Structure and Thermal Behavior of EPDM/POSS Composite Fibers Prepared by Electrospinning

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ABSTRACT: Polyhedral oligomeric silsesquioxane (POSS)-containing ethylene-propylene-diene monomer (EPDM) composite fibers have been prepared by electrospinning method, with an average diameter of micron grade and fibrous structural morphology. The results of transmission electron microscopy, Fourier transform infrared, and UV-Vis spectra reveal that POSS moieties have been dispersed in polymer matrix homogeneously. A combination of thermogravimetric analysis and thermogravimetric-differential scanning calorimetry (TG-DSC) united analysis was used to investigate the thermal behavior of the resulting fibers at elevated temperatures. The results show that composites exhibited great increase of thermal decomposition temperature and large reduction of total heat release compared with pure EPDM. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polyhedral oligomeric silsesquioxane (POSS) is a novel hybrid molecule composed of a well-defined cubic octameric silica cage surrounded by eight organic corner groups,[1] which can be methyl, ethyl, phenyl, and epoxides, etc. Because of its excellent mechanical and thermal properties,[2] POSS-containing polymers are emerging as a new technology for accessing organic–inorganic nanocomposites.[3] The nanoscale of POSS enables its segments to effectively reinforce polymer chain segments and control chain motion at the molecular level through maximizing the surface area and chemical interactions of the nano-reinforcement with the polymer.[4]

During the past years, there has been extensive work reported in the literature on organic–inorganic hybrid thermoplastic or thermoset nanocomposites containing POSS.[5–8] But how to disperse POSS into the polymeric matrix homogeneously to express its maximal effect is still a technological challenge in research at present.[9] Xu et al. reported a kind of POSS-containing polymethylmethacrylate (PMMA) hybrid nanocomposites using radical polymerization technique.[10] But in this way, it need various complicated functional modified treatments on original POSS. Thus, seeking a new preparation method, which does not need functional modified treatment to obtain evenly dispersed POSS-containing polymeric composite material, will be very significant for practical application.

Electrospinning is a simple and effective technique to generate continuous polymeric fibers ranging from micrometer to nanometer size in diameters.[11–14] This technique has recently been used to produce fibrous POSS-based polymeric materials, in which POSS macromer could be dispersed homogeneously. Meanwhile, POSS can be added into polymer electrospinning solution directly, without any functional modified treatment. However, only a few studies of electrospun polymer systems, containing POSS monomer, have been reported so far.[15–20] They always used a graft polymerization or solution blend method to prepare POSS-based polymeric electrospinning mixed solution. By this way, poly(vinyl alcohol),[15] PMMA,[16] cellulose acetate,[17] sulfonated poly(arylene ether sulfone),[18] poly(ethylene glycol),[19] and poly(N-isopropylacrylamide)[20] were used as polymer matrixes to prepare electrospun nanofibers with POSS added in them. But studies about electrospun polymer/POSS composite fibers using rubber elastomer as matrix have not been reported at present.

Ethylene-propylene-diene monomer (EPDM) exhibits better physical characteristics such as high elasticity, abrasion resistance, corrosion resistance, and highly filled feature. These properties of EPDM have led to their utilities in a variety of industrial areas.[21] In order to expand its useful life in kinds of severe environments, the heat-resistant quality or thermal stability of EPDM would be enhanced by filling other additives.[22]

Considering the advantages of POSS, we make use of POSS as nano-additive into EPDM to improve its thermal behavior.

In this article, for the first time we report on the electrospun EPDM/POSS nanocomposite fibers, prepared by dissolving both EPDM and solubility enhanced octaphenyl POSS (ph-POSS) in the tetrahydrofuran (THF) solvent. From this approach, the POSS macromer can be evenly dispersed into the EPDM matrix at a nanometric level to get a composite with excellent compatibility. The dispersion of POSS within EPDM fibers was analyzed; furthermore, the structural and thermal properties of various EPDM/POSS composite fibers with different amounts of POSS content were investigated. The composite fibers exhibited great increase of thermal decomposition temperature and large reduction of total heat release (THR) compared with pure EPDM, which may be beneficial for producing special rubber material applied in some high temperature conditions. Besides, detailed further studies on the practical application of these elecrospun nanocomposites are in progress.

