

# *In-Situ* Polymerized Phenolic Resin for Reinforcement of Chloroprene and Ethylene–Propylene Rubber Vulcanizates

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**ABSTRACT:** Phenolic resin (PF) was incorporated into rubbers by *in situ* polymerization at the vulcanization conditions of rubbers. The PF with a localized three-dimensional network structure was formed in chloroprene rubber (CR), whereas the fabric PF was formed in ethylene–propylene rubber (EPDM). The study results showed that the PF phase was effective on reinforcing these rubbers. Depending on the morphologies of the formed PF phases, various rubber properties could be significantly enhanced. In the case of CR rubber, the tensile strength, tear strength, and modulus could be considerably enhanced, but the elonga-

tion and resilience properties were limitedly affected by PF addition. For EPDM rubber, all mechanical properties were improved, particularly the elongation, about 26% increase. The substantial improvements of mechanical properties of CR and EPDM rubbers were attributed to their morphology, high flexibility, moderate stiffness, and excellent bonding with rubber matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1177–1184, 2009

**Key words:** chloroprene rubber; ethylene–propylene rubber; phenolic resin; reinforcement

## INTRODUCTION

The incorporation of small particle size fillers to crosslinked elastomer matrix results in substantially improved mechanical properties.<sup>1,2</sup> The efficiency of fillers in polymer composites is known to strongly depend on the aspect ratio of the fillers and on their size.<sup>3–6</sup> 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<sup>7–9</sup> that could improve the rubber–filler interaction and better filler dispersion.<sup>10,11</sup> The localized rubber phase would contribute in a special way to the reinforcement and viscoelastic property of the elastomers<sup>12–14</sup> due to the formation of covalent bounds between rubber and fillers.<sup>11,15</sup> Recently, modification of polymers with carbon nanofibers<sup>16,17</sup> or nanotubes<sup>18,19</sup> has been paid much attention because of their high aspect ratio and low density.

Natural fillers such as the soy protein aggregates<sup>20</sup> and modified starch<sup>21</sup> have been studied to replace carbon black for strengthening of styrene butadiene

rubber (SBR). The results showed that the natural fillers have good compatibility with rubber matrix and their reinforcement effect is superior to that of carbon black. Synthetic polymers ultra-high molecular-weight polyethylene (UHMWPE) and polyaniline have also been studied to improve the mechanical properties of various types of rubbers.<sup>22–24</sup> These materials have some similar chemical properties to those of rubbers, but much higher stiffness and hardness and reasonable flexibility and they are ideal reinforcement candidates for elastomers. However, the method of incorporating this range of materials into elastomers needs more scientific studies. The formation of reinforcement constitute *in situ* seems to be a promising route. In our previous studies, we have studied the reinforcement effects of polymerized phenolic resin on the acrylonitrile-butadiene rubber vulcanizates.<sup>25</sup> In this study, two types of rubbers were modified using low molecular weight polymer, PF formed *in situ* and its effects on rubber mechanical properties were studied in correlation with microstructure investigations.

## EXPERIMENTAL MATERIALS AND METHODS

### Materials

Chloroprene rubber (CR) (Chongqing Chemical, China), ethylene–propylene (EPDM) rubber (EP-33,

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**TABLE I**  
**The Rubber Compositions and Vulcanization Conditions**

Rubber types	Rubber compositions (phr)	Vulcanization
EPDM	EPDM 100, ZnO 5, SA 1, M 0.5, carbon black 40, cyclohexane 35, Olefin 0.5, TMTD 1.5, S 1.5	160°C, 20 min
CR	CR 100, ZnO 5, MgO 4, SA 0.5	150°C, 20 min

Japan Synthetic Rubber, Japan) and carbon black (30 nm, Qingdao Rhone-poulenc, China) were used as received. The chemicals tetramethyl thiuram disulfide (TMTD), 2-mercaptobenzthiazole (M), and stearic acid (SA) were supplied by ICI UK. Phenolic resin (PF) (molecular weight 3500), sulfur (S), zinc oxide (ZnO), and aluminum hydroxide (Al(OH)<sub>3</sub>), olefin, naphthene, toluene, acetone, cyclohexane were obtained from Shanghai Chemical, China.

