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# Enhancement of Ablative and Interfacial Bonding Properties of EPDM Composites by Incorporating Epoxy Phenolic Resin

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**Abstract**:

Effects of epoxy phenolic resin (EPR) on ablative and interfacial bonding properties of EPDM composites were evaluated. Ablative properties of EPDM composites were enhanced by 2 folds with incorporating 10 phr EPR. This significant enhancement was attributed to positive effect of EPR on thermal stability and thermal insulating properties of EPDM composites as well as formation of compact char layer onto composites. Furthermore, interfacial shear strength of EPDM composites with carbon fiber/epoxy (CF/EP) composites was increased by 55.6 % with incorporating 10 phr EPR, due to interfacial chemical reaction of epoxide groups of EPR molecule from EPDM composites with amine group of hardener from CF/EP composites.

**Keyword:** B. Thermal properties; B. Interface; A. Polymer-matrix composites; D. Mechanical testing

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## 1.Introduction

Thermal insulators, used as heat-barrier materials between the case and the propellant, were essential components of rocket motors, and they should have good thermal resistance and good ablation properties. At present, the elastomers like ethylene-propylene-diene monomer (EPDM) were conventionally used as matrix for thermal insulating materials because of their low thermal conductivity, high thermal stability and low density [1-3]. With the aim to enhance the integrated performance of elastomer-based thermal insulator, many sorts of fillers were widely incorporated into the system in the literatures [1,4-6]. In our previous works, polysulfonamide pulp was pretreated and used to enhance the ablative, thermal and mechanical properties of EPDM thermal insulating composites [7-9]. However, with the fast development of rocket motor technologies, high performance thermal insulators were required to form strong char layer after carbonization and endure the severe conditions of high temperature combustion gases [2,10,11]. The reported EPDM-based thermal insulator did not meet this requirement well since such insulator alone could not form a strong char layer after carbonization. Therefore, more stable and advanced fillers should be applied in the thermal insulator to improve their integrated thermal insulating properties. Among various fillers, the phenolic type materials were favorable due to their high thermal stability and char yield in the high temperature condition [12,13], which implied that such materials would greatly contribute to building up the strong char layer after carbonization. However, there have been few reports on EPDM composites modified with phenolic type materials up to now.

In addition, the continuous fiber reinforced epoxy composites have replaced the metal materials to be used as the motor case along with the fast development of rocket motor technologies due to their advantages of high strength and low density [14-16]. In this new application environment of the thermal insulator, the state of its interfacial bonding with the composite case, which was the vital factor to ensure the safe running of solid rocket motor, has attracted much more attention than before,

since EPDM as a non-polar elastomer could not achieve good adhesion with other materials. To overcome this problem, a lot of researchers focused on developing the external adhesives for the interfacial bonding of such insulator and composite case [17-20]. For instance, Park et al. examined the effects of fabrication and adhesive parameters on adhesion between composite and insulator rubber [17]. Unexpectedly, the enhancement of the interfacial bonding strength by using adhesives was limited, and such efforts led to some negative factors such as increasing the corresponding cost and processing difficulty of the materials. On the other hand, it was noticed that the chemical activation of interfacial bonding ability of EPDM-based thermal insulator was the feasible way to enhance its interfacial bonding with other materials [21]. However, to the best of our knowledge, there was a large uncertainty and lack of understanding on improving the autologous interfacial bonding ability of EPDM-based thermal insulator.

To bridge this gap, effects of epoxy phenolic resin (EPR) on ablative and interfacial bonding properties of EPDM-based thermal insulating composites were investigated in detail. To this end, (i) EPDM-based thermal insulating composites with EPR were prepared; (ii) effects of EPR on ablative properties, thermal stability and thermal insulating properties of EPDM composites were evaluated along with the characterizations of thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and energy disperse X-ray spectroscopy (EDS); and (iii) the interfacial shear strength associated with micro-morphology of interfacial region was studied to elucidate the effect of EPR on autologous interfacial bonding ability of EPDM composites with carbon fiber/epoxy (CF/EP) composites.