EXPERIMENTAL

Materials
EPDM (Vistalon 7001, ExxonMobil Chemical) was used as received, with a Mooney Viscosity of 60 MU, containing 73.0 wt % ethylene ingredients and 5.0 wt % ethylidene-norbornene content. Solubility enhanced ph-POSS, with a molecular weight (M_W) = 1033.53 g/mol, and 98.5% purity, was provided by Liaoning Am Union Composite Materials. THF purchased from Tianjin Damao Chemical Reagents was used as solvent. All chemicals were of analytical purity or higher quality and were used without further purification.

Solution Preparation
The polymer solutions for electrospinning were prepared by dissolving EPDM granules and ph-POSS powders into THF solvent successively, and then stirred by a magnetic stirrer at 50°C for several hours until the mixtures completely dissolved. The EPDM concentration was 2.5% (w/v, EPDM:THF), and the weight ratios of POSS to EPDM were set as 2, 5 and 10 wt %, respectively. Thus EPDM/POSS solutions with lucid appearance and fine liquidity were obtained, and a pure EPDM solution without POSS was prepared as a comparison at the same time.

Electrospinning Process
In this experiment, a high-voltage power supply (DW-N503-4ACCD, Tianjin Dongwen HVPS, China) capable of generating voltages up to 50 kV was used. Each POSS-based EPDM solution prepared above was poured in a 5-mL syringe fixed on a microsyringe pump (LSP02-1B, Baoding Longer Precision Pump, China), which was in charge of controlling the solution flow rate. The syringe was connected to a stainless-steel blunt-ended needle with an inner diameter of 1.2 mm by an original perfusor-tubing (PE material, B. Braun Melsungen AG). The needle was placed at the center of a disk-type electrode vertically, below that there was a grounded flat collector covered with Al foil. The sample solution was electrostatically drawn from the tip of the needle by applying high voltage between the disk electrode and the collector. The experimental parameters were adopted with applied voltage 20 kV, tip-to-collector distance 20 cm, and flow rate of the solution 3 mL/h, respectively. All the electrospinning processes were carried out at 25°C with the relative humidity 45%, and the resultant fibrous electrospun EPDM/POSS meshes were dried overnight to remove the residual solvent.

Characterization
The morphology of the electrospun fibers after gold coating was observed with a field emission scanning electron microscope (SEM) (Sirion 200, FEI) at an accelerating voltage of 10 kV. The fiber diameters and distributions were determined with an image analyzer (Image-Pro Plus, Media Cybernetics).[23,24] Mean diameters of the electrospun fibers and the standard deviations were measured from 30 randomly chosen fibers in SEM images.[25]

Transmission electron microscopy (TEM) analysis was performed with high resolution equipment (JEM-2010, JEOL). Ultrathin sections of fibers, about 200 nm thickness, were cut with a resin embedding method by a Power Tomex microtome, and placed on a 200 mesh copper grid.[17] The energy-dispersive X-ray spectroscopy (EDS) analysis was carried out at the same time.

Fourier transform infrared (FTIR) spectra of the electrospun fibers were recorded at the ambient temperature on a Nicolet MAGNA-IR 750 spectrometer (Nexus, Nicolet Instrument) over the range of 400–4000 cm^{-1}. UV-Vis spectra were recorded on a spectrophotometer (CARY-5 E, VARIAN, Australia) between 200 and 700 nm. Above two kinds of spectra were performed with a membrane testing method.

