

## An excellent ablative composite based on PBO reinforced EPDM

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**Abstract** Short poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) fibers were first used to reinforce ethylene–propylene–diene terpolymer (EPDM) as thermal insulation materials. The effects of PBO fiber length and content on the mechanical and ablative properties of the composites were investigated in detail. Comparing with the severe breakage occurred in short aramid fibers as fillers, only some necking deformation is observed in PBO fibers filled EPDM after processed. After ablated by oxyacetylene flame, the carbonized PBO fibers still keep solid fibrous structure instead of hollow one of carbonized aramid fibers in the char layer. As a result, the PBO fibers/composites show significantly higher tensile strength and ablation resistant abilities than the aramid fibers/composites. Moreover, with the length and content of PBO fibers increasing, both the tensile strength and the ablation resistance of the composites increase gradually though the break elongation reduces sharply. Considering the properties requirement of thermal insulator, PBO fibers with 3.42–5.56 wt% in content and 3–4 mm in length are preferred. The mass loss rate and the erosion rate as low as 0.05 g s<sup>-1</sup> and 0.10 mm s<sup>-1</sup> are observed in the optimal samples, respectively, which is evidently lower than that of the best aramid fibers/EPDM-based insulations reported so far.

**Keywords** PBO fiber · EPDM · Insulation composites · Ablative rate

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## Introduction

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. Thermal insulation materials, namely ablative materials, located between the solid propellant and the motor chamber, are important components of high performance solid propellant rocket motors in many aerospace and military application [1, 2]. During the rocket motors working, these materials are subjected to high temperature (above 3,000 °C) and high velocity (6.8–3,400 m s<sup>-1</sup>) ablation resulting from the combustion gas and the particles of the burning solid propellant [3–5]. Under these extreme conditions, the insulation materials would be degraded continuously and then carbonized to form a char layer. A sharp temperature gradient would be formed in the char layer, which slows down the penetration of the heat in the insulator and provides thermal protection for the motor chamber. Therefore, the mechanical strength of the char layer is crucial for the ablation resistant properties of these insulation materials [6–8].

Usually, flexible elastomer [such as butadiene–acrylonitrile (NBR), ethylene–propylene–diene terpolymer (EPDM)] is utilized as a matrix of these thermal insulation composites for its advantages in easy processing, low density, and low thermal conductivity. However, these elastomer matrixes alone could not form a strong char layer after carbonized. Therefore, they have to be reinforced with fibers (chopped or woven fabric of graphite, carbon, glass, or Kevlar) or fillers (silica, metal oxides, asbestos, or silicates) [9]. Recently, more and more inorganic fibers are rejected for their pollution and poor reinforcement. For example, asbestos has been discarded for its environment pollution and potential cancer threat to human health [1, 10]. In addition, glass fiber and carbon fiber have poor reinforcement on the rubber matrix for their further breakage during mixing with rubber and other additives [11]. Therefore, organic fibers attract more and more interests during the past decade. First, polyacrylonitrile (PAN) fiber, for its high carbon residue (about 45% at 1,000 °C) in nitrogen, is expected to be a good choice to improve the mechanical and ablative properties of EPDM-based insulation composites [12]. Unfortunately, some studies show that PAN fiber has the same problem of breakage during the mixing process as glass fiber. Meanwhile, our study shows that PAN fiber during the ablation is not carbonized as expected as it happens in nitrogen, which may attribute to its low pyrolysis temperature (below 285 °C) [13]. The degradation temperature of PAN fibers and EPDM matrix is very close and they would decompose synchronously. As a result, the PAN fiber does not exhibit effective reinforcement on the matrix and the composite insulator could hardly survive under the oxyacetylene flame. Then the interest has been turned to aramid fiber for its higher mechanical strength and better thermal stability, which allows it to be degraded much slower than that of matrix. So far, aramid fiber is still mostly utilized as the organic filler in the insulation composites [5, 14–16]. However, our studies show that aramid fiber has the problem of breaking as well as exfoliating during processing [17, 18]. After mixed with rubber matrix, its actual length and diameter are both reduced. Moreover, the SEM study shows that the aramid fibers present

**Table 1** Comparison of mechanical and thermal properties between aramid fiber and PBO fiber

Properties	Aramid fiber	PBO fiber
Supplier	Akzo Co. Ltd., Holland	Toyobo Co. Ltd., Japan
Trade name	Twaron-1001	Zylon-HM
Tensile strength (GPa)	3.0	5.8
Tensile modulus (GPa)	125	280
Elongation at break (%)	2.3	2.5
Density (g cm <sup>-3</sup> )	1.44	1.56
Limiting oxygen index (Vol.%)	29	68
Pyrolysis temperature (°C)	550	675

hollow structure after ablated by the heat flux, which would greatly lower the mechanical strength of the carbonized fibers, and so does the char layer.

