thermal conductivity coefficient (W/m/K)
Kevlar	525	45.3 ± 0.3	1.4	0.04
Carbon fiber	582	63.5 ± 0.5	1.9	6.4
Borax	–[a]	70 ± 0.6	1.73	0.6

[a] Weight loss observed at the temperature range of about 100-250°C was due to the water evaporation.

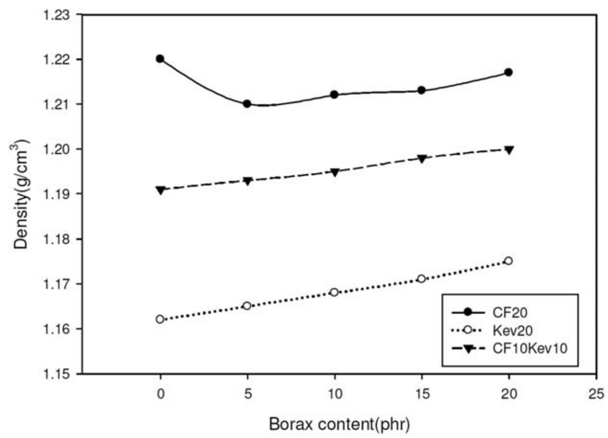

Figure 2. Variation of density with the Borax content in the three EPDM-based compounds.

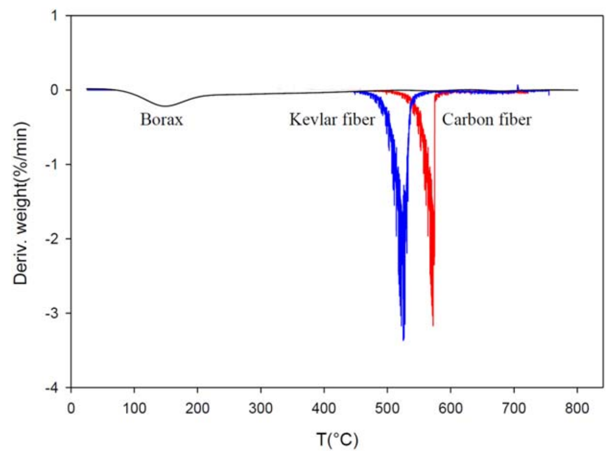

Figure 4. DTG diagram of Borax, carbon fiber, and Kevlar under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

582°C. TGA curve of Borax shows gradually mass loss at the temperature range of 100-250°C due to the evaporation of the water molecules and then reaches to a stable state without mass loss up to 700°C. Thus, the main structure of Borax has higher thermal stability than both carbon fiber and Kevlar.

Moreover, due to the existence of water molecules in the structure of Borax, it acts as flame retardant. The water evaporation process in the structure of the Borax molecules is endothermic, which takes place in the temperature range of 100–250°C. This process causes gradual loss in weight, but some Borax molecules remain stable without weight loss up to 700°C that can act as a thermal shield to prevent more decomposition of sub-layers.

DTG and DTA thermograms of Borax are shown in Figure 5. At the temperature range of about 100-250°C, the removal of water from the structure of Borax was occurred (30 wt % H_2O, about 5 mole H_2O). An exothermic peak can be observed at 565°C which can be attributed to the crystallization and internal rearrangement of the dehydrated Borax. Finally at 736°C, an endothermic peak related to the Borax melting can also be observed.[33]

Weight loss of the prepared composite samples occurs during three stages (Figure 6).The first stage relates to the volatile substances such as process aid materials. The second stage corresponds to the decomposition of composite matrix polymer. Decomposition of reinforcement filled materials also occurs during the third stage. The char yield of samples reinforced with 20 phr Kevlar (Kev20) is low (16%) (Table V) while the CF20 sample has 27% char yield. Therefore, use of the carbon fiber and Kevlar (CF10Kev10) can stabilize insulator char yield, which improves its ablation resistance and thermal conductivity. Borax along with the carbon fiber and Kevlar were added to the compound in order to strengthen the ablative performance and approaching to ablation rate of the asbestos-reinforced insulator. This situation has an important effect on their enforcing of the char yield. The stable and dense char layer produced by decomposition of Borax forms an excellent thermal protective layer. Moreover, Borax compared with carbon fiber has a lower thermal conductivity. However, addition of the Borax to the insulators reinforced with carbon fiber