Thermogravimetric (TG) analysis was carried out with an analyzer (Pyris TGA, PerkinElmer) by heating from 50 to 700°C under a nitrogen atmosphere at a heating rate of 20°C/min. Besides, heat release case and thermo-oxidative degradation during the heating process were characterized with an equipment (DTG-60H/DSC-60, Shimadzu, Japan) by heating from room temperature to 800°C under an air atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Morphology
The diameters of electrospun fibers are mainly influenced by the following four experimental parameters, solution concentration, applied voltage, tip-to-collector distance, and flow rate.[23] So it needs firstly sight these parameters by electrospinning pure EPDM, and find out the most suitable parameters, mentioned in previous experimental section. It can be seen that the fibers have a smooth surface and their average diameter is approximately 2.3 ± 0.32 μm [Figure 1(a)]. They can hardly be considered as nanofibers, nevertheless their average diameter is about one order of magnitude smaller than ordinary EPDM fibers obtained by conventional wet or melt spinning,[26] so we can regard them as ultra-fine fibers. Then, several EPDM/POSS solutions with different POSS contents were electrospun according to the experimental parameters of pure EPDM. The resultant electospun fibers are named as EPDM/POSS2, EPDM/POSS5, and EPDM/POSS10 by the percentage of POSS to EPDM. It is observed that the electrospun fibers are deposited as a randomly oriented states, forming a highly porous structure, which is held together by some connecting sites such as
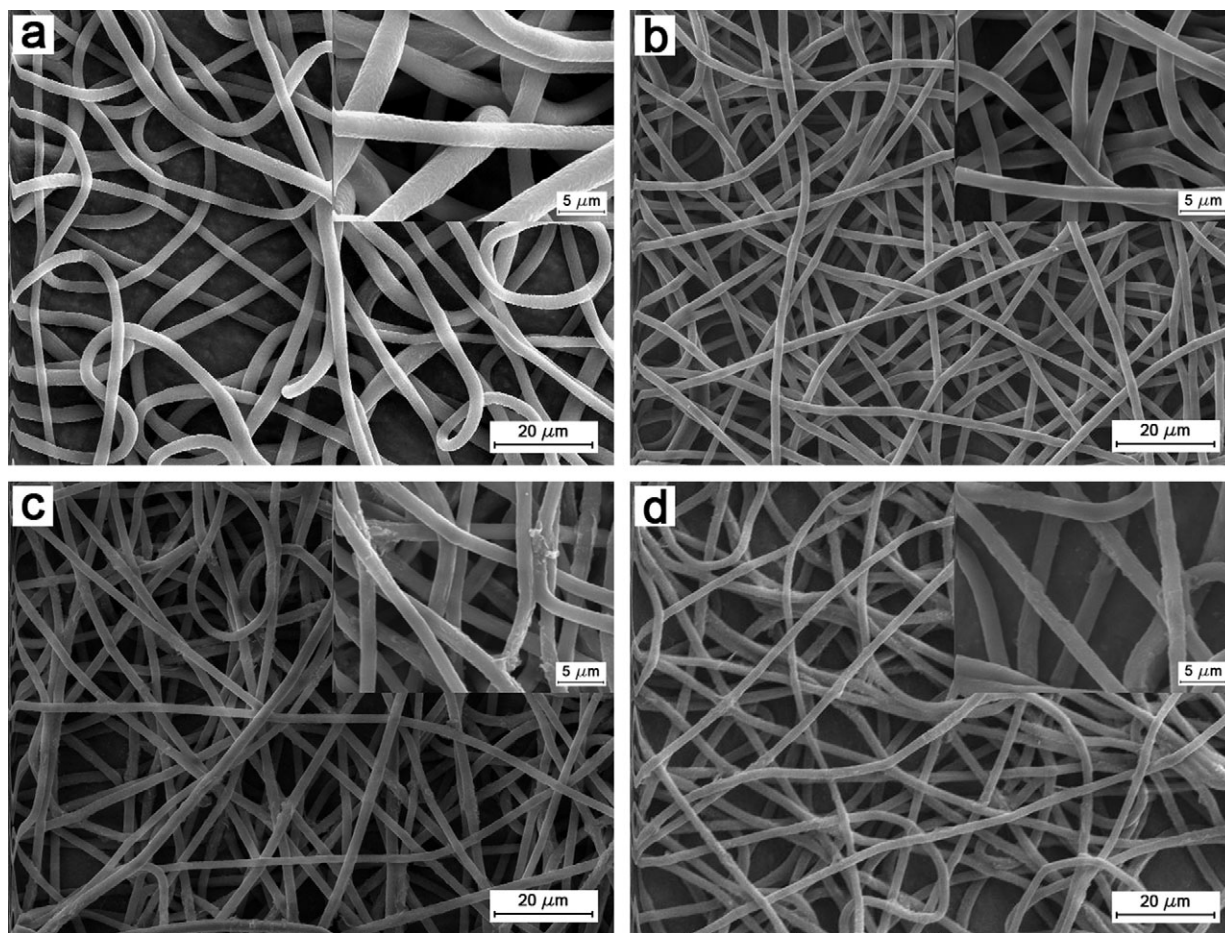
Figure 1. SEM images of electrospun EPDM/POSS composite fibers with various POSS weight percentages: (a) 0 wt %, (b) 2 wt %, (c) 5 wt %, (d) 10 wt %.

electrostatic crossing and bonding between the fibers.[15,17] Because in the electrospinning process, the fibers are ejected from the needle tip by several long ones simultaneously and deposited layer upon layer continuously.

