Mechanical Properties and Microstructure of Acrylonitrile–Butadiene Rubber Vulcanizates Reinforced by *In Situ* Polymerized Phenolic Resin

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ABSTRACT: The phenolic resin (PF) was incorporated into acrylonitrile–butadiene rubber (NBR) vulcanizates by *in situ* polymerization during the vulcanization process. It was found that the tensile strength, tearing strength, and tensile strength (300% elongation) could be considerably enhanced 59.4, 80.2, and 126.4%, respectively, at an optimum PF content of only 15 phr, but the elongation at break and shore A hardness were only slightly affected on the basis of silica-reinforced NBR vulcanizates. A systematic study of the PF structure formed within the NBR matrix using various experimental schemes and procedures has revealed that the PF resin would form the localized discontinuous three-dimensional interconnected network structures in the NBR matrix. The substantial reinforcement of PF on the mechanical properties of vulcanized NBR were attributed to the morphology, high flexibility, and moderate stiffness of the PF phases and their excellent bonding with rubbers through ''rubber to rubber'' and interface layer. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3851–3857, 2007

Key words: acrylonitrile–butadiene rubber; phenolic resin; vulcanization; reinforcement; networks

INTRODUCTION

The rubber reinforcement by means of hard fillers such as silica and carbon has been used for decades. The filler dispersion status, filler structure, and filler-elastomer interactions are the key factors for the reinforcement.[1–6] The enhanced filler-elastomer interaction has been achieved using various coupling agents.[7] It was also found that the localized rubber phase would contribute in a special way to the reinforcement and viscoelastic property of the elastomers.[8–10] Small and well-dispersed silica has also been generated by *in situ* sol–gel process for rubber strengthening and the results demonstrated that the strengthening effect was depended on using the silane-coupling agent.[11–13] Yuko et al.[12] reported that the dispersion of *in situ* silica particles (15–33 nm) using the tetraethoxysilane as a silica precursor was much more homogeneous than using conventional silica particles and the resulting butadiene rubber was radically improved in mechanical properties. Recently, the modification of polymers with carbon nanofibers[14,15] or nanotubes[16,17] has been paid much attention because of their high aspect ratio and low density. But, the strengthening effect was closely affected by their dispersion status and rubber-filler interactions.

In addition to silica and carbon materials, the soy protein aggregates[18] and modified starch[19] have demonstrated good compatibility with rubber matrix and their reinforcement effects are superior to that of carbon black. Synthetic polymers such as ultrahigh molecular-weight polyethylene and polyaniline could also be used to improve the mechanical properties of various types of rubbers.[20–22] These materials are ideal reinforcement candidates because they have some similar chemical properties to those of rubbers, but much higher stiffness and reasonable flexibility. However, the methods of incorporating this range of materials into elastomers need more scientific studies and the formation of reinforcement constitute *in situ* seems to be a promising route. In this study, the low molecular weight phenolic resin (PF) prepolymer was dispersed in the raw rubber matrix during the mixing process, the thermosetting PF dispersed phases were *in situ* polymerized in acrylonitrile–butadiene rubber (NBR) matrix during vulcanization process, and the influence of PF phases on the mechanical properties of NBR vulcanizates were studied in correlation with microstructure investigations.

EXPERIMENTAL

Materials

The NBR (N41 type, Lanzhou Chemical, China), tetramethyl thiuram disulfide (TMTD), cyclohexyl benzthiazyl sulfenamide (CZ), polymerized 1,2 dihydro

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TABLE I
The Sample Preparation Schemes

Samples	Compositions and conditions	Purpose
Scheme 1	NBR 100, ZnO 5, SA 2, CZ 1.2, RD 1, silica 40, TMTD 0.5, S 1.5 vulcanization condition: 150°C, 15 min	To determine the mechanical properties and microstructures of original NBR vulcanizates.
Scheme 2	NBR 100, ZnO 5, SA 2, CZ 1.2, RD 1, silica 40, TMTD 0.5, S 1.5, with 5, 10, 15 or 25 phr PF additions vulcanization condition:150°C, 15 min	To determine the mechanical properties and microstructure of original NBR vulcanizates with PF modifications.
Scheme 3	NBR 100, ZnO 5, SA 2, CZ 1.2, RD 1, silica 40, with 5, 10, 15 or 25 phr PF additions press molding:150°C, 15 min (nonvulcanization).	To determine the morphologies of PF phase within NBR rubbers.

