Synthesis of a Novel Intumescent Flame Retardant and Its Application in EVM

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ABSTRACT: A novel phosphorous-nitrogen structure containing intumescent flame retardant, 4,4-diaminodiphenyl methane bi(2,2-dimethyl-1,3-propanediol) phosphoramidate (DBDPP) was synthesized and characterized. Thermal stability and flammability properties of ethylene vinyl-acetate copolymer rubber(EVM)/DBDPP composites were investigated by thermogravimetric analysis (TGA), limiting oxygen index (LOI) test and UL-94 measurement, respectively. The results showed that the addition of DBDPP enhanced the thermal stability and flame retardancy of EVM significantly. The weight of residues improved greatly with the addition of DBDPP. SEM investigations revealed that a strong charred layer was formed from EVM/DBDPP composites during combustion. It is confirmed that the char structure was a critical factor for flame retardancy of EVM rubber. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1544–1551, 2012

Key words: ethylene vinyl-acetate copolymer rubber; intumescent flame retardant; flammability; thermal stability

INTRODUCTION

Ethylene vinyl acetate (EVA) copolymers represent one of the most important engineering polymers and have wide applications ranging from food packaging (2–18% vinyl acetate content) and wire and cable insulation to melt adhesives (above 50% VA). They are also widely used in competition with plasticized vinyl resins or vulcanized rubbers. For most of these applications, additives often have to be used to improve both mechanical properties and fire retardancy of the EVA materials.[1-3] Ethylene vinyl-acetate copolymer (EVM) rubber, as a copolymer of ethylene and high content of vinyl acetate, is suitable for use as wire and cable insulating or sheathing materials because of its good compatibility with inorganic materials, good resistance to oil and good flame-retardant properties[4] (compare with flammable rubbers, such as ethylene propylene rubber and polypropylene).

Halogen-containing flame retardants and their synergistic systems containing antimony trioxide are the most effective and show a good ratio of property to price in flame retardancy of polyolefins.[5] Traditionally, halogen-containing compounds are the main flame retardants of EVM. However, these systems are known to be a source of corrosive, obscuring and toxic smoke during combustion. Therefore, the present tendency aims at the limitation of using halogen-based flame retardants (FRs) and research and development turns towards halogen-free FR formulations.[6] Halogen-free compounds are regarded as promising FRs due to their environmentally friendly properties. Metal hydroxides, such as aluminum hydroxide ($Al(OH)_3$) and magnesium hydroxide ($Mg(OH)_2$) are commonly used.[7-10] But high loading (more than 60 wt %) of the metal hydroxides is required to obtain the same flame retardant level in EVM compared with halogen-containing retardants, and mechanical properties can be destroyed obviously.[5,11] So silicon additives and layered double hydroxide compounds are used in ethylene vinyl acetate to enhance the mechanical properties and flame retardancy.[12-17] But high filler loading of flame retardent have not changed.

A promising way to improve fire resistance of flammable materials is to use intumescent flame retardants (IFR) which have many advantages such as high efficiency and production of low smoke and nontoxic gases.[18-20] An intumescent flame retardant system is usually composed of three active ingredients, i.e., an acid source, a carbon source, and a blowing agent.[21] Ammonium polyphosphate(APP) as a typical and widely adopted IFR is also used in ethylene vinyl acetate.[22-24] But ammonium phosphates are water-soluble and they have a poor compatibility with the polymer. Thus, problems of migration and solubility may occur.[21]

In recent years, intumescent flame retardant systems and flame retardant mechanisms have been developed rapidly. Many flame retardants are synthesized for EVA.[25,26] They can produce a layer of foamy carbonaceous char, which protects the polymer surface from the flames. Expandable graphite is also used in polyolefins and make a good performance in them.[27] But it is used limited for its black colour. However, intumescent flame-retardant mechanisms are quite complicated, there may be different mechanisms with different matrix resins and different flame retardants,[28] And it need to be further studied and understood.