SEM images are allowed to evaluate the influence of POSS on the final fibers' morphologies and diameters. The morphologies of both pure EPDM and EPDM/POSS composite fibers are similar on the whole, but with the POSS content increasing, the fibers' surfaces change from smooth to rough gradually. It can be seen that there are numerous unobvious tiny dots adhering to the electrospun fibers' surfaces with relatively higher POSS contents [Figure 1(c, d)], which may be the additive POSS moieties. Afterward, fiber diameters were manually measured by image software and the diameter distributions were calculated, shown in Figure 2. Compared with pure electrospun EPDM fibers, the diameters of EPDM/POSS composite fibers are smaller and their distributions narrower, presumably due to the incorporation of POSS moieties, containing Si atoms, which might increase the conductivity of the solutions, and be potentially able to promote the elongation force of the ejected jets, favoring the formation of thinner fibers.[17] When the POSS content is 2 wt %, the average fiber diameter reaches its minimum value and then increases gradually with the POSS content added. On the one hand, the electrostatically charged fibers

tend to adhere to each other forming local structure of spindled fibers.[17] On the other hand, the aggregation of POSS moieties occupies the inner volume of fibers and dilates the fibers, and maybe these effects gradually exceed the conductance effect. As a result, the average diameters of all the EPDM/POSS composite
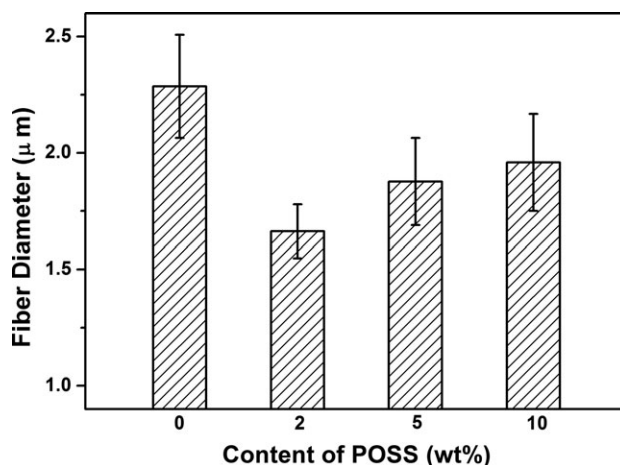

Figure 2. Influence of POSS content on fiber diameter (error bars show standard deviations).
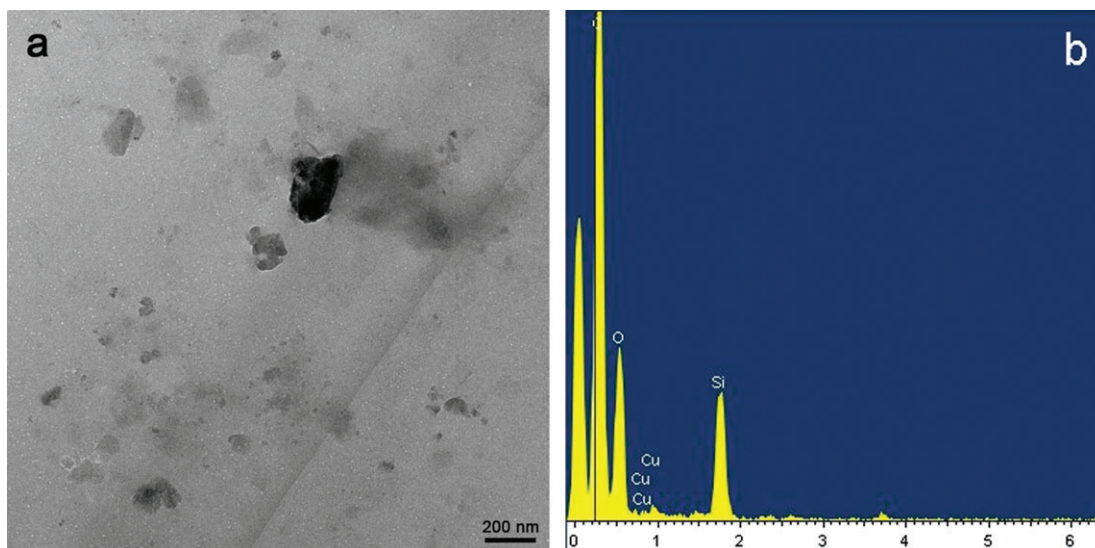
Figure 3. TEM (a) and EDS (b) images of electrospun EPDM/POSS10 composite fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

fibers increase slightly as increasing the concentration of POSS moieties,[19] and are approximately in the range from 1.66 ± 0.12 (2 wt %) to 1.96 ± 0.21 μm (10 wt %).