2,2,4-trimethyl quinoline (RD), and stearic acid (SA) were supplied by ICI, UK. The alkaline PF (molecular weight 3500), sulfur (S), and zinc oxide (ZnO) were obtained from Shanghai Chemical, China.

Rubber-modification processes and characterizations

To study the effects of PF on the mechanical properties of NBR vulcanizates, three experimental schemes have been adopted as shown in Table I. The samples from Scheme 1 were used to determine the properties of NBR vulcanizates before using PF modification. The samples obtained from Scheme 2 were used to study the properties and microstructures of PF-reinforced NBR vulcanizates. The samples produced from Scheme 3 were utilized to study the formed PF structure within NBR matrix because the NBR was not vulcanized in this scheme and it could be removed from the NBR/PF composites, leaving the polymerized PF for microstructure studies.

Mixtures of NBR and additives were mixed and then sheeted out on a two-roller mill. The compounds were pressured to a 2-mm-thick sheet at 150°C for 15 min. Tensile properties were measured with dumbbell-shape specimens according to ASTM D412. Tear strength was tested according to ASTM D624 using the unnotched 90° angle test piece. Both tensile and tear tests were performed on a universal testing machine (AI-7000M, Taiwan Gaotie Technology, China) at a crosshead speed of 500 mm/min. The impact resilience of the obtain specimens were measured using Laizhou Lab Instrument, China. Shore A hardness was determined using a handheld Shore A Durometer according to ASTM D2240. All tests were carried out at 23°C.

For microstructure investigations of the vulcanizates, three experimental procedures have been adopted. In procedure 1, the NBR rubbers with or without PF modification were put into 20 wt % NaOH solution at room temperature; two weeks later, the samples were washed using deionized water and then dried at room temperature, followed by immersing into liquid nitrogen. After several seconds of freezing, the samples were fractured into pieces. The fracture surfaces were observed to determine the possibility of interconnection of PF phase within the NBR matrix. In procedure 2, the NBR vulcanizates with or without PF modification were fractured into pieces after freezing in liquid nitrogen. Then, the fractured samples were put into a 20 wt % NaOH solution for 2 weeks. The observations of fracture surface were carried out to determine the PF phase distribution within NBR matrix. In procedure 3, the nonvulcanized rubbers with PF addition were etched first with acetone at room temperature for 2 weeks to dissolve the NBR matrix in composites adequately. The remnant substance were further etched with 20 wt % NaOH solution for 2 weeks to dissolve the PF resin completely; last, the existence of indiscerptible remnant can determine the reaction between PF and NBR. For all samples subjected to field-emission scanning electron microscopy (FE-SEM, 6700F, Jeol, Japan) or atomic force microscopy, (AFM, 4410 Liestal, Nanosurf Scan Easy, Swiss) observations were washed by deionzed water.

RESULTS AND DISCUSSION

The modification of elastomers using hard filler was aimed to increase the mechanical strength of the materials. However, with increasing the filler content, the mechanical strength increases generally, however, the elongation at break would be also reduced accordingly.