## 2. Experiment

### 2.1. Composite preparation

The materials including EPDM, liquid EPDM, polysulfonamide pulp, nano silica, additives and curing agents were selected in accordance with our previous works [7-9], except the new filler, epoxy phenolic resin (EPR) (Wuxi Resin Factory of Bluestar Chemical Co., China). The content of EPR was adjusted to 0, 5, 10, 15 and 20 parts per hundred grams (phr) of EPDM composites. The EPDM composites were prepared following the process reported in our previous works [7-9]. The specimens of EPDM composites adhered with carbon fiber/epoxy (CF/EP) composites were prepared by placing uncured EPDM composites on CF/EP prepreg with amine hardener and subsequent curing together at 120 °C for 30 min and 150 °C for 3 hr under the pressure of 10 MPa.

**2.2. Analysis and characterization**

**2.2.1. Ablative properties**

The composite plaques in 10 mm thickness were cut into round ablative specimens with a 30 mm diameter. Ablative testing was conducted on an oxy-acetylene ablation tester (Xi'an Tianguan Sci. Co., Ltd., YS22) in accordance with ASTM E 285.

**2.2.2. Thermogravimetric analysis (TGA)**

TGA of the specimens (10–12 mg) was performed using a TA instrument (NETZSCH STA 449C) under an argon atmosphere at a purge rate of 40 ml/min. The specimens were heated from 35 to 800 °C at a heating rate of 10 °C/min.

**2.2.3 Thermal insulating properties**

Thermal insulating testing was contacted on a butane-torch. Temperature evolution at the various thickness locations were tested by a thermocouple and were synchronously recorded by a multi-recorder (CF30R16, Beijing Chidufangyuan Sensor Element Co., Beijing, China).

**2.2.4 Morphology observation and element analysis**

Observations of char layers and fractured surfaces of EPDM composites were carried out by scanning electron microscopy (SEM, HITACHI S4700). The composite specimens were coated with

a thin layer of a gold alloy. The elements of char layers of EPDM composites were analyzed under energy disperse X-ray spectroscopy (EDS, EDAXGENESIS2000). The final value of each element content was the average of five measurements on different specimens.

**2.2.5. Mechanical properties**

The mixture plaques composed of EPDM composites in 2 mm thickness and carbon fiber/epoxy (CF/EP) composites in 2 mm thickness were cut into rectangle specimens with 20×120 mm size with a 20×20 mm square contact area in accordance with ASTM D 1002. Interfacial shear strength was measured by tensile testing machine (Instron 1121) at a crosshead speed of 500 mm/min using 200 N load.

## 3. Results and discussion

### 3.1. Ablative properties

Fig.1 shows effect of epoxy phenolic resin (EPR) content on ablation rate of EPDM composites. With the increase of EPR content, there was a rapid decrease to 0.044 mm/s at 10 phr content of EPR, and then a smooth increase in the ablation rate. Compared to EPDM composites without EPR, ablative properties of EPDM composites were enhanced by 2 folds with incorporating 10 phr EPR. For the contrast, the ablation rate of EPDM composites with 10 phr phenol formaldehyde resin, a similar material to EPR, was measured to be 0.045 mm/s. This manifested that the contribution to ablative rate decrease of EPDM composites was comparable for both EPR and phenol formaldehyde resin. However, EPR was selected as the proper filler in our present study, since EPR had the epoxide groups in the chemical structure and showed significant advantage on enhancing interfacial bonding of related composites (which will be discussed in Part 3.4 ). Furthermore, the initial decrease of ablation rate in Fig.1 could be explained by the enhancement of thermal stability and the increment of char yield of the composites with the addition of phenolic type materials [13]. However, the tenacity