All the studies suggest that the reinforcement of the carbonized fibers on the char layer depends on their mechanical strength and thermal stabilities, which may closely relate to the mechanical strength and thermal stability of the original fibers [5, 19, 20]. This promotes us to apply stronger and more stable fibers as fillers in the thermal insulation composites to improve their thermal insulation properties. It has been reported that the thermal decomposition temperature and the carbon residue of poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) fiber under nitrogen at 1,000 °C are much higher than that of aramid fiber [21]. The properties of aramid fiber and PBO fiber are compared and shown in Table 1 [22]. All the properties indicate that PBO fiber may be a better choice to improve the mechanical, especially the ablative properties of the insulation materials for its higher mechanical and ablative properties than that of aramid fiber. However, as far as we know, no study on PBO fiber reinforced elastomer composite insulation materials has been reported, although a lot of papers focus on the surface treatment and the thermal degradation of pure PBO fiber [23–25].

In this study, a thermal insulation material with outstanding mechanical and ablative properties is reported, which consists of PBO fibers for length 2.0, 3.0, 4.0, and 5.0 mm as filler and EPDM rubber as elastomer matrix. The fiber length in the final insulation is well characterized. The effects of the length and content of PBO fiber on the mechanical and ablative properties of the insulator have been investigated in detail. For comparison purpose, the results of short aramid fibers reinforced EPDM system processed in the same procedure are listed as well.

## Experimental part

### Materials and specimen preparation

Poly(*p*-phenylene-2,6-benzobisoxazole) (PBO, Zylon-HM) fibers were supplied by Toyobo company (Japan) with an average diameter of 15.0 μm. The PBO fibers for

**Table 2** Formula of the insulation composites

Materials	Purity	Supplier	Content (wt%)
EPDM (trade name, EPDM4045)	Commercial grade	Jilin Chemical Co. China	56.5
DCP	Laboratory grade	Shanghai Fangruida Co. Ltd., China	2.26
Chlorinated Paraffin-70	Laboratory grade	Shanghai Jieren Chemical Co., China	5.65
Antimony trioxide	Laboratory grade	Huachang Antimony Industry Co. Ltd., China	2.82
Boron phenolic resin (trade name, FB89)	Laboratory grade	Xi'an Taihang Fire Retardant Co., China	11.83
Fumed Silica (trade name, A200)	Commercial grade	Jilin Shuanglong Chemical Co. Ltd., China	11.83
PBO fiber (trade name, Zylon-HM)	Commercial grade	Toyobo Co. Ltd., Japan	2.31–6.63 (2–5 mm)
C <sub>5</sub> petroleum resin (trade name, PR1-100)	Laboratory grade	Shandong Landun Petroleum Resins Co. Ltd., China	5.65

length 2.0, 3.0, 4.0, and 5.0 mm were controlled by a computer during being chopped. Aramid fibers for length 4.0 and 5.0 mm and for diameter 12  $\mu\text{m}$  were purchased from Twaron1001, Akzo Co. Ltd., Holland. The composites were prepared by mixing the short fibers, fumed silica, boron phenolic resin, and C<sub>5</sub> petroleum resin with the EPDM rubber on a laboratory-sized (160  $\times$  320 mm) two-roll mill, model XK-160. Then the flame retardants (chloroparaffin-70 and antimony trioxide) and the vulcanization agent [dicumyl peroxide (DCP)] were also added into the rubber mixtures, respectively. The detailed formula was listed in Table 2.

After the short PBO fibers and other additives were well dispersed in the EPDM rubber on the two-roll mill for about 20 min, the compounds were vulcanized in the molds with a dimension of 210  $\times$  160  $\times$  2 mm for tensile test and a dimension of  $\varnothing 30 \times 7$  mm for ablation measurement, respectively, at 160  $^{\circ}\text{C}$  and 15 MPa for 55 min.

Aramid fibers reinforced EPDM composite was prepared following the same procedure for comparison.

## Properties test

### *Mechanical properties test*

The mechanical properties of the insulation materials, such as tensile strength and break elongation, were measured on a CMT7304 electron tensile machine according to ASTM D3039 at room temperature. The tensile speed was 100  $\text{mm min}^{-1}$  and the gauge length was 25 mm. The tensile test was carried out along the machine rolling direction. Generally, the short fibers (such as aramid fiber) will be broken

severely by the shear strength of the rollers when they are blended with other additives and EPDM matrix on the two-roll mill. As a result, the real length of short fiber in the composites will decrease heavily and display a normal distribution. It is well known that the reinforcement of short fibers on the composites will be affected mainly by fibers' real length instead of their original length. Therefore, the real length of short fibers in the composites should be measured. In this study, the real length of the short fibers in the composites was measured with an optical microscope after the fibers were separated from the unvulcanized composites with toluene and transferred onto a glass-dish [26]. We selected randomly 550 pieces short fibers and measured their length on the optical microscope. Then the average length of those 550 pieces short fibers was regarded as the real length of short fiber in the composites.