#### Rubber modification process and characterization

To study the effects of low molecular weight polymer (LMWP) phenolic resin (PF) on the properties of different rubbers, the experimental procedure has been carefully designed and three groups of samples have been prepared. For the first group of samples, the rubbers without addition of PF were mixed using a laboratory-size internal mixer at 50°C for 15 min (Shanghai Rubber Machinery, China) followed by vulcanization (flat plate, Shanghai Rubber Machinery, China) according to the compositions and conditions shown in Table I. This group of samples was used to determine the rubber properties before modifications. For the second group of samples, the rubbers with addition of phenolic resin were vulcanized according to the same conditions described in Table I. For the third group of samples, the rubbers and resins were mixed together without sulfur addition followed by hot pressing under the vulcanization conditions. Therefore, the resins were cross-linked leaving the rubber without vulcanization and the nonvulcanized rubbers could be removed from the rubber matrix to obtain the polymerized PF for microstructure studies.

For the purpose of studying the morphologies of PF within rubbers, the PF must be removed or isolated from the rubbers. The EPDM and CR rubbers mixed with resins, but without vulcanizations, were immersed into acetone, toluene, acetone/cyclohexane, respectively, for two weeks to remove the rubber phase to determine the morphologies of PF phases within the rubbers by using scanning electron microscopy (Jeol-6700F, Jeol, Japan). For fracture surface observation, the rubber specimens were fractured immediately after embrittled in liquid nitrogen. Before the microstructure study, all sam-

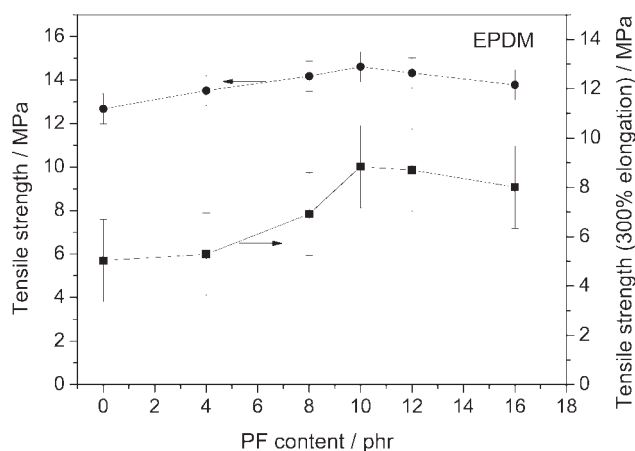
ples were washed by deionized water followed by drying in an oven at 40°C. For EPDM rubber, the rubber thermal degradation was carried out at 70°C for 48 h. The chemical resistances to alkali and acidic media were tested by contacting the rubbers with NaOH (20%) and H<sub>2</sub>SO<sub>4</sub> (30%) solutions for 24 h separately at room temperature. The degradation of properties was evaluated by comparing the mechanical properties before and after treatments. The oxygen indexes of the CR rubbers modified by PF (10 phr) and/or Al(OH)<sub>3</sub> (30 phr) were measured by using the oxygen indexer (XYZ-450, Changchun Xinke Instrument, China).

The rubbers were also punched into standard Dumbbell samples (75 × 4 × 2 mm<sup>3</sup>) for mechanical property testing using a universal testing machine (AI-7000M, Taiwan Gaotie Technology, China) at a crosshead speed of 500 mm/min. The resilience (Lupke Rebound) and shore hardness (Laizhou Lab Instrument, China) were also measured for both modified and nonmodified rubbers.