Hence, there exists an optimum addition level of the filler, which provides a better strength as well as acceptable elongation at break. In practical, the silica was added at a mass content of 40 phr. Further increase of the hard filler-reinforced rubber properties without lowering elongation is a technical challenge in this field. In this work, a low molecular weight prepolymer PF was polymerized *in situ* in the NBR matrix to strengthen its mechanical properties. It was found that the *in situ* formed PF could significantly enhance the silica-reinforced NBR
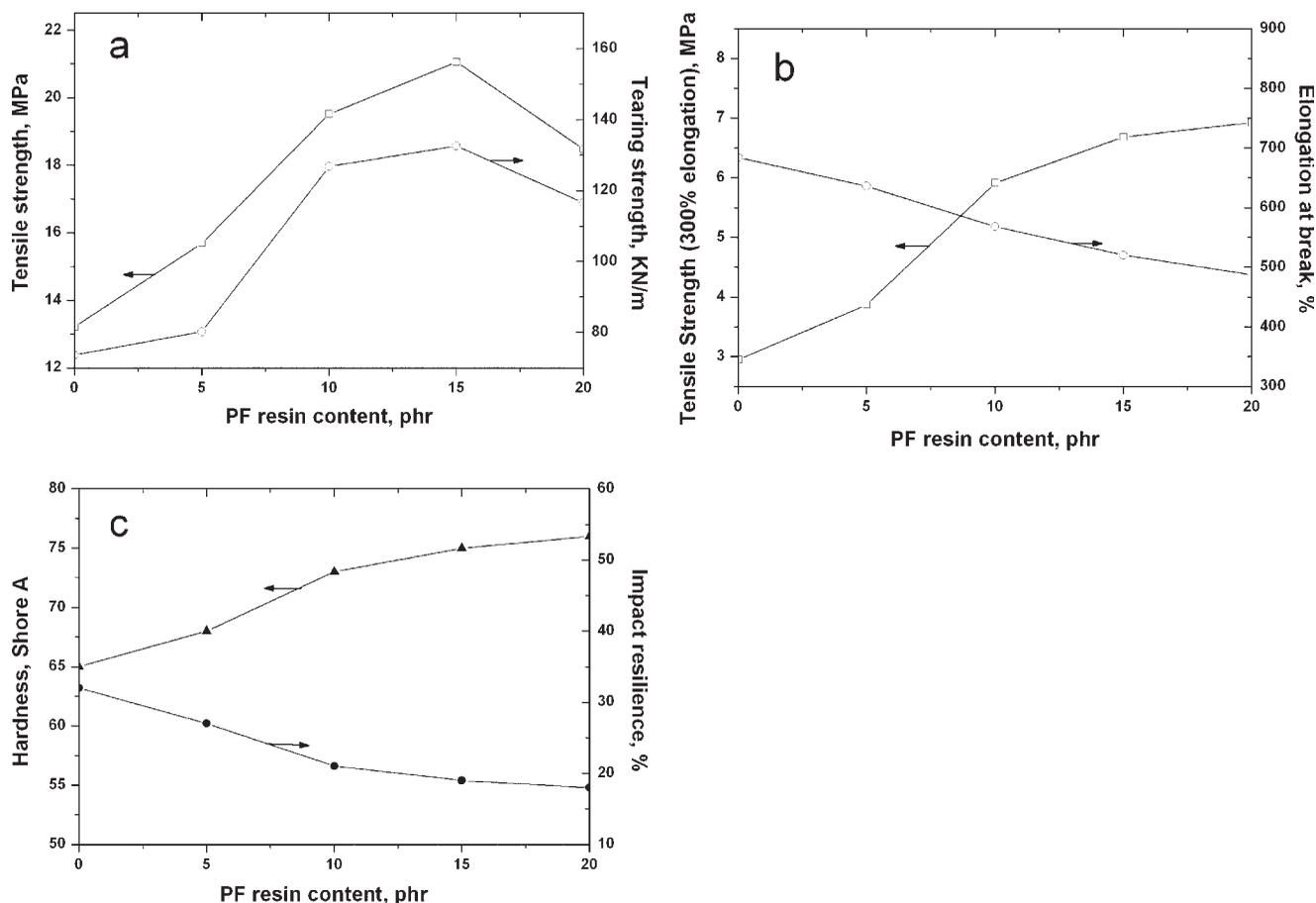
Figure 1 The mechanical properties of the NBR vulcanizates as a function of PF contents. (a) Tensile strength and tearing strength; (b) Tensile strength (300% elongation) and elongation at break; (c) Surface hardness and impact resilience.

vulcanizates as shown in Figure 1. Both tensile and tearing strength increased almost linearly with increasing PF content until 15 phr, followed by slight decline thereafter. Other properties such as shore hardness, elongation at break, and impact resilience gradually deteriorated with increasing PF content, but they were still in the accepted ranges for most applications. At the optimum PF addition of 15 phr, the tensile strength, tear strength, tensile strength (300% elongation), and shore hardness were increased about 59.4, 80.2, 126.4, and 13.3%, respectively, while the elongation at break and impact resilience were decreased about 23.9 and 40.6%, respectively. This improvement was significant because it was based on the silica-reinforced NBR rather than on unreinforced one. The present investigation results have clearly demonstrated the feasible approach for further increasing the strength of the silica-reinforced NBR vulcanizates with limited worsening of other properties.

