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Zirconium phosphate functionalized by hindered amine: A new strategy for effectively enhancing the flame retardancy of addition-cure liquid silicone rubber

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ABSTRACT

Functionalized zirconium phosphate (F-ZrP) was prepared by intercalating 1,2,2,6,6-pentamethyl-4-(vinyldiethoxysiloxy) piperidine (PMVP) into α-zirconium phosphate (α-ZrP), and was used to flame-retard addition-cure liquid silicone rubber (ALSR). X-ray diffraction (XRD) and transmission electron microcopy (TEM) were used to characterize the structural morphology of F-ZrP and ALSR/F-ZrP. The results indicated that PMVP was successfully intercalated into α-ZrP, and F-ZrP existed with a structure of the intercalated and exfoliated components in the ALSR matrix. F-ZrP could significantly improve the flame retardancy of ALSR. When only 4 phr of F-ZrP was added, the flame-retardant ALSR could pass the UL-94 V-0 rating with the LOI value of 31.0%. Such an efficient flame retardancy of F-ZrP was attributed to the synergism of the catalyzing carbonization and free-radical quenching mechanism.

1. Introduction

Silicone rubber (SR) is playing an increasingly significant role in many application fields with high requirement of flame retardancy, such as electric transmission and electronic products [1–4]. However, SR is combustible due to the formation of flammable products which are mainly generated by the free-radical reaction and the random scission reaction when exposed to fire [5]. At present, aluminum trihydrate [6] (ATH) and magnesium hydroxide [7] (MH) are the most widely used halogen-free flame retardants of silicone rubber, which release water to cool the substrate and dilute flammable gases during combustion. However, a high loading (> 50 wt%) is required for adequate flame retardancy, which severely deteriorates the mechanical property and the processability of SR. Therefore, it is imperative to develop a new strategy for effectively enhancing the flame retardancy of SR.

α-Zirconium phosphate (α-ZrP) is a new type of layer nanomaterials and is attracting enormous interests in many fields due to its surface area and aspect ratio, ion exchange and catalytic properties [8], which are more superior to those of montmorillonite (MMT) [9]. Moreover, α-ZrP acts as a solid acid that can catalyze dehydrogenation of polymers to promote the charring of polymers, suggesting its potential application in improving the flame retardancy of SR [10,11]. It's also worth noting that hindered amine is a good candidate for flame-retarding polymers, because it can produce regenerable free-radical scavengers, suppressing and interrupting the free-radical reaction during combustion [12].

In this work, the functions of the catalyzing carbonization and the free-radical quenching were tactfully coupled through functionalizing α-ZrP with 1,2,2,6,6-pentamethyl-4-(vinyldiethoxysiloxy)-piperidine (PMVP) to enhance the flame retardancy of addition-cure liquid silicone rubber (ALSR), and the flame-retardant mechanism of functionalized zirconium phosphate (F-ZrP) was proposed.

2. Experimental section

2.1. Materials

α-ZrP was synthesized according to Sun et al. [13]. Vinyltriethoxysilane (VTES) and 1,2,2,6,6-pentamethyl-4-piperidinol (PMPO) was supplied by Energy Chemical Co., Ltd., China. Tetrabutyl titanate (TBT) was purchased from Tianjin Fuchen Chemical Reagent Factory, China. Vinyl-terminated poly(dimethylsiloxane) (VPDMS, viscosity was 20,000 mPa.s, vinyl content was 0.12 wt%), ploy(hydromethylsiloxane) (PHMS, viscosity was 160 mPa.s, hydride content was 0.70 wt%), and platinum(0) – 1,3-divinyl-1,1,3,3-tetramethydisiloxane complex (Karstedt's catalyst, 3000 ppm) were supplied by Guangzhou Tinci Silicon Technology Co., Ltd.,

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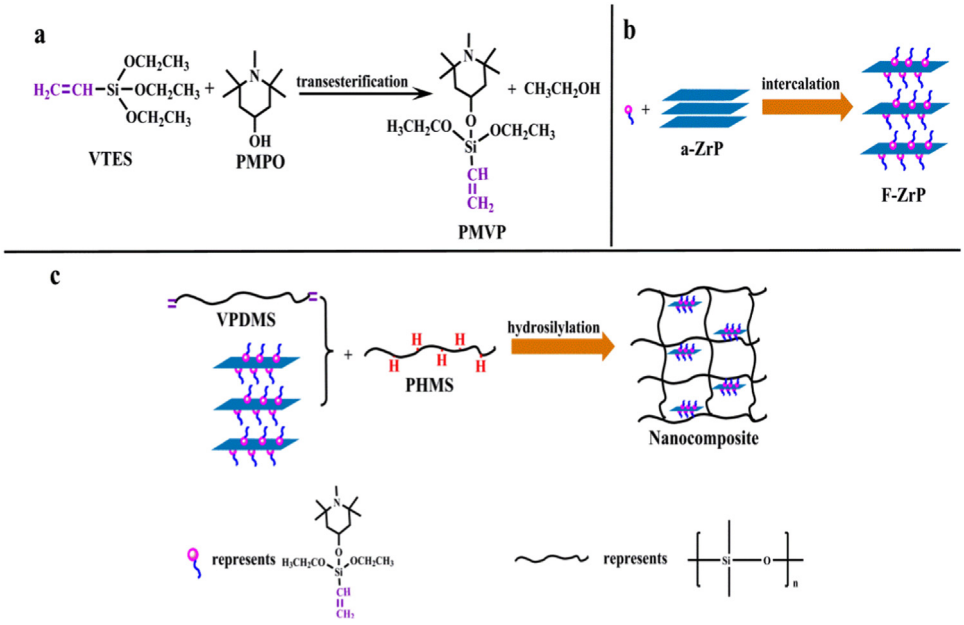