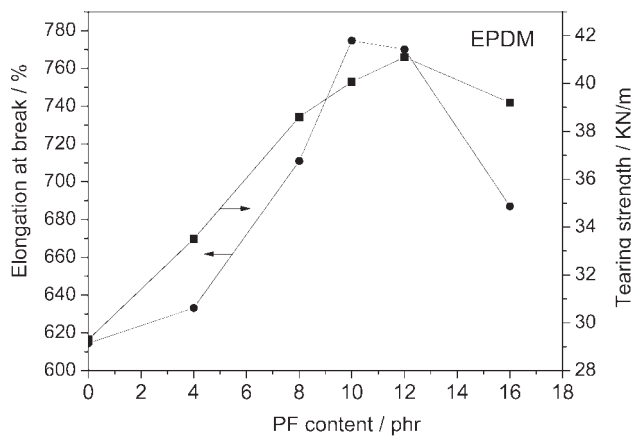
## RESULTS AND DISCUSSIONS

### The mechanical properties and microstructures of EPDM modified with PF

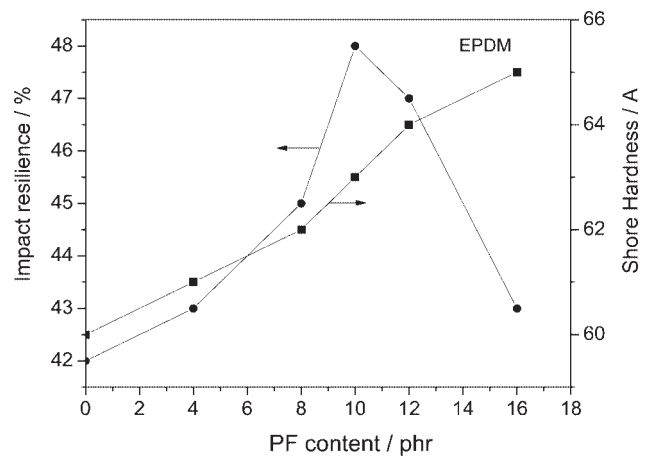
Different mechanical properties of the EPDM rubber modified with various contents of PF are shown in Figures 1–3. Both the tensile strength and tensile strength at 300% elongation increased with increasing PF content until 10 phr followed by a decrease. The maximum of elongation at break occurred at a PF content of 10 phr, whereas the tearing strength was the highest at a PF content of about 12 phr. The impact resilience increased also with PF content until about PF content of 10 phr followed a decrease. The shore hardness increase almost linearly with PF content as expected. At the optimal PF content,