EVM is very important but flammable polymer. Neopentyl glycol and phosphorus oxychloride have been used for synthesizing intumescent flame retardant to improve polymer's flame retardancy.[29,30] In this work, a novel phosphorouse-nitrogen containing intumescent flame retardant, 4,4-diaminodiphenyl methane bi(2,2-dimethyl-1,3-propanediol) phosphoramidate (DBDPP) is synthesized by using Neopentyl glycol, phosphorus oxychloride and 4,4'-Diaminodiphenyl methane (DDM). The structure of DBDPP is characterized by FT-IR, ^{31}PNMR, and ^{1}HNMR. Its thermal degradation behavior and flammability properties in EVM are investigated by thermogravimetric analysis (TGA), LOI test and UL-94 measurement. The residues after combustion are investigated by scanning electronic microscopy (SEM).

EXPERIMENTAL

Materials

All the starting materials and solvents were commercially available. The EVM rubber (Levapren 550HV) was obtained commercially from Bayer AG, Germany. Neopentyl glycol (NPG) of C.P. grade was obtained from Sinopharm Chemical Reagent, Phosphorus oxychloride ($POCl_3$) of A.R. grade was obtained from Chengdu Kelong Chemical Reagent Plant. 4,4'-Diaminodiphenyl methane (DDM) of C.P. grade was the product of Chengdu Gracia Chemical Technology Chloroform of A.R. grade was obtained from Sinopharm Chemical Reagent Acetonitrile of A.R. was purchased from Tianjin Damao Chemical Reagent Plant.

Synthesis of 2,2-dimethyl-1,3-propanediol phosphoryl chloride (DPPC)

Neopentyl glycol (25 mmol) and chloroform (20 mL) were mixed in a 100-mL glass flask equipped with a globose condenser and tail gas absorber, then the mixture was heated to 50°C, phosphorus oxychloride (25 mmol) was dropped into the glass flask with constant pressure funnel in 1–1.5 h.The mixture was

heated up to 62°C gradually and stirred until no HCl gas was emitted. Successively, the reaction mixture was cooled slowly to room temperature and removed the chloroform solvent. The white solid was washed once with 30 mL hexane and twice with 30 mL ether. The powdery product was dried at 70°C under vacuum to a constant weight (73% yield). The melting point of purified product was 95–96°C. Elemental analysis for $C_5H_{10}O_3PCl$ (184.5): C, 32.52%; P, 16.8%; Cl, 19.24% (theoretically). C,32.23%; P, 16.60%; Cl, 19.18% (experimentally).

Synthesis of 4,4-diaminodiphenyl methane bi(2,2-dimethyl-1,3-propanediol) phosphoramidate (DBDPP)

DPPC (25 mmol, excess) and DDM (10 mmol) were added in a glass flask and dispersed by acetonitrile (30 mL). Triethylamine was added as acid scavenger. The mixture was stirred and gradually heated with nitrogen protection. The reaction would be completed after 16 h at 80°C, when no HCl could be detected. The product obtained was filtered and purified using a filter with water and acetone, then dried to constant weight at 80°C in vacuum drying box. The white solid powder was obtained (50% yield). The melting point of purified product was 262°C. Elemental analysis for $C_{23}H_{32}O_6P_2N_2$ (494): C, 55.87%; N, 5.67%; P, 12.55% (theoretically). C, 55.54%; N, 5.72%; P, 12.24% (experimentally).

Preparation of flame-retardant EVM

EVM rubber with different DBDPP content were prepared by using JTC-752A two-roll mixing mill equipment (Guangdong Zhanjiang Machinery Factory, China). All ingredients were of commercial grade and the vulcanization was performed at 165°C for 12 min under 14 MPa. The vulcanizing agent was dicumyl peroxide (DCP). Then the compositions was taken out to cool to room temperature.

Measurements

The FT-IR spectrum was applied with a WQF-410 infrared spectrophotometer (Beijing The Second Optical Instrument Company) using KBr pellets.

The ^{1}HNMR and ^{31}PNMR spectra were performed on a INOVA-400 (Varian, USA) using d_6-DMSO as a solvent and TMS as an internal standard.

Elemental analyses were performed using a Heraeus CHN-O-S-Rapid elemental analyzer.