The exceptional reinforcement behavior of PF on NBR vulcanizates was further studied by microstructure analyses. FE-SEM observation results of the fracture surfaces of NBR vulcanizates with or with-

out PF modification after etching with NaOH solution (samples from procedure 1) were shown in Figure 2. It can be seen from this figure that the vulcanized NBR without PF modification displayed a smooth fracture surface with no pore found [Fig. 2(a)] and the well-dispersed fine silica particles could be easily identified in the NBR vulcanizates matrix [Fig. 2(b)]. On contrary, the NBR with PF addition revealed many small pores [Fig. 2(c)] on the surface indicating that the solvent has penetrated into the internal structure of NBR rubber through the channel of removed PF phase. The internal surface of the pores was very rough [Fig. 2(d)], and hence to provide a good mechanical bonding between the PF phase and rubber matrix. AFM observation of the surface of PF-reinforced NBR vulcanizates exhibited that the PF phase on the vulcanizate surface layer has been removed leaving the needle-like NBR phase, as shown in Figure 3. This investigation result may suggest that the PF phase within the NBR matrix is not continuous and has limited interconnection.

To study further the structure and distribution of the PF phase within the NBR rubbers, the etched
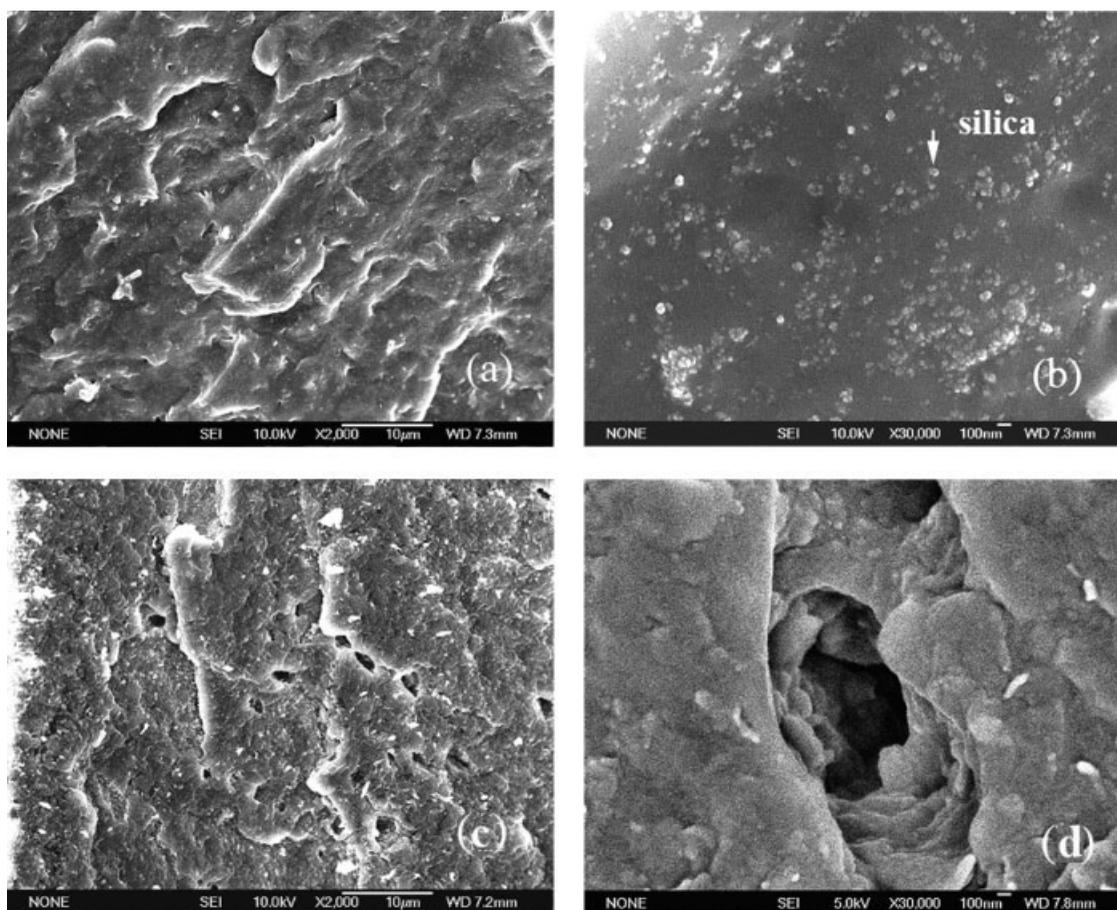
Figure 2 The fracture surface of NBR vulcanizate without PF modification (a,b) and with PF modification (c,d) after etching by NaOH solution (20%) for PF removal.