**Figure 1** The changes of the tensile strengths as a function of PF content in EPDM rubber.



**Figure 2** The changes of the elongation at break and tearing strength as a function of PF content in EPDM rubber.

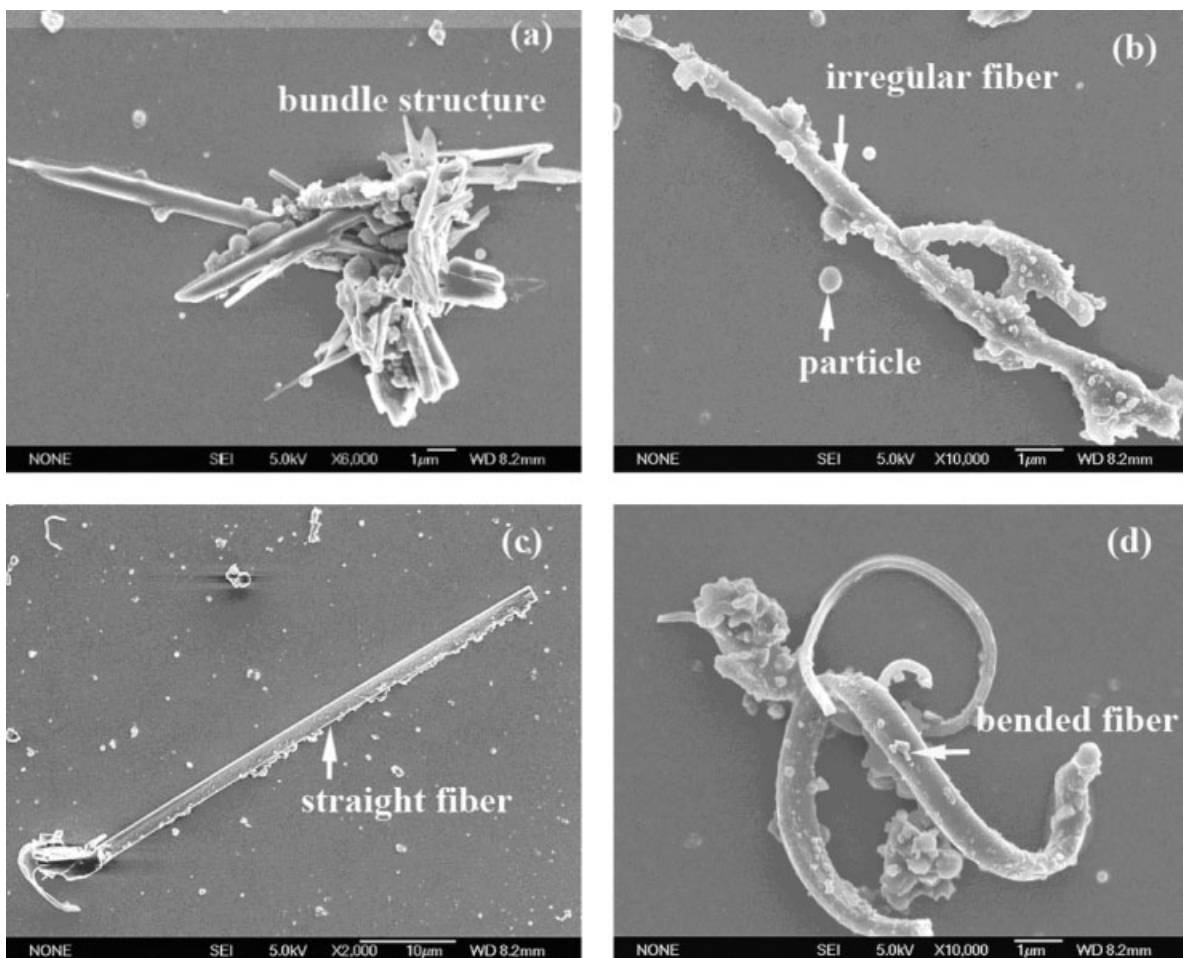


**Figure 3** The changes of the impact resilience and shore hardness as a function of PF content in EPDM rubber.

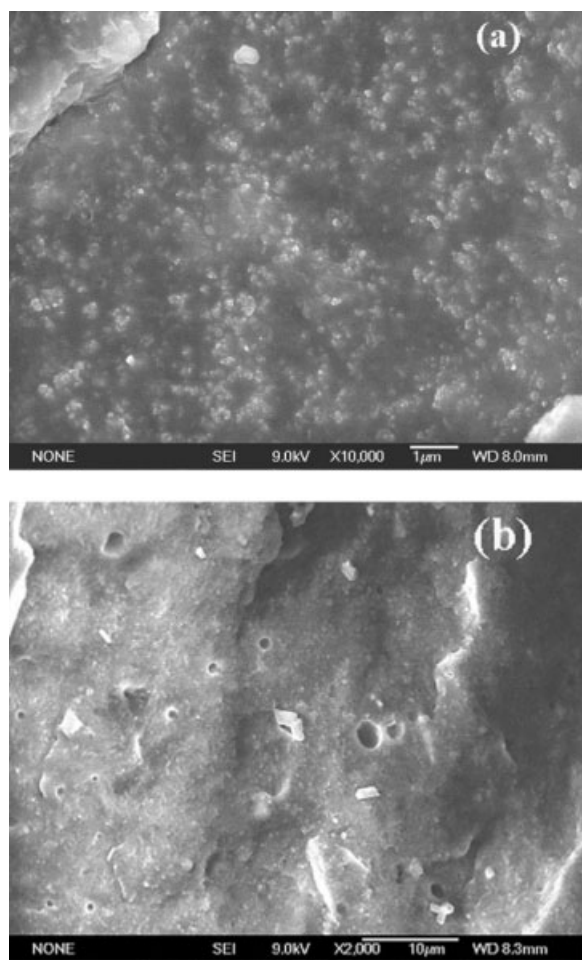
10 phr, the tensile strength, tear strength, modulus, and elongation were significantly increased about 15, 37, 76, and 26%, respectively.

The PF phase within EPDM was obtained by removing the EPDM phase using toluene solvent

and its morphologies were shown in Figure 4. It can be seen from this figure that the polymerized PF phases were mostly in the forms of bundle structure [Fig. 4(a)], irregular fiber and particle [Fig. 4(b)], straight fiber [Fig. 4(c)], and bended fiber [Fig. 4(d)].



**Figure 4** The morphologies and structures of PF formed in EPDM rubber. (a) Bundle structure, (b) irregular fiber, (c) straight fiber, and (d) bended fiber.



**Figure 5** The fracture surface of EPDM vulcanizate without PF modification (a) and with PF modification (b) after etching by NaOH solution (20%) for PF removal.

