

Preparation of Novel Dendritic Flame-Retardant Polymer and Its Application in EPDM Composites

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ABSTRACT: Flame-retardant polymer, dendritic tetramethylolphosphonium chloride (FR-DTHPC), was prepared by condensation polymerization between THPC, the monomer we prepared, and boric acid. It was then characterized by Fourier transform infrared spectroscopy, intrinsic viscosity, and matrix assisted laser desorption ionization time of flight mass spectrometer. This FR-DTHPC was used in the preparation of flame-retardant ethylene propylene diene monomer (EPDM) composites. Different types of EPDM/FR-DTHPC composites were prepared with different amounts of FR-DTHPC. Then, the cure characteristic, tensile properties, flame-retardance, and thermal stability were researched and compared. Results showed that the addition of this novel additive can improve some mechanical and flame-retardant properties of EPDM composites. Mechanisms of reinforcing and flame-retardance were proposed. The dendritic polymer may reduce the amount and size of voids in EPDM composites, and thus may increase their tensile properties. Meanwhile, the degradation products from nitrogen, phosphorus, and boric acid in FR-DTHPC can increase the amount of carbonaceous layers, and thus can inhibit the pyrolysis degree of EPDM composites during burning and improve their flame-retardant performance. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40855.

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INTRODUCTION

Ethylene propylene diene monomer (EPDM) is one of the most widely used and fastest growing synthetic rubbers having both specialty and general-purpose applications. EPDM elastomers are valuable for their excellent resistance to heat, oxidation, ozone, and weather aging due to their stable and saturated polymer backbone structure. As nonpolar elastomers, they have good electrical resistivity, as well as resistance to polar solvents, such as water, acids, alkalis, phosphate esters, and many ketones and alcohols. However, one setback of these synthetic rubbers that limits their usages for highly demanding applications is its inherently high flammability.¹

The use of flame-retardant additives allows the optimization of anti-fire properties of EPDM elastomers.^{2,3} Recently, a new class of macromolecules, dendrimers, has received more attention due to their special structures, such as porous and three-dimensional networks, plenty of functional end groups, difficult to crystallize, and high compatibility with other polymers.⁴ Dendrimers exhibit characteristics of both molecular chemistry and polymer chemistry. Molecular chemistry like properties come from their step by step controlled synthesis while they show polymer chemistry like properties as they are made up of

monomers.^{5,6} In addition, phosphorous, nitrogen, and boron elements can be introduced in the structure of dendritic polymers, and thus can improve their flame-retardance and smoke inhibition abilities.

In this study, a novel type of flame-retardant polymer, dendritic tetramethylolphosphonium chloride (FR-DTHPC), was prepared by condensation polymerization between tetramethylolphosphonium chloride (THPC), the monomer, and boric acid. The FR-DTHPC was analyzed by Fourier transform infrared (FTIR) spectroscopy, intrinsic viscosity, and matrix assisted laser desorption ionization time of flight mass spectrometer (MALDI-TOF-MS). Then, the application of this FR-DTHPC in EPDM composite was studied. The properties of EPDM/FR-DTHPC composites, such as cure characteristics, tensile strength, elongation at break, thermal stability, and flame-retardance were researched and compared.

EXPERIMENTAL

Materials

THPC, methyl acrylate, diethanolamine, methanol, toluene-p-sulfonic acid, boric acid, and aluminum hydroxide (AH) were supplied by Shanghai Guoyao Chemical Company (Shanghai,

Table I. Formulation of Rubber Vulcanizates

Component	phr
EPDM	100
Sulfur	2.5
Zinc oxide	5.0
Stearic acid	1.0
2-bezothiazolethiol	1.2
Tetramethyl thiuram disulfide	0.2
Diphenyl guanidine	0.3
Antioxidant T	1.0
FR-DTHPC/AH/CB	0,5,10,15,20

China). Carbon black (CB), industrial grade, was supplied by Shanghai Kabote Co. (Shanghai). EPDM, industrial grade, was obtained from Zhedong Rubber Co. (Zhejiang, China). *N, N*-dihydroxyl-3-aminomethyl propionate was prepared as reported before.⁷

The formulation, which was shown in Table I, was used for the application of this novel FR-DTHPC into rubber vulcanizates.

Preparation of G-1, G-2, and G-3

A 250 mL of four-necked flask with a mechanical stirrer, thermometer, and a tube with N₂ atmosphere was used as a reactor. *N, N*-dihydroxyl-3-aminomethyl propionate of 0.4 mol was gradually added to a prior prepared solution of 0.1 mol of THPC, 0.07 g of toluene-*p*-sulfonic acid (catalyst), and acetone. The resultant suspension was vigorously stirred for 10 h, distilled, and a viscous liquid, G-1, was obtained. Yield: ~90%.

N, N-dihydroxyl-3-aminomethyl propionate of 0.8 mol was gradually added to a prior prepared solution of 0.1 mol of G1, 0.20 g of toluene-*p*-sulfonic acid (catalyst), and acetone. The resultant suspension was vigorously stirred for 10 h, distilled, and a viscous liquid, G-2, was obtained. Yield: ~80%.

N, N-dihydroxyl-3-aminomethyl propionate of 1.6 mol was gradually added to a prior prepared solution of 0.1 mol of G2, 0.40 g of toluene-*p*-sulfonic acid (catalyst), and acetone. The resultant suspension was vigorously stirred for 10 h, distilled, and a viscous liquid, G-3, was obtained. Yield: ~70%.

Preparation of FR-DTHPC

G-3 of 0.1 mol and 1.6 mol of boric acid were added into a three-necked flask provided with a stirrer. The mixtures were treated at 75–80°C for about 2 h. The liquid product was distilled, and thus, FR-DTHPC was obtained. Yield: ~85%.

