Preparation of Novel Hyperbranched Flame-Retardant Polymer and Its Application into Natural Rubber Systems

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ABSTRACT: Flame-retardant hyperbranched pentaerythritol (FR-HPER) was prepared by condensation polymerization between pentaerythritol (PER), the monomer, and phosphate acid we prepared. It was then characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance, thermogravimetric analysis, and matrix-assisted laser desorption ionization time of flight mass spectrometer (MALDI-TOF-MS). This FR-HPER was used in the preparation of natural rubber (NR)/FR-HPER composites. Different types of NR/FR-HPER composites were prepared with different amounts of FR-HPER, and compared with the composites directly incorporated with PER. Then, the tensile, wear resistant, thermal, and FR properties were researched and compared. Results showed that some mechanical and FR properties of NR/FR-HPER composites showed obvious improvements compared with that of NR and NR/PER systems. Schemes of toughening, wear resistant, and FR mechanism were proposed. The hyperbranched polymer may reduce the amount and size of voids in NR matrix, and thus increase the tensile properties. Meanwhile, the synergistic effect between nitrogen in PER and phosphorus in phosphate acid can increase the amount of carbonaceous layers, and thus may inhibit the pyrolysis degree of NR matrix during burning. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Natural rubber (NR) is a material that has shown its worthiness both as a "commodity polymer" and as an "engineering elastomer" by virtue of its unique combination of physico-mechanical properties. One of the setbacks of most natural and synthetic rubbers that limit their usages for highly demanding applications is its inherently high flammability.[1]

The use of flame-retardant (FR) additives allowed their fire properties to be optimized.[2,3] Potential approaches for fire retarding of NR were focused on two main approaches, that is, halogenated additives or high loadings of aluminum hydroxide (ATH), neither of which were satisfactory. The traditional halogens FR additives can reach better FR effect, but it will release poisonous hydrogen halogens air and have harm to the human body and environment. Inorganic FR fillers, ATH, need high quantity to satisfy the FR requirement, and this may influence the application properties of polymeric materials. ATH were identified for use, and zinc borate was considered as synergists with ATH.[4] Expandable graphite was identified for use in other elastomers and had potential for polyisoprene.[5] Alternative nanoscale fire retardants such as montmorillonite clay[6] and

multiwalled carbon nanotubes[7] were reported typically as a secondary additive to hydrated fillers. Other potential approaches were identified including the use of phosphorus- and nitrogen-based additives, such as phosphorus and pentaerythritol (PER), as intumescent char formers, and with zeolites as char catalysts.[8–10] This FR system is beneficial for the environmental, but has yet to make a successful transition to further and deeper investigation.

Hyperbranched macromolecules had received special attention in the field of flame retardancy because of its high thermal stability, sub-microparticle size, and reinforcing properties.[11] Hyperbranched macromolecules had porous and three-dimensional structure and plenty of functional end groups. This can make them more reactive. For high degree of branched structure, they were difficult to crystallize and had higher compatibility with other polymers. In addition, the addition of phosphorus element in hyperbranched polymers can improve the FR ability of hyperbranched polymers.

In this study, a novel type of FR hyperbranched polymer (FR-HPER) was prepared by condensation polymerization between PER, the monomer, and phosphate. Then, the application of

this FR-HPER in NR system was studied. The FR-HPER was analyzed by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), and matrix-assisted laser desorption ionization time of flight mass spectrometer (MALDI-TOF-MS). The properties of NR/FR-HPER composites, such as tensile strength, elongation at break, abrasion loss, thermal stability, and flame-retardance were researched and compared. Results showed that the use of FR-HPER can improve some mechanical and FR properties of NR matrix due to toughening and synergistic effects in these composites.

EXPERIMENTAL

Materials

PER, methyl acrylate, diethanolamine, methanol, toluene-*p*-sulfonic acid, and phosphate acid were supplied by Shanghai Guoyao Chemical Company (China).

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

Synthesis of Monomer

Diethanolamine (0.1 mol), 0.1 mol of methyl acrylate, and 10 mL of methanol were added into a three-necked flask provided with a stirrer. The mixtures were treated at 35°C for about 4 h at N_2 atmosphere. The product was separated by separatory funnel method and distilled by rotary evaporator until no methanol was remained. The product, *N, N*-dihydroxyl-3-aminmethyl propionate, was obtained as stable transparent oil liquid. Yield: ~85%.

Synthesis of Intermediate

A 250 mL of four-necked flask with a mechanical stirrer, thermometer, and a tube with N_2 atmosphere was used as a reactor. *N, N*-dihydroxyl-3-aminmethyl propionate (0.06 mol) was gradually added to *a prior* prepared solution of 10 g of PER, 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 was obtained. Yield: ~90%.

Synthesis of FR-HPER

Intermediate (0.1 mol) and 0.2 mol of phosphate 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-HPER was obtained. Yield: ~85%.

Preparation of NR Composites

Different additives were added into the NR systems on a double roller plasticator. After mixing for 20 min, PER or FR-HPER was added, and different types of NR composites were prepared. PER or FR-HPER was cured at 150°C before they were applied into NR matrix. Then, the mixtures were molded in a dumbbell mould. Curing was conducted at 150°C for 10 min, after which elastic vulcanizates were obtained.

Characterization

FTIR spectra of PER and FR-HPER were obtained using a FTIR spectrometer, model Avatar 370 from Nicolet corporation. The scan 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.

^{1}H-NMR (Bruker AV600 spectrometer) was used to analyze the components of PER and FR-HPER. These liquids were dissolved by using tetrahydrofuran. Tetramethylsilane was used as an internal standard.

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.

The molecular weight of FR-HPER was verified by MALDI-TOF-MS (Voyager-DE STR spectrometer, Applied Biosystem Lab). The accelerating voltage was 25 kV, the acquisition mass range was 9500–17,000 Da, and the number of laser shots was 100/spectrum.