The diameter of the fibers was in the range of 0.5–1  $\mu\text{m}$  with the aspect ratios of about 30. The fracture surfaces of EPDM vulcanizates with or without PF modifications after removing the PF phases were shown in Figure 5. Clearly, the fracture surface of EPDM without addition of PF was very smooth [Fig. 5(a)]. There were holes within the EPDM-modified PF phase due to the removal of PF phase.

The PF has a higher strength than that of rubber, therefore, the formed PF short fibers within the rub-

ber matrix could behave as the strengthening materials, and the mechanical properties of EPDM were significantly enhanced as shown in Table III. The resilient property and elongation were simultaneously increased rather than decreased. This was attributed to the higher strength and toughness of the formed PF fiber and the molecules of PF and EPDM could be partially in a miscible state at the boundary. The increased strain at break could be due to the adequately loose chain entanglements between PF and EPDM molecules.<sup>22,24</sup> Therefore, under external stress, the short fibers were elastically deformed and returned to original shape after stress release. As a result the resilient property and elongation were enhanced. It was also noticed that the obtained rubber surface finish was excellent. This investigation has demonstrated that the modification using PF could be a plausible route for EPDM property enhancement.

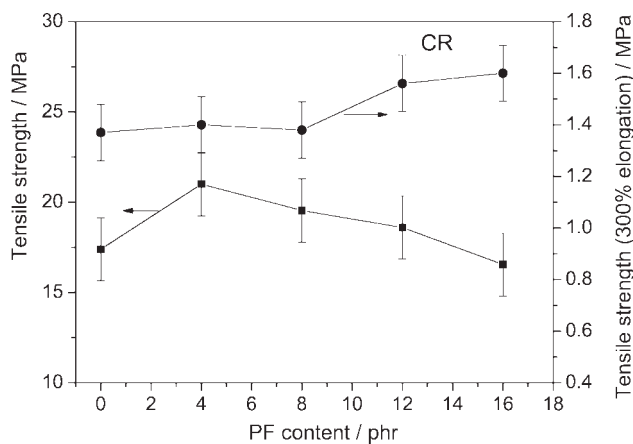
Because EPDM is mainly used in the harsh conditions such as acidic, alkaline, and hot environments, its property stability will be significant for the material application. Table II shows that the variations in properties after degradation in these environments for EPDM with or without PF modification were very limited demonstrating that the modification with PF had no significant effect on the degradation behaviors of EPDM.

#### The mechanical properties and microstructures of CR modified with PF

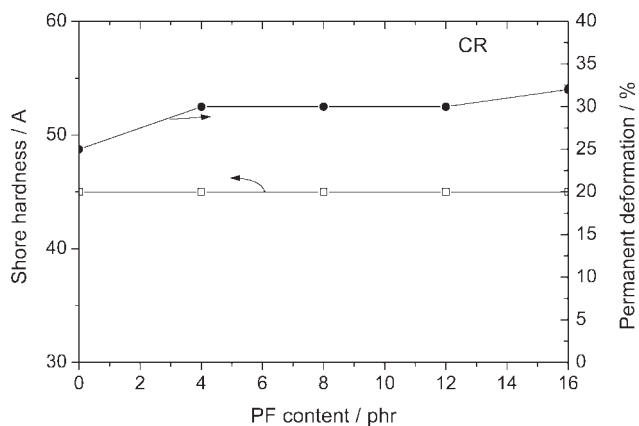
The effects of PF on the mechanical properties of crystalline CR are shown in Figures 6–8. The tensile strength was significantly increased by 23% with 4 phr of PF addition, while it was decreased with further PF increase (Fig. 6). Interestingly, the tensile strength at 300% elongation was limitedly affected when PF content was below 8 phr, whereas it was dramatically increased with further PF addition (Fig. 6). The elongation at break increased almost linearly with PF content until 8 phr followed by a decrease. The tearing strength, however, increased with PF content until 12 phr followed by a decrease (Fig. 7).