of the char layer on the surface of the composites was greatly influenced by the content of EPR, which dominated the adhesion between char layer and virgin material. When the content of EPR was high, that is, greater than 10 phr, the tenacity of the char layer on the surface of the composites decreased obviously. During the intensive impingement of high-temperature combustion gases, the poor tenacity resulted in the fracturing and sloughing of the formed char layer. Then, the underlying virgin material was exposed, and this led to the ablation rate increasing. Therefore, EPDM composites with 10 phr EPR showed the optimal ablative properties which were the critical performance for thermal insulating materials. In addition, according to the findings in our previous works [7], the ablative properties of the composites was also related to the thermal stability and thermal insulating properties as well as the microstructure of char layer on the composites, which was elucidated in the following parts of our present study.

### 3.2. Thermal properties

Fig.2 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of EPDM composites without and with 10 phr EPR. It could be seen that only one major degradation step at around 474 °C characterized the decomposition of both composites. However, the TG curves showed that the residue yield of EPDM composites with EPR at 800 °C was 24.1 % higher than 21.2 % of the composites without EPR, as well as the DTG curves exhibited that the peak degradation rate was lower for the former composites than for the latter composites. The observed increased residue yield was attributed to the high char yield of EPR since the benzene rings contained in the chemical structure of EPR would deposit to form much char [12,13]. These results indicated that the addition of EPR enhanced thermal stability and char yield of the composites, which was beneficial to the enhancement of ablative and thermal insulating properties according to Deuri [22] et al.

Fig.3 shows the temperature evolution with ablation time along the thickness direction for EPDM composites without and with EPR. It could be noted that, with the increasing of the ablation time and the decreasing of the distance from the flamed surface, the temperature increased obviously for both composites. Furthermore, the slopes of the temperature increasing in both composites were much higher at the location closer to the flamed surface than at the other location far from the flamed surface. However, compared to EPDM composites without EPR, the temperature increasing at the same thickness location was far slower with ablation time for EPDM composites with EPR. For instance, at the thickness location of 1 mm for EPDM composites without and with EPR, the temperatures at the ablation time of 10 s were 146 and 204 °C respectively, while the values at the ablation time of 60 s were 826 and 906 °C, accordingly. This phenomenon manifested that the addition of phenolic type resin could improve the thermal insulating ability of EPDM composites, which was resulted from the high specific heat capacity, low thermal conductivity and long degradation half-life of phenolic type materials [12,23].

**3.3. Micro-morphologies**

On the basis of the established ablation model by many researchers [24,25], the internal insulating materials were divided into three regions consisting of char layer, decomposition layer and virgin layer. The heat was absorbed by the materials with the changing of chemical or physical state of these materials. The interfaces between these regions were somewhat indistinct, but even so the regions could be defined by the principal phenomena found in each. Judging from internal real-time temperature distribution in both composites without and with EPR shown in Fig.3, the part from 0 to 1.5 mm thickness was the char layer which was carbonized already, where the temperature increased rapidly beyond 600 °C at the 1.5 mm thickness location after ablation for 60 s. The part from 1.5 to 2.5 mm thickness was considered as the decomposition layer, where the temperature increased slowly than the char layer and the loose structure with big pores (which will be shown in Fig.4(c) and (d))