The limiting oxygen index (LOI) values were measured on a HC-2 oxygen index meter (Changzhou Thermal Instrument Company, China) with sheet dimensions of 130 mm × 6.5 mm × 3 mm according to ASTM D2863-97.
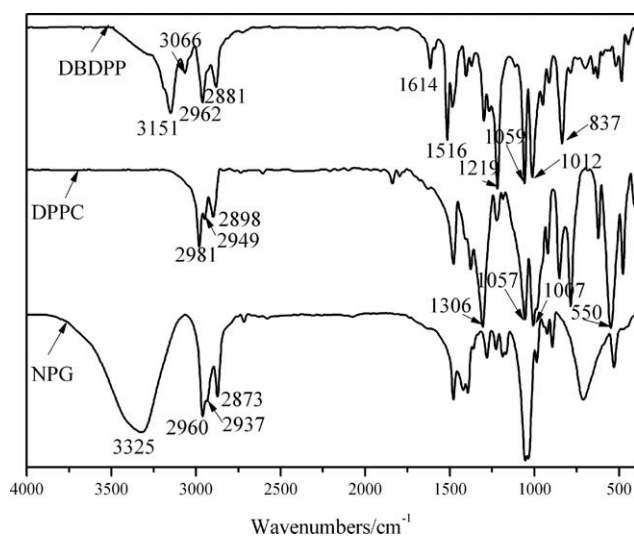
Figure 1 FT-IR spectrum of DPPC and DBDPP.

Fire retardency performance was evaluated according to the UL-94 vertical test protocol, using standard bars of 130 mm × 13 mm × 3 mm according to ASTM D 3801-06.

Thermogravimetric analysis (TGA) was conducted on a NETZSCH STA 449C thermogavimetric analyzer (Germany). Totally, 10 mg of samples (Platinum Pan) were heated from room temperature to 550°C at a heating rate of 10°C /min under nitrogen with a flowing rate of 60 mL/min.

Scanning electronic micrograph (SEM) and Energy dispersive spectrometer (EDS) observed on a FEI QUANTA-2000 (FEI, USA) to investigate the residues of the EVM/DBDPP system, which were obtained after LOI test.

The tensile strength and elongation at break were measured at room temperature with Shimadzu XLL-50 tensile tester (Guangzhou Material testing machine plant) according to IEC-502. The samples were kept at room temperature for 24h.

RESULTS AND DISCUSSION

Synthesis and characterization of DPPC and DBDPP

Because $POCl_3$ is very active, nonprotonic solvents such as DMSO, acetonitrile, toluene, chloroform, etc. are used to synthesize the DPPC and DBDPP. To avoid severe reaction and prevent volatilization of $POCl_3$, controlling the temperature is important. In this work, chloroform and acetonitrile are used as solvent, the dropping temperature of $POCl_3$ is kept at 50°C.

Figure 1 shows FT-IR spectrum of DPPC and DBDPP. There are some specific absorption peaks for DPPC: 1306 cm^{-1} (P=O), 1007 cm^{-1}, and 1057 cm^{-1} (cyclic P—O—C), 550 cm^{-1} (P—Cl), which is consistent with the previous report,[31] the peak of NPG at 3325 cm^{-1} (—OH) is disappeared, it proves the reaction of $POCl_3$ and NPG. In the FT-IR spectrum of DBDPP, the absorption peaks at 3151 cm^{-1} (—NH—), 3066 cm^{-1} (C—H in the phenyl), 1516 cm^{-1} and 1614 cm^{-1} (C=C in the phenyl), 1219 cm^{-1} (P=O), 1012 cm^{-1} and 1059 cm^{-1} (cyclic P—O—C), 837 cm^{-1} (P—N) are found. The disappearance of the peak at 550 cm^{-1} (P—Cl) indicates the completion of synthesis.

The ^{1}HNMR spectrum of DBDPP is showed in Figure 2. The peaks of H: 0.860–1.099 ppm (—CH_3 in the cyclic structure, a), 3.734 ppm (—CH_2— in DDM, c), 3.925–4.009 ppm (—CH_2— in the cyclic structure, b), 6.935–7.057 ppm (benzene ring, d, e), 7.907–7.933 ppm (P-NH-, f) confirm the final structure of DBDPP.