The tensile properties of the vulcanizates were measured with dumbbell specimens (6 mm wide in cross section) according to

Table I. Formulation of Rubber Vulcanizates

Component	Information	Phr
NR	3#, industrial grade, provided by Hainan Rubber Company, Hainan, China	100
Sulfur	Chemical pure, provided by Shanghai Guoyao Chemical Agent Company, Shanghai, China	2.5
Zinc oxide		5.0
Stearic acid		1.0
2-Bezothiazolethiol		1.2
Tetramethyl thiuram disulfide		0.2
Diphenyl guanidine	Chemical pure, provided by Shanghai Lingfeng Chemical Agent Company, Shanghai, China	0.3
Antioxidant D	Chemical pure, provided by Shanghai Gaoqiao Chemical Agent Company, Shanghai, China	1.0
PER or FR-HPER	PER, chemical pure, provided by Shanghai Nanwei Chemical Agent Company, Shanghai, China; FR-HPER, self-prepared	1, 3, 5, 7, 9

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 wear resistant tests of the vulcanized rubber composites were conducted on a WML-76 Akron abrasion testing machine. The rotate velocities of the sample wheel and the empery wheel were 76 rpm and 33 rpm, respectively, and the angle between the shafts of the two related wheels was 15°. A pressure of 26.7 N was loaded on the sample during the wearing.

The horizontal burning tests were carried out on a YG815 horizontal burning tester according to the standards ASTM D635, respectively, on sheet 127 mm × 12.7 mm × 3.2 mm. Limiting oxygen index (LOI) was measured using a Stanton Redcroft instrument on sheets ($100 \times 10 \times 3$ mm^3) according to ASTM 2863.

Scanning electron microscope (SEM) of the fractured surface of NR/PER and NR/FR-HPER was observed using a Hitachi S-2150 SEM. The SEM was taken using an electron beam potential of 25 kV.

RESULTS AND DISCUSSION

Analysis of FR-HPER

The FTIR spectra of PER and FR-HPER were shown in Figure 1.

In the spectrum of PER, as shown in Figure 1(a), the peaks at 3000–3500 cm^{-1}, 2800–3000 cm^{-1}, 1400 cm^{-1}, and 1050 cm^{-1}

Figure 2. ^{1}H-NMR of (a) PER and (b) FR-HPER. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were ascribed to the stretching or bending vibration of —OH, C—H, and C—O bonds. These were attributed to the hydroxyl and methylene groups existed in PER. In the spectrum of the monomer, as shown in Figure 1(b), the 3250–3650 cm^{-1} peaks were caused by the stretching of the two hydroxyl groups. The peaks between 2800 and 3000 cm^{-1} resulted from the stretching vibration of C—H bond in the monomer structure. The appearing of strong peaks at 1760 and 1100 cm^{-1} was attributed to the —C=O and —C—O— bonds in —CH$_2$CH$_2$COOCH$_3$. The evidence of the successful addition reaction between methyl acrylate and diethanolamine was obtained from a sharp peak at 1230 cm^{-1} in its spectrum (C—N stretching). This was the result of successful application of the "slow monomer addition" method.[12,13] Zhang et al.[14] also synthesized a water-soluble amino-terminated hyperbranched polymer from methyl acrylate and diethylene triamine by polycondensation. Figure 1(c) gave the spectrum of FR-HPER we synthesized. The new peaks at 2350, 1650, and 1250 cm^{-1} were caused by the stretching vibration of —P=O, P—O, and C—N bonds in —POOCH$_2$CH$_3$— and C—N(C)(C) structures. These groups came from the hyperbranched repeat units and the phosphate acid ester grafted over the surface of PER.[15]

The ^{1}H-NMR spectra of PER and FR-HPER were illustrated in Figure 2. Two bands of PER were observed between 1.5 and 1.6
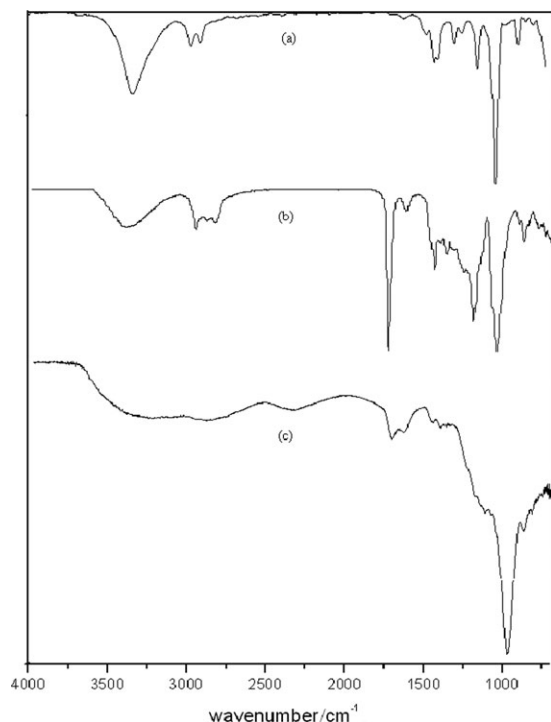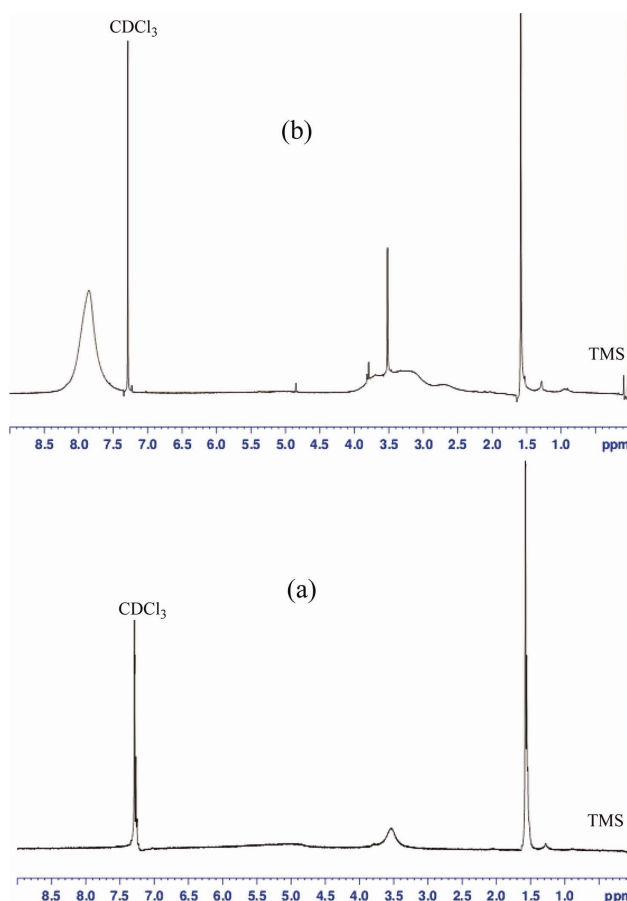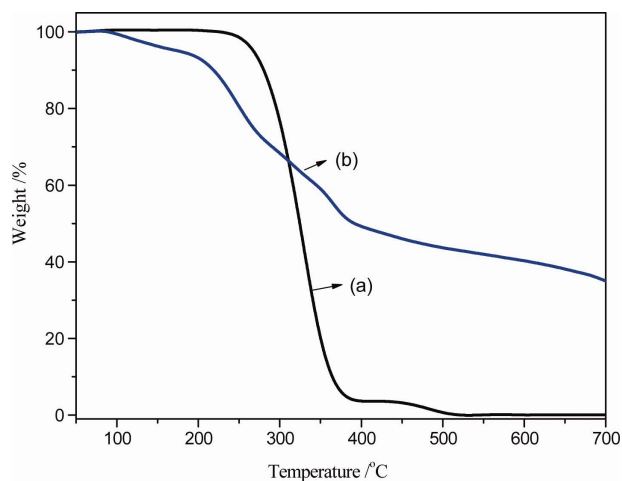