were generated. It could be inferred that the heat was not transferred effectively beyond 2.5 mm thickness during ablation of butane-torch in our experiment so that the decomposition of both composites did not take place in the virgin layer in the condition of slight increasing of corresponding temperature. Fig.4 shows SEM images of each layer of three-layer structure, optical images of ablated specimens and EDS results of char layer for EPDM composites without and with EPR. As shown in Fig.4(a-f), EPDM composites showed distinct microscale three-layer structure after ablation. It could be seen that the virgin layers were compact without holes while the decomposition layers showed porous microstructure. There was no much difference observed in the microstructure of virgin layer as well as decomposition layer for EPDM composites without and with EPR. Nevertheless, the morphologies of char layers on surfaces of EPDM composites without and with EPR were clearly different. During ablation, the surfaces of EPDM composites were eroded by the flame combustion, resulting in the formation of macro-scale pits on the surface char layer. However, as shown in the left parts of Fig.4(g) and (h), it could be noted that the surface pit of EPDM composites without EPR was centered and sharply deep, whereas that of EPDM composites with EPR was smooth and relatively shallow. This difference could be explained from the micro-structure and element composition of char layers of both composites. As shown in Fig.4(e) and (i), the char structure of EPDM composites without EPR was loose with a large amount of visible big cracks and holes from about 50 to 200 μm and the final content of carbon element was 90.6 %. In contrast, the char structure of EPDM composites with EPR in Fig.4(f) and (j) was relatively compact with higher carbon element content of 96.7 % in consistence with the results in Fig.2, which contributed to the enhancement of ablative properties of EPDM composites. Therefore, the ablative properties were superior for EPDM composites with EPR as shown in Fig.1.

**3.4. Interfacial bonding properties**

Fig.5 shows interfacial shear strength of EPDM composites with carbon fiber/epoxy (CF/EP) composites. The interfacial shear strength was increased by 55.6 %, from 2.7 to 4.2 MPa, when 10 phr EPR was incorporated, which was even higher than corresponding strength values of 2.1 and 3.0 MPa, respectively, resulted from acrylate based adhesive and EPDM based adhesive as well as the values reported in the literatures [27,28]. This indicated that the strong interfacial bonding was built up between the EPDM thermal insulating materials and the composite case, which was verified from the optical and SEM images of interfacial regions between EPDM composites and CF/EP composites in Fig.6. As shown in Fig.6(a) and (c), the interfacial bonding area was clearly separated for EPDM composites without EPR after shearing testing, and the debonding and cracking were obviously found on the interfaces due to the non-reactivity of EPDM matrix. While, as shown in Fig.6(b), the materials from the side of EPDM composites with EPR was firmly adhered onto the other side of CF/EP composites after shearing testing, and there was no cracking observed for EPDM composites with EPR shown in Fig.6 (d) because of high reactivity of EPR in EPDM composites with the harder of CF/EP composites. All these results revealed that strong interfacial bonding was formed between EPDM composites with EPR and CF/EP composites in accordance with the results from Fig.5. Noticeably, the significant enhancement of the interfacial bonding of EPR filled EPDM composites with CF/EP composites was within our experimental expectation. As shown in Fig.7, the epoxide groups of EPR molecule from EPDM composites were reacted with the amine group of the hardener from CF/EP composites. With this reaction proceeding, the three-dimensional crosslinked network structure was formed on the interface between the two composites. Therefore, such chemical adhesion contributed to the observed enhancement of interfacial bonding properties of EPR filled EPDM composites with CF/EP composites.

**4. Conclusions**

The ablative properties of EPDM composites were significantly enhanced by the addition of epoxy phenolic resin (EPR) and this observed enhancement was related to the positive effect of EPR on the thermal stability and thermal insulating properties of EPDM composites as well as the formation of compact char layer on the composites. Moreover, the addition of EPR contributed to enhancing the interfacial bonding of EPDM composites with carbon fiber/epoxy composites due to the interfacial chemical reaction between the two kinds of composites.