#### *Thermogravimetric analysis (TGA)*

The TGA curves of PBO fibers, matrix, and the composites were carried out with a thermogravimetric analyzer (Q1000DSC+LNCS+FACS Q600SDT, TA Co., America) under nitrogen from 20 to 1,000 °C at a heating rate of 20 °C min<sup>-1</sup>.

#### *Thermal conductivity*

The thermal conductivities of EPDM matrix, aramid fiber/composites, and PBO fiber/composites were carried out according to ASTM D5470-2005 on a DRP-II thermal conductivity instrument (Xiangtan Instrument Co. Ltd., China) using a method of steady-state plate. The dimension of the samples was Ø30 × 10 mm. Furthermore, the temperature and the relative humidity of the air were 27 °C and 60%, respectively. The average value was taken from the result after repeating the test with five specimens.

#### *Ablation experiment*

In order to evaluate the ablation resistant properties of the insulation composites, an oxyacetylene flame test was carried out according to ASTM E285-80 (2002) on a machine (AO-III, made by the Fourth Academy of China Aerospace Science Company) in this research. A hot gas flow as high as about 3,000 °C and  $4.2 \times 10^6 \text{ W m}^{-2}$  heat flux would be created in this test. The velocity of the hot combustion gas was controlled by the flow rate and pressure of acetylene (1,116 L h<sup>-1</sup> and 0.095 MPa) and oxygen (1,512 L h<sup>-1</sup> and 0.4 MPa), respectively. The vulcanized sample was fastened on a plate and the oxyacetylene flame was burst onto the center of the cylindrical specimen surface. The inner diameter of the flame nozzle was 2.0 mm. The distance between the specimen surface and the flame nozzle was 10 mm. After ablated by oxyacetylene flame for 20 s, the center of the specimen surface would be eroded very severely and the ablative properties of the composites could be characterized with an erosion rate and a mass loss rate [18]. In this research, the erosion rate referred to the maximum difference in thickness between original and ablated specimen per second. And the mass loss rate was the

difference in weight between original and ablated specimen per second. Generally, after the composites were ablated for some time, four zones including ablation zone, porous char layer, pyrolysis zone, and virgin material were observed in the longitudinal profile of the insulation material [13]. Importantly, the porous char layer provides the thermal and ablation resistant protection for the whole ablative materials effectively. In other words, the erosion resistant properties of the composites were affected directly by the very char layer. Thus, the composites with dense and strong char layer were necessary when facing the hot and high-speed combustion gas flow. The aim of all previous studies is to strengthen the char layer by adding some fibers into the matrix.

### *Morphology analysis*

The tensile fractographs of the composites and the ablative morphology of the carbonized fibers in the char layer were observed on a scanning electron microscope (SEM, Model Philips Quanta 200).

## **Results and discussion**

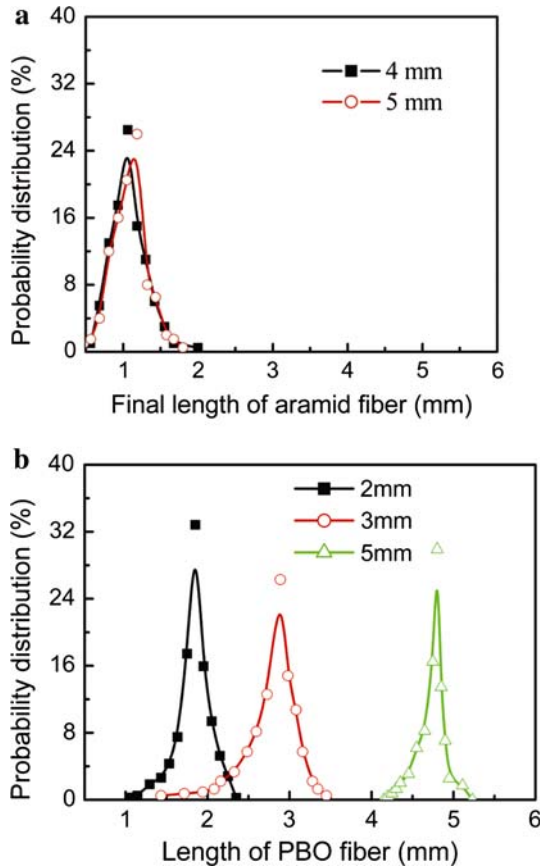
### Real length of aramid fibers and PBO fibers in the composites