Structural Property

To investigate the dispersity of POSS among the EPDM matrix interior at the finer size-scale level, the composite fibers have been characterized by TEM [Figure 3(a)] to accurately evaluate the internal structure. If POSS and its matrix are combined by simple physical blend, POSS particles will form micron-sized aggregates or even macroaggregates dispersed in matrix, probably formed during the melt state of the processing.[9] However, when POSS and its matrix are conjoined by solution electrospinning, they could combine with each other more tightness, and POSS particles can be found to make nanoscale aggregates evenly dispersed in EPDM. Different from the other general inorganic nanoparticles, POSS itself is an organic–inorganic hybrid system and it has an amorphous morphology. Thus, although there are aggregations of POSS moieties in some areas, it is still considered as a good distribution. The photograph reveals that POSS particles have ellipsoidal and irregular shape exhibiting a size lying between 20 and 80 nm, so this kind of electrospun EPDM/POSS fibers could be regarded as a nanocomposite actually. In addition, the additive POSS moieties are dispersed in the EPDM matrix almost homogeneously, which could express its excellent mechanical and thermal properties to enhance the polymeric fibers better. Moreover, the noticeable existence of Si element peak in the EDS result [Figure 3(b)] proves that POSS moieties truly exist in the composite fibers.

To confirm the composition of products, the electrospun pure EPDM fibers and EPDM/POSS composite fibers with different POSS content were identified by FTIR spectrometer, as shown in Figure 4. It is observed that the band at 721 cm^{-1} is assigned to the methylene [—$(CH_2)_n$—, where $n > 5$] rocking vibration due to the presence of ethylene sequences in the EPDM backbone, the band at 1377 cm^{-1} is attributed to the —CH_3 sym-

metrical bending vibration from the propylene unit, and the absorption intensity at 1468 cm^{-1} is attributed to the —CH_2— bending vibration.[27] We also find that the strong absorption bands at 2850 and 2920 cm^{-1} correspond to the C—H symmetric and asymmetric stretching vibration of the saturated aliphatic backbone, respectively. All the above bands represent the IR absorption peaks of EPDM, which appear both in pure EPDM fibers and in EPDM/POSS composite fibers. However, there are two new obvious absorption peaks in the 900–1200 cm^{-1} range, which exist not in pure EPDM fibers but only in EPDM/POSS composite fibers. Among them, the band around 1020 and 1120 cm^{-1} are associated with the Si—C and Si—O stretching vibrations of the POSS monomer, respectively.[5,7] Furthermore, as the POSS content increased, the intensities of these two absorption bands also increase,[15] and these two peak
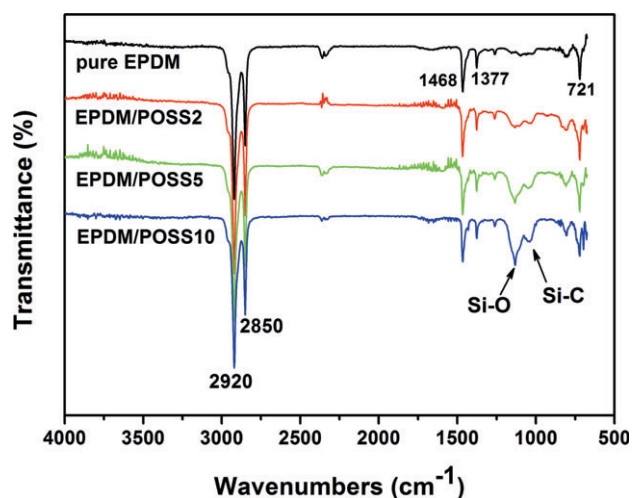

Figure 4. FTIR spectra of electrospun pure EPDM and EPDM/POSS composite fibers with different POSS content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