fracture surfaces (samples from procedure 2) were observed by FE-SEM. Figure 4(a) shows that without PF modification, the surface was still very smooth, similar to that shown in Figure 2(b), because there was no dissolvable phase within the matrix. In contrast, many homogenously distributed cracks, some of which were interconnected, were found on the surface of NBR vulcanizate with PF modification [Fig. 4(b)]. These cracks were attributed to the removed PF phases that should exist in a three-dimensional network structure rather than one-dimensional structure (linear shape). The formation of this network structure was further confirmed by direct observation of the isolated PF phase obtained by removing NBR nonvulcanizates from NBR/PF composites (samples from procedure 3) as shown in Figure 5(a,b). The PF phase was in the form of small or big three-dimensional interconnected structures (from about 10 to over 100 μm) consistent to the surface morphology observed in Figure 5(a). The network structures were formed locally and discontinuously, but with very limited contact points among them. Otherwise, the rubber will become rigid without any resilience.

The formed PF phase as shown in Figure 5(a) was further etched with NaOH solution (20%) to remove the PF phase to determine if there were chemical
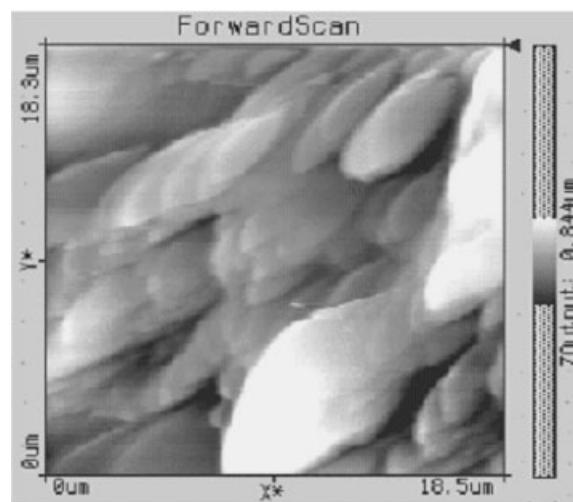

Figure 3 The AFM image of the surface of NBR vulcanizate modified with 15 phr PF after etching by NaOH solution (20%).
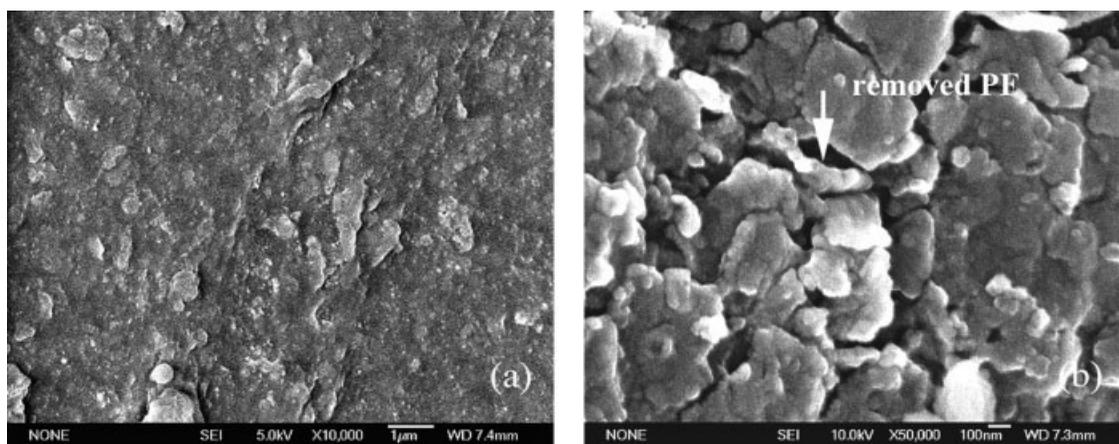
Figure 4 The etched fracture surfaces of vulcanized rubbers with or without PF modifications. (a) Without PF modification, (b) with PF modification.