Preparation of EPDM Composites

Different additives were added into EPDM elastomers on a lab twin roll mill. After mixing for 20 min, FR-DTHPC was added, and different types of EPDM composites were prepared. Then, the mixture was molded in a dumbbell mold. Curing was conducted at 170°C for 30 min, after which elastic vulcanizates were obtained. To compare the tensile and flame-retardant properties of these novel composites, standard reinforcing fillers, CB, and standard flame-retardants, AH, were added in EPDM

matrix, respectively, and EPDM/CB and EPDM/AH composites were obtained.

Characterization

FTIR spectra of THPC, different generations, and FR-DTHPC were obtained using a FTIR spectrometer, model Avatar 370 from Nicolet Corporation. The scanning range was from 4000 to 700 cm⁻¹ with a resolution of 2 cm⁻¹. Sixty-four scans were necessary to obtain spectra with good signal-to-noise ratios.

The intrinsic viscosity measurements were carried out using an Ubbelohde viscometer in a temperature-regulated water bath (25°C).

The molecular weight of FR-DTHPC was verified by MALDI-TOF-MS (Voyager-DE STR spectrometer, Applied Biosystem Lab). The accelerating voltage was 25 kV, the acquisition mass range was 500–17000 Da, and the number of laser shots was 100/spectrum.

The curing parameters of EPDM composites were determined on an oscillating disk rheometer (MDR-2000, Wuxi, Liyuan, China) according to ASTM D 2084-81. The compositions were then vulcanized at 170°C during the respective optimum cure time under 15 MPa pressure on an electrically heated press. To compare test results conveniently, all of the uncured mixes and vulcanizates in this article were prepared using the above conditions and the formulation shown in Table I.

The tensile properties of EPDM composites were measured with dumbbell specimens (6-mm wide in cross section) according to the Chinese National Standard GB 528-82. The value for each sample was taken as the median value of five specimens. These tests were carried out at room temperature on a universal tensile testing machine (TCS-2000, Dongguan, China) with a crosshead speed of 500 mm/min. The tensile specimens for each composition were tested and the stress and strain at break determined.

The horizontal burning tests of EPDM composites were carried out on a horizontal and vertical burning tester (5400, Kunshan, China) according to the standards ASTM D 635, respectively, on sheet (125 ± 5 mm) × (13.0 ± 0.5 mm) × 3.0(0.0 + 0.2 mm). Limiting oxygen index (LOI) was measured using a Stanton Redcroft instrument on sheets (100 × 10 × 3 mm³) according to ASTM 2863.

Thermogravimetric analysis (TGA) was carried out at 20°C/min heating rate from ambient temperature to 700°C at nitrogen atmosphere using a Linseis PT-1000 microbalance, controlled by Version 3.0 software. In each case, the mass of the sample used was fixed at 10 mg and the samples were positioned in open vitreous silica pans.

RESULTS AND DISCUSSION

Analysis of FR-DTHPC

Mechanism for synthesis of FR-DTHPC. The photos of THPC, different generations, and FR-DTHPC were shown in Figure 1.

Three flame-retardant dendrimers, G-1, G-2, and G-3, have been synthesized by polycondensation reaction using an approach reacting the monomer, *N, N*-dihydroxyl-3-aminomethyl propionate, with different amounts (Scheme 1). During the

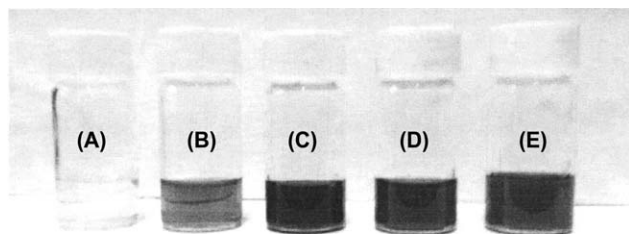


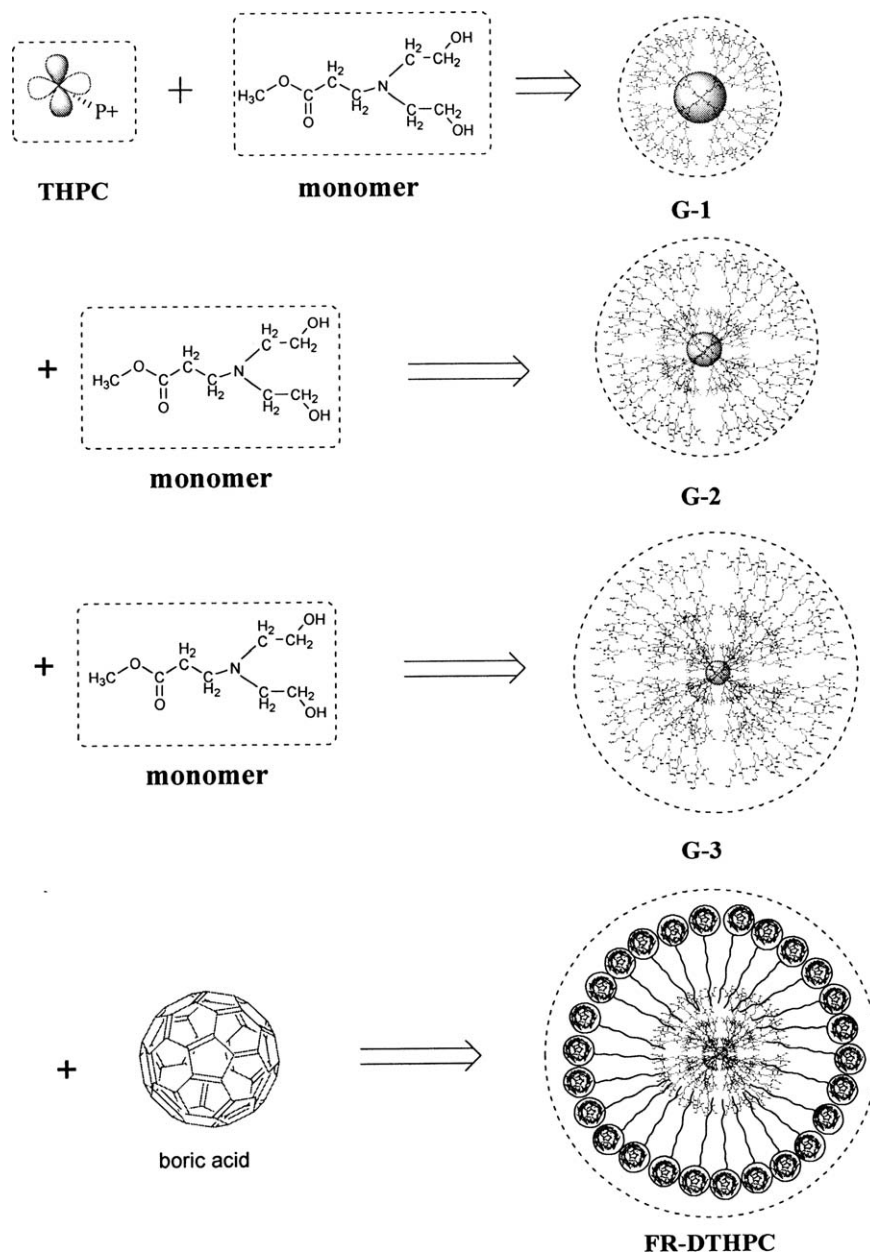
Figure 1. Photos of (A) THPC, (B) G-1, (C) G-2, (D) G-3, and (E) FR-DTHPC.