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**List of Figures**

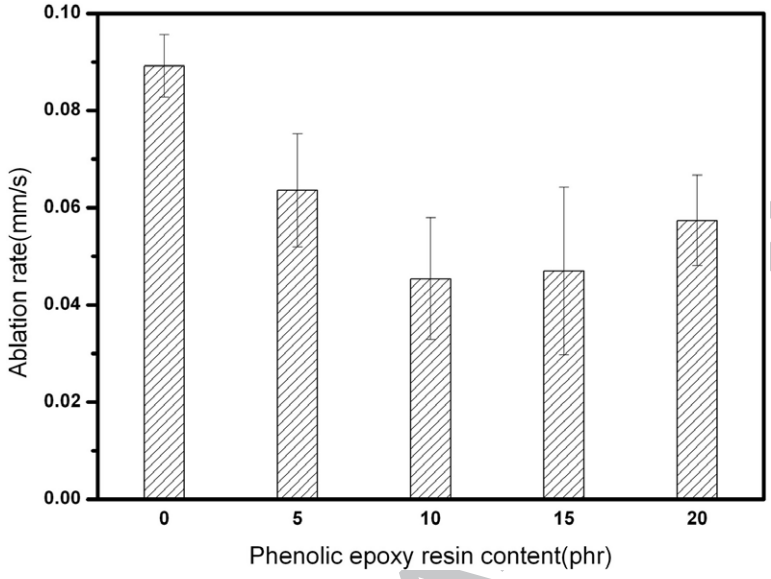


Fig. 1. Effect of EPR content on ablation rate of EPDM composites.

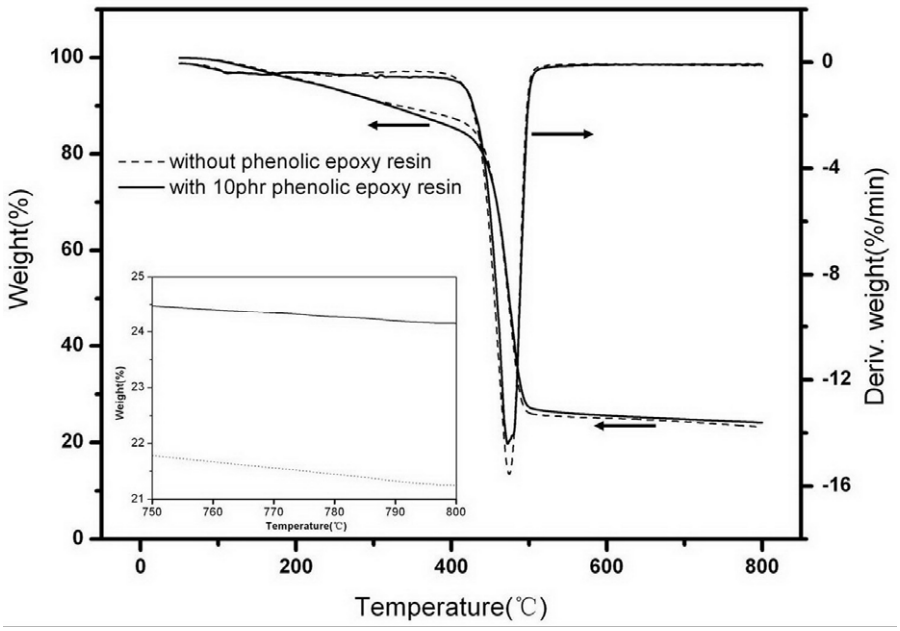


Fig. 2. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of EPDM composites without and with 10 phr EPR. The TG and DTG curves are labeled by arrows.