Figure 1. FTIR spectra of (a) PER, (b) monomer, and (c) FR-HPER.

Figure 3. TGA of (a) PER and (b) FR-HPER. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ppm [Figure 2(a)]. This was assigned to —CH_2 groups. The chemical shifts between 3.3 and 3.7 ppm were resulted from —OH groups due to the electron-withdrawing effect of oxygen atoms. Chemical shifts between 7.5 and 8.4 ppm were ascribed to hydrogen in the spectrum of phosphate acid [Figure 2(b)]. Many bands appeared between 2.7 and 4.0 ppm for FR-HPER. This was attributed to the —CH_2 groups in the different environment resulted from the repeat units of the branched polymers. This suggested the successful hyperbranched reactions in these systems.[16]

TGA

TGA curves of PER and FR-HPER were presented in Figure 3. The FR-HPER had an obviously enhanced thermal behavior in comparison with that of PER in the temperature range of 320–700°C. PER was a kind of FR additive, and almost two degradation steps can be seen from Figure 3(a). PER first showed initial

weight loss at 250°C. This may be due to the pyrolysis of —OH or —CH_2 in the powder. The second step was observed between 390 and 700°C. This was ascribed to the decomposition of oxidated materials in the residual. Figure 3(b) showed TGA study of FR-HPER we synthesized. It demonstrated that its thermal stability was increased after the hyperbranched reaction. Its degradation occurred in three successive steps. The first step started at about 100°C. This had something to do with the degradation of physical water in the surface of the hyperbranched polymer. The second step occurred between 200 and 320°C, and the third step was from 320 to 700°C. The weight loss in the temperature range of 320–700°C for FR-HPER was about 22%. This may be attributed to the decomposition of the main component of the hyperbranched polymer.[17]

An increased molecular weight of FR-HPER was achieved compared with that of PER (Figure 4). FR-HPER was prepared in-house from PER, the core material, and the monomer we synthesized, via condensation polymerization. To limit polydispersity and increase the molecular weight, the monomer was added to the reactant steadily using "slow monomer addition" method. However, the measurement of molecular weight of hyperbranched polymer by common gel permeation chromatography (GPC) method could not get the accurate results. As reported previously, the molecular weight measured by common GPC method might be lower due to the unsuitable and inapplicable standard materials used. Here, MALDI-TOF-MS was thus used and a molecular weight about 14,000 was obtained. This was the exact feature of the hyperbranched polymers.[18–20]