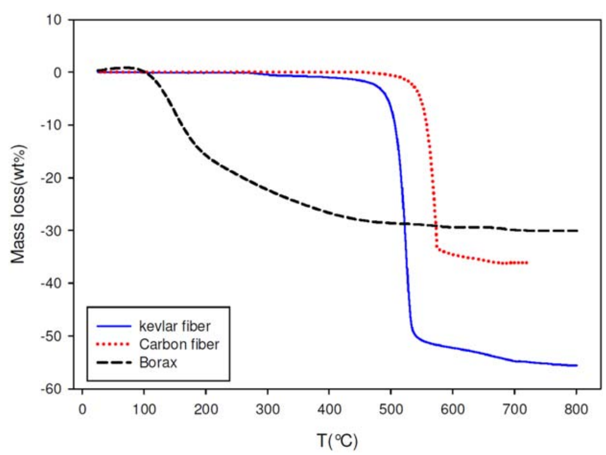

Figure 3. Thermo gravimetric (TGA) curves of Borax, carbon fiber, and Kevlar under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

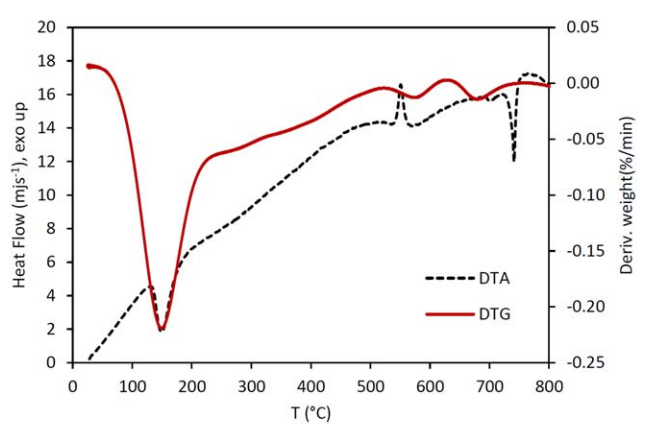

Figure 5. DTG and DTA thermograms of the Borax. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

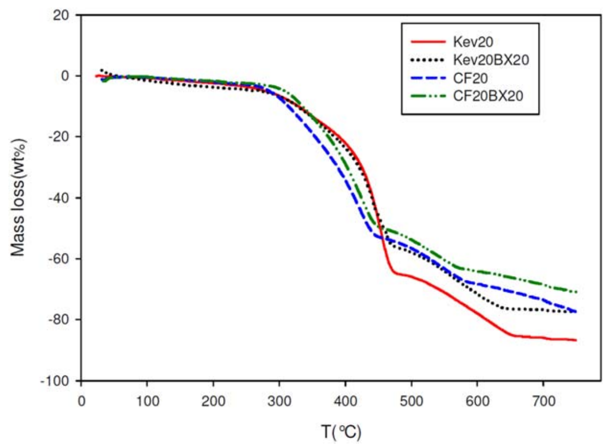

Figure 6. TGA thermograms for various insulator formulations under air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

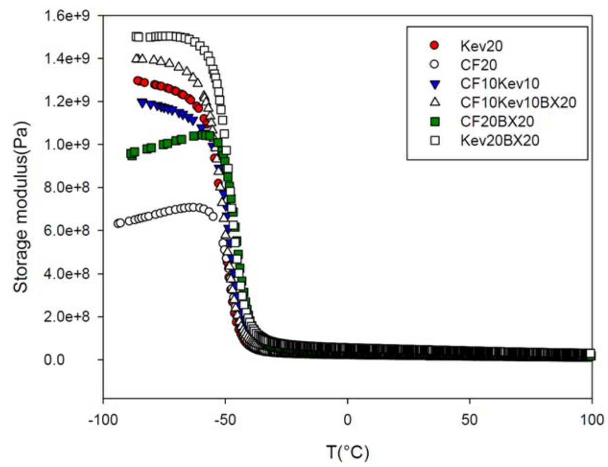

Figure 7. Storage modulus as a function of temperature for EPDM-based insulator formulations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and Kevlar (CF10Kev10), cannot have a large influence on the thermal conductivity.