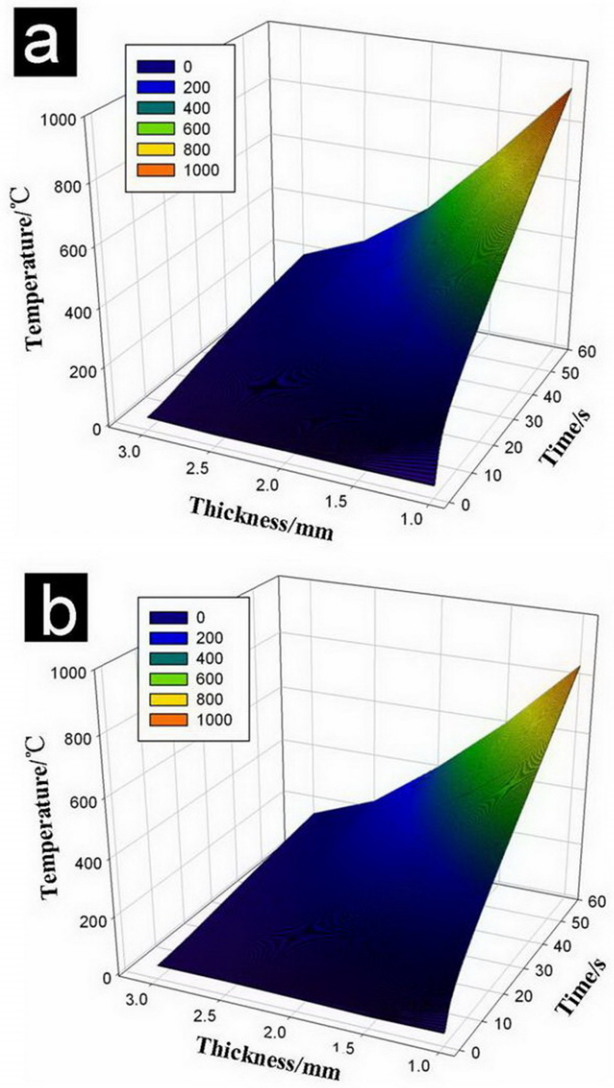


Fig. 3. The temperature evolution with ablation time along the thickness direction for EPDM composites (a) without and (b) with 10 phr EPR.