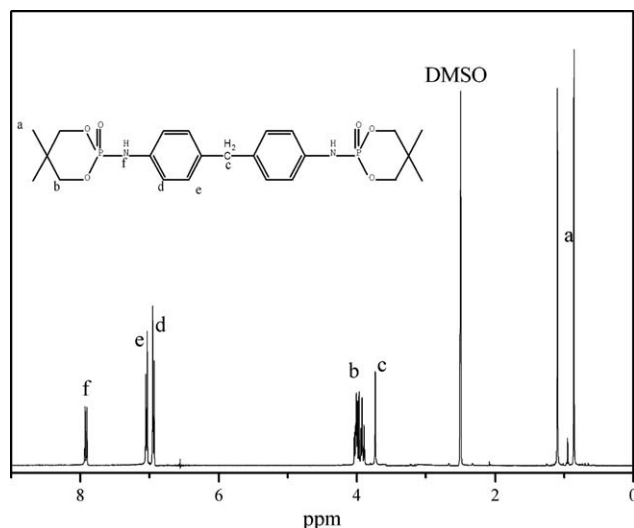Figure 3 is the ^{31}PNMR spectrum of DBDPP. The only one peak of 1.947 ppm (–1.604 ppm for the

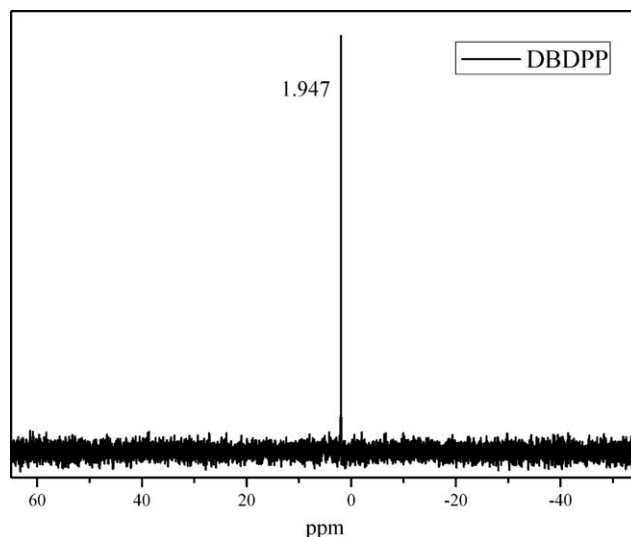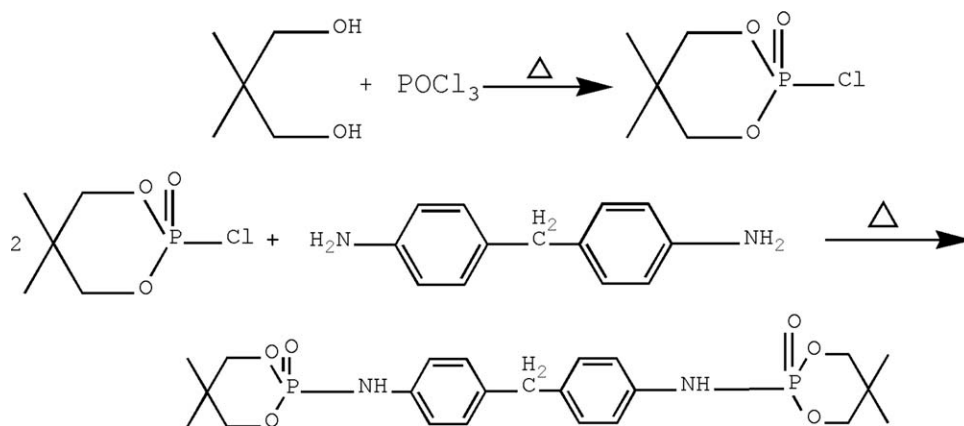**Figure 2** The ^{1}HNMR spectrum of DBDPP.

Figure 3 The ^{31}PNMR spectrum of DBDPP.

Scheme 1 Schematic procedure of synthesis for DBDPP.

intermediate) further validates the purity and structure of DBDPP. All the information above confirm the formation of the structure shown in Scheme 1.

Thermal stability

Figures 4 and 5 show the TGA and DTG thermograms of DBDPP, pure EVM and EVM/DBDPP composites respectively. TGA result shows that DBDPP starts decomposing at 271.5°C and has a residue of 27.5% at 550°C in N_2. The high char weight indicates that DBDPP is an efficient char-forming agent. DTG result indicates that DBDPP has two weightloss stage which can be assigned to the scission of the phosphate ester bonds (at about 302°C) and intumescent char formation (at about 327°C).[32] The sufficient thermal stability can meet the processing temperature of engineering plastics and rubber.