Ablation Rate

Ablation rate is generally used to report ablative properties of the composites.[34] Evaluation of the remaining weight (char yield) at 670°C from TGA thermograms in Figure 6 shows a significant enhance in char yield by increasing Borax content. Boron oxide can act as a refractory and late melting layer that helps to form stable char as a protective barrier layer. It also prevents reaching heat and oxygen for more burning sub-layers. So, the formation of a stable and late melting char plays the main role to improve the ablation resistance of the Borax- filled samples. Moreover, evaporation of water in Borax structure is an endothermic process, which causes drop in flame temperature and prevents flame spread.

The effect of Borax content on the ablation rates of CF20, Kev20, and CF10Kev10 composites is shown in Table V. The ablation rates of all composites were decreased by increasing Borax content. The initial reduction of the ablation rate can be explained by the enhancement of the thermal stability of the composites with increasing Borax content. However, tenacity of the char layer formed on the surface of the composites are the main factors that can increase the ablation resistance because it

Table V. Thermal Conductivity, Thermal Diffusivity, Heat Capacity, Char Yield, and Ablative Properties of the Samples with Different Formulations

Sample code	Thermal conductivity coefficient (W/m/K)	Ablation rate (mm/s)	Char yield[a] (%)	Thermal diffusivity[b] (mm^2/s)	Specific heat capacity (J/g/C)
CF20	0.390	0.21±0.008	27±0.2	0.179	1.80
CF20BX5	0.381	–	–	0.17	1.82
CF20BX10	0.365	0.15±0.006	30± 0.25	0.162	1.79
CF20BX15	0.359	–	–	0.155	1.76
CF20BX20	0.35	0.12±.004	32±0.29	0.151	1.61
Kev20	0.221	0.43±0.017	16±0.12	0.131	1.45
Kev20BX5	0.232	–	–	0.136	1.46
Kev20BX10	0.244	0.32±0.12	19±0.15	0.14	1.48
Kev20BX15	0.250	–	–	0.143	1.49
Kev20BX20	0.262	0.25±0.01	22.5±0.18	0.146	1.52
CF10Kev10	0.271	0.3±0.012	24±0.19	0.142	1.61
CF10Kev10BX5	0.272	–	–	0.143	1.59
CF10Kev10BX10	0.278	0.22±0.008	28±0.25	0.145	1.60
CF10Kev10BX15	0.281	–	–	0.145	1.61
CF10Kev10BX20	0.287	0.13±0.005	30±0.25	0.147	1.63
As20	0.285	0.10±0.004	31±.26	0.157	1.51

[a] TGA remaining weight at 670 °C.
[b] Data were measured with a tolerance of ± 0.0001.

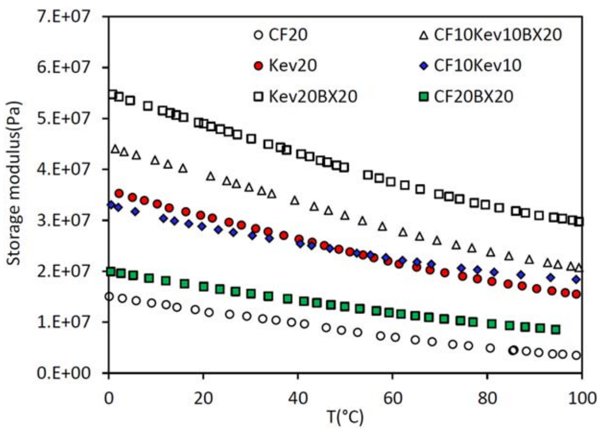

Figure 8. Storage modulus versus temperature in the temperature range of 0–100°C for EPDM-based insulator formulations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