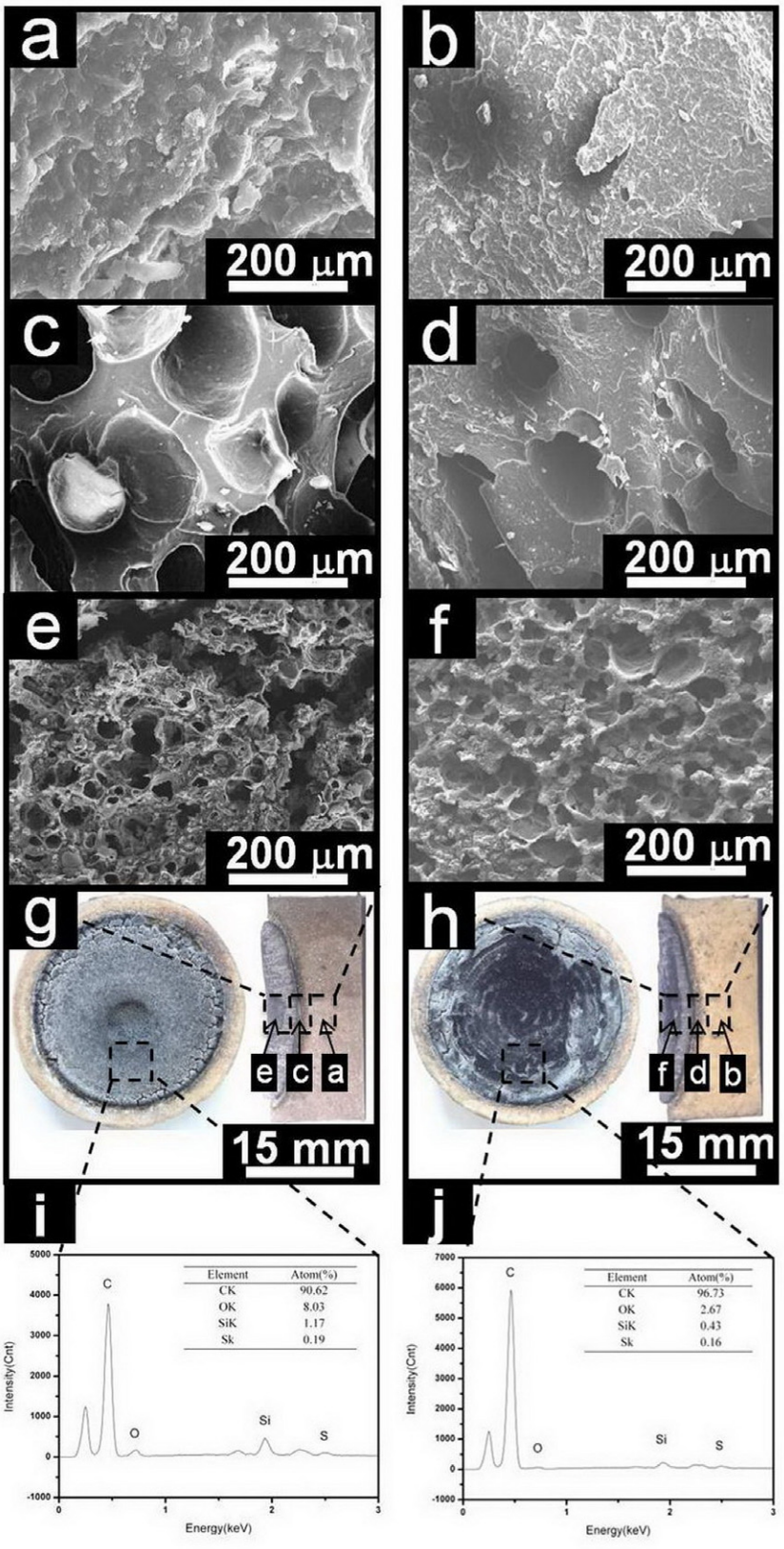


Fig. 4. SEM images of (a, b) virgin layer, (c, d) decomposition layer and (e, f) char layer; (g, h) optical images of ablated specimens and (i, j) EDS results of char layer for EPDM composites. In

these images, (a, c, e, g, i) for EPDM composites without EPR and (b, d, f, h, j) for EPDM composites with 10 phr EPR. In the right parts of images (g, h), the transverse cross-sections of ablated specimens show the three-layer structure, corresponding to the SEM images (a-f).

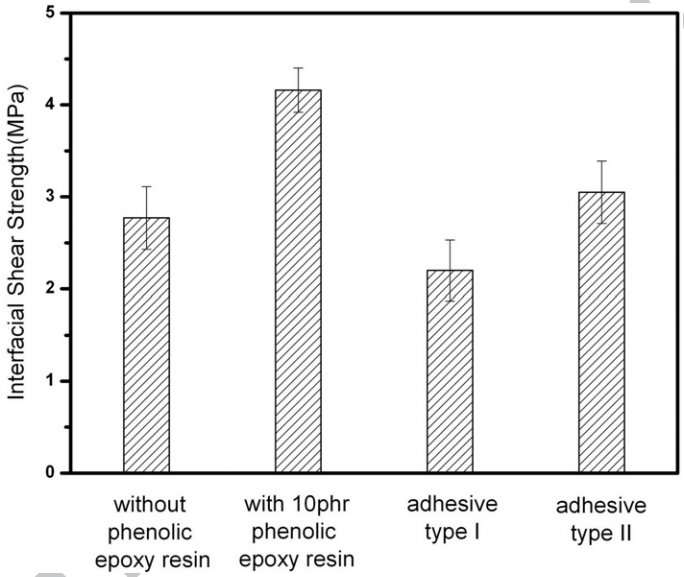


Fig. 5. Interfacial shear strength of EPDM composites with CF/EP composites. The specimens of EPDM composites (without EPR) adhered with CF/EP composites by two types of external adhesives were used as contrast samples. Adhesive type I is a kind of ethyl α-cyanoacrylate based adhesive. Adhesive type II is a kind of EPDM based adhesive.