Mechanism for Synthesis of FR-HPER

The reaction for synthesis of the monomer was illustrated in Scheme 1(a). It belonged to Michael additional reaction. The H atom of —NH— in diethanolamine was very reactive and was able to react with —C=C— in methyl acrylate to produce . The methanol used here was a kind of solvent and
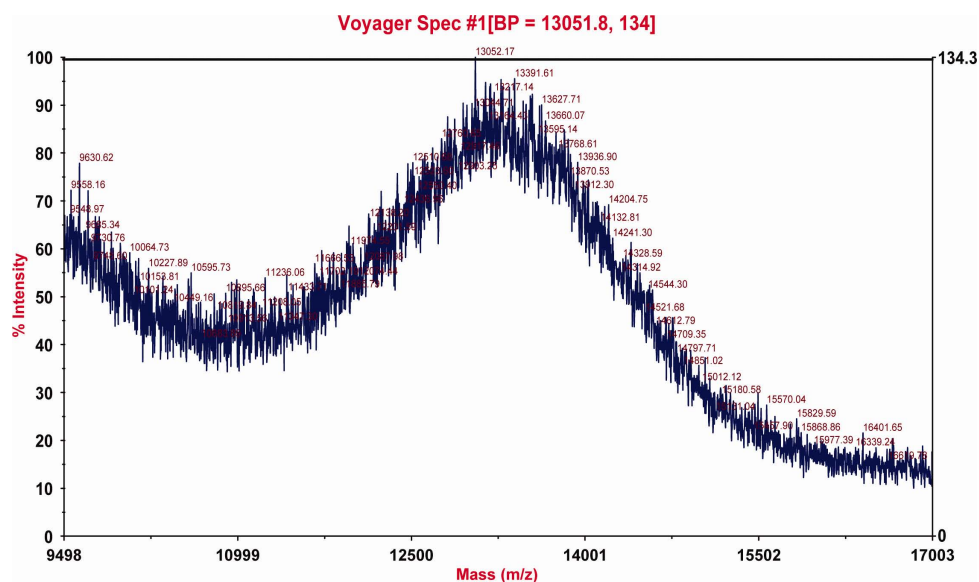
Figure 4. MALDI-TOF-MS spectra of FR-HPER. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
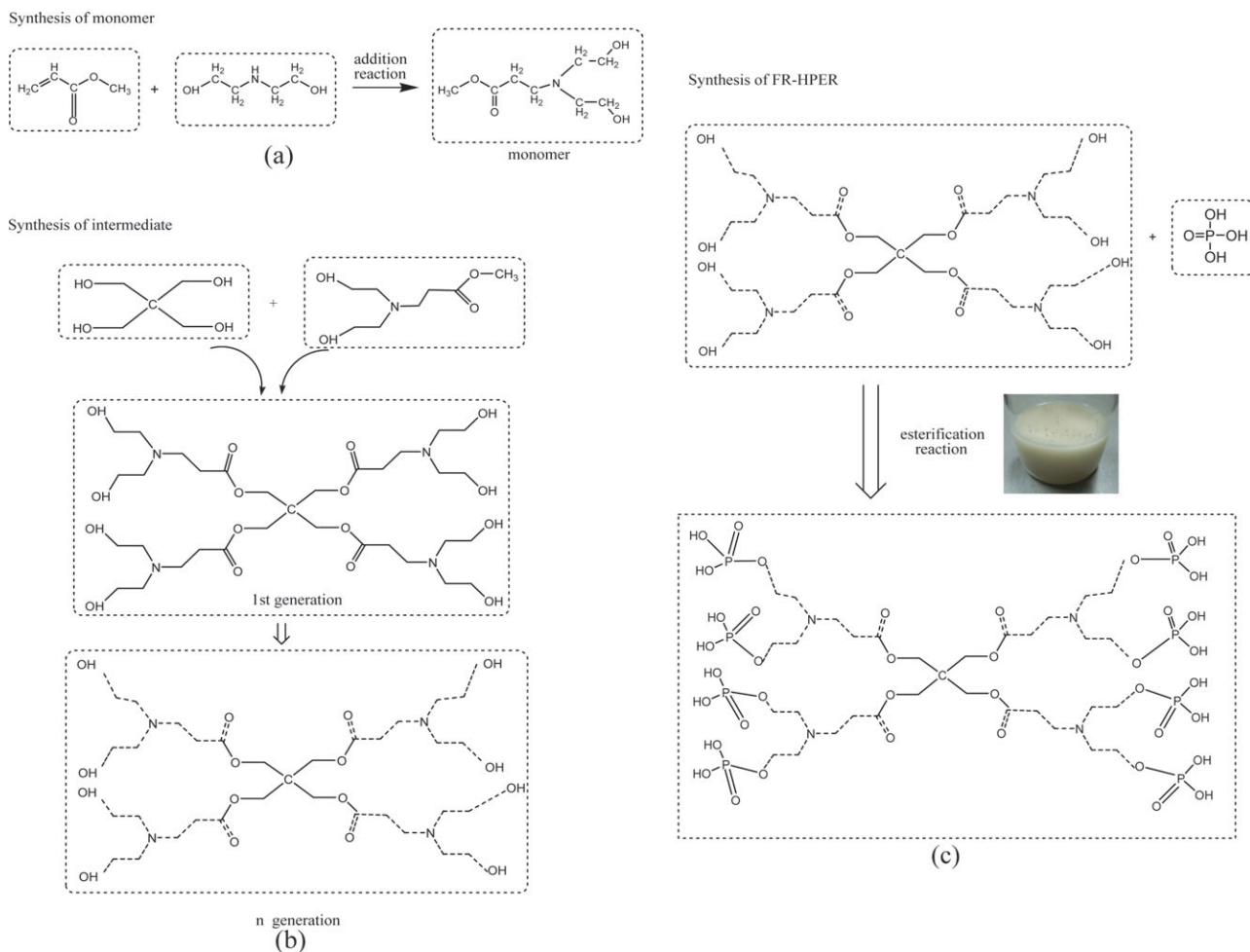
Scheme 1. Preparation process of (a) monomer, (b) intermediate, and (c) FR-HPER. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phase-transfer agent. It can accelerate dissolution of the two reactants and improve their reaction rate.

The transesterification reaction between PER and the monomer was illustrated in Scheme 1(b). In the process of reaction, transesterification of —OH groups with —COOCH$_3$ groups occurred yielding small molecules (methanol) which were continuously removed, resulting in decrease of hydroxyl value. This was in good accordance with what Wang et al.[16] depicted in the synthesis of hyperbranched poly(amide-ester) polyol by a melt polycondensation technique. A viscous white liquid was obtained after the esterification reaction occurring between the hydroxyl in the intermediate and phosphate acid [Scheme 1(c)].

Analysis of NR/FR-HPER Composites
Tensile Properties. The tensile strength and elongation at break of pure NR and different NR composites were shown in Figures 5 and 6. When the FR-HPER amount was less than 5 phr, these properties were increased with the increase of FR-HPER amount. The tensile strength and elongation at break of NR/FR-HPER-5 composite was increased from 17.1 to 21.2 MPa, 382.3–947.5%, and 1.24 and 2.48 times that of the pure NR, respectively. When FR-HPER amount was higher than 5 phr,

these properties were decreased, which may be caused by the aggregates of the FR-HPER in the composites.[21] In addition, the tensile strength and elongation at break of NR/FR-HPER-5 were better than that of NR directly added with 5 phr of PER. These may be ascribed to the better compatibility between FR-HPER and NR matrix. Further evidence of dispersion for PER and FR-HPER in the different NR composites was supported by SEM photomicrographs shown in Figure 7. With the addition of 5 phr of PER in NR, the surface was rougher, and voids of various sizes could be seen [Figure 7(a)]. This was probably a consequence of the agglomeration of some PER powders. That was why this composite had inferior tensile properties. However, the fractured surfaces of NR/FR-HPER-5 [Figure 7(b)] owned scattered FR-HPER. The fractured surface showed no voids and no deformed portions, which, in some extent, could confirm the better mechanical properties of this system.[21]