may dominate adhesion between the char layer and virgin material.[3] In high-loaded EPDM composite with fiber, the tenacity of the char layer on the surface of the composites was decreased. It can be attributed to the decreasing of binder/filler ratio in the elastomer compound. Thus, the composites were loaded up to 20 phr carbon and Kevlar fibers to maintain the adhesion between the char layer and virgin material. The enhancement of ablative properties through increment of Borax loading in CF20 can be explained by improvement of thermal stability of the composite insulators, reduction in thermal conductivity, and martial loss during ablation.

Comparison of the ablation properties of prepared samples showed that the samples with 20 phr Borax have the closest ablation rate to asbestos-reinforced insulator, i.e., As20. Among them, ablative and thermal properties of CF10Kev10BX20 were almost similar to As20 (Table V).

Storage Modulus and Char Stability

Figures 7 and 8 show storage modulus plots for various EPDM-based composites. It is clear from this figures that samples containing Kevlar have higher storage modulus as compared to the samples reinforced with carbon fiber samples. These results can be attributed to the brittleness of carbon fiber under shear force of compounding process. Due to the high strength and flexibility of Kevlar, breaking of its fibers during compounding could

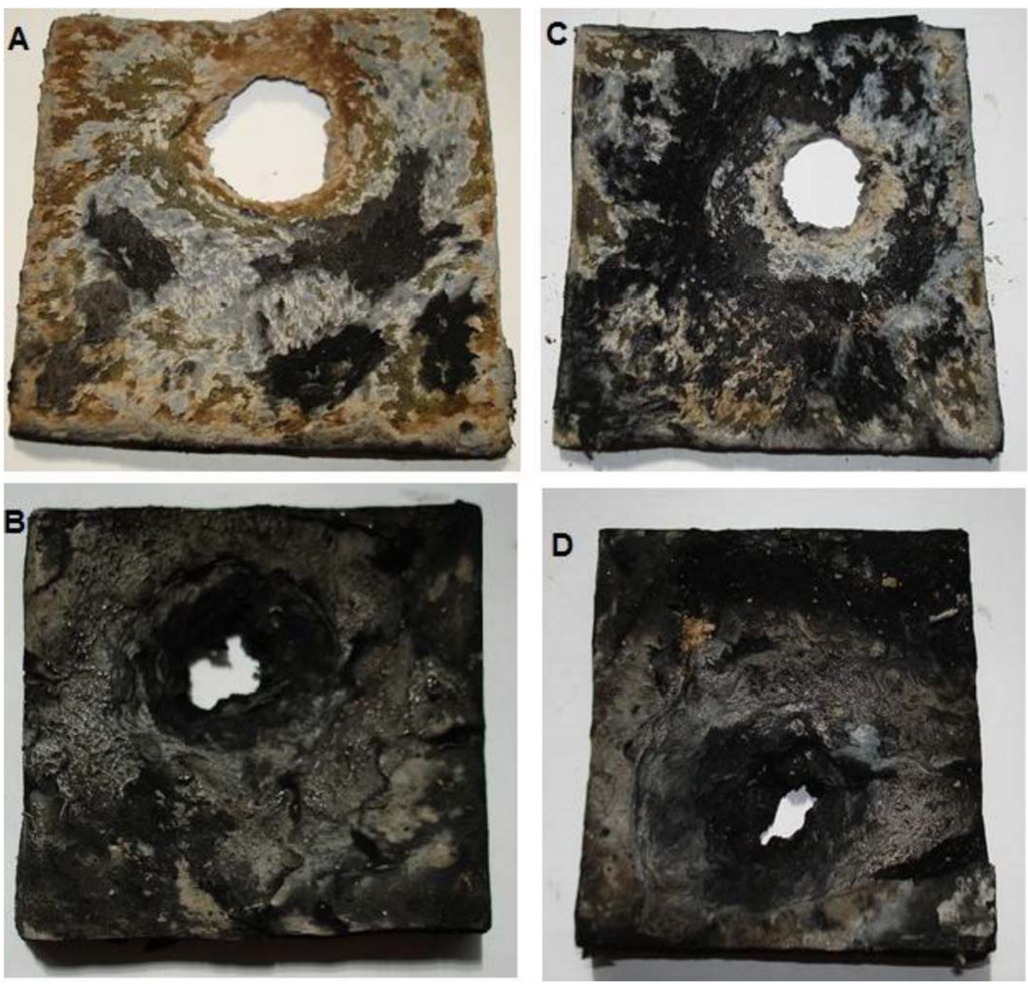