preparation process, transesterification between $-\text{OH}$ groups and $-\text{COOCH}_3$ groups occurred yielding small molecules (methanol) which were continuously removed, resulting in a decrease of hydroxyl value. This was in good accordance with

what Wang et al.⁸ depicted in the synthesis of hyper-branched poly(amide-ester) polyol by a melt polycondensation technique.

To achieve a convergent dendrimer synthesis using toluene-*p*-sulfonic acid as an activation agent, an AB_2 building block containing one ester and two hydroxyl groups, *N,N*-dihydroxyl-3-aminomethyl propionate, was selected. For the synthesis of G-1, 1.1 to 1.5 equiv of THPC were required. We assumed that THPC was partially decomposed or converted to THPO due to hygroscopic property. The AB_2 building block reacted with THPC to afford G-1 in 85% yield after recrystallization from acetonitrile.

Similarly, G-2 and G-3 were prepared by repeating the same reaction sequence, using *N,N*-dihydroxyl-3-aminomethyl propionate as described above. The activation time of the ester and the time



Scheme 1. Schematic preparation process of FR-DTHPC.

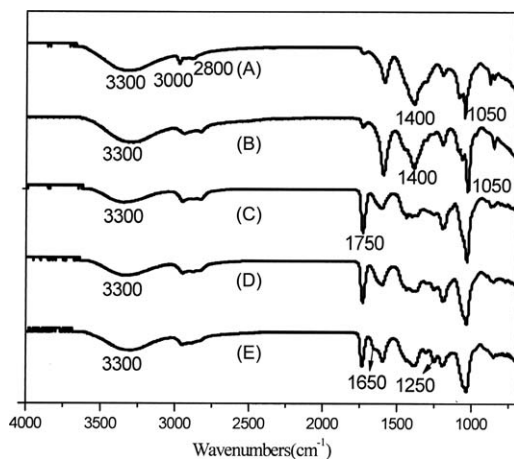
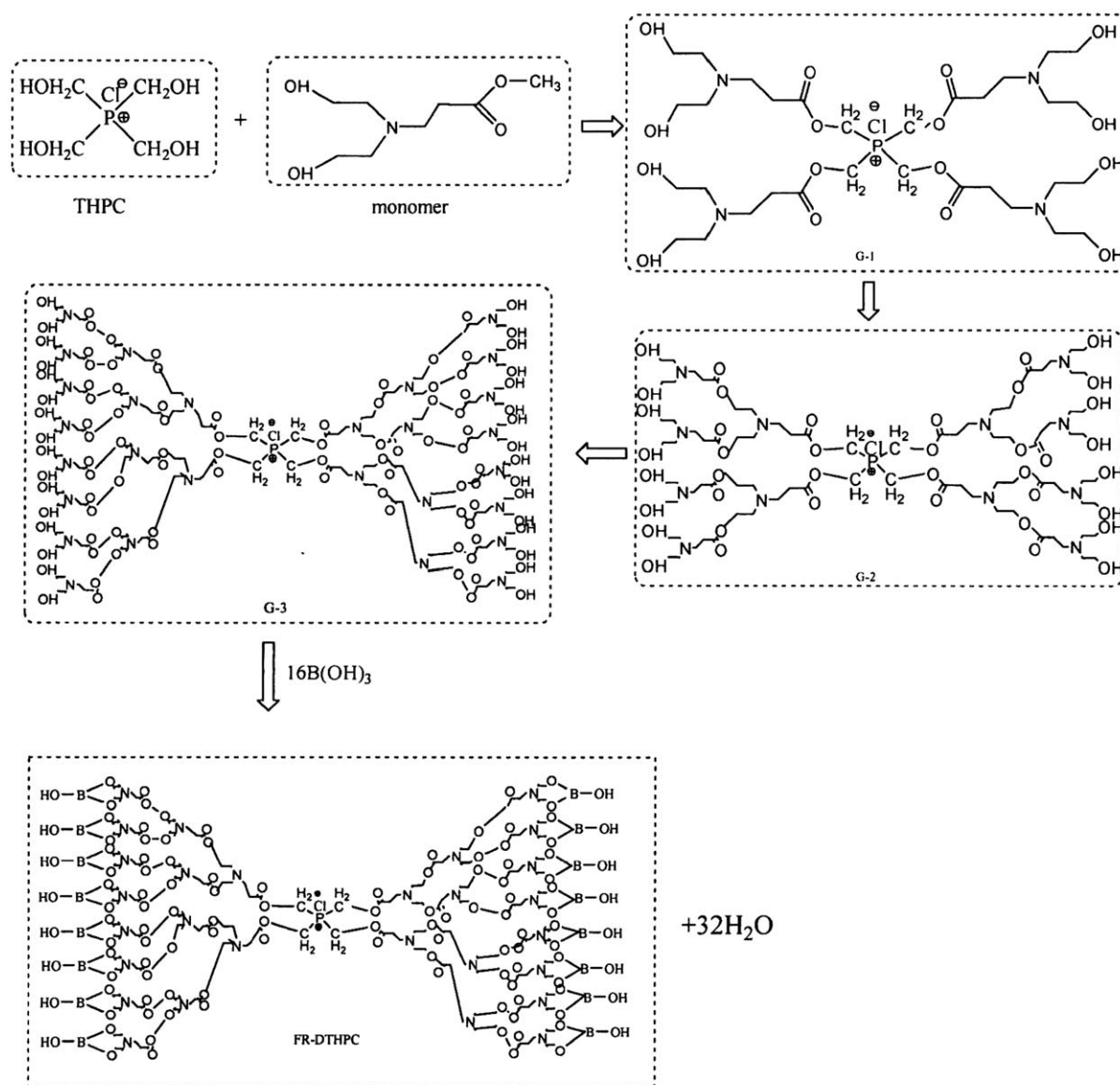