In Table I, the detailed TGA and DTG data, for example, initial decomposition temperature (T_{onset}) and the temperature of maximum weight-loss rate (T_{max}) for pure EVM, DBDPP and its composites are summarized. Two decomposition steps around 300–500°C are found for pure EVM under nitrogen. The first step is attributed to the loss of acetic acid from EVM, and the second step is main chain scission of EVM. EVM rubber decomposes at 304.8°C, leaving negligible char above 500°C. Both T_{onset} and T_{max} in TGA curve and DTG curve of DBDPP in N_2 are lower than those of EVM rubber, which means DBDPP degrades early. For EVM/DBDPP samples, T_{onset} of DBDPP contained samples is lower than that of the uncontained one due to the earlier degradation of DBDPP, however, T_{max} of the major degradation step increases for the DBDPP contained samples, indicating the thermal enhancing effect of DBDPP. The weights of residues improve greatly with the increase of DBDPP addition.

Results from TGA and DTG thermograms show that the addition of DBDPP reduces the initial degradation temperature but enhanced the thermal stability at high temperature. The proper gap of initial degradation temperature between polymers and intumescent flame retardants is necessary for the
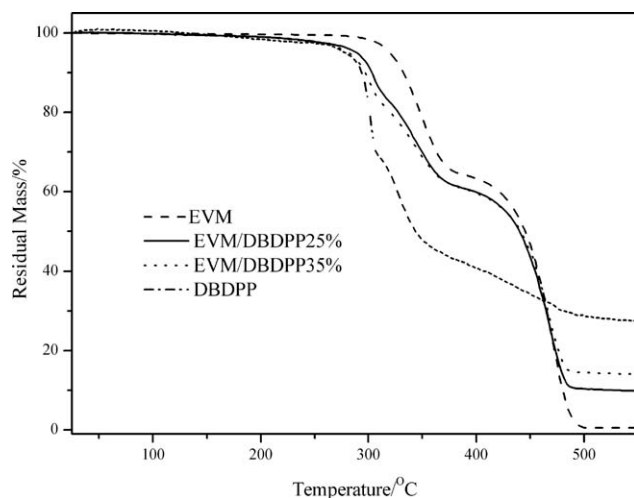

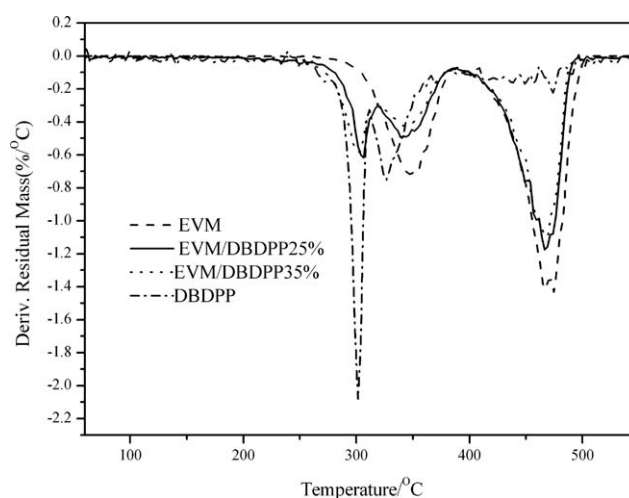**Figure 4** The TGA thermograms of DBDPP, pure EVM, and EVM/DBDPP composites.

Figure 5 The DTG thermograms of DBDPP, pure EVM, and EVM/DBDPP composites.

Samples	T_{onset} (°C)	Residue at 550°C (%)	T_{max} (°C)		
			Stage 1	Stage 2	Stage 3
EVM	304.8	0.5	–	347.3	467.3
DBDPP	271.5	27.5	301.5	326.5	–
EVM/25%DBDPP	289.0	9.8	306.5	343.0	467.5
EVM/35%DBDPP	282.1	14.0	302.1	347.1	468.1

T_{onset}: initial decomposition temperature; T_{max}: maximum weight-loss temperature.

flame-retardant systems because phosphoric and polyphosphoric acids have to be produced in the beginning of combustion to accelerate the reaction of esterfication and carbonization (but the T_{onset} of flame retardants should not be lower than the processing temperature).[33]

Flammability properties

The results of LOI tests and UL-94 measurement for EVM and its composites are listed in Table II. The LOI value of EVM rubber is 18 indicating its inherent flammability properties. The flame retardance of the treated EVM composites increase consistently with the increasing amount of DBDPP, which is reflected in the increase of LOI value. When the addition of the DBDPP is 35%, this system can pass UL-94 V-0 rating. At the same time, the dripping tendency during combustion becomes weaker. The results of LOI test and UL-94 measurement show that DBDPP is an effective flame retardant for EVM rubber.

