



# Exploiting arene-perfluoroarene interactions for dispersion of carbon black in rubber compounds

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## ABSTRACT

Coupling agents are intended to promote filler dispersion by providing a bridge between the filler and the rubber phase. This study investigated the ability of a novel physical coupling agent, poly(butadiene-graft-pentafluorostyrene) in a mixture with polypentafluorostyrene, to improve rubber-filler interactions and suppress filler-filler networking in carbon-black-reinforced styrene-butadiene rubber (SBR), and thereby decrease hysteresis. The electron-rich aromatic rings of carbon black are involved in arene-perfluoroarene interactions with the electron-poor pentafluorostyrene aromatic rings of the coupling agent. The SBR chains in the rubber compound have an affinity for the polybutadiene backbone of the coupling agent. The interactions between carbon black and the coupling agent were analyzed using Raman spectroscopy, transmission electron microscopy, zeta potential measurements, surface area measurements, and scanning electron microscopy. Filler flocculation analysis showed that the coupling agent improves the dispersion and lowers the energy of dissipation. The hysteresis loss, quantified in terms of loss tangent values at 60 °C, was reduced by up to 12% due to the coupling agent's promotion of better filler-rubber interactions. The influence of the PPFS graft length was also studied.

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## 1. Introduction

The concept of rolling resistance is explained in various forms in the literature; one simple definition is the force required to make tires roll on road surfaces. According to the United States Department of Transportation, 240 million light trucks and passenger cars consume approximately 135 billion gallons of motor fuel each year in the United States [1]. In this context, rolling resistance is among several factors that determine the fuel economy. For example, approximately 2 billion gallons of fuel would be saved each year in the United States alone if the rolling resistance was decreased by 10% [2]. An improvement in fuel economy leads to reduced CO<sub>2</sub> emission and improved air quality.

The material packages used in tire tread formulations directly impact the rolling resistance (RR) of the resulting compounds. Two major avenues to improve the RR of tire tread compounds are the use of a rubber matrix with lower inherent values of RR and an increase of the rubber-filler interactions via the use of coupling agents. The first series of articles on filler-elastomer interactions

was published by Wang and coworkers [3,4]. These investigators explained the impact of filler-filler networks and surface energies of filler particles on dynamic mechanical properties of the compounds. Another approach to improve the dynamic mechanical properties is by controlling the filler microstructures [5] and filler dispersion [6]. For filled rubber systems, the loss ( $G''$ ) and storage ( $G'$ ) moduli values are determined from the state of filler networking along with hydrodynamic effects. The hydrodynamic effects depend strictly on the filler loading, while the values of  $G'$  are related to the filler networks that remain intact with the applied strain. The values of  $G''$ , however, are associated with the breakdown and reformation of filler-filler networks [7]. Luginsland et al. [8] reported that filler-filler interactions compete in both silica- and carbon black-filled systems.

A number of studies focused on increasing the rubber-filler interactions using covalent coupling agents in silica-filled rubber compounds [8–12]. Bis(triethoxysilylpropyl)tetrasulfide is a common covalent coupling agent for silica-filled rubber. In comparison, rubber-carbon black (CB) interactions did not receive much attention, except for studies involving nitroso compounds [13,14], unsaturated hydroxy organic acid [15], dinitroamines [16], dinitrodiamides [17], and isocyanates [18]. Nitroso compounds are

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carcinogenic with unfavorable health effects [5,19] while diamines more effectively enhance filler-polymer interactions compared to the dinitramides [17,20]. The isocyanate-based coupling agents require introduction of NCO groups onto carbon black surfaces. However, such groups are very sensitive to moisture and require further stabilization by masking the isocyanate groups by reversible addition of a weak acid across the N=C double bond [21].

This study introduces a novel physical coupling agent (CA) for carbon black (CB) based on arene-perfluoroarene interactions [22] between aromatic hydrocarbons and aromatic fluorocarbons. Arene-perfluoroarene interactions were first noted by Patrick and Prosser [21] when one equivalent of benzene ( $T_m = 5.5^\circ\text{C}$ ) mixed with one equivalent of hexafluorobenzene ( $T_m = 5^\circ\text{C}$ ) formed a transient complex that melted at  $24^\circ\text{C}$ , which is much higher than that of either component. Similarly, an equimolar solution of methylnaphthalene ( $T_m = 35^\circ\text{C}$ ) and hexafluorobenzene generate an isolatable crystalline complex that melts at  $56^\circ\text{C}$  [22]. The formation of these crystals was attributed to interaction of the electron-rich aromatic hydrocarbon and the electron-poor aromatic fluorocarbon. These arene-perfluoroarene interactions are a type of face-to-face  $\pi$ - $\pi$  stacking interactions that are used to provide physical crosslinks [23], aid in orienting reactants for polymerization [24] and photodimerization [25], and stabilize less ordered liquid crystalline phases [26].