It is well known that owning strong shear strength is very important for all the rollers to disperse the short fibers and other additives into rubber matrix. However, this shear strength can break the short fibers severely after a mixing process. As a result, the reinforcement of short fibers on the final composites will be affected mainly by the fibers' real length instead of their original length. The real length distributions of aramid fibers with 4.0 and 5.0 mm and PBO fibers with 2.0, 3.0, and 5.0 mm in the composites are measured and shown in Fig. 1a, b. After mixed with EPDM rubber and other additives in the two-roll mill, 4.0- and 5.0-mm-long aramid fibers present the similar length distributions which both gather at around 1.1 mm in the final composites. That means they are broken about 4 and 5 times, respectively. However, the real lengths of PBO fibers measured in the final composites are about 1.9, 2.9, and 4.8 mm, while their corresponding original lengths are approximate 2.0, 3.0, and 5.0 mm. Therefore, PBO fibers hardly break during the mixing process with EPDM matrix. As shown in Table 1, both the tensile strength and the tensile modulus of PBO fibers are much higher than that of aramid fibers. As a result, the shear strength of the rollers is not sufficient to break those PBO fibers though it could result in the severe breakage and exfoliation of aramid fibers during the mixing process.

### Morphology of aramid fibers and PBO fibers in the composites

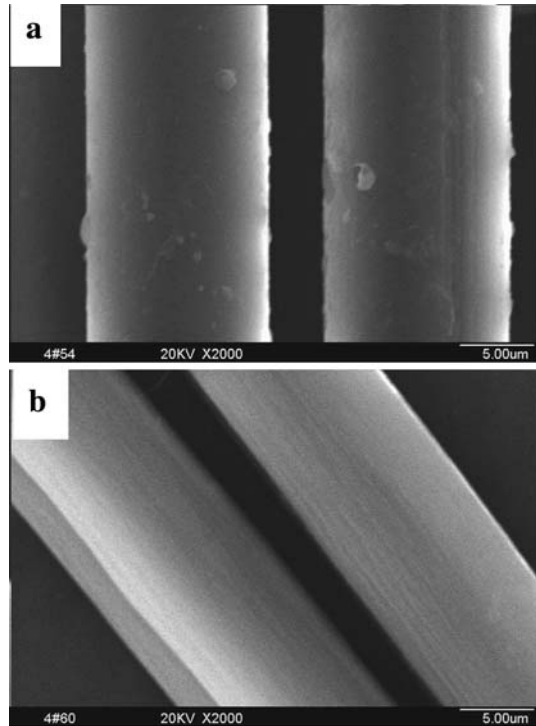
Figure 2a, b shows the morphology of aramid fibers and PBO fibers before mixed with rubber matrix, respectively. The SEM pictures indicate that both aramid fibers and PBO fibers present a smooth surface. However, after a mixing process on the

**Fig. 1** The length distributions of aramid fibers for length 4.0 and 5.0 mm (a) and PBO fibers for length 2.0, 3.0, and 5.0 mm (b) in the composites



two-roll mill, both the fibers show quite different morphology in the final composites. As shown in Fig. 3a, aramid fibers have been exfoliated severely by the shear strength of the rollers and many fibrils in the fracture surface of aramid fibers are observed. However, only some necking deformations on the PBO fibers surface are obtained as shown in Fig. 3b, which are attributed to the shear strength of rollers. In other words, the shear strength of rollers during processing is sufficient to exfoliate aramid fibers severely but not enough for breaking or exfoliating PBO fibers. This confirms the results of fiber lengths in the final composites measured with optical microscope. The breakage and exfoliation of aramid fibers during processing would increase their overall surface area, which is useful to improve the tensile strength of the composites. However, the reduction in length would decrease their reinforcement on the composites sharply. Hence, the overall influence of processing on the strength of the composites is rather vague. For PBO fibers, the necking deformations would improve the interfacial adhesive strength between the fibers and the matrix, which will cause the great improvement of tensile strength of composites with the increasing of PBO fiber contents.