Char-forming mechanism

To elucidate how the formation of intumescent char affects the combustion of the flame-retarded EVM composites, the morphologies were examined by taking photographs with a digital camera. The microstructures of the char after combustion were investigated with SEM. The elements of the char are analyzed by EDS spectrum.

Figure 6 displays the digital photos for the residues of EVM/25% DBDPP sample after LOI tests. The pure rubber is almost burnt out, but for EVM/

TABLE II
Results from LOI and UL-94 Measurements

Samples	LOI/%	Dripping	UL-94
EVM	18.0	Yes	No rating
EVM/25%DBDPP	28.0	Little	V-2
EVM/35%DBDPP	31.5	No	V-0

25% DBDPP sample, a swollen char layer covers the surface of material and provides resistances of both mass and heat transfer, protects the inner materials and postpones its degradation to form a combustible substance.

Figure 7 shows the micromorphologies of the outer (a, b) and inner (c, d) surface of the char for EVM/25% DBDPP composite. Outer surface of the char exhibits a cohesive and dense structure, the sphere-like swollen bubbles are not broken, indicating formation of a strong charred layer during combustion. Many honeycomb cavities scatter in the inner char, these cavities become pathways of gas fragments generated from the combustion and heat evolved during burning process.

The temperature after the maximum weight-loss rate of DBDPP remain at approximately 400°C. So the FT-IR spectrum of the swollen char of DBDPP after heating at 400°C for 30 min is given in Figure 8. The broad speaks ranging from 3000 cm^{-1} to 2500 cm^{-1} and 1220 cm^{-1} were attributed to the stretching vibration of P—OH[34] and P=O groups.[35] The absorbing peaks of P—O—C were observed at 1000 cm^{-1}.

The EDS spectrum of the intumescent residual char for EVM/25% DBDPP composite is given in Figure 9, and the elemental composition of the char is showed in Table III. Al, Si, Ca are a spot of elements in commercial EVM rubber. The high content of P and O provide positive evidence that DBDPP produces phosphoric and polyphosphoric acids during thermal degradation, which served as the dehydration agents and are the driving force for the formation of the heat resistant carbonaceous char by carbonization. The major characteristic of an intumescent coating is its ability to swell. The low N content can show that NH_3 was created during the combustion process. NH_3 is essential factor to form a dense and porous char layer.
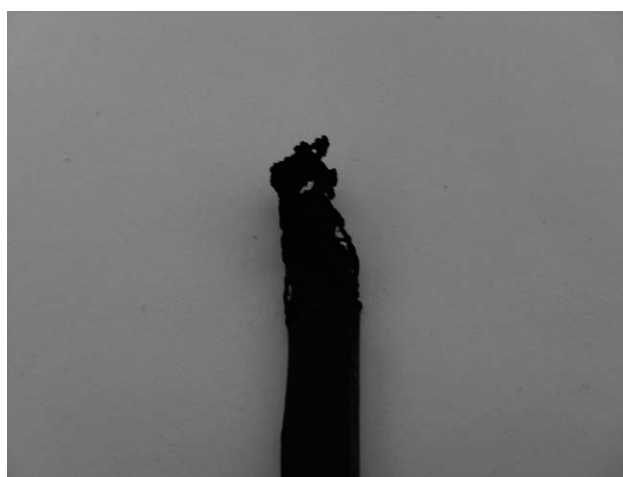