interactions between the rubber phase and PF. It was found that there were residual substances left in the solution and their surface revealed irregular crevices attributed to the removed PF as shown in Figure 5(c). Because this substance could not be dissolved by NaOH solution or acetone, it should be the reaction product between PF and NBR, which

could provide a good bonding media or interface between PF and NBR.

The present works have clearly demonstrated that the *in situ* polymerized PF is very effective for strengthening NBR vulcanizates. It should be noted that the property enhancement was based on the silica-reinforced vulcanizates, and therefore, this
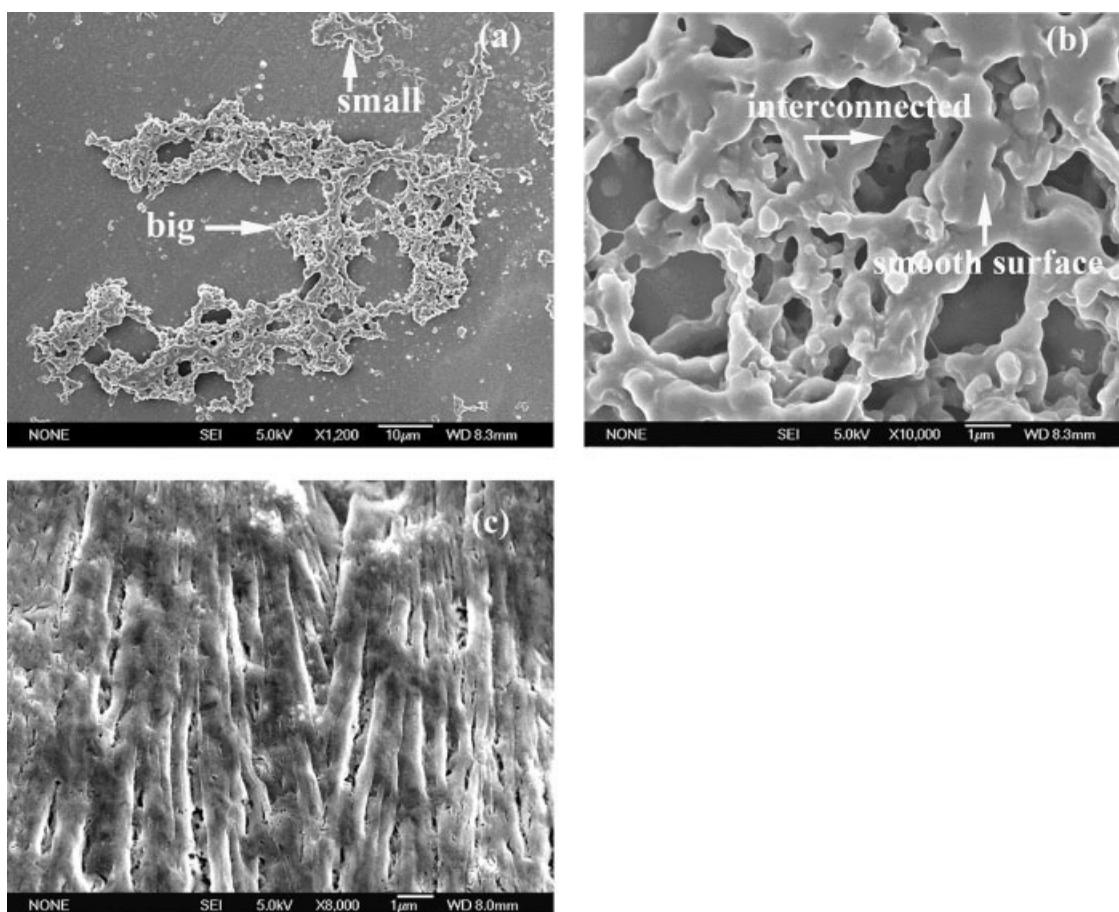