**Fig. 2** SEM picture of aramid fiber (a) and PBO fiber (b) before added into EPDM mixture



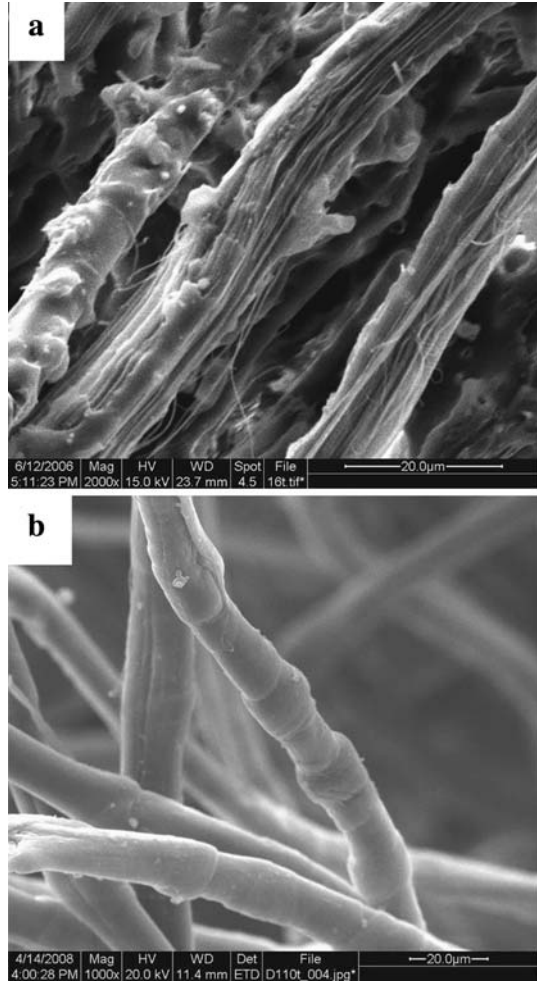
### TG curves and ablative morphology of aramid fibers and PBO fibers

Figure 4 shows the TG curves of the matrix, aramid fibers and PBO fibers at a heating rate of  $20\text{ }^{\circ}\text{C min}^{-1}$ . Under the protection of nitrogen, the main decomposition and weight loss of matrix compound, aramid fibers and PBO fibers appear at about 460, 580, and  $730\text{ }^{\circ}\text{C}$ , respectively. Apparently, the thermal decomposition temperature of PBO fiber is much higher than that of the matrix and the aramid fibers. Moreover, the final carbon residue of PBO fibers (about 64.4%) is much higher than that of the matrix (only about 20.5%) and the aramid fibers (about 40.0%) at about  $1,000\text{ }^{\circ}\text{C}$ . As discussed previously, the decomposition temperature and carbon residue of fibers should be as high as possible [21]. When the matrix is degraded and carbonized, the fibers still keep their fibrous structure and high strength, which will anchor the carbonized matrix grains together to form a hard char layer to resist the violent mechanical erosion of hot gas flow. Moreover, even when these fibers have been carbonized, their higher carbon residue could also ensure the higher mechanical strength of the carbonized fibers.

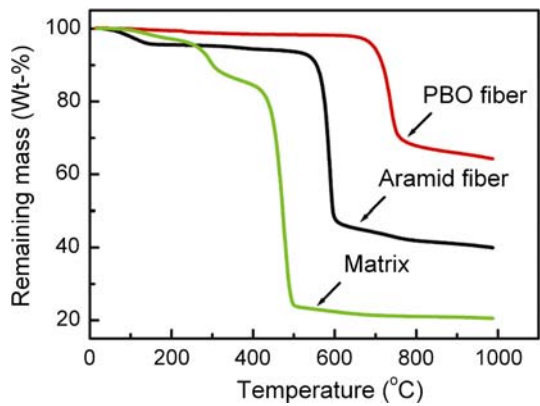
Besides the TG results, the ablative morphologies of aramid fibers and PBO fibers could also confirm that PBO fibers are better than aramid fibers to improve the ablation resistant properties of the insulation composites. As shown in Fig. 5a, the PBO fibers still keep the solid fibrous morphology in the char layer, which would reinforce the carbonized matrix strongly and form a hard char layer. However, as



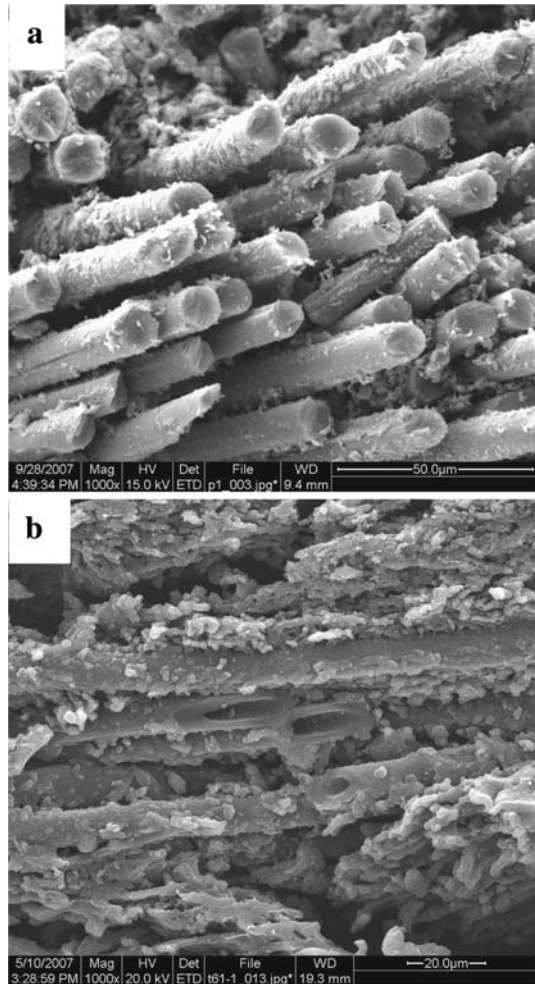
**Fig. 3** SEM picture of aramid fiber (a) and PBO fiber (b) after mixed with EPDM mixture