Figure 6 The digital photos for the residues of EVM/25% DBDPP sample after LOI tests.
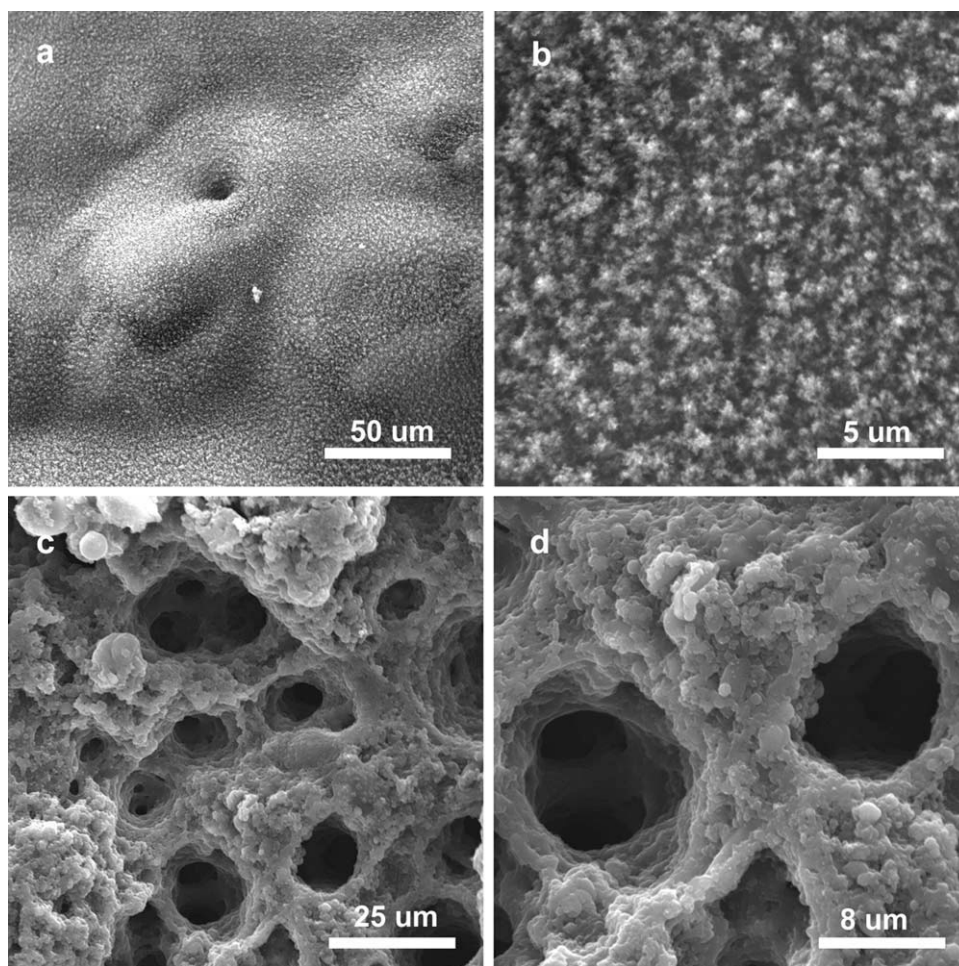
Figure 7 SEM of the chars for EVM/25% DBDPP composite.

On the basis of the phenomena mentioned above, the structure having a relatively strong charred layer is important to minimize the heat transfer and provide good protection for the rubber. It is clear that the blowing agent, DDM, plays a very important role which leads to the formation of honeycomb structure in the char of EVM/DBDPP composites. The formation of intumescent chars is responsible for the
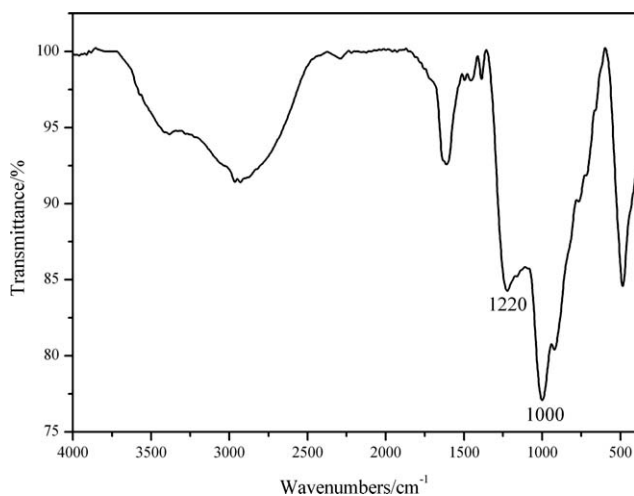