Figure 9. Comparison of the ablation pit for burnt materials of (a) Kev20, (b) Kev20BX20, (c) CF20, and (d) CF20BX20. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

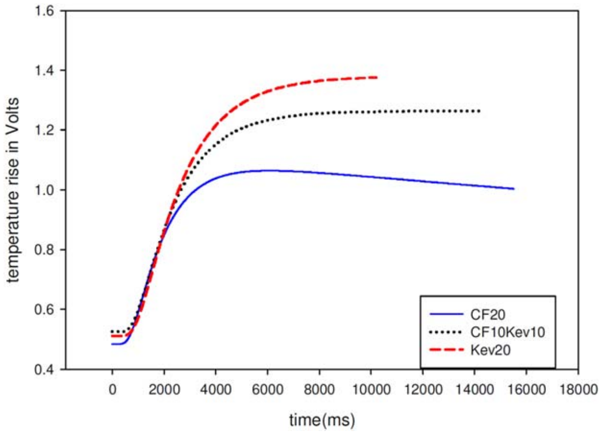

Figure 10. Monitoring of the temperature rise on the opposite face of sample as a function of time for the various samples (to be used for determination of $t_{1/2}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

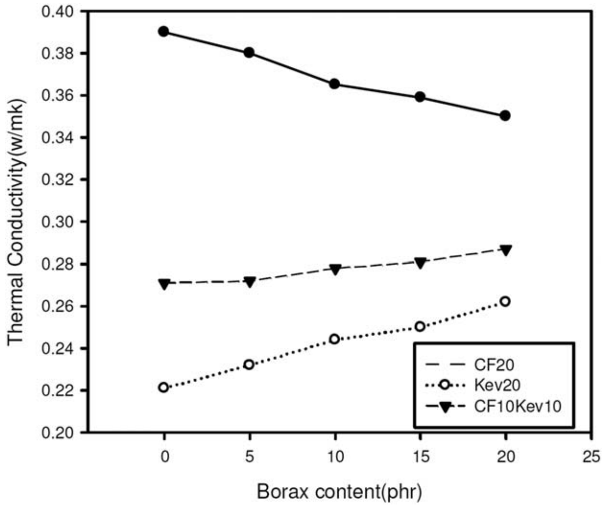

Figure 11. Effects of Borax content on the thermal conductivity of carbon fiber- and Kevlar- reinforced EPDM.

not readily possible in comparison with the carbon fiber. Moreover, Kevlar has high degree of fibrillation[32] that leads to tangled fiber network and samples with higher storage modulus. The fibrillation capability in Kevlar produces a compact and stable thin char layer. So, using carbon fiber and Kevlar in insulator compound can produce compact, stable, and high efficiency char layer. The extent of the destruction was visible in burnt materials (Figure 9). It is clear from this figure that char structures of Borax-loaded samples are porous with small ablation pit while the EPDM composites without Borax have compact char with relatively large ablation cavity. The char layer in Kevlar-filled samples was compact in comparison with the carbon fiber-loaded samples. It can be attributed to the breaking of carbon fiber during compounding and high aromatic rigid structure of Kevlar.