**Fig. 4** TG curves of matrix, aramid fiber and PBO fiber under nitrogen (heating rate = 20 °C min<sup>-1</sup>)



**Fig. 5** Ablative morphology of PBO fiber (a) and aramid fiber (b) in the char layer

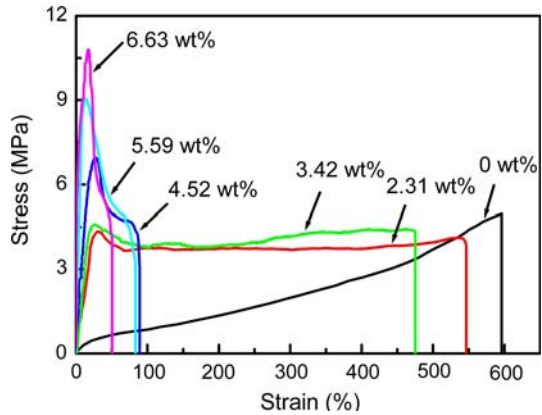


shown in Fig. 5b, the aramid fibers in the char layer are hollow after ablated though they could be carbonized like the PBO fibers. Apparently, the mechanical strength of these hollow carbonized fibers must be lower than that of the solid ones, so does their reinforcement on the char layer.

#### Mechanical properties of the insulation materials

During the rocket motor working, the motor chamber will undergo a huge thermal deformation and a high thermal stress [27]. Therefore, certain high tensile strength as well as break elongation is required for the thermal insulation materials [2, 28]. The effect of the PBO fiber content on the stress–strain curves of the composites is shown in Fig. 6. The fibers with 2.31, 3.42, 4.52, and 5.59 wt% in content and 4 mm in original length are introduced, respectively. Compared with the pure

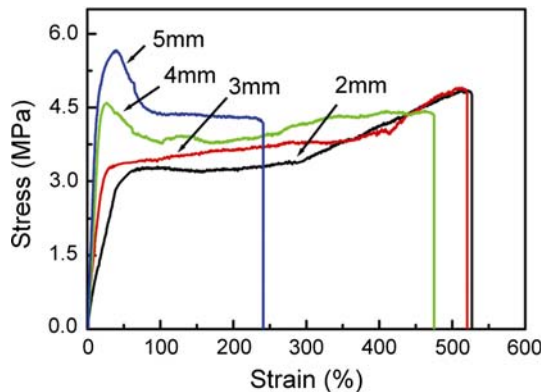
**Fig. 6** Stress–strain curves of insulation composites reinforced by short PBO fibers for length 4.0 mm and for content 0–6.63 wt%



matrix, the introduction of short fibers leads to obvious improvement on tensile strength and great reduction on tensile elongation. This is quite normal phenomena in short fibers reinforced elastomer system, which is mainly attributed to the higher tensile strength of the short fibers and their restriction on the elongation of elastomer matrix.

The influence of the short fiber length on the stress–strain curves of the composites is presented in Fig. 7. The original length of PBO fibers is 2.0, 3.0, 4.0, and 5.0 mm and the fiber content is 3.42 wt%. As the fiber length increases, the tensile strength is improved and the elongation is reduced consistently even the fibers are introduced with the same content. Theoretically, the reinforcement effect of the fibers on the composites would be improved as fiber length increases. However, the reinforcement of short fibers on the composites is usually found to be independent on the length, but just dependent on the content of short fibers introduced in the short fiber/elastomer system. The main reason is that the short fibers, such as glass fibers, carbon fibers, or aramid fibers, would break by the high shear strength of the rollers during processing as discussed in section “[Real length of aramid fibers and PBO fibers in the composites.](#)” As a result, the real length of the fibers in the composites is almost the same no matter how long the original short

**Fig. 7** Stress–strain curves of insulation composites reinforced by short PBO fibers for length 2–5 mm and for content 3.42 wt%