**TABLE II**  
The Degradation of Properties of EPDM Modified with 10 phr PF in Acidic, Alkaline and Hot Environments (The PF content was 10 phr)

Rubber compositions	Tensile strength (MPa)/variation (%)	Modulus (300%), (MPa)/variation (%)	Elongation (%) / variation (%)	Degradation environments
EPDM	13.54/6.8	4.96/−1.4	653.93/6.4	Acidic, 24 h
EPDM+PF	15.23/4.2	8.84/0.0	774.65/0.0	
EPDM	12.95/2.1	5.02/−0.2	625.06/1.7	Alkaline, 24 h
EPDM+PF	15.28/4.6	8.74/−1.1	778.08/0.4	
EPDM	13.0/2.5	5.22/3.8	611.76/−0.4	Hot air, 48 h
EPDM+PF	15.15/3.7	9.22/4.3	737.02/−4.9	



**Figure 6** The changes of the tensile strength and tensile strength at 300% elongation as a function of PF content in CR rubber.

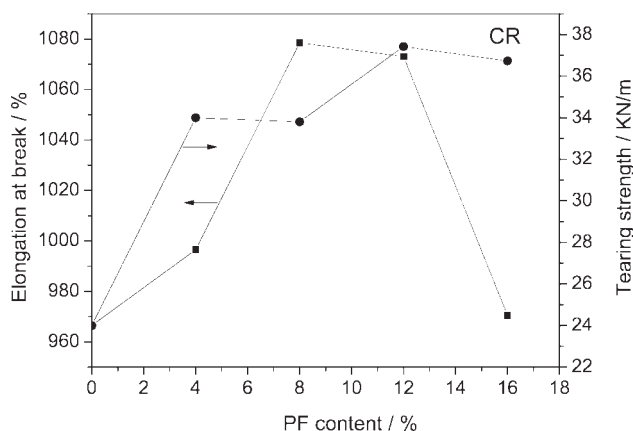


**Figure 8** The changes of the shore hardness and permanent deformation as a function of PF content in CR rubber.

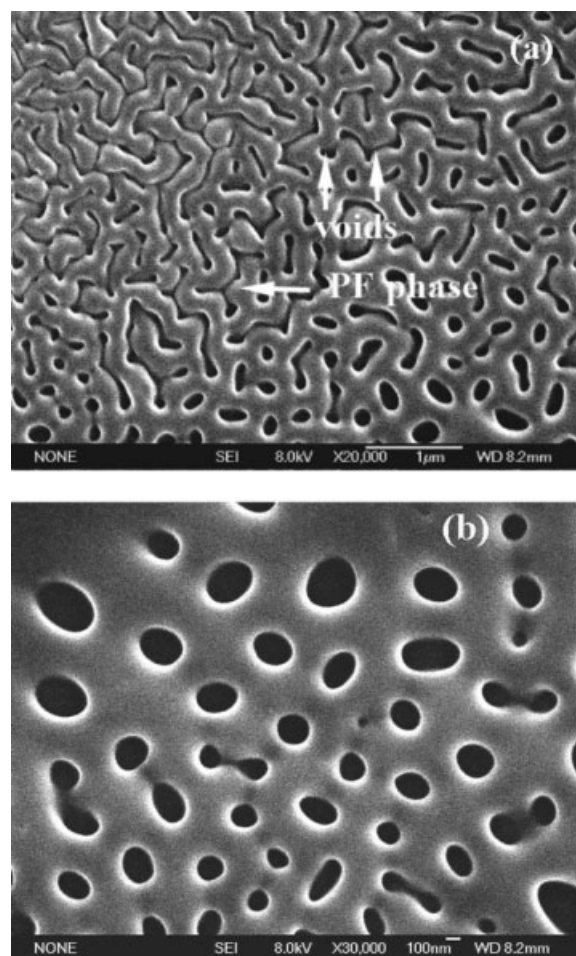
Very interestingly, not like the case for EPDM rubber, the shore hardness was almost unchanged within the PF addition levels studied. The possible reason is that PF phase within CR rubber has a three-dimensional network structure with a larger size (or volume) as confirmed by SEM studies shown in Figure 9, rather than PF short fibers formed within EPDM rubber. Therefore, the PF phase will have less effect on the localized deformation, i.e., hardness. The permanent deformation increased with PF content in CR, as generally expected.

that there was no apparent transitional boundary between CR and PF phases. This PF structure is finer and more homogeneous than that formed in NBR<sup>25</sup> and hence, it could provide stronger strengthening