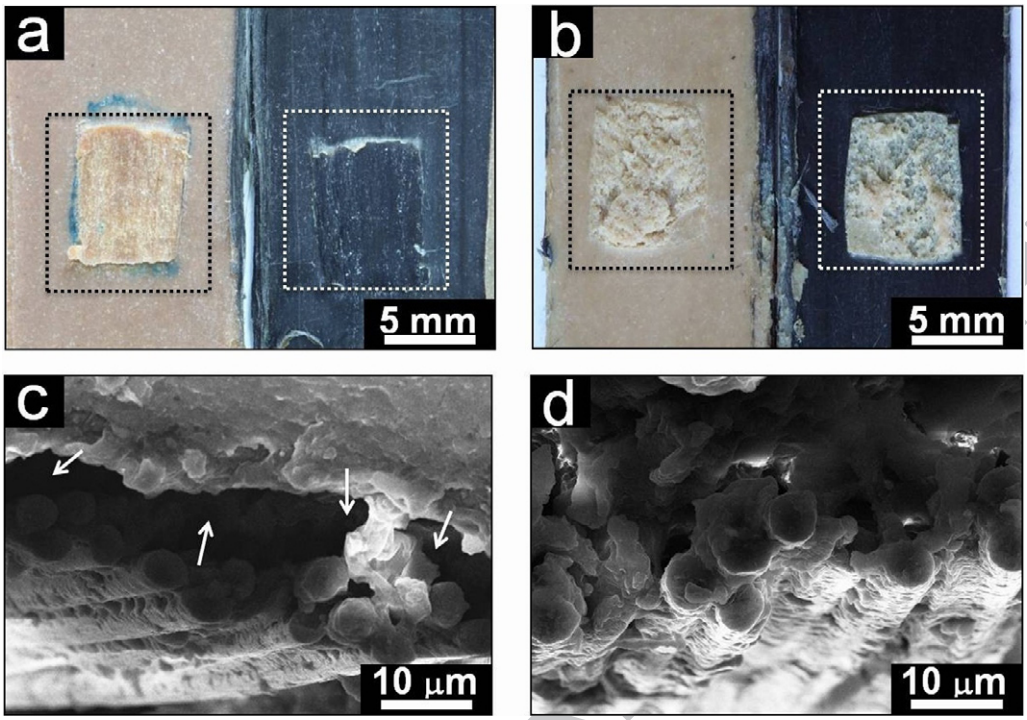


Fig. 6. (a, b) Optical and (c, d) SEM images of interfacial regions between EPDM composites and CF/EP composites after fracturing. In these images, (a, c) for EPDM composites without EPR and (b, d) for EPDM composites with 10 phr EPR. The dotted rectangles in part (a) and (b) show the interfacial bonding regions between EPDM composites and CF/EP composites after fracturing. In part (c), the arrows show the debonding and cracking existing in the interfacial bonding regions between CF/EP composites and EPDM composites without EPR.

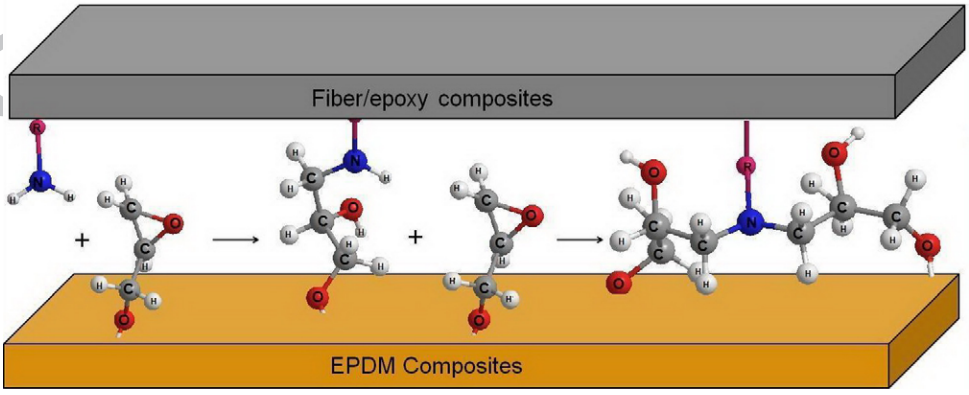


Fig. 7. Schematic of interfacial chemical reaction between EPR filled EPDM composites and CF/EP composites.