Figure 2. FTIR of (A) THPC, (B) G-1, (C) G-2, (D) G-3, and (E) FR-DTHPC.

for condensation were different depending on the types of dendrons as shown in Scheme 1. The dendrimers, G-2 and G-3, were isolated in 77 and 71% yield, respectively. A viscous white liquid was obtained after the esterification reaction occurring between boric acid and the hydroxyl groups in the intermediate.

FTIR Analysis. The FTIR spectra of THPC, different generations, and FR-DTHPC were shown in Figure 2.

In the spectrum of THPC, as shown in Figure 2(A), the peaks at 3000–3500, 2800–3000, 1400, and 1050 cm^{-1} were ascribed to the stretching or bending vibration of —OH, C—H, and C—O bonds. These were attributed to the hydroxyl, methyl, or methylene groups existed in THPC. In the spectrum of G-1, G-2, and G-3, as shown in Figure 2(B–D), the peaks at 3250–3650 cm^{-1} were caused by the stretching vibration of the two hydroxyl groups. The peaks between 2800 and 3000 cm^{-1} were resulted from the



Scheme 2. Chemical formula for preparation of G-1, G-2, G-3, and FR-DTHPC.

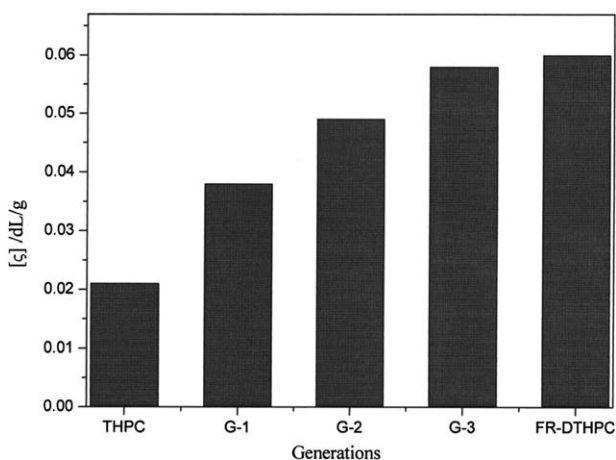


Figure 3. Intrinsic viscosity of THPC, G-1, G-2, G-3, and FR-DTHPC.

stretching vibration of C—H bond in the monomer structure. The appearing of strong peaks at 1750 cm^{-1} was attributed to C=O and C—O bonds in $-\text{CH}_2\text{CH}_2\text{COOCH}_3$. These flame-retardant dendrimers have been synthesized by polycondensation reaction using the monomer, *N*, *N*-dihydroxyl-3-aminomethyl propionate. Figure 2(E) gave the spectrum of FR-DTHPC we synthesized. Compared with that of G-3, the new peaks at 1650 and 1250 cm^{-1} were caused by the stretching vibration of B—O bonds in the new structure.⁹ Boric acid was a typical Lewis acid. When boric acid was added into glycerol or other polyol, $\text{B}(\text{OH})_4^-$ can be ionized out from this solution and can react with the hydroxyl groups. This reaction was a type of ester reaction and a stable complex with two six-membered rings was formed after stripping off four water molecules.¹⁰ The chemical formulas of above reactions were illustrated in Scheme 2.

Intrinsic Viscosity Analysis. The intrinsic viscosity of THPC, different generations, and FR-DTHPC was measured and shown in Figure 3. THPC was found to have a viscosity of 0.021 dL/g . The low viscosity was resulted from the smaller size of the molecules and larger space between the molecules facilitating the free movement of the molecular chains. With the increase of generations, the intrinsic viscosity was increased to 0.038 , 0.049 , and 0.058 dL/g , respectively. The increased molecular weight and the decreased movement space of molecules can increase the interactions between branched chains and solvent. This can increase the intrinsic viscosity of these dendrimers. However, the intrinsic viscosity of FR-DTHPC only increased a little when boric acid reacted with the end groups of G-3. This was due to the decreased amount of hydroxyl groups and the resulting less hydrogen bonds formed in the molecules.¹¹

MALDI-TOF-MS Analysis. FR-DTHPC was prepared in-house from THPC, the core material, and the monomer we synthesized, via condensation polymerization. MALDI-TOF-MS was used, and a total molecular weight of about 4750 , 15024 , and 19973 Da were obtained corresponding to G-1, G-2, and G-3, respectively (Figure 4). An increased molecular weight of G-1, G-2, and G-3 was achieved compared with that of THPC. This was the exact feature of the dendritic polymers.^{12,13} However, the molecular weight, 525.2 , 671.3 , and 671.3 , was obviously

lower compared with the calculated molecular weight, 827 , 2099 , and 4643 Da . The reason for such a decrease may be ascribed to the generational defects and branching defects came from following aspects.^{14,15} First, some THPC molecules may turn into derivatives, for example, tetrakis (hydroxymethyl) phosphonium, the oxidation of trimethylolphosphine (THPO), the product of tris(hydroxymethyl) phosphine.^{16,17} This may cause more defects in the core of the dendrimer and decrease its branching degree. Second, G-3 may contain trailing generations and oligomers and, thus, in principle may contain particles with molecular weights ranging from about 800 Da (G-1) to 4000 Da (G-3). This may cause significantly different biodistributions of different sized materials. These generational defects may cause substantial portions of the sample population with significantly lower molecular weights.

