Study on the Ablation Properties of Nano-graphite Modified EPDM Insulators

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Abstract. To improve the anti-ablative property of EPDM-based composites, nano-graphite powder as anti-ablation filler was introduced to optimize the EPDM insulation material formulas. Characterization of anti-ablation performance showed that the composite at the nano-graphite content of 10phr exhibited the best anti-ablation and mechanical performances, such as: a linear ablation rate of 0.062 mm/s, a mass ablation rate of 0.048 g/s, tensile strength of 5.69 MPa and Elongation at break of 391.2%. The nano-graphite was proven to be an effective material which is beneficial to improve the anti-ablation of the EPDM composites.

1. Introduction
As an important part of the solid propellant charge, the basic function of the insulator is to control the burning area of the propellant grain and to ensure that the charge burns according to the desirable pressure-time profile for a specific mission requirement [1~4]. At the same time, the combustion chamber wall is protected not to be burned out from the high temperature gas produced by the propellant charge combustion. It is not only directly related to the interior ballistic performance of the solid rocket motor, but also to one of the important factors of the service life of it.

The thermal protection materials based on Ethylene Propylene Diene Monomer rubber (EPDM) have been widely used in internal insulators of solid rocket motor and inhibitors of propellant charges [5~7] because EPDM has excellent low temperature properties, outstanding resistance to oxidation and lower density among elastomers. The inhibitor based on EPDM matrix is often made up of some fibers [8~12], nanoparticle fillers [13,14], flame retardants, phenolic resins and the like are applied in the ablators based on EPDM to improve the integrity and quality of char layer. Golla Rama Rao et al. nano-clay into phenolic resin composites to reduce mass ablation rates owning to nano-clay increasing thermal stability of composites. As fire retardants, graphite-based compounds can always be valid candidates to improve the anti-ablation property of EPDM based inhibitors. Maurizio et al. studied the effect of different carbon black nano-particles contents on the ablation properties and the results showed that the ablation properties of phenolic resin were improved obviously. Nano-graphite is known to be high temperature resistance, low thermal expansion and the possibility to be dispersed in organic rubbers. As ablation resistance fillers, nano-graphite is widely used in the insulators for solid rocket engine motors. In this work, nano-graphite was introduced in EPDM-based ablative composites based on the effect of their characteristics on char layer structure. And the influence of nano-graphite filler contents on the char layer morphology, ablative resistance and mechanical properties were investigated.
2. Experimental

2.1. Materials

EPDM rubber (NORDEL™ IP 4820P) having ethylene and ethylidene norbornene (ENB) content 80.0 wt.% and 4.9 wt.%, was purchased from Shanghai Kai-yin chemical co., Shanghai, China. Nano-graphite (C03041) having nano-graphite content 98.7 wt.% and particle size 50–70nm was purchased from Qingdao Hua-tai Lubrication Technology Co., Ltd, China. The polyimide pulp (SOP) (Jiangsu Shino New Materials Technology Co., LTD, China, Changzhou, China) was selected that it was chopped into staples, 0.5–3mm in length. The ablative and mechanical properties of EPDM rubber nano-composites were examined using oxyacetylene torch tests and Static tensile testing machines. The effects of nano-graphite fillers content on the ablative and mechanical properties of the composites were examined, also.

2.2. Preparation of modified EDPM insulators

This EPDM rubber was mixed with liquid plasticizers followed by addition of polyimide pulp, and nano-graphite fillers together with 0.1 phr of coupling agent (Silane A-151) and a master mixer was obtained. Antioxidant (TQ), Activator (ZnO) and the curatives are mixed with the master mixer by a double roll open miller. The mixing rubber was vulcanized at 165°C for 30 min by a plate Vulcanizing Machine at 6 MPa pressure to obtain nanocomposite sheet.

The formulations of the EPDM based inhibitor for double-based propellant composites are given in Table 1. EPDM rubber was loaded with different levels of nano-graphite fillers. The polyimide pulp loading 5 phr was kept constant while varying nano-graphite the content from 0 phr to 10 phr.

The samples for mechanical and ablative properties experiment were carried out.

|   | 1   | 2   | 3   | 4   | 5   |
|---|-----|-----|-----|-----|-----|
| EPDM | 100 | 100 | 100 | 100 | 100 |
| Paraffin oil | 15  | 15  | 15  | 15  | 15  |
| nano-graphite | 0   | 3.0 | 5.0 | 8.0 | 10.0|
| polyimide pulp | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| silica | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Zinc oxide | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Antioxidant | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Peroxide | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 |

2.3. Characterization

Mechanical properties of composites were measured with tensile testing machine (Instron 1121) at strain rate 500mm/min. All of measurements were conducted with GB/T528-2009. Ablative properties of composites were performed with an oxy-acetylene ablation tester under the following test conditions as flow velocity of O₂, 0.35m3/h; flow velocity of C₂H₂, 0.35 m³/h and the characteristic values were calculates based on ASTM E285-80. Micro-structure of samples were obtained by using scanning electron microscopy (SEM, Tescan VEGA-II).

3. Results and discussion

3.1. Mechanical test results

Stress strain diagrams of modified EPDM nanocomposites were shown in Fig.1. When the nano-graphite fillers content is from 1 phr to 7 phr, the stress–strain curves of the composites are similar to that of EPDM rubber. The effect on nano-graphite fillers filling into EPDM matrix for the improvement in mechanical properties of EPDM composites is evident at different level of filler loadings (1, 3, 8 and 10 phr) shown in Table 2. The tensile strength, elongation at break values increased progressively with increasing filler loadings. It is well researched that nano-graphite as a filler shows a very strong filler networking. There is a moderate increase of 27% strength with the addition of 10 phr of nano-graphite in EPDM from Benchmark to No.5. The reinforcing effect of nano-graphite fillers in rubber compounds
was interpreted from an understanding of structure property relationship for carbon black filled natural rubber. It was reported that mechanical properties of a composite are also affected a number of parameters: the size, shape, aspect ratio and distribution of the reinforcing particle.