Fig. 1. Schematic illustration for preparation of the ALSR/F-ZrP nanocomposite: (a) synthesis reaction of PMVP, (b) intercalation process for F-ZrP, (c) hydrosilylation reaction for ALSR/F-ZrP nanocomposite.

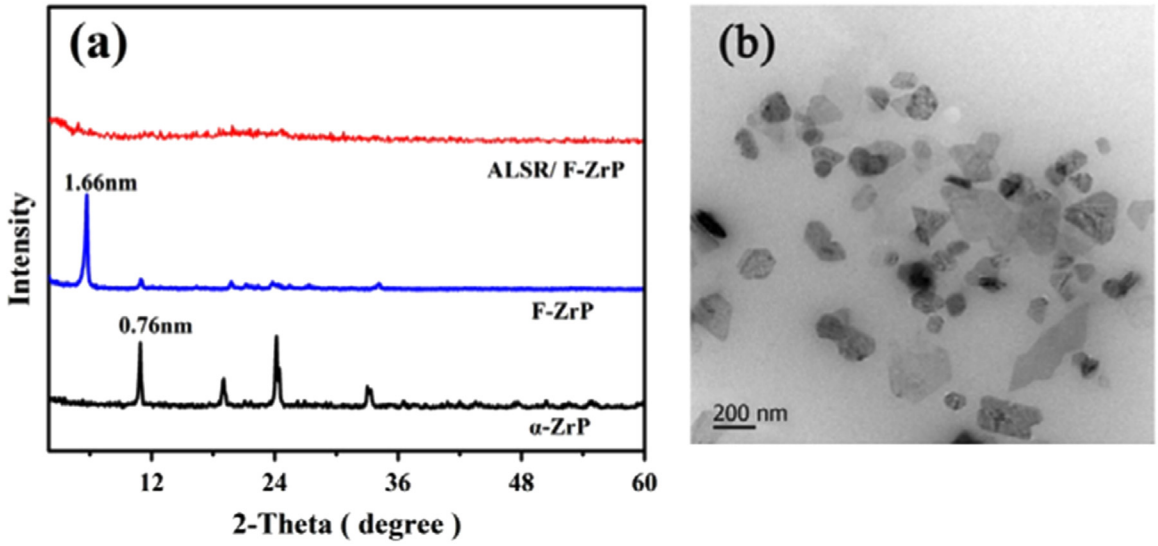

Fig. 2. (a) XRD patterns of α-ZrP, F-ZrP and ALSR/F-ZrP; (b) TEM image of ALSR/F-ZrP.

Table 1
Flame retardancy of ALSR and its composites.

Sample	α-ZrP (phr)	PMVP (phr)	F-ZrP (phr)	LOI (%)	UL-94	Self-extinguishing
ALSR	0	0	0	28.0 ± 0.2	NR	No
ALSR/α-ZrP	4.0	0	0	28.3 ± 0.1	NR	No
ALSR/α-ZrP	2.13	0	0	28.2 ± 0.2	NR	No
ALSR/PMVP	0	4.0	0	28.9 ± 0.2	NR	Yes
ALSR/PMVP	0	1.87	0	29.1 ± 0.1	NR	Yes
ALSR/α-ZrP/PMVP	2.13	1.87	0	29.5 ± 0.2	NR	Yes
ALSR/F-ZrP	0	0	4.0	31.0 ± 0.1	V-0	Yes

Note: NR means no rating.

China. Fumed silica (M-5) was purchased from Cabot Co., Ltd., USA.

2.2. Functionalization of zirconium phosphate

VTES (0.1 mol) and TBT (0.5 wt% of the total mass of the reactants) were added into 200 mL toluene, and the mixture was heated to 70 °C. PMPO (0.1 mol) was added dropwise to the mixture, and the reaction lasted for 2 h at 70 °C. Then, the reaction was maintained for another 2 h under the reduced pressure and the toluene was removed to obtain PMVP (Fig. 1a). The chemical