Analysis of EPDM/FR-DTHPC Composites

Curing Properties. The cure curves of different EPDM composites were shown in Figure 5. The curves were similar and the theoretical curing time was about 30 min . The maximum torque (M_m) has some relationship with the cross-linking density of the composites, as shown in Figure 5(A). However, the maximum torque of most EPDM/FR-DTHPC composites was relatively decreased in comparison with that of pure EPDM composites. Compared with the following tensile data of these composites, the torque had no close relationship with this property. This may be resulted from the different sensitivity to the degree of dendrimer dispersion in polymer matrix for the tensile strength and the maximum torque. The small stacks were probably responsible for these less than expected decreased results.¹⁸

In addition, the data of other cure characteristics, such as T10 (scorch time, the time during which a rubber compound can be safely worked at a given temperature before curing begins in rubber manufacture) and T90 (optimum cure time, the time taken for the rubber to rise to its maximum point, and at 90% of this level) of different amounts of FR-DTHPC-filled EPDM systems were illustrated in Figure 5(B). Scorch time is a parameter that is used to determine the safety of rubber products processing. The longer was the scorch time, the safer the process was. Compared with pure EPDM composite, it can be seen that the addition of FR-DTHPC ($5\text{--}20\text{ phr}$) can decrease scorch time (T10) and make the process unsafe. The decreased scorch time for these EPDM composites was attributed to the adsorption of a curative, the sulphate agent, by the dendrimers.¹⁹ Technical cure time is the shortest time that is used for the rubber to reach the maximum cross-linking degree during vulcanization process. It can be deduced from the decreased technical cure time (T90) that less energy was used in the curing process after the addition of different amounts of FR-DTHPC.

Tensile Properties. The tensile properties of EPDM/FR-DTHPC and EPDM/CB composites can be seen from Figure 6. They showed different reinforcing abilities and trends. The tensile strength and elongation at break of EPDM/FR-DTHPC composites showed the “first increase, then decrease” trend. The tensile strength and elongation at break showed a remarkable increase after the addition of 5 phr of FR-DTHPC. The tensile strength

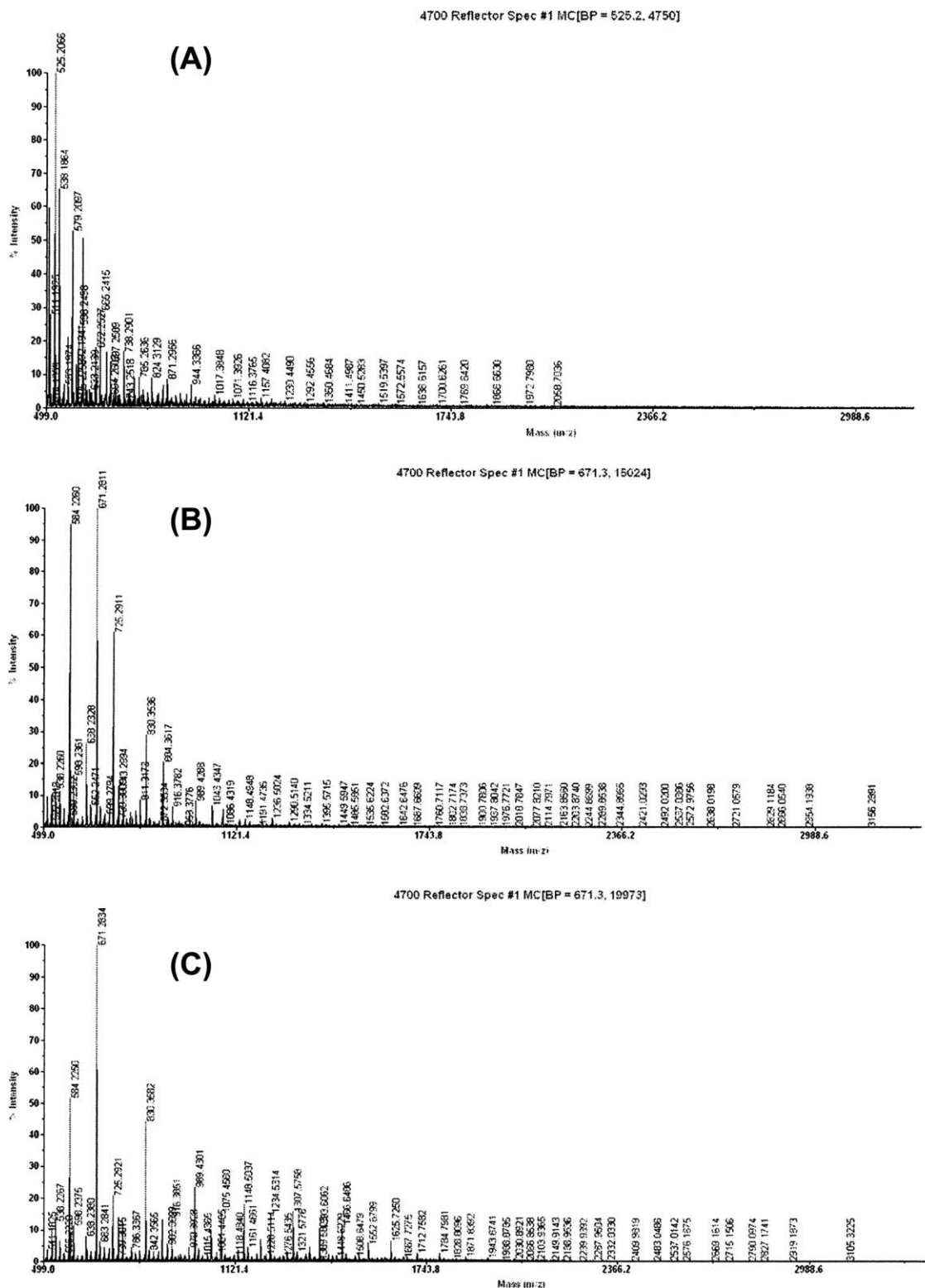


Figure 4. MALDI-TOF-MS spectra of (A) G-1, (B) G-2, and (C) G-3.