![Stress strain curve of EPDM nanocomposites with different loadings of nano-graphite](image)

**Figure 1.** Stress strain curve of EPDM nanocomposites with different loadings of nano-graphite

**Table 2.** Mechanical properties of EPDM nanocomposites with different loadings of nano-graphite

| No. number | Sample designation | Tensile strength (MPa) | Elongation at broken(%) |
|------------|--------------------|------------------------|------------------------|
| 1          | Benchmark          | 4.48                   | 306.1                  |
| 2          | 1                  | 3.17                   | 346.3                  |
| 3          | 2                  | 4.34                   | 350.2                  |
| 4          | 3                  | 4.31                   | 370.2                  |
| 5          | 4                  | 5.69                   | 391.2                  |

### 3.2. Ablation properties

To study the ablation properties of the modified EPDM composites samples, the samples were burned by an oxyacetylene flame, using a testing bed made by Xi’an Zhi Rui Industrial Systems Engineering Co., Ltd. The test was carried out with the oxygen-acetylene gas flow rate of 1512 L/h and 1116 L/h and actual value of heat flux reached to 457 W/cm². Hyperthermia oxyacetylene flame was placed in the center of samples vertically, with the ablation process lasting 20s.

The linear ablation rate (LAR) and mass ablation rate (MAR) and percentage char yield were calculated according to the following equations.

\[
R_m = \frac{m_2 - m_1}{t} \quad (1) \\
R_d = \frac{d_1 - d_2}{t} \quad (2) \\
\text{Char yield} = \frac{m_2}{m_1} \times 100\% \quad (3)
\]

where \(R_m\), \(R_d\) and \(\text{Char yield}\) represent the mass ablation rate (g/s), linear ablation rate (mm/s) and percentage char yield(%), respectively, \(m_1\), \(m_2\), \(d_1\) and \(d_2\) are the mass (g) and thickness (mm) of samples before and after ablation testing, \(t\) means the working time (s).

Thus, the \(R_d\) was widely used to the analysis of ablative resistance.

The ablation properties of various modified EPDM composites are summarized in Table 3. The \(R_m\), \(R_d\) and the char yield of the ablated samples were measured using Eq. (1) - Eq. (3) respectively and plotted in Fig. 2.

| No. number | Sample designation | \(R_m\) (g/s) | \(R_d\) (mm/s) | Char yield (%) |
|------------|--------------------|--------------|---------------|---------------|
| 1          | Benchmark          | 0.112        | 0.236         | 88.45         |
| 2          | 1                  | 0.054        | 0.198         | 89.20         |
| 3          | 2                  | 0.053        | 0.183         | 91.21         |
| 4          | 3                  | 0.050        | 0.093         | 90.81         |
| 5          | 4                  | 0.048        | 0.062         | 91.30         |
Figure 2 illustrates that the increase of nano-graphite fillers in modified EPDM compositions leads to the gradual decrease of linear and mass ablation rates. $R_d$ decreases from 0.236 mm/s to 0.062 mm/s when nano-graphite fillers were increased from 0 to 10phr, respectively. The same observation can be seen for $R_m$ which decreases from 0.112 g/s to 0.048 g/s. The high char yield values (88.45%) are obtained for modified EPDM without nano-graphite fillers and only polyimide pulp as a filler while char yield comes up to 91.30% with 7phr of nano-graphite as a filler.

From Table 3 and Fig. 2, it can be concluded that the incorporation of nano-graphite and polyimide pulp in modified EPDM compositions enhances their ablation performance.

3.3. Morphological analysis of char layers
The difference in ablative resistance of modified EPDM composites can be ascribed to the diversity in structure of char layers formed in ablation test. The SEM images of char layer surface of nano-graphite fillers and polyimide pulps modified EPDM composites were displayed in Fig.3.

Figure 3 SEM images of char layer surface: No 3 and No 5

Combination of nano-graphite fillers and polyimide pulps was exploited to overcome the drawbacks of unmodified EPDM char layer and the variation in ablation rate with nano-graphite fillers ratios can be reflected and explained from the diversity of char layer morphology. All of this demonstrate that the limitation of either nano-graphite fillers or polyimide pulps impedes the formation of dense and intact char layer to withstand hot gas erosion and realize favorable ablative resistance. SEM micrographs of char layer surface with the content of nano-graphite 5phr and 10phr are illustrated in Fig. 3. Because of the degradation of matrix, nano-graphite fillers and polyimide pulps can survive and the char layer...
surface is gradually shielded by nano-graphite with the nano-graphite content increasing, forming a protection layer spontaneously.

4. Conclusion
In this work, an attempt was made to utilize nano-graphite modified EPDM nanocomposites in the field of double based propellant. Nano-graphite fillers and polyimide pulps can take their advantages in thermal stability to consolidate char layer and resist heat flow erosion, to reduce ablation rate and formation of intact char layer. In addition, the relationship between char layer structure and ablative resistance was analyzed. Based on the effect of filler on char layer, this combination of two fillers with different characteristics provides a facile approach to construct char layer with a desirable structure and guides the expansion of new ablative composites.

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