Figure 5 The structures and morphologies of formed PF phase (a,b) and residual phase (nondissolvable phase) (c).
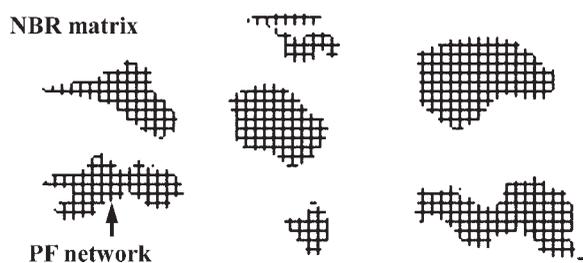
Figure 6 The schematic show of the cross section view of PF three-dimensional interconnected network in NBR rubber matrix.

investigation results have practical meanings in this field. The strengthening mechanism, however, was complicated and could not be fully explained from this work. Traditionally, it was widely accepted that the increase of strength imparted by active filler might be regarded as the product of two terms. One involves a hydrodynamic effect arising from the inclusion of rigid particles such as widely used silica and carbon black. The second term involves an increase in the crosslinking density created by polymer-filler interactions that depend strongly on the coupling effect between particle and rubber.[23,24] Nevertheless, these classical theories ignore the important role of the filler polymer interactions as a result of the aggregation of filler particles to large clusters and their associated huge surfaces and the deformation of filler materials.[7] Apparently, the above-mentioned theories are not applicable to the present studies because in this study, the strengthening component could not be deemed as either hard particle or fiber. In our research, the PF prepolymer was dispersed in the NBR matrix during the mixing process and then polymerized into thermosetting materials during the course of vulcanization process. The PF-reinforcing agent formed *in situ* is in the form of three-dimensional network structures and there is rubber filled within this structure making it extremely difficult to quantify its strengthening effect theoretically.

In addition, PF either in fabric or three-dimensional structure has much higher flexibility and allow a higher degree of elastic deformation under stress than other inorganic materials such as carbon or silica. This would resolve the drawbacks of hard fillers that could cause significant brittleness, low elongation at break, and poor impact resilience when their contents exceed a critical level. The density of silica is 2.65 g cm^{-3}, while PF has a density of about 1.1 g cm^{-3}. Therefore, for the NBR modified with 15 phr of PF, the volume of PF (about 13 cm^3/100 g of NBR) within rubber matrix almost equals to that of 40 phr of silica (about 15 cm^3/100 g of NBR). Hence, without the advantageous mechanical property of PF, the NBR vulcanizates modified with

about 15 phr of PF would reveal a considerable brittle nature and significantly reduced elongation. Additionally, the NBR vulcanizates was filled in the three-dimensional structure forming a localized strengthened "cluster" with excellent bonding to rubber matrix through "rubber to rubber" interaction and interface layer rather than rubber to surface coupling groups, as schematically shown in Figure 6. Under stress, the localized strengthened "clusters" could be deformed relatively easier and absorb more energy during the deformation process without reinforcing agent slipping as for the case of silica or carbon fillers. Consequently, the tensile strength and tearing strength of NBR vulcanizates were significantly improved with increasing PF content as shown in Figure 1(a), while the elongation at break and impact resilience decreased accordingly. Nevertheless, when the PF content is too high, 20 phr, the rigid nature of PF will be significant leading to a decreased mechanical strength, further reduced elongation, and resilience.

CONCLUSIONS

The *in situ* polymerized PF could significantly enhance the mechanical properties of NBR rubbers reinforced by silica. At the optimum PF content of 15 phr, the tensile strength, tearing strength, and tensile strength (300% elongation) were increased about 59.4, 80.2, and 126.4%, while the properties of elongation at break, shore A hardness only slightly deteriorated. Using various experimental methods, the PF was determined in the form of localized discontinuous three-dimensional interconnected network structure. The strengthening effects were attributed to the unique structure of formed PF, the mechanical properties of PF, and strong reinforcing agent-rubber bonding through the mechanism of "rubber to rubber" and interface layer. This study has demonstrated the practical route to reinforce carbon- or silica-filled NBR rubber vulcanizates further without significant scarification of other properties.

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