Figure 5. UV-Vis absorption spectra of electrospun pure EPDM and EPDM/POSS composite fibers with different POSS content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].
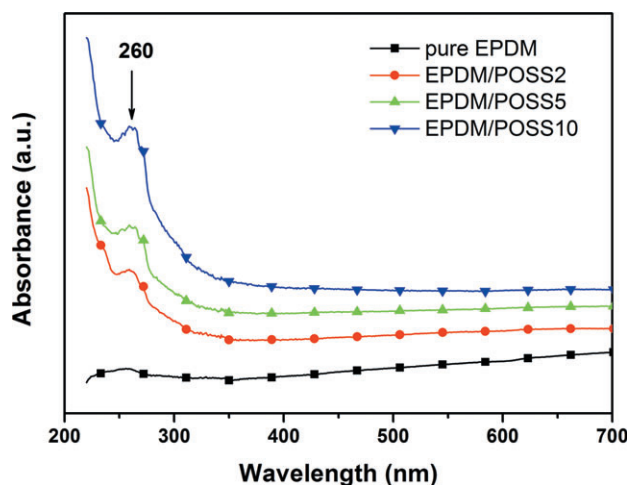
positions transfer to the high-frequency direction. For example, from EPDM/POSS2 to EPDM/POSS10, these two peak positions shift from 1018 and 1099 cm^{-1} to 1038 and 1132 cm^{-1}, respectively. This phenomenon should attribute to the Steric Hindrance Effect, which always occurs when the large size of groups within a molecule compels the bond angles of its adjacent groups waned, and the vibration frequencies of them to shift higher. Here in the ph-POSS macromer, it is the phenyl groups that influence the frequencies of its adjacent Si—C and Si—O bonds in the silsesquioxane cage structure.

The typical UV-Vis absorption spectra of the electrospun pure EPDM fibers and EPDM/POSS composite fibers with different POSS content are shown in Figure 5. It mainly can not be seen any obvious absorption band in the electrospun pure EPDM fibers, but there is a absorption peak in the electrospun EPDM/POSS composite fibers, and the maximum absorption wavelength locates at 260 nm, which is assigned to the $\pi \rightarrow \pi^*$ electronic transition of the corresponding conjugated benzene chromophore in our used ph-POSS macromer. We know that the standard characteristic absorption band of benzene chromophore is at 256 nm, less than the above value. Because the phenyl group grafting on the POSS monomer is amount to that Si atom substituting the benzene ring, the POSS monomer could act as an auxochrome of benzene chromophore. Therefore, both Si—O bond in POSS and benzene ring will arouse a hyper conjugation effect, which could cause a bathochromic shift in the UV absorption band. It is also noteworthy that the relative intensity of the absorption band increases with the chromophore content increasing in the electrospun composite fibers. In sum, the appearing of new peaks both in FTIR and UV-Vis spectra prove that POSS moieties are really dispersed in the composite fibers from another point of view.

Thermal Behavior

The TG and differential thermogravimetry (DTG) results of electrospun pure EPDM and partial EPDM/POSS composite fibers are respectively shown in Figure 6 and summarized in Table I. The thermal decomposition of pure EPDM in nitrogen
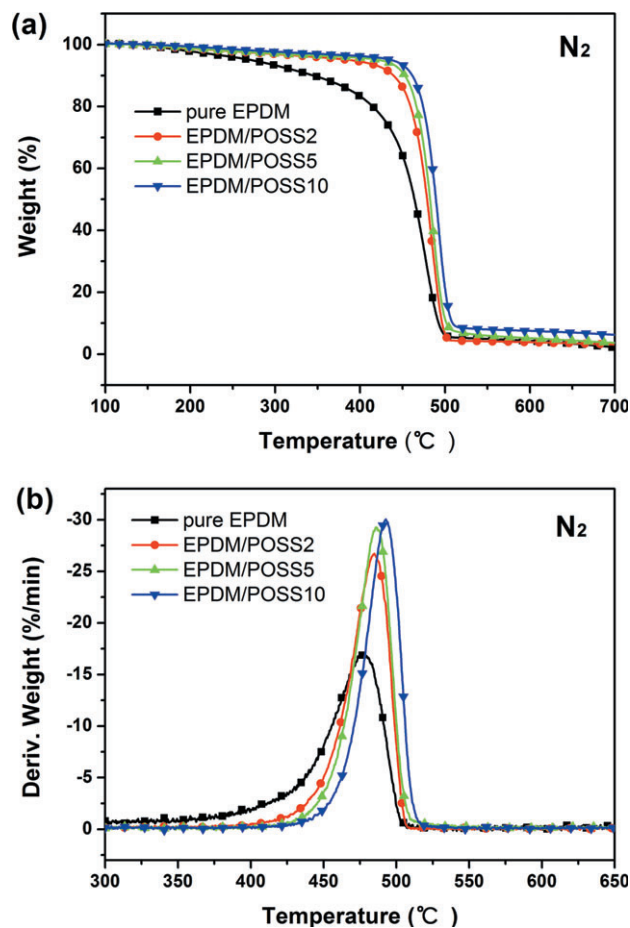