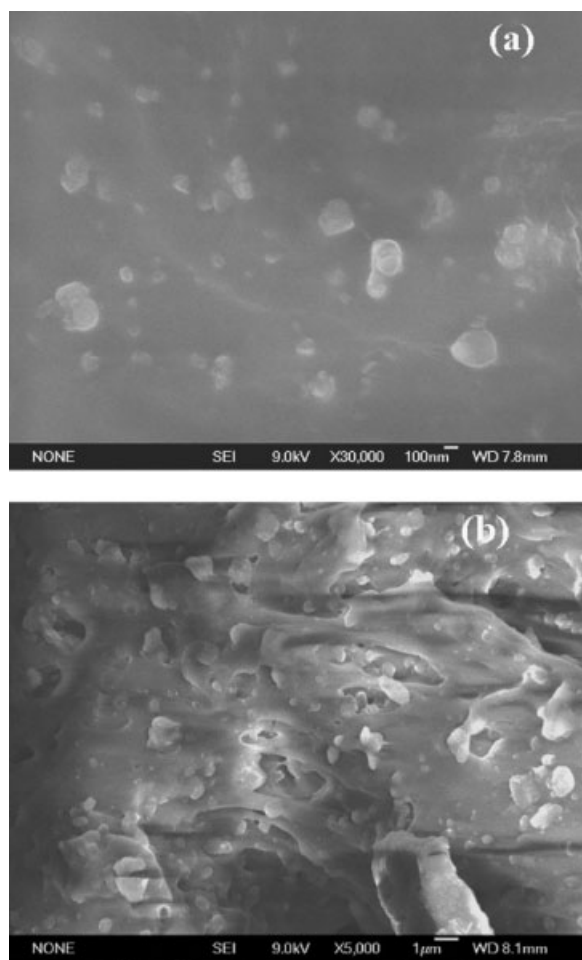
The structure of formed PF phase within CR was studied by hot pressing CR and PF blend at the vulcanization condition without using sulfur. After removing the CR phase, the morphologies and structures of formed PF phases at the vulcanization temperature examined by SEM are shown in Figure 9. It can be seen clearly from Figure 9(a,b) that the PF phase formed a three-dimensional interconnected structure with a strut diameter from 100 to 300 nm. The surface of PF was very smooth and it seems



**Figure 7** The changes of the elongation at break and tearing strength as a function of PF content in CR rubber.



**Figure 9** The morphologies and structures of PF formed in CR rubber. (a) Interconnected fiber-like structure, (b) PF sheet with holes.



**Figure 10** The fracture surfaces of CR vulcanizates without PF modification (a) and with PF modification (b) after etching by NaOH solution (20%) for PF removal.

effect for the CR rubber leading to radically enhanced rubber mechanical properties. The fracture surfaces of CR vulcanizates with or without PF modifications after etching by NaOH solution (20%) for PF removal are shown in Figure 10. Smooth surface was observed for CR without PF addition, whereas the voids and holes were found on the surface of CR with PF modification due to the removal of PF phase.

The CR rubber was also sensitive to commonly used retarding agent  $\text{Al}(\text{OH})_3$ . Table III shows that

the tear strength, modulus, permanent set, shore hardness and oxygen index were considerably increased with addition of 30 phr of  $\text{Al}(\text{OH})_3$ , whereas the tensile strength was weakened. However, the addition of 10 phr of PF into the CR containing 30 phr  $\text{Al}(\text{OH})_3$  would enhance the tear strength, modulus, shore hardness and elongation. At the same time, the tensile strength was almost unchanged. This investigation results indicates that PF phase is compatible to the CR rubber containing the retarding agent  $\text{Al}(\text{OH})_3$ .

### Mechanical property and microstructure correlations

This investigation has clearly demonstrated that the PF could be an effective additive for strengthening various rubber materials. It should be noted that the property enhancement was based on the silica or carbon reinforced rubbers and therefore, this 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 modulus imparted by active filler might be regarded as the product of two terms: one involving a hydrodynamic effect arising from the inclusion of rigid particles. It is quantitatively taken into account by the Guth and Gold expression.

$$G = G_0(1 + 2.5\phi + 1.44\phi^2) \quad (1)$$

where  $G_0$  is the modulus of the unfilled matrix and  $\phi$  is the volume fraction of filler. In the absence of polymer–filler interaction as it would be expected in NR or SBR filled with silica without the use of a coupling agent, only hydrodynamic reinforcement is obtained. The second term involves an increase in the crosslinking density created by polymer–filler interactions. When there are polymer–filler interactions present, the obtained  $G_0$  using the above formula is lower than that obtained experimentally for the filled network. This result can only be explained by the presence of filler–rubber interactions. Nevertheless, these classical theories and most of their