**Table 3** Comparison of the mechanical properties between aramid fiber/composites and PBO fiber/composites

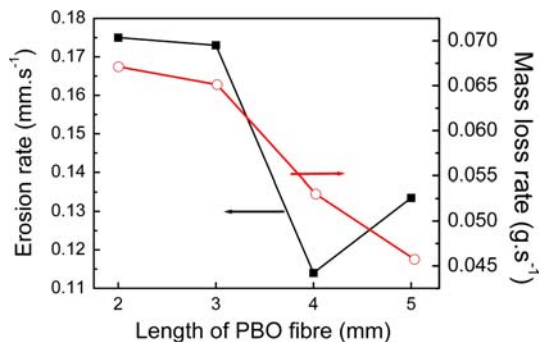
Properties	Aramid fiber	PBO fiber
Original length of short fiber (mm)	5.0	5.0
Contents in composite (wt%)	3.42	3.42
Real length in composites (mm)	1.09	4.80
Tensile strength of composites (MPa)	5.17	5.67
Elongation of composites (%)	527	241

fibers are. However, the length of PBO fibers in the final composites is rather close to the original length thanks to their high mechanical strength and no obvious breakage is observed during processing. Therefore, the effect of fiber length on the reinforcement of elastomer-based composites is exhibited just as found in many short fiber reinforced plastic systems. Considering the requirement of the thermal deformation and thermal stress of the insulation materials during the motor working, the PBO fibers with 3–4 mm in length and 2.31–5.56 wt% in content are preferred.

Comparing with the aramid fibers with lower tensile strength, PBO fibers possess obvious advantages on reinforcing the composites. The mechanical properties of EPDM-based composites filled with aramid fibers and PBO fibers with the same content (3.42 wt%) and original fiber length (5.0 mm) are listed in Table 3. After processed in the two-rollers and vulcanized, much smaller fiber length is observed in aramid fibers (only about 1.09 mm) filled composites than that of PBO fibers (about 4.80 mm) filled composites. This may account for the lower tensile strength of aramid fiber/EPDM composites than that of PBO fiber/EPDM composites. PBO fibers possess many advantages since their excellent reinforcement effect on the composites. For example, the content of PBO fibers could be lower than that of aramid fibers when the same mechanical properties are reached.

#### Ablative properties of the insulation materials

Generally, the ablative properties of the composites are characterized with erosion rate and mass loss rate after the composites are ablated by oxyacetylene flame [3]. As shown in Fig. 8, with the original length of PBO fibers increasing from 2.0 to

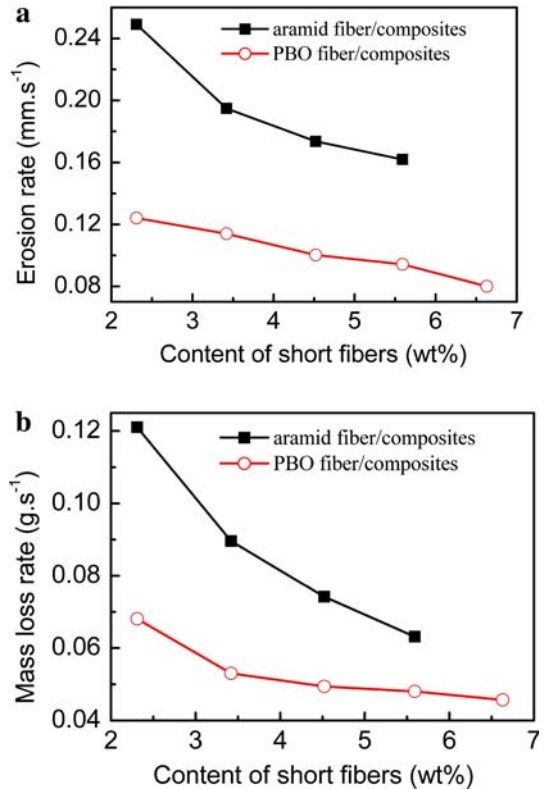
**Fig. 8** Effect of the original length of PBO fibers (3.42 wt%) on the ablative rates

5.0 mm, the mass loss rate drops consistently but the erosion rate decreases first until the length of PBO fibers is 4.0 mm then increases slightly at 5.0 mm. It is well known that the fiber filler with high carbon residue and thermal stability would reinforce the char layer via eliminating the stress generated during thermal degradation and carbonization of the composites [20]. Therefore, the actual length of short fibers inside the composites would affect their reinforcement ability on the char layer as well. The longer fibers are able to anchor more carbonized matrix grains and a harder char layer is formed. Thus, the ablation resistant abilities of the composites are improved gradually when the original length of the PBO fibers increases from 2.0 to 4.0 mm. However, this conclusion is based on the fact that all the fibers are straight and well dispersed in the composites. When the fibers are sufficient long, the entanglement of the fibers would happen. As a result, the effective length of the fibers is much smaller than that of the original. This could account for the higher erosion rate of composites filled with 5 mm PBO fibers than those filled with 4 mm PBO fibers. However, the mass loss rates mainly come from the thermal degradation of the composites, which is affected by the entanglement of fibers less than that of erosion rate.