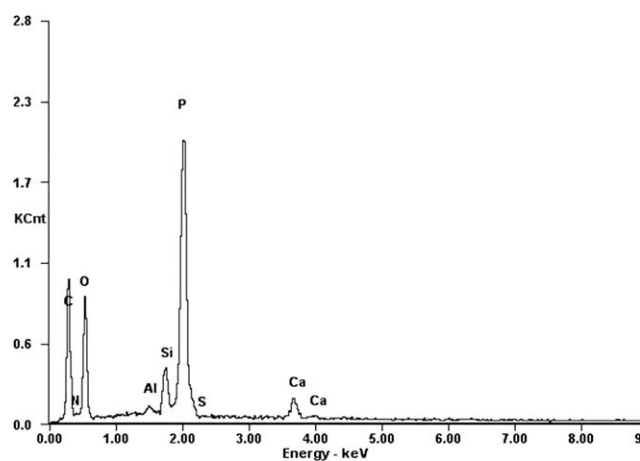**Figure 8** FT-IR spectrum of the swollen char of DBDPP after heating at 400°C for 30 min.

Figure 9 The EDS spectrum of the intumescent residual char for EVM/25% DBDPP composite.

TABLE III
Elemental Composition of the Char for EVM/25% DBDPP Composite

Element	wt %	At/%
C	52.34	64.04
N	04.45	04.67
O	24.44	22.45
Al	00.34	00.19
Si	02.12	01.11
P	14.61	06.93
Ca	01.69	00.62
S	00.00	00.00

thermal stability and flammability properties. The formation of the efficient char for EVM/DBDPP composites can prevent the heat transfer between the flame zone and the rubber, and thus protect the underlying materials from further burning and pyrolysis.

Mechanical properties of EVM/DBDPP composites

With increase in the loading of DBDPP in EVM/DBDPP composite, mechanical properties of EVM/DBDPP composite gradually decreased. When 25 wt % DBDPP added to EVM/DBDPP system, tensile strength and elongation of EVM/DBDPP composite are 10.4 MPa and 550% respectively. When 35 wt % DBDPP added to it, tensile strength fall to 8.11 MPa, and elongation is 525%. It is found that DBDPP affect tensile strength more than elongation. According to mechanical properties, we considered that the effect of DBDPP on mechanical properties of EVM/DBDPP system is not obvious.

DBDPP consistent with EVM rubber as it shows in Figure 10, there is no obvious phase separation
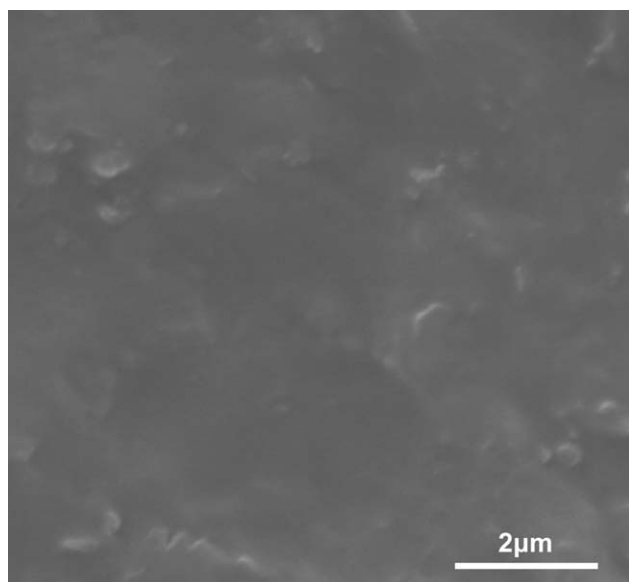

Figure 10 SEM of the section of EVM/DBDPP composite.

between DBDPP and EVM rubber, the surface of the composite is symmetrical. This is important to the mechanical properties.

CONCLUSIONS

A novel phosphorous-nitrogen structure containing intumescent flame retardant, 4,4-diaminodiphenyl methane bi(2,2-dimethyl-1,3-propanediol) phosphoramidate was synthesized and characterized. Investigation of thermal degradation behavior for DBDPP and EVM/DBDPP systems from DTG reveals that the addition of DBDPP enhances the thermal stability of EVM rubber at high temperature, but decrease T_{onset} of EVM/DBDPP composites. The residues from TGA improve greatly with the addition of DBDPP. The DBDPP can increase the LOI value of EVM/DBDPP composites. Residual chars contain polyphosphoric or phosphoric acid, which play an important role in the process of carbonization. The intact intumescent char is formed for EVM/DBDPP composites after combustion. DBDPP can reduce the mechanical properties of EVM/DBDPP composites, but not greatly. This has adequately proved that DBDPP is a very effective intumescent flame retardant in EVM.

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