The different characteristics of NR/PER-5 and NR/FR-HPER-5 under tensile strength are depicted in Figure 8. The failure of the two specimens upon tensile strength started with small cracks. If the elastomeric network was capable of dissipating the inputted energy (e.g., by converting into heat), then it can withstand higher stresses. In NR/PER-5, numerous PER were
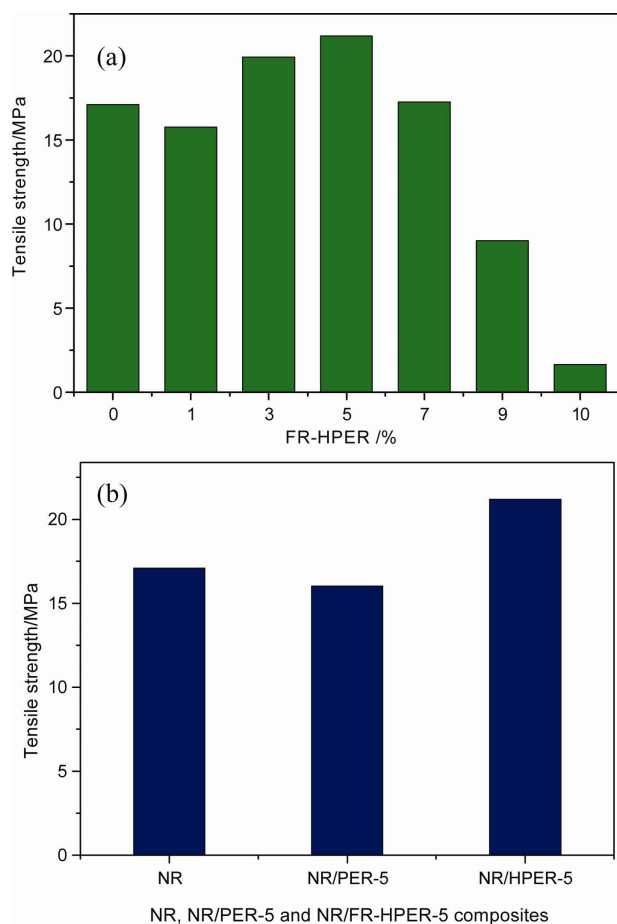
Figure 5. Tensile strength of (a) different NR/FR-HPER composites, (b) NR, NR/PER-5, and NR/FR-HPER-5 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aggregated, and voids (subcritical cracks) appeared during drawing and cracks can be generated via voiding [shown in Figure 8(a)]. While in NR/FR-HPER-5, the hyperbranched polymers can fill the void in the matrix, like various creeks flowing into small valleys. This can improve the cross-linking degree of the NR matrix [Figure 8(b)]. The "anchor" effect between the hyperbranched polymer and molecular chains in NR can restrict the movement of polymer chains, and thus may improve the tensile properties of this composite.[22]

Hardness Test. Figure 9 showed the hardness of pure NR and different NR composites. It can be seen that with the increasing amount of FR-HPER agent, the hardness showed decreased trend. When compared with that of pure NR and NR/PER-5, 47 and 46, the hardness of NR/FR-HPER-5 composite was 32, decreased about 32%. This may be due to the decreased cross-linking density in the FR-HPER filled matrix. However, this may be beneficial for the application of these additives in some fields that need this property.

Wear Resistant Properties. Figure 10 presented the abrasion loss value of various systems with the different fillers. The abrasion loss of NR/PER-5 was 0.19 cm^3, nearly 12% increase, compared with the neat NR system, 0.17 cm^3. However, the system

