The ceramifying process and mechanical properties of silicone rubber/ ammonium polyphosphate/ aluminium hydroxide/ mica composites

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ABSTRACT

The ceramifying process and mechanical properties of silicone rubber/ammonium polyphosphate/ aluminium hydroxide/mica composites (hereinafter referred to as SRAAM) are investigated. The changes in microstructures and phase compositions of SRAAM during ceramifying process at different calcined temperatures are studied. At 300 °C, SRAAM residues exhibit porous structure due to gas evolution from the thermal decomposition of APP, $Al(OH)_3$ and silicone rubber, but mica does not react with them. Although the flexural strength of SRAAM residues are low, the generation of aluminium phosphate ($AlPO_4$) and $NH_4AlP_2O_7$ improves the self-supporting. With no new phase generated, SRAAM residues maintain certain degree flexural strength due to the adhesive effection of aluminium phosphate during 300–600 °C. The reactivity of mica is increased by eliminating hydroxyl at temperature up to 800 °C, and then the chemically interactions between active mica and phosphates are able to generate $Al_2O_3 \cdot 2SiO_2$, and $KAlP_2O_7$ compounds improving the flexural strength. Further reactions between mica and $KAlP_2O_7$ could generate $KAlSi_3O_8$ at 1000 °C and the density of residual product is improved by low melting point phosphate filling pore to form relatively dense structure increasing the flexural strength. SRAAM with high flexural strength and good self-supporting from low to high temperatures is expected to be a kind of excellent ceramifying performance of flame retardant materials.

1. Introduction

Ceramifying polymer composites ideally have the dual performance characteristics of polymers at room temperature and ceramics at elevated temperatures, consisting of polymer matrix, mineral powder filler, structure control agent and other auxiliaries [1–3]. Mica is a ratio of 2:1 layered aluminosilicate (ideal formula $KAl_2(Si_3Al)O_{10}(OH)_2$), one of the most popular flame retardant fillers in silicone polymer especially for electric cable applications [4,5], due to its high dielectric strength, high heat resistance and excellent corona resistance etc. For instance, Hanu et al. reported that silicone polymer composites filled with mica, glass frit, ferric oxide and/or a combination of these were developed as a part of a ceramifiable polymer range for electrical power cables. They found that mica played a significant role on the thermal stability of silicone polymer [6]. Al-Hassany et al. reported another ceramifiable

polymer composites with non-silicone based for fire protection application. Their results revealed that introducing APP, mica and $CaCO_3$ to the poly(vinyl acetate) improved the ceramifying residue strength after calcination at 400 °C and 1050 °C (0.64 MPa and 0.79 MPa respectively) [7]. Zhang J et al. found that a two-layer structure of fire residue on the surface of material formed during burning the high-impact polystyrene/organically modified montmorillonite nanocomposite, containing a thin and condensed skin layer at the top and a loose and expanded cellular layer under the skin layer, which were composed of mainly montmorillonite platelets to form a nanoscale network structure by aggregating [8]. The non-silicone based ceramifiable composites modified with inorganic substances show good ceramifiable capacity and resistance to combustion due to the formation of char, which can protect the underlying materials from combustion [9–11].

In order to further improve the mechanical properties of ceramifying residue, silicon-based polymers had attracted great attention in the past years [12,13]. Silicon-based polymers such as silicone rubbers with high bond strength Si–O had been proven to

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promote the ceramifying process during combustion [14–16]. For example, Mansouri et al. studied the mechanism of ceramization structure of mica-poly(dimethylsiloxane) composite after firing. They showed that mica reacted via a eutectic reaction with silica and the formation of a barrier layer is expected to improve fire performance properties and the flexural strength after calcination at 600 °C, 800 °C and 1000 °C (0.3 MPa, 1.2 MPa and 2.2 MPa, respectively) [14]. Glass frits could be added into silicon-based polymers reacting via a eutectic reaction with the aim to improve low temperature ceramification at elevated temperatures. On the basis of these, Mansouri et al. studied the influence of various glass frits on the ceramization residue and thus dimensional changes at different temperatures. The flexural strength of ceramifying residue is improved by adding glass frits D with softening point of 525 °C, which has a composition of SiO_2: 37.7%; Al_2O_3: 1.2%, CaO: 1.2%; Na_2O: 14.6%; K_2O: 10.6%; TiO_2: 16.0%; P_2O_5: 1.3%; Fe_2O_3: 3.0% and other minor oxides and volatile components: 14.4%, after calcination at 600 °C, 800 °C and 1000 °C (0.88 MPa, 2.30 MPa and 3.53 MPa, respectively), due to the formation of more liquid phase that allows densification via liquid phase sintering [15].