of EPDM/FR-DTHPC-5 was 2.4 MPa, which was improved about 85% compared with that of pure EPDM, 1.3 MPa. The elongation at break was also improved from 200 to 990%, a remarkable enhancement, 395%. The complex interplay between the dendritic polymer and the induced decrease in the apparent

weak points was the reason for such an increase.²⁰ When more FR-DTHPC was added, their tensile properties were decreased due to the aggregation of more dendrimers in the composites. However, the tensile strength and elongation at break of EPDM/CB composites showed “a linear increasing trend” after the

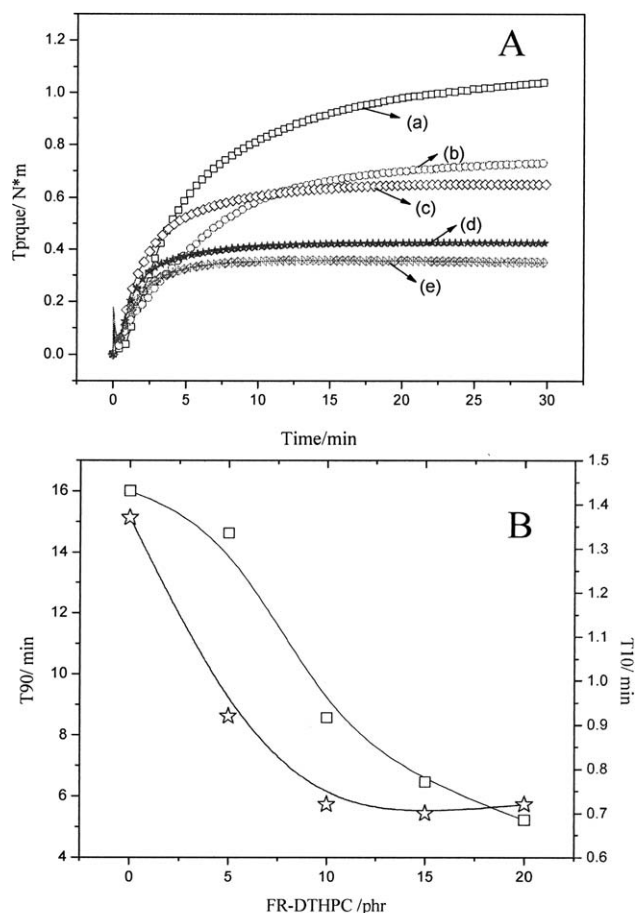


Figure 5. Cure curves of different EPDM composites A: (a) EPDM, (b) EPDM/FR-DTHPC-5, (c) EPDM/FR-DTHPC-10, (d) EPDM/FR-DTHPC-15, and (e) EPDM/FR-DTHPC-20. B: T10 and T90.

addition of different amounts of CB. The tensile strength of EPDM/CB-20 was 2.3 MPa, which was improved about 77% compared with that of pure EPDM. The elongation at break was improved from 200 to 490%, an increase of about 145%.

The failure of this specimen, EPDM/FR-DTHPC-5, on tensile strength started with small cracks (Figure 7). If the elastomeric network was capable of dissipating the inputted energy (e.g., by converting into heat), then it can withstand higher stresses. In EPDM/FR-DTHPC-5, the dendrimer can fill the void in the matrix, like various creeks flowing into small valleys. This can decrease the amount of weak points in this composite. The “anchor” effect between the end groups of dendrimer and molecular chains of EPDM can restrict the movement of polymer chains, and thus may improve the tensile properties of this composite.²¹

Figure 8 showed the hardness of different EPDM/FR-DTHPC composites. It can be seen that with the addition of 5 phr of FR-DTHPC, the hardness was slightly increased. This may have something with the increasing amounts of cross-linking networks in this composite. However, when more FR-DTHPC was added, the hardness was decreased. This was resulted from the loosing structures of the dendrimer. This may be beneficial for the application of this additive in some fields that need this property.

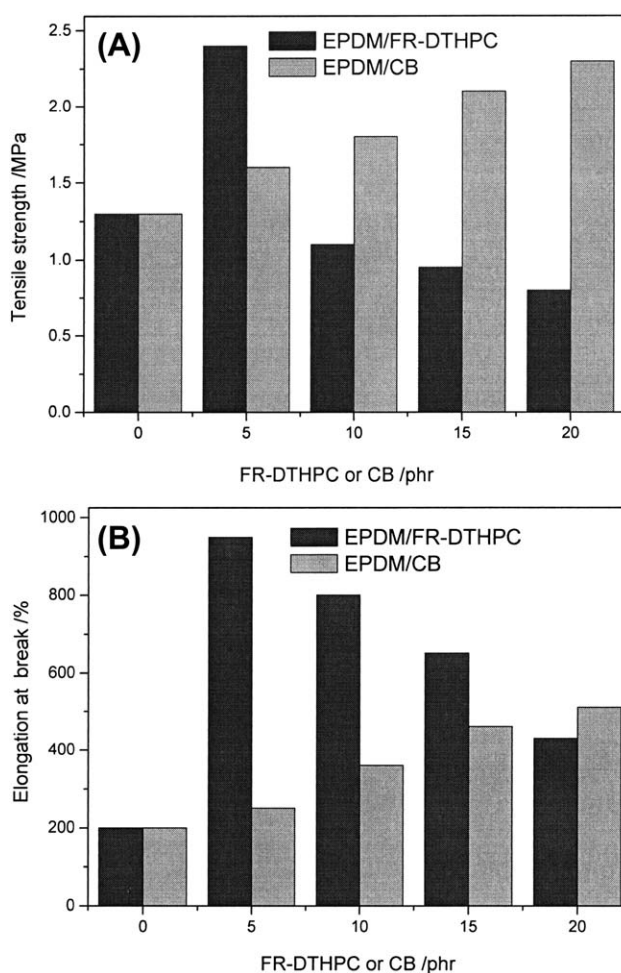


Figure 6. Tensile properties of different EPDM composites (A) tensile strength and (B) elongation at break.