showed the worse wear resistant property after the addition of FR-HPER. The abrasion loss of the NR/FR-HPER-5 was 0.25 cm^3, 32% increase, compared with that of NR/PER-5 composite.[23] The reason for the decreased wear resistant property of FR-HPER may be resulted from the less cross-linking degree of the hyperbranched polymers.

Generally, wear resistance were thought to affect not only the performance but also the life of rubber products. The abrasion loss of the NR composites changed significantly with the addition of PER and FR-HPER. In this experiment, the abrasion was a kind of micro-cutting caused by the sanding between the grinding wheel of Akron machine and the soft rubber surface. This belonged to the line abrasion mechanism proposed by Burwell.[24] This abrasion process was described in Figure 11. First, as shown in point A in Figure 11(a), crack initiated in the rubber surface when the shearing force produced from friction exceeded the limited shearing strength the rubber can stand. Second, the tongue-like material was produced after the initiation of crack. The tongue-like material showed fatigue failure point in point B, and this was illustrated in Figure 11(b). Third, the tongue-like material ruptured and broke off the rubber matrix during the periodical friction, and thus, the ridge-like
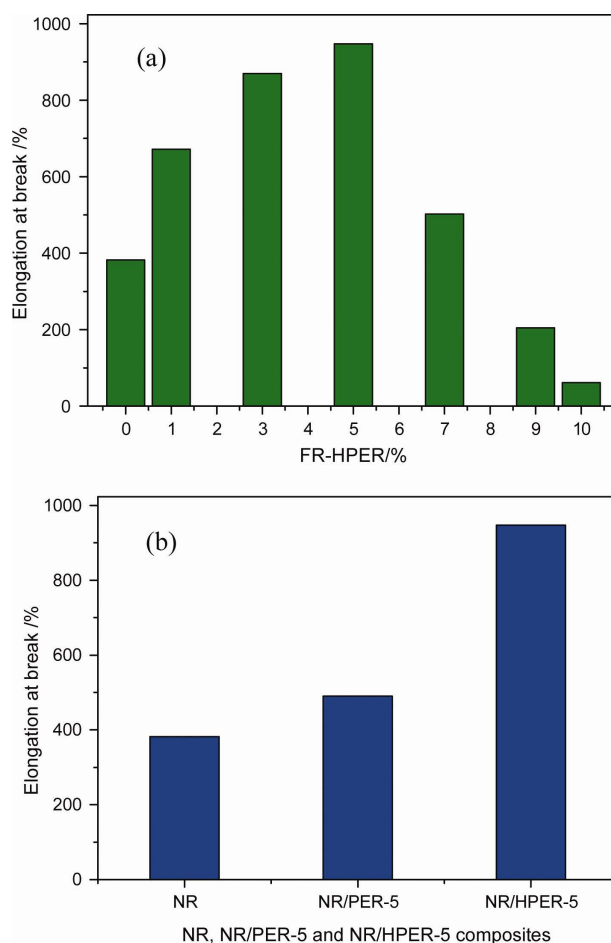
Figure 6. Elongation at break of (a) different NR/FR-HPER composites, (b) NR, NR/PER-5, and NR/FR-HPER-5 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
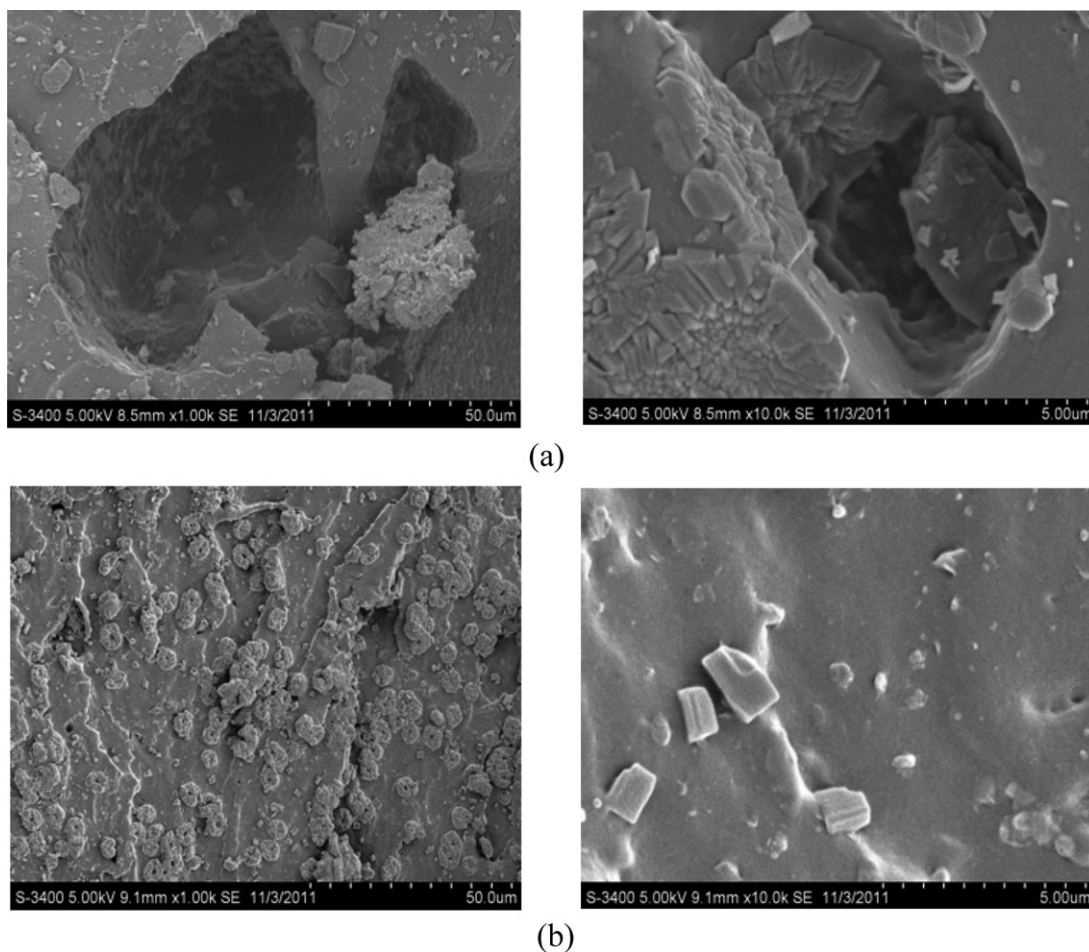
Figure 7. SEM of (a) NR/PER-5 and (b) NR/FR-HPER-5.

