Polymer Degradation and Stability 96 (2011) 949–954

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Effect of polyphenylsilsesquioxane on the ablative and flame-retardation properties of ethylene propylene diene monomer (EPDM) composite

Yunyun Jiang, Xu Zhang, Jiyu He*, Liang Yu, Rongjie Yang

School of Material Science and Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, PR China

ARTICLE INFO

Article history:
Received 30 November 2010
Received in revised form
17 January 2011
Accepted 28 January 2011

Keywords:
EPDM
Polyphenylsilsesquioxane
Ablative
Flame retardancy
Char structure

ABSTRACT

Polyphenylsilsesquioxane (PPSQ) microspheres with ladder structure synthesized in the laboratory have been incorporated into ethylene propylene diene monomer (EPDM) composite in order to study the effect of PPSQ on the ablative and flame-retardation properties of EPDM composites. The results showed that PPSQ microspheres serve as an effective ablative additive and flame retardant for EPDM composites. Thus, PPSQ greatly improved the ablative properties of EPDM composites, with a 4.8 wt% loading leading to a remarkable reduction in the linear ablation rate of EPDM by about 50%. Moreover, this loading of PPSQ improved the flame retardancy and smoke suppression, and significantly reduced the PHRR of EPDM composite from 504 kW/m^2 to 278 kW/m^2. Moderate tensile strength could be obtained and the breaking elongation was improved for the EPDM/PPSQ composites. TGA results showed that PPSQ had little influence on the thermal decomposition of EPDM. SEM, CONE, and TG-FTIR tests showed that the char structure of EPDM composites was the primary factor through which PPSQ affected the ablative and flame-retardation properties of EPDM. The chars formed during the ablation of EPDM composites containing PPSQ had better structural stability and thermal stability, owing to the fact that they were denser, remained intact, and had an ordered arrangement of holes.

1. Introduction

Ethylene propylene diene monomer (EPDM) is the polymer prepared from ethylene, propylene, and ethylidene norbornene or 1,4-hexadiene or dicyclopentadiene monomers. EPDM composite is a good internal insulating material for solid rocket motors by virtue of various advantageous features, such as low density (0.87–0.89 g/cm^3), low ablation rate, high thermal decomposition temperature, high specific heat, low brittle temperature, good aging resistance, and good air-tightness, and its tensile strength and elongation are in full accord with those required for this application [1]. However, EPDM matrix itself does not meet the requirements for the environment of gas flow at high temperature and high speed with high-pressure eroding in a solid rocket motor, and so various fillers have to be added to enhance its ablative properties [2,3].

Poly(organic-silsesquioxane) is a kind of polysiloxane with the formula $(RSiO_{1.5})_n$, where R is hydrogen, or any alkyl, alkylene, aryl, or arylene group, or even an organic-functional derivative of such groups. It combines the properties of inorganic compounds and organic polymers, and can be blended with various organic polymers to form organic–inorganic hybrid reinforced polymers [4–6]. At high temperatures, an insulating ceramic layer may be formed on the surface of a material containing poly(organic-silsesquioxane), which displays more remarkable thermal stability and ablative properties than a char layer derived from the ablation of common polymer materials. In previous work [7], Jiyu He studied the effect of oligomeric octaphenyl silsesquioxane (OPS) on the fire and ablation performances of EPDM composites, and found that OPS lowered the linear ablation rate of these composites and improved their mechanical properties and flame retardancy. Compared to OPS, polyphenylsilsesquioxane (PPSQ) has superior thermal stability (Fig. 1). This is because PPSQ is a ladder polymer with a stereoregular double Si–O chain structure (Fig. 2). On the one hand, the Si–O bond is not easy to break due to its high bond energy (422.5 kJ/mol); on the other hand, even if there is local chemical bond breakage within the ladder structure of the PPSQ chain, this will not have a significant impact on the structural integrity of the whole chain [8–10]. In the work described herein, PPSQ microspheres with ladder structure synthesized in the laboratory [11] have been incorporated into EPDM composite in order to study the effect of PPSQ on the ablative and flame-retardation properties of EPDM composites. The mechanism of action of PPSQ in the flame-retardation of EPDM composites is also discussed.

* Corresponding author.
E-mail address: hejiyu@bit.edu.cn (J. He).

0141-3910/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2011.01.034

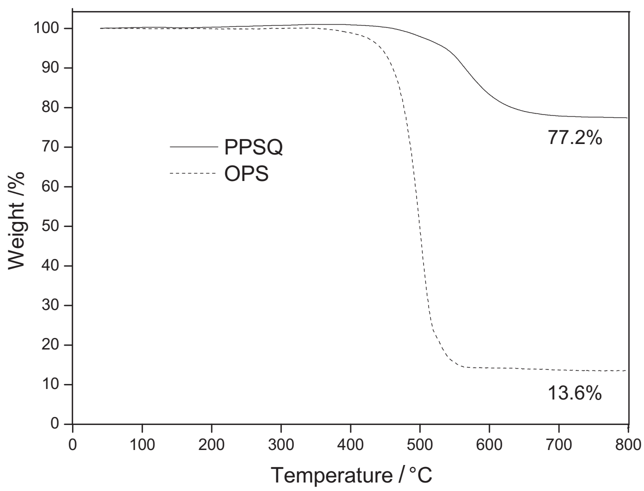

Fig. 1. TGA curves of PPSQ and OPS in N_2.