Besides the fiber length, the content of short fiber is another important factor affecting the ablative properties of the composites. The effects of fiber content on the erosion rate and the mass loss rate of the composites filled with short aramid fibers and short PBO fibers are shown in Fig. 9a, b, respectively. The original length of short fibers is 4.0 mm. As shown in Fig. 9a, the erosion rates of the composites reinforced by aramid fibers and by PBO fibers both reduce continuously with the fiber content increasing from 2.31 to 6.63 wt%. However, the erosion rate of the PBO fiber/composites is much lower than that of the aramid fiber/composites when the fibers content is the same. For example, when the content of the short aramid fibers increases to 5.59 wt%, an erosion rate as high as  $0.162 \text{ mm s}^{-1}$  is obtained in aramid fibers reinforced composite. However, only 2.31 wt% of PBO fibers is required to reach an erosion rate of  $0.124 \text{ mm s}^{-1}$ . This may be attributed to the longer fiber in the final composites as well as higher thermal stability and carbon residue of PBO fibers. As discussed in section “[Real length of aramid fibers and PBO fibers in the composites](#),” the strong shear strength during processing causes severe breakage of aramid fibers but no obvious breakage of PBO fibers. As a result, the actual fiber length in the composite is rather different. As discussed above, the larger real fiber length in the composites shows significant reduction on the erosion rate of the composites. Meanwhile, the higher thermal stability and carbon residue of PBO fibers lead to a solid carbonized fibrous structure, while a hollow structure is observed in aramid fibers. The higher mechanical strength of solid structure than that of hollow one also benefits the erosion rate. Both the effects could account for the lower erosion rate of PBO fibers than that of aramid fibers filled composites.

For the mass loss rate, the similar results as the erosion rate could also be obtained with the increasing of fiber content as shown in Fig. 9b. The mass loss rates of the two kinds of composites are decreasing sharply via enhancing the fiber contents. However, the PBO fiber/composites present a further lower mass loss rate than the aramid fiber/composites even the fibers are introduced in the same content. It is well known that the mass loss of the ablative materials consists of two parts.

**Fig. 9** Effect of the contents of aramid fibers or PBO fibers for length 4.0 mm on erosion rate (a) and mass loss rate (b)



The main part is from the pyrolysis gas generated during the thermal degradation of the composites, which will be affected by the thermal conductivity of the composites. The other part is from the char layer peeled off by the high-speed gas flow, which could also be regarded as the mass erosion rate. As shown in Table 4, the thermal conductivities of EPDM matrix, aramid fiber/composites and PBO fiber/composites are 0.218, 0.254, and 0.247  $\text{W m}^{-1} \text{K}^{-1}$ , respectively. Obviously, the thermal conductivity of PBO fiber/composites is less than that of aramid fiber/composites, which strongly confirms that the thermal degradation of the PBO fiber/composites is less than that of the aramid fiber/composites. In other words, the thermal protection of the former is much better than that of the latter. Moreover, as the fiber content increases, the mechanical properties of char layer are enhanced gradually thanks to the improved reinforcement of fibers. Therefore, the thermal

**Table 4** Thermal conductivity of EPDM matrix, aramid fiber/composites and PBO fiber/composites

Properties	EPDM matrix	Aramid fiber/composites	PBO fiber/composites
Length of fibers (mm)	–	5.0	5.0
Content of fibers (wt%)	–	3.42	3.42
Thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )	0.218	0.254	0.247

degradation is slowed as well as the erosion rate, so does the overall mass loss rate. Comparing with aramid fibers, PBO fibers with larger length, higher carbon residue and stronger structure in the composites show more effective reinforcement on the char layer. Therefore, the composites filled with PBO fibers exhibit lower thermal degradation rate, mass erosion rate, and hence overall mass loss rate than that filled with aramid fibers.

## Conclusions

PBO fibers instead of aramid fibers are introduced to fill EPDM composites and a series of thermal insulation composites with excellent mechanical and ablative properties are obtained. Thanks to their higher mechanical strength than aramid fibers, the strong shear strength during processing causes no breakage and exfoliation in PBO fibers. The carbonized PBO fibers exhibit solid fibrous structure instead of hollow structure of aramid fibers due to their higher thermal degradation temperature and carbon residue. As a result, the composites filled with PBO fibers show significantly higher mechanical strength and ablative properties than those filled with aramid fibers. And with the increasing of fiber length and content, both the tensile strength and ablation resistant abilities of the PBO fibers/composites increase gradually though their break elongation reduces sharply. For application purpose, the preferred length and content of PBO fiber are 3–4 mm and 3.42–5.59 wt%, respectively. The mass loss rate of  $0.05 \text{ g s}^{-1}$  and erosion rate of  $0.10 \text{ mm s}^{-1}$  under the oxyacetylene flame test are observed in the optimal samples, which is evidently lower than the best aramid fibers/EPDM-based composites reported so far.

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