morphology developed. This was shown in Figure 11(c). Fukahori and Yamazaki[25,26] researched the factors that influenced the space d [shown in Figure 11(c)] between the ridges in ridge-like surfaces. They reported that during abrasion, two periods existed, that is, self-stimulated abrasion vibration and wee vibration. They thought that the abrasion morphology came from these two periods, space d_1 and d_2. The space d_1 of the wee vibration equaled the ratio of average friction velocity v and the inherent frequency f_0, that is, v/f_0. The space d_2 of the self-stimulated abrasion vibration equaled to the ratio of average abrasion velocity v and its frequency F_0, that is, v/F_0. The improvement of frequency f_0 and F_0 can decrease space d and thus increase the wear resistant properties of the corresponding matrix. A careful examination showed that the space between the ridges in the worn surfaces of NR/PER-5 and NR/FR-HPER-5 systems was different. The space of the ridges of NR/FR-HPER-5 system was relatively larger than that of the NR/PER-5 system. This may lead to the lower wear resistant property of this system.

FR Performance

The horizontal burning time of NR, NR/PER, and NR/FR-HPER systems were shown in Figure 12. The burning time value of pure NR was relatively lower (414.21 s). By adding

1–10 phr of FR-HPER into pure NR, the burning time value was changed. The NR/HPER-5 showed a longer burning time, 504.41 s compared with that of NR/PER-5 composite, 436.71 s. This was probably due to the synergistic effect between PER, the repeat unit of the hyperbranched structure, and phosphate
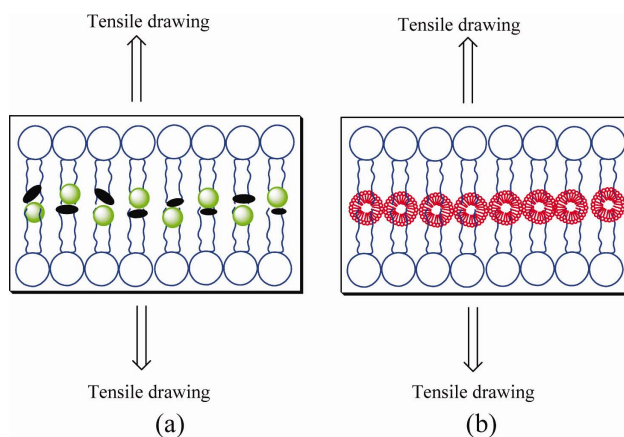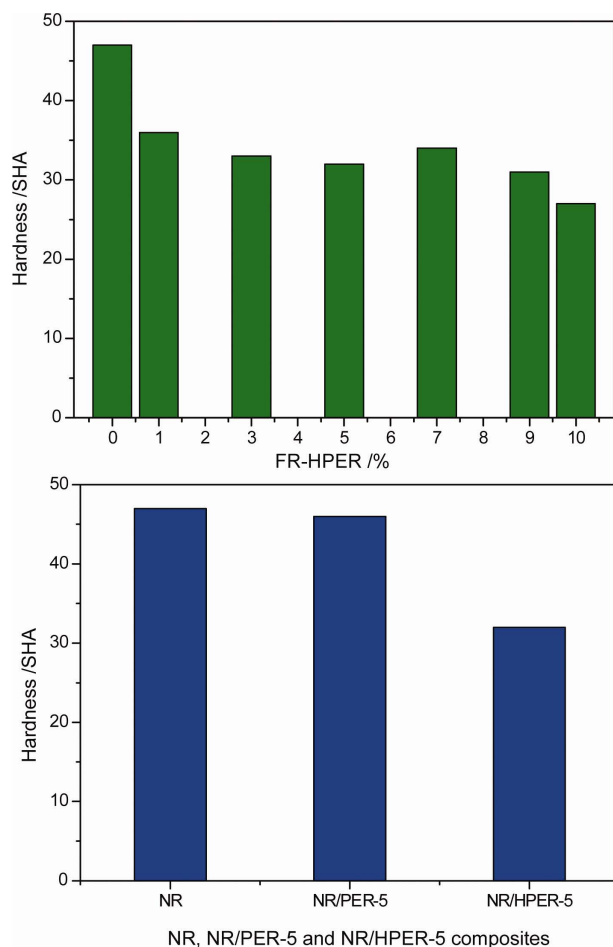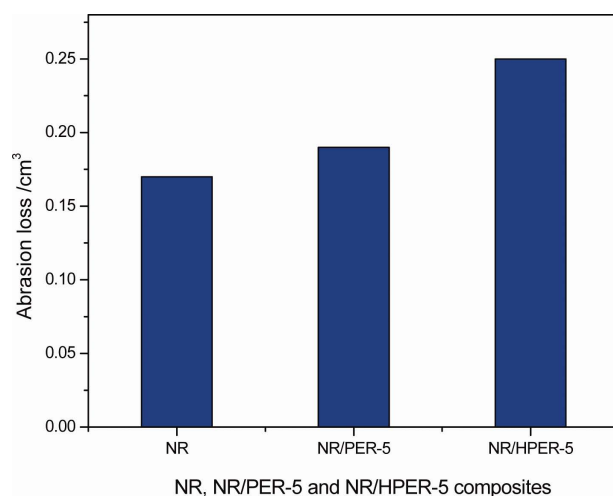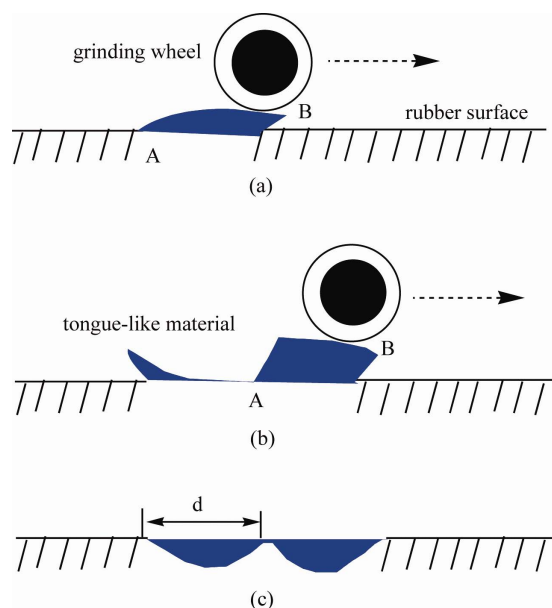

Figure 8. Toughening mechanism of (a) NR/PER-5 and (b) NR/FR-HPER-5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
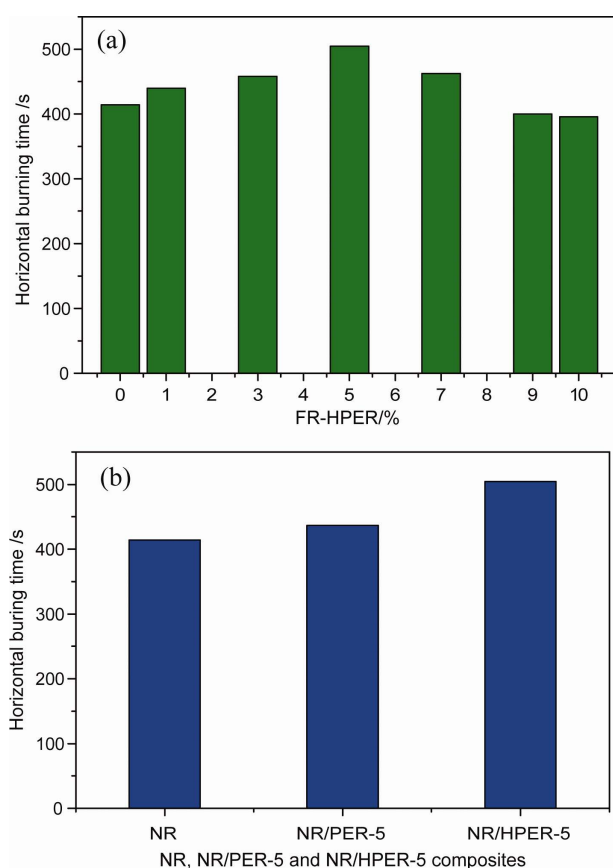
Figure 9. Hardness of (a) different NR/FR-HPER composites as well as (b) NR, NR/PER-5, and NR/FR-HPER-5 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]