FR Performance. The horizontal burning time, burning rate, and LOI value of EPDM/FR-DTHPC and EPDM/AH composites were summarized in Table II. The burning time of pure EPDM was relatively shorter (250 s). By adding 5–20 phr of FR-DTHPC into pure EPDM, the burning time was changed. The EPDM/FR-DTHPC-5 showed a longer burning time, 355 s, due to the flame inhibition effect of FR-DTHPC. However, with addition of more FR-DTHPC into EPDM, these composites showed a decreased burning time. This was probably due to the damaged structure and the resulted more holes, which were beneficial for the oxygen to flow into and helpful to the burning behavior of these composites.²² However, by adding 5–20 phr of AH into pure EPDM, the burning time showed a linear increase. This was the FR effect reflection of this metal hydroxide. The LOI value of pure EPDM was 20.0%, which meant that this polymer was flammable in an air environment. By adding 5 phr of FR-DTHPC or 20 phr of AH into EPDM, the LOI value was increased to 26.0 and 25.0%, respectively. They showed better fire protection.

Regarding the improvement of flame-retardance of EPDM/FR-DTHPC composites, we may explain, as shown in Figure 9, that the carbonaceous layers that formed during burning had great

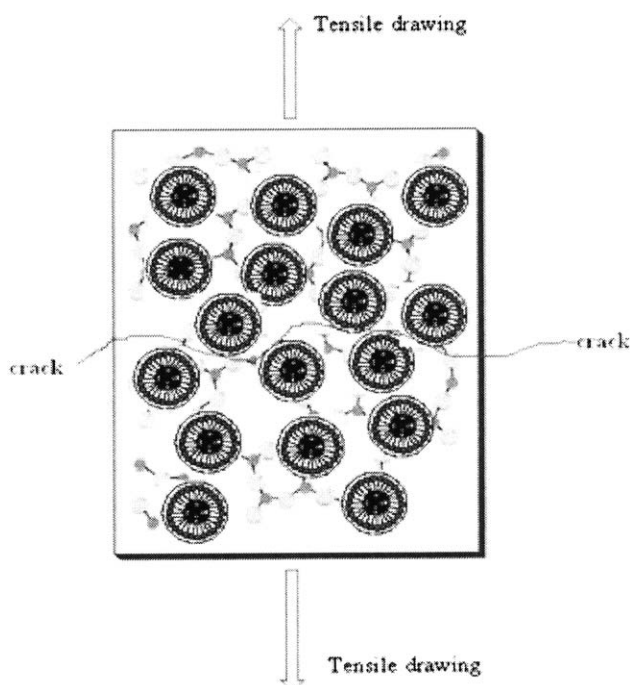


Figure 7. Reinforcing mechanism of EPDM/FR-DTHPC-5.

effect on the flame-retardant properties. In all, the EPDM system containing FR-DTHPC may have following flame-retardant mechanism. First, aromatic compounds may be formed from the degradation process and products coming from phosphorus, nitrogen, and boric elements in the dendrimer. Second, FR-DTHPC and EPDM decomposed at high temperatures, and carbonaceous layers were produced from the degradation products of EPDM and methylene groups in the dendrimer. They can act as a physical barrier and prevent combustible gases from feeding the flame, and also separate oxygen from the burning material.²³

Thermal Stability. TGA curves of different EPDM composites were shown in Figure 10. To compare their thermal stabilities

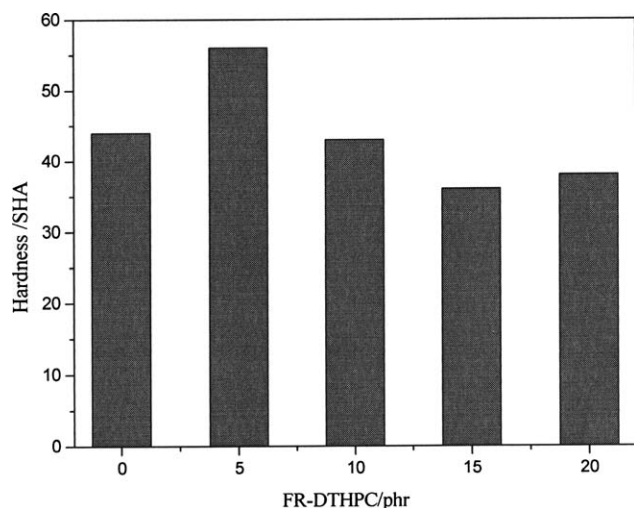


Figure 8. Hardness of different EPDM composites.

Table II. Horizontal Burning (HB) and LOI Test Results of Different EPDM Composites

Materials	Horizontal burning test			LOI (%)
	Burning distance (mm)	Burning time (s)	Burning rate (mm s^{-1})	
EPDM	75	250	0.300	20
EPDM/FR-DTHPC-5	75	355	0.211	26
EPDM/FR-DTHPC-10	75	278	0.270	24
EPDM/FR-DTHPC-15	75	230	0.326	19
EPDM/FR-DTHPC-20	75	225	0.333	18
EPDM/AH-5	75	261	0.287	21
EPDM/AH-10	75	278	0.270	22
EPDM/AH-15	75	291	0.258	24
EPDM/AH-20	75	305	0.246	25

clearly, three parameters were measured from TGA curves, that is, the onset temperature of thermal degradation (T_{onset} , the temperature at which weight loss is 5%), the center temperature of thermal degradation (T_{max} , the temperature at which weight loss is the fastest), and the yield of charred residue at 700°C .²⁴ The results were summarized in Table III.