Most studies of silicone-based ceramifying composites have been focused on its preparation and ceramifying mechanism at high temperatures [3,14,16], the flexural strength of composites is improved as a result from eutectic reactions at the interfaces between the mica particles and silica formed from decomposition of the silicone polymer matrix [12,14,15]. In spite of the silicone-based ceramifying composites based on the previous studies, very little is known about the phase composition evolution, microstructure and ceramifying processes during heating. Moreover, the flexural strength of the residues is usually weak at the meso-low temperatures, in addition, glass frits increase conductivity duo to ionic conduction of the glass phase produced by eutectic reactions at high temperatures [2,15], so that adding glass frits is harmful to produce electrical power cables. The mechanism of ceramifying process of silicone-based ceramifying composites is the interactions in the inorganic substances essentially, but the understanding of their ceramifying process is not fully understood and it should be investigated.

In our previous work, it has been shown that the reaction of ammonium polyphosphate and aluminium hydroxide in silicone rubber could reduce the ceramifying temperature and improve the mechanical properties in meso-low temperature to replace the glass frits. Moreover, the reactions in the phosphates, decomposition products of silicone rubber and mica can enhance the mechanical properties in high temperatures. The silicone rubber/ammonium polyphosphate/aluminium hydroxide/mica composites (hereinafter referred to as SRAAM) are prepared by the combination of ceramifying of mica [5] and synergistic flame retardance between ammonium polyphosphate and aluminium hydroxide [17] in this paper. Here, the phase compositions and microstructures evolution of SRAAM during ceramifying process are studied using field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD), moreover this paper reportes on the thermal degradation of SRAAM that converted to ceramic residues of improved flexural strength when fired in air up to 1000 °C. The formation of a ceramic layer has been identified, which is expected to be advantageous for fire performance polymers.

2. Experimental procedures

2.1. Raw materials

A high-temperature vulcanized silicone rubber (SiR, brand name CENUSIL® R250CN, methyl vinyl silicone rubber with molecular weight of 500,000) purchased from Wacker Chemie Company was used as the silicone matrix in this work. Ammonium polyphosphate (APP) of commercial grade (crystalline form II, polymerization degree exceeds 1500) was supplied by Xingxing Fire-retardants Co., Ltd, Jiangsu, China. Dicumyl peroxide in powder form was used as the curing agent supplied by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Aluminium hydroxide ($Al(OH)_3$) was from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Mica was from Huayuan mica Co., Ltd, Hebei, China, with a mean particle size of 100 μm. The chemical compositions of the mica, determined by X-Ray Fluorescence (XRF), are given in Table 1. The microstructures of the $Al(OH)_3$, APP and mica are shown in Fig. 1a,b and c, respectively.

2.2. Preparation of the silicone rubber/ammonium polyphosphate/ aluminium hydroxide/mica composites (SRAAM)

All SRAAM were prepared using a conventional two-roll mill, with silicone rubber first softened at room temperature and fillers then added until a homogeneous batch was obtained. The curing agent was then added and processed until a visually good dispersion was achieved. Fillers were progressively mixed according to the compositions set out in Table 2. Silicone compounds were moulded and cured into flat sheets by compression moulding at 165 °C for 15 min at 10 MPa pressure firstly, and then cured into draught drying cabinet at 200 °C for 240 min.

The obtained of flat sheet samples of SRAAM were thermally heated from room temperature to target temperature at a heating rate of about 10 °C/min in a muffle furnace in air atmosphere. The solid residues were obtained when heated to 300, 400, 600, 800, 1000 °C, respectively, holding for 60 min.

2.3. Characterization of the composites

Chemical compositions of mica were analyzed by the X-ray fluorescence method using a PANalytical B.V Axios advanced XRF spectrometer.

X-ray diffraction spectra of SRAAM after heat treatment were obtained using a Brucker AXS D8 X-ray diffractometer. Each scan was conducted from a 2θ angle of 5–55° at a scan rate of 4°/min.

After calcining, the apparent porosity of SRAAM residues was measured according to Archimedes displacement method using distilled water. The expansion of samples were measured by heating flat sheet sampales to 300, 400, 600, 800, 1000 °C, respectively, holding for 60 min in air. To avoid any bloating effects, the length and width changes of the samples were measured and the average calculated, correcting for any changes in the thickness of the samples that may have arisen from bloating.

The residues of SRAAM were observed with field emission scanning electron microscope (Quanta-FEG250, FEI Co., USA) at an accelerating voltage of 20 kV. Samples were sputter-coated with gold using a Polaron Sputter coater unit.

Thermogravimetric analysis was performed on a thermogravimetric analyzer (STA449c/3/G, NETZSCH, Germany) at a heating rate of 10 °C/min (air atmosphere, flow rate of 50 ml/min). Samples were analyzed in the temperature range from 100 to 1000 °C. The calculated TG or DTG curves were summed up by the TG or DTG curves of the mixture ingredients, weighted by their contents [19].

Table 1
Chemical composition of mica.

Components	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
	49.97	27.30	5.32	1.12	0.037	0.46	9.85
wt%	TiO_2	P_2O_5	ZrO_2	Rb_2O	CeO_2	BaO	LOI
	0.79	0.026	0.045	0.024	0.075	0.028	4.82