Figure 11. Scheme of the process of abrasion pattern (a) crack start, (b) tongue-like material, and (c) ridge-like rubber surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10. Abrasion loss of NR, NR/PER-5, and NR/FR-HPER-5 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 12. Horizontal burning time of (a) different NR/FR-HPER composites as well as (b) NR, NR/PER-5, and NR/FR-HPER-5 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
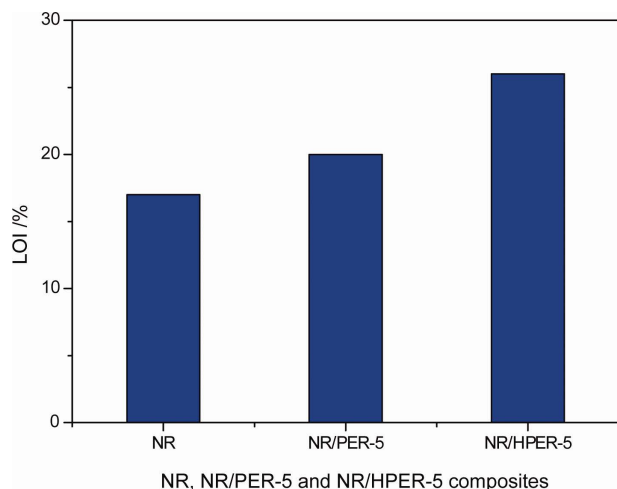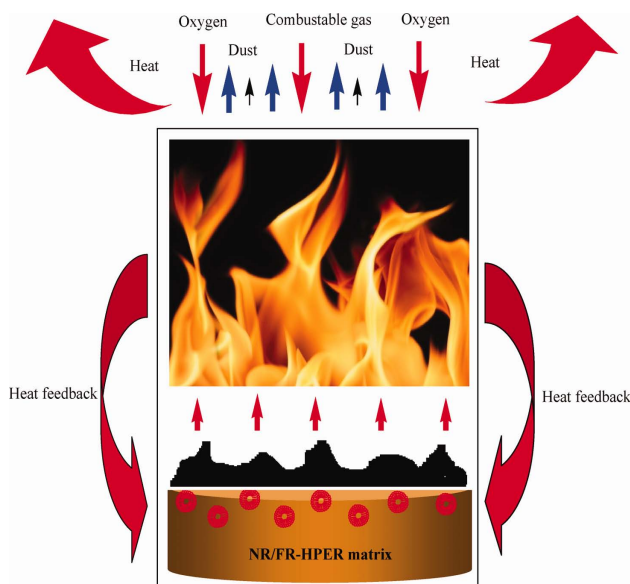
Figure 13. LOI of NR, NR/PER-5, and NR/FR-HPER-5 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 15. TGA of (a) NR, (b) NR/PER-5, and (c) NR/FR-HPER-5 composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
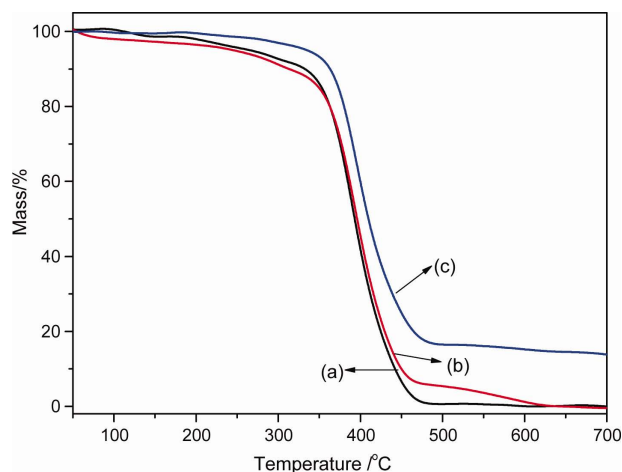
acid. However, with addition of more FR-HPER into NR, these composites showed decreased burning time. This was probably due to the damaged structure and the resulted more holes, which were beneficial for the oxygen to flow into and helpful to the burning behavior of these composites.

The LOI of NR, NR/PER-5, and NR/FR-HPER-5 systems were shown in Figure 13. The LOI value of pure NR was very low (17.0%), which meant that NR was easily flammable. By adding 5 phr of PER into NR, the LOI value was increased to 20.0%. In addition, the LOI value increased to 26.0% with the addition of 5 phr of FR-HPER agent. They showed better fire protection for NR.

Regarding the improvement of FR performance for NR/FR-HPER composites, we may explain, as shown in Figure 14, that

Figure 14. FR mechanism for FR-HPER in NR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the carbonaceous layers that formed during burning had great effect on the fire-retardant properties. In all, the NR system containing FR-HPER may have following FR mechanism and synergistic effect. First, aromatic compounds were developed from the synergistic effect between nitrogen in PER and phosphorus in phosphate acid in the hyperbranched polymer. Second, PER and NR decomposed at high temperatures, and carbonaceous layers were produced from the degradation products of NR and methylene groups in PER. They can act as a physical barrier and prevent combustible gases from feeding the flame, and also separate oxygen from the burning material.[27]

Thermal Stability

The TGA curves of NR composites were shown in Figure 15. To compare their thermal stabilities clearly, three parameters were measured from the TGA curves, that is, the onset temperature of thermal degradation (T_{onset}, the temperature at which weight loss is 5 mass %), 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. The results were summarized in Table II.

Overall, the thermal stability of NR/PER-5 and NR/FR-HPER-5 composites was better than that of pure NR. The T_{onset} and T_{max} of the composites were higher than those of pure NR. At loading of 5 phr of PER, T_{onset} and T_{max} were 250°C and 405°C as well as 20°C and 5°C higher than that of pure NR. This was mainly attributed to the thermal stability of PER. Moreover, significant improvement of T_{onset} and T_{max} was obtained when 5

Table II. TGA Results for the Thermal Degradation of Different NR Composites

	T_{onset} (°C)	T_{max} (°C)	Residual mass (%)
NR	250	400	5
NR/PER-5	270	405	5
NR/FR-HPER-5	350	430	19

phr of FR-HPER was added into NR, that is, T_{onset} and T_{max} was increased about 100°C and 30°C. This was due to the improvement of thermal stability caused by the hyperbranched polymer chains. The well dispersed FR-HPER not only hindered the evaporation of decomposition products but more effectively hindered the access of oxygen to the polymer, reducing the rate of initiation of polymer chain scission to produce volatile small products. The high decomposition temperature indicated the improved thermal stability of the composites.[28]

CONCLUSIONS

Hyperbranched PER was a type of effective liquid for improving the mechanical and FR properties of NR composites. It was demonstrated that the condensation reactions between PER, the monomer, and phosphate acid was beneficial for the improvement of toughening and FR property for NR. Experimental results demonstrated that incorporation of 5 phr of FR-HPER into neat NR system can improve the tensile strength and elongation at break from 17.1 to 21.2 MPa and 382.3 to 947.5%, respectively. However, the abrasion loss of the NR/FR-HPER-5 was 0.25 cm^3, 32% increase, compared with that of the NR directly added with 5 phr of PER. In addition, with the addition of FR-HPER into NR systems, the horizontal burning time was increased, and its thermal stability was also improved.

The mechanism for more toughening, less wear resistance, and improved FR ability for FR-HPER was proposed. Modification of PER powder by hyperbranched polymer can improve the cross-linking degree of the NR matrix, and thus may improve the tensile properties of NR composites. In addition, synergistic FR effect occurred in these novel FR additives, and carbonaceous layers were developed which can inhibit the pyrolysis degree and improve the FR property of NR matrix.

ACKNOWLEDGMENTS

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