Overall, the thermal stability of EPDM/FR-DTHPC-5 was better than that of pure EPDM and EPDM/FR-DTHPC-20. At loading of 5 phr of FR-DTHPC, T_{onset} and T_{max} was 320 and 490°C , and these were higher than that of pure EPDM. This was mainly attributed to the thermal stability of the dendrimer. The well dispersed FR-DTHPC not only hindered the evaporation of decomposition products but also more effectively hindered the access of oxygen to the polymer, reducing the rate of polymer chain degradation to volatile products. The high-decomposition

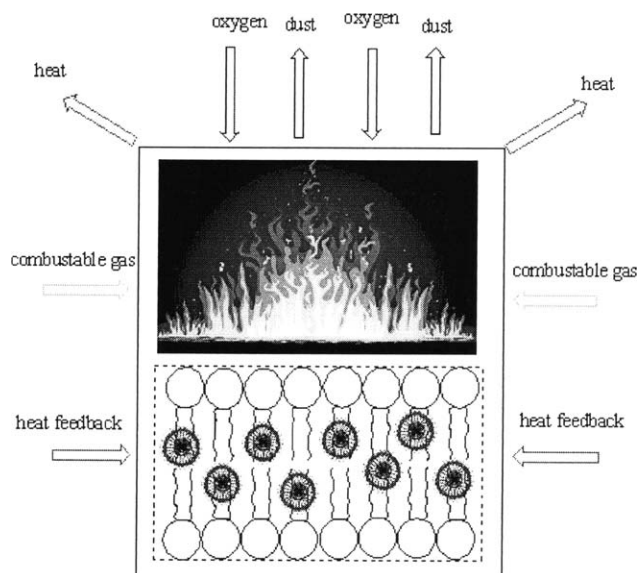


Figure 9. Flame-retardant mechanism of FR-DTHPC in EPDM.

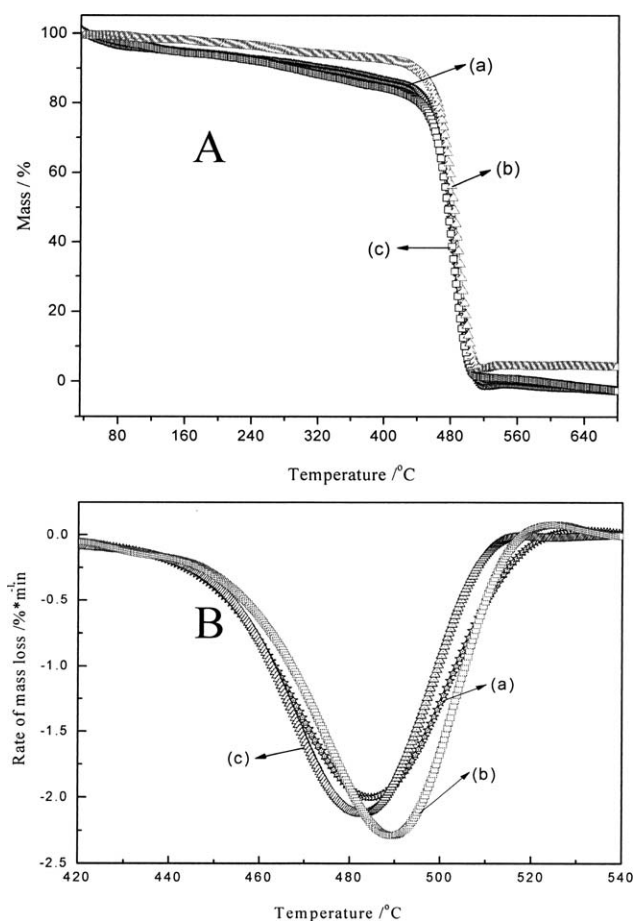


Figure 10. TGA (A) and Derivative thermogravimetric analysis (DTG) (B) of (a) EPDM, (b) EPDM/FR-DTHPC-5, and (c) EPDM/FR-DTHPC-20.

temperature indicated the improved thermal stability of the composites.²⁵ Moreover, significant decrease of T_{onset} and T_{max} was obtained when 20 phr of FR-DTHPC was added into EPDM. T_{onset} and T_{max} of EPDM/FR-DTHPC-20 were decreased about 110 and 9°C, respectively. This was due to the decreased thermal stability caused by the damaged structure resulting from more aggregated dendrimers in the composites.

CONCLUSIONS

Dendritic flame-retardant polymer was a type of effective liquid for improving the mechanical and flame-retardant properties of EPDM composites. It was demonstrated that the condensation reaction between THPC, the monomer, and boric acid was beneficial for the improvement of reinforcing, toughening, and flame-retardant property of EPDM composites. Experimental

Table III. TGA Results of Thermal Degradation of Different EPDM Composites

	T_{onset} (°C)	T_{max} (°C)	Residual mass (%)
EPDM	250	489	4
EPDM/FR-DTHPC-5	320	490	9
EPDM/FR-DTHPC-20	210	481	3

results demonstrated that incorporation of 5 phr of FR-DTHPC into neat EPDM system can improve the tensile strength and elongation at break from 1.3 to 2.5 MPa, and 210 to 990%, respectively. These tensile properties were better than that of EPDM/CB-5 composite. In addition, the horizontal burning rate was decreased from 0.300 to 0.211 mm/s, and the LOI value was increased from 20 to 26%. These flame-retardant properties were better than that of EPDM/AH-5 composite. The thermal stability of EPDM/FR-DTHPC-5 was also improved. It was demonstrated that T_{onset} and T_{max} was 320 and 490°C, and these were higher compared with that of pure EPDM.

The mechanisms of the improved reinforcing and flame-retardant abilities of FR-DTHPC were proposed. Modification of THPC by dendritic polymer can increase the amount of cross-linking networks in the EPDM matrix, and thus may improve the tensile properties of these composites. In addition, degradation behavior occurred in these novel flame-retardant additives and carbonaceous layers were formed. This can inhibit the pyrolysis degree and improve the flame-retardance of EPDM composites.

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