2. Experimental

2.1. Materials

EPDM-0, a non-vulcanized EPDM composite containing definite proportions of EPDM, reinforcing agent, ammonium polyphosphate (APP), coupling agent, curing agent, and accelerator, was obtained from the Fire Safety and Materials Engineering Centre, Beijing Institute of Technology. PPSQ, with a high content of ladder polymer without hydroxyl groups, was synthesized in the laboratory [11]. The diameters of the spherical PPSQ particles were in the range 0.5–1.5 μm.

2.2. Preparation of EPDM/PPSQ composites

PPSQ microspheres were incorporated at different levels into EPDM-0 by means of a two-roller mixer (SRR-Z4, Shanghai Rubber Machinery Factory). The respective blends were then transferred to a specific mould. The final EPDM/PPSQ composites were obtained by curing for 50 min in a curing press (QLB-350 × 350 × 2, Shanghai First Rubber Machinery Factory) at 160 °C and 15 MPa. EPDM composite without PPSQ was submitted to the same conditions as a control. The sample compositions are shown in Table 1, and were separately code-named as EPDM-00, EPDM/PPSQ-1, EPDM/PPSQ-2, and EPDM/PPSQ-3.

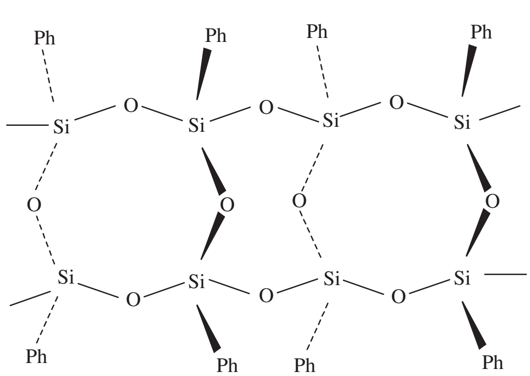

Fig. 2. Typical chemical structure of the PPSQ molecule.

Table 1
The compositions of the EPDM/PPSQ composites.

Code	EPDM-0/g	PPSQ/g	PPSQ/wt%
EPDM-00	200	0	0
EPDM/PPSQ-1	200	5	2.4
EPDM/PPSQ-2	200	10	4.8
EPDM/PPSQ-3	200	15	7.0

2.3. Measurements

Linear ablation rate was measured using oxygen–acetylene ablation testing equipment according to GJB323A-96. The nozzle diameter of the equipment was 2 mm, the ablation distance and ablation time were 10 mm and 20 s, respectively, and the oxygen and acetylene flow rates were 0.42 m^3/s and 0.31 m^3/s, respectively. The linear ablation rate was calculated according to the following formula: linear ablation rate = (original thickness − residual thickness)/ablation time.

The mechanical properties were measured by means of a universal testing machine (DXLL-5000, Shanghai D&G machinery equipment Co., Ltd.) according to GB/T 528-92.

Thermal gravimetric analysis (TGA) was performed over the temperature range 40–800 °C on a Netzsch 209 F1 thermal analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere.

Fourier-transform infrared spectroscopy (FTIR) was performed with a Thermofisher 6700 spectrometer at a resolution of 4 cm^{-1} with a total of 32 scans.

Scanning electron microscopy (SEM) experiments were performed with a ZEISS SUPRA 55 field-emission scanning electron microscope. Samples for SEM were the char residues from ablation testing and were prepared by sputtering the surface with gold.

Combustion experiments were performed with a cone calorimeter (Fire Testing Technology) according to ASTME-1354. Samples of dimensions 100 × 100 × 3 mm^3 were exposed to a radiant cone (50 kW/m^2).

3. Results and discussion

3.1. Mechanical and ablative properties

Compared to EPDM-00, the tensile strength was somewhat decreased and the elongation at break was increased for the EPDM/PPSQ composites (Table 2). Linear ablation rate is a very important parameter in evaluating the performance of insulating materials, and a lower linear ablation rate means a lower loss rate for materials under the dual influence of a hot flame and gas flow. In other words, the materials retain the integrity of the original structure, which plays a crucial role in heat insulation and fire proofing. The data in Table 2 show that PPSQ significantly improved the ablative properties of the EPDM composite. The linear ablation rates of the EPDM/PPSQ composites were significantly decreased compared to that of EPDM-00. Specifically, the linear ablation rate was reduced

Table 2
Effect of PPSQ content on the mechanical and ablative properties of EPDM composites.

Sample	Tensile strength/MPa	Elongation at break/%	Linear ablation rate/mm/s
EPDM-00	10.9 ± 0.3	332 ± 11	0.093 ± 0.007
EPDM/PPSQ-1	9.3 ± 0.2	403 ± 13	0.080 ± 0.006
EPDM/PPSQ-2	9.4 ± 0.2	375 ± 11	0.047 ± 0.004
EPDM/PPSQ-3	8.4 ± 0.3	346 ± 10	0.047 ± 0.005