Figure 6. TG (a) and DTG (b) curves of electrospun pure EPDM and EPDM/POSS composite fibers under nitrogen condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

atmosphere is characterized by a single degradation step, beginning from 223°C ($T_{-3\%}$) with the maximum mass loss rate at 478°C. Only a few residues (2.15 wt %) are remained at 700°C, indicating that many gas-phase products release in the pyrolytic process. When POSS is added, the decomposition behavior has no fundamental change and one degradation step is also apparently observed in a temperature range between 425 and 510°C. However, the onset temperature of weight loss and the solid

Table I. TG and DTG Data for Electrospun Pure EPDM and EPDM/POSS Composite Fibers Under Nitrogen Condition

Sample	$T_{-3\%}$[a] (°C)	$T_{-50\%}$[b] (°C)	T_{max}[c] (°C)	Residue[d] (wt %)
Pure EPDM	223	464	478	2.15
EPDM/POSS2	295	479	485	3.06
EPDM/POSS5	304	482	486	3.65
EPDM/POSS10	349	489	493	6.21

[a]temperature at weight loss 3 wt %.
[b]temperature at weight loss 50 wt %.
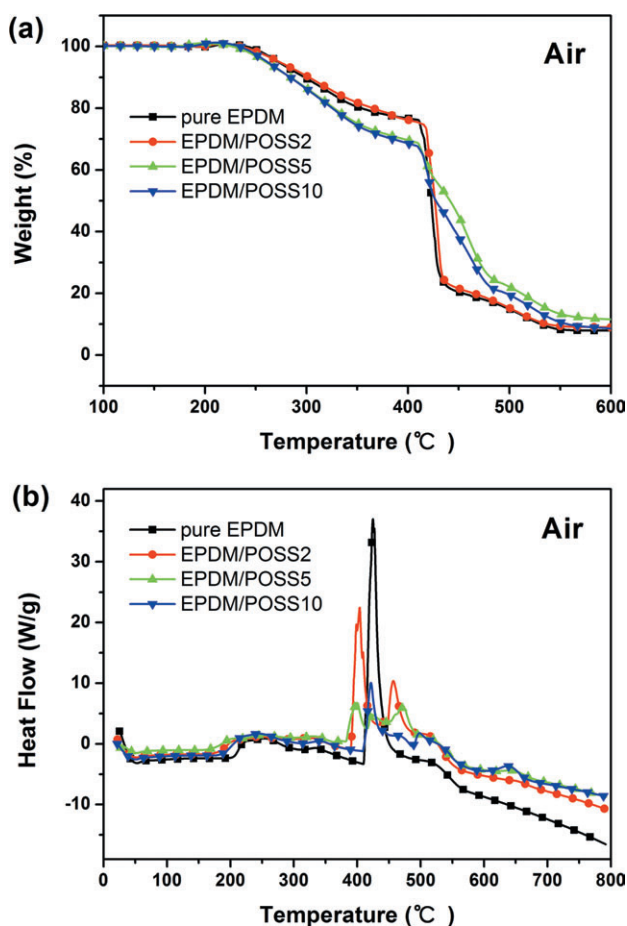[c]temperature at weight loss peak.
[d]at 700°C.

Figure 7. TG (a) and heat release (b) curves of electrospun pure EPDM and EPDM/POSS composite fibers obtained from TG-DSC united analysis under air condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

residue are different. The initial decomposition temperatures of EPDM/POSS composite fibers shift to a much higher value, and the temperatures also increase with the POSS adding more. Meanwhile, there are similar variations among the decomposition temperatures both at mass loss of 50 wt % and at the maximum mass loss rate. At the end of the test, the residue slightly increases to 6.21 wt % for EPDM/POSS10. Furthermore, the slopes of the TG curves are different; the curves with POSS have more gradient slope than that without POSS. In our point of view, there is a strong interaction between the additives and the polymer matrix, as a result, the times of the degradation become short and the pyrolytic temperatures are delayed. These results agree with the fact of DTG curves.

As shown in Figure 6(b), the DTG curves of EPDM/POSS composite fibers have the similar shape of peaks at the same temperature when the degradation speed is the fastest, and have narrower and sharper peaks compared with the pure EPDM curve. It indicates that POSS changed the thermolysis speed and the temperature range of the composites. Therefore, the presence of POSS makes the thermal stability of composite fibers further enhanced.