Thermal Conductivity

Thermal conductivity is the measure of a materials ability to conduct heat. The thermal diffusivity (α) of a medium is the thermophysical property that determines the speed of heat propagation by conduction during changes of the temperature with time. The higher the thermal diffusivity is, the faster the heat propagation will be. For a given volume of material, a heat required to raise the temperature with a given amount depends on its heat capacity and the density. When the product of heat capacity and density is high, the thermal diffusivity may be low. So the thermal conductivity depends on thermal diffusivity, heat capacity, and density of material.

Specific heat and thermal conductivity of EPDM composites strongly depend on the content of fillers such as silica, carbon fiber, Kevlar and Borax. Specific heat and thermal conductivity of the rubber decrease as content of the fumed silica increases. This behavior can be attributed to the low specific heat and thermal conductivity of silica.[35] It is clear from Figure 10 that the order of $t_{1/2}$ could be considered as Kev20>CF10-Kev10>CF20, while the values of α for these three composites have order of the CF20> CF10Kev10>Kev20. It is clear from Table V that the Kev20 sample has the lowest thermal conductivity, which confirms that the Kevlar containing composites have high thermal protection properties. Moreover, the carbon fiber composites such as CF20 have the highest thermal conductivity. Therefore, the thermal conductivity of composites is reduced gradually as the carbon fiber weight percent decreases. As indicated in Table IV, the thermal conductivities of carbon fiber, Kevlar and Borax are 6.4, 0.04 and 0.6 W/m/K, respectively. In other words, the thermal conductivity of Borax is about one-tenth of the carbon fiber. Thus, replacement of a portion of the carbon fiber with the Borax can decrease thermal conductivity beside improvement of the insulator ablation resistance. The advantages of carbon fiber are high ablation resistance and char yield but those for Kevlar are high tensile strength and low thermal conductivity. Therefore, the use of Kevlar/carbon fiber composition has a good performance from the view point of the mechanical and thermal properties. Effects of Borax content on the thermal conductivity of carbon fiber- and Kevlar- reinforced EPDM is shown in Figure 11, indicating that thermal conductivity of the CF10Kev10 composite is 0.271 W/m/K which is in an optimal range defined for the internal insulation of the rocket motors.[11,22] Meanwhile, the ablation resistance of this sample can be improved with loading of the Borax. The ablation rate of CF10Kev10BX20 was reached to 0.13 mm/s, which is near to the ablation rate of asbestos filled sample (As20), while the thermal conductivities of both CF10Kev10 and CF10Kev10BX20 samples were very close to each other.

CONCLUSION

In the present work, effect of the Borax on the mechanical and physical properties as well as the ablation and thermal properties of EPDM insulator reinforced with the carbon fiber and Kevlar was investigated. All formulations contained 30 phr fumed silica powder and 10 phr paraffinic oil. Thermo-physical properties of samples showed that Kevlar-reinforced EPDM creates an insulator with low thermal conductivity and low density. But due to the lower char yield and weak ablation resistance, it is necessary to use other supplementary material in the Kevlar-filled rubber insulators. Despite some advantages of the carbon fiber- reinforced EPDM compared with the Kevlar- filled insulator, the carbon fiber- reinforced EPDM has a high thermal conductivity. Due to the high char yield and good ablation resistance, Borax particulate filler can compensate disadvantages of the carbon fiber- and Kevlar- filled EPDM compounds. The content of 20 phr Borax in the EPDM rubber compounds filled with the carbon fiber reduces substantially (about 10%) of the thermal conductivity and density of the composite insulator. For EPDM samples reinforced with 20 phr Kevlar, the addition of 20 phr Borax can increment the char yield and ablation resistance. The addition of Borax to the composite samples containing carbon fiber, Kevlar or their mixture with an equal ratio can increase the tensile strength, elastic modulus and hardness. Slightly decrease in the elongation of rubber samples was also observed. The results of DMTA have shown that samples loaded with the Kevlar have a higher storage modulus in comparison with that loaded with the carbon fiber. Thus, composites containing Kevlar produce compact and stable char. The sample CF10Kev10BX20 has the closest thermal and ablation properties to the asbestos- filled sample. So, suitable combination of Kevlar, carbon fiber and Borax in EPDM compounds can be used instead of the asbestos- based insulators.

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