**TABLE III**  
The Effects of PF and  $\text{Al}(\text{OH})_3$  Additions on the Mechanical Properties of Vulcanized CR Rubbers

Rubber compositions	Tensile strength (MPa)	Tear strength (kN/m)	Modulus (300%) (MPa)	Shore hardness (A)	Elongation at break (%)	Permanent set (tension set) (%)	Oxygen index
CR	20.56	22.72	1.09	45	1063	10	36
CR + 10 phr PF	22.4	30.54	1.62	48	1051	15	36
CR + 30 phr $\text{Al}(\text{OH})_3$	13.6	30.9	1.77	53	923.7	18	43
CR + 30 phr $\text{Al}(\text{OH})_3$ + 10 phr PF	14.1	39.4	2.82	59	943	25	44

extensions 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, the deformation of filler materials. Besides, the filler property itself should also contribute significantly on the final properties. Especially, the heterogeneities of these surfaces yield a peculiar dynamic behavior of the polymer chains close to them.<sup>15</sup> Recent studies have also shown that at a given strain, the tensile stress increased with increasing the interfacial interactions between rubber molecules and silica surface, and simultaneously the chain scission became remarkable.<sup>26</sup>

Apart from the filler-polymer interactions, the aspect ratio (length/width) of the particles is also expected to affect the properties of final materials. Acicular fillers such as fibers or nanotubes, characterized by two dimensions in the nanometer range, yield materials with exceptional mechanical properties only in the direction of the fiber as a result of the high anisotropy and high orienting capability of this type of materials. As for this study, an elongation increase of about 26% was observed as a result of the formation of PF with anisometric fiber structure in EPDM rubber. This enhancement behavior could not be simply explained by filler-rubber interaction. Generally, the hard filler, either in the form of particles or fibers, will increase the strength, but lower the elongation. However, for PF fibers with high flexibility and moderate stiffness, the strong interaction between filler and rubber would make the filler to be part of the rubber solid. This would result in the stretching of not only the rubber molecules but also the PF molecules along the stress direction. Hence, a higher resilience property and significantly improved mechanical property were achieved. On the other hand, for CR rubbers modified with PF, the CR vulcanizates will fill in the three-dimensional PF structure forming a localized strengthened "cluster" with excellent bonding to rubber matrix through "rubber to rubber" interaction. Therefore, the reinforcement mechanism of the PF phase is not explainable by the theory applicable to fiber materials.

There is now a general agreement that filler-rubber interaction is an important factor in reinforcement, depending on the characteristics of filler particles such as particle size, surface area, structure and surface activity.<sup>27</sup> However, the reinforcement of rubbers with PF could not be fully explainable by present theories because of special mechanical and chemical properties associated with PF materials and formed PF morphologies besides the filler effect and filler-rubber interactions. PF either in fabric or three-dimensional structure has much higher flexibility than other inorganic materials such as carbon or silica. Its resilience properties were lower than those

of rubber but much higher than those of carbon or silica because of the possibility of molecule stretching. Therefore, it can absorb more energy during the deformation process. This difference was demonstrated by the enhancement of strength and elongation at the same time. Nevertheless, the present study could not fully elucidate the strengthening mechanisms and much more studies will be needed to clarify the present suggestions.

## CONCLUSIONS

CR and EPDM rubbers have been modified by formation of PF *in situ* at the vulcanization conditions. The PF will form different morphologies in different rubbers. The PF with a localized three-dimensional network structure was formed in CR rubber, whereas the fabric PF was formed in EPDM rubber. For CR rubber, the tensile strength, tear strength, modulus and elongation were significantly improved at a PF content of 8–10 phr, whereas the hardness and permanent deformation were limitedly affected. For EPDM rubber, however, all mechanical properties were significantly enhanced at a PF content of 10 phr, especially, the tear strength, modulus, elongation, and resilience. The strengthening mechanisms involved in using PF for rubber modification were suggested to relate to the properties of filler materials, strong filler-rubber bonding or interactions and the morphologies of *in situ* formed PF.

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