The heat release properties were characterized by TG-DSC united analysis that measures the heat flow of the gases evolved during controlled heating of milligram-sized samples under air atmosphere, with the thermo-oxidative degradation results obtained at the same time. The TG and heat release results of electrospun pure EPDM and partial EPDM/POSS composite fibers are respectively shown in Figure 7 and summarized in Table II. The thermo-oxidative degradation of pure EPDM is characterized by three decomposition steps, 230–410°C, 410–435°C, and 435–550°C, respectively [Figure 7(a)]. They maybe related to the polyolefinic main chain scission, short chain scission, and branch chain scission. When low content of POSS is added into EPDM fibers, there are no apparent changes in these steps. But in the fibers with high content of POSS, such as 5 or 10%, the decomposition temperature during the first step brings forward obviously. It is proved that POSS take the lead in decomposition during the low temperature range, like the first step, which promotes the thermal degradation of EPDM/POSS composites at the initial stage. On the other hand, the latter two steps are delayed in EPDM/POSS composites. The addition of POSS which contains organic groups enhances the crosslinking reaction of the composite matrix. Therefore, both the rapid thermal degradation of POSS at the low temperature range and the high degree of crosslinking for EPDM/POSS composites promote the formation of a physical protective barrier on the surfaces of the materials at the initial stage, which could limit the oxygen and heat diffusion.[28] So, in order to break though this barrier, they need a higher decomposition temperature in the latter two steps.

Figure 7(b) shows that EPDM is a labile polymer material under high temperature state, so it has high peak of heat flow (PHF) and THR. Compared with pure EPDM, the heat release curves of EPDM/POSS composites shows lower and disrupt peaks resulting form the decomposition of POSS. It is proved that the incorporation of POSS make the heat release process undergoing not a single narrow but a wide separate temperature district. The PHF value decreases from 37.0 W/g for pure EPDM to 6.77 W/g for EPDM/POSS5 with a reduction of 82%. It indicates that the presence of POSS could further reduce thermal degradation case of EPDM fibers. The heat release capacity (HRC) is another important index to measure thermal degradation hazard of a material, which is defined as the maximum

Table II. Heat Release Data of Electrospun Pure EPDM and EPDM/POSS Composite Fibers Obtained from TG-DSC United Analysis Under Air Condition

Sample	PHF[a] (W/g)	T_{PHF}[b] (°C)	THR[c] (kJ/g)	HRC[d] (J/g K)
pure EPDM	37.0	425	17.6	26.4
EPDM/POSS2	22.5	404	16.3	24.4
EPDM/POSS5	6.77	400	12.7	16.8
EPDM/POSS10	10.1	421	12.6	16.8

[a]peak of heat flow.
[b]temperature at PHF.
[c]total heat release.
[d]heat release capacity.

heat release rate divided by the constant heating rate in the test.[29] In comparison with pure EPDM, the HRC value of EPDM/POSS10 is reduced by 36%. What is more, the THR value also decreases from 17.6 kJ/g for pure EPDM to 12.6 kJ/g for EPDM/POSS10 with a reduction of 28%, although its PHF value and temperature at PHF (T_{PHF}) have a slightly increase above those of EPDM/POSS5. Based on the thermal-oxidative decomposition analysis, it is indicated that POSS promotes the pyrolysis of EPDM matrix in the initial stage and probably reacts with EPDM leading to the reduction of combustible gases. The formation of thermally stable residue or called barrier could further inhibit the release of flammable products and protect the underlying material from the action of the heat flux. Consequently, with the incorporation of POSS, the thermal degradation hazard of EPDM fibers has been ameliorated significantly and the heat-resistant property under high temperature state has been improved.

CONCLUSIONS

In summary, we have demonstrated a simple and effective strategy to produce highly thermal stable EPDM fibers by adding a ph-POSS molecule via electrospinning, which can be successfully used as an alternative approach to disperse POSS at a nanoscale to a polymer matrix. The morphologies of the resultant EPDM/POSS composite fibers are regular with the fiber diameter ranging from 1.6 to 2.3 μm. It is observed that the POSS moieties are dispersed in EPDM matrix homogeneously by TEM, and there are new characteristic peaks of functional group appearing in both FTIR and UV-Vis spectra, which prove that POSS macromers have a compact interaction with EPDM polymer to a certain extent. Furthermore, TGA and TG-DSC united analysis were used to investigate the potential pyrolytic risks of various EPDM composite fibers. For the fibers containing POSS, the thermal decomposition temperature is delayed, besides HRC and THR, which are important indicators of material pyrolytic hazards, are reduced by 36% and 28% respectively. In other words, the thermal stability of EPDM composite fibers has been apparently improved. Finally, it is expected that such electrospun EPDM/POSS composite fibers mat with a fibrous structure and heat-resistant property may be a promising special material applied in some high temperature conditions.

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