As exemplified by the structure in Fig. 1, carbon black (CB) contains graphite-like microcrystalline substructures amongst its amorphous elemental carbon chemical make-up [27]. Most compounded rubber is reinforced with CB [28,29]. The graphitic content makes CB amenable to arene-perfluoroarene interactions with perfluoroarene materials. Paz-Pazos and Pugh reported the grafting of polybutadiene with 2,3,4,5,6-pentafluorostyrene using free radical initiation, to produce a mixture of the graft copolymer and polyperfluoroarene homopolymer [30]. Fig. 2 presents a representative structure of the resulting PB-g-PPFS (polybutadiene-graft-polyperfluoroarene) copolymer. The chemical structures of the copolymer's polybutadiene backbone and the rubber matrix are similar and will therefore interact well, while the electron-deficient pentafluorostyrene (PFS)  $\pi$ -system and the electron-rich graphitic CB can interact by arene-perfluoroarene interactions. This is the first study to exploit the physical, arene-perfluoroarene interactions to promote CB particle dispersion in rubber compounds. We recently demonstrated that the mixture of polybutadiene-graft-polyperfluoroarene and PPFS is an effective coupling agent for improving the dispersion of polar hybrid lignin-coated carbon black particles in non-polar rubber [31].

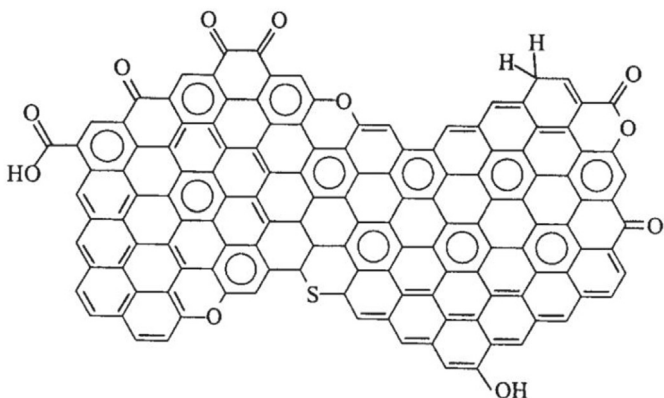


Fig. 1. Representative chemical structure of carbon black [32].

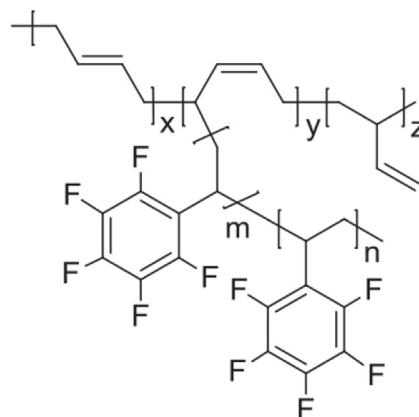


Fig. 2. Simplified structure of polybutadiene-g-polyperfluoroarene (PB-g-PPFS).

## 2. Experimental

### 2.1. Materials

Butylated hydroxytoluene (BHT, Alfa-Aesar), carbon black (CB, donated by Eastman Chemical, grade N234), polybutadiene (BR donated by Goodyear; 0.8% 1,4-trans, 97.7% 1,4-cis, 1.5% 1,2-vinyl;  $M_n = 1.25 \times 10^5$  Da,  $\bar{D} = M_w/M_n = 4.6$ ), styrene-butadiene rubber (donated by Eastman Chemical Company (Akron, OH); 25 wt% styrene, 42 wt% vinyl content; grade BUNA VSL VP PBR 4041) were used as received. Antioxidant antiozonant PD2, *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine and the ingredients used for rubber curing, *N*-*t*-butyl-2-benzothiazyl sulfenamide (TBBS) accelerator, Rubber Maker (sulfur curing agent), stearic acid (flakes), and zinc oxide (powder) were used as donated by Akrochem Corporation. Benzoyl peroxide (BPO, 97%, Aldrich) was stored at  $<-10^\circ\text{C}$  in a freezer after recrystallization in a refrigerator from 1:3 (v/v) chloroform/methanol. The inhibitor was removed from 2,3,4,5,6-pentafluorostyrene (Apollo Scientific) prior to each use by passing it through a small amount of basic activated alumina. Tetrahydrofuran (THF, reagent grade, Aldrich) used for polymerizations was dried and distilled under  $\text{N}_2$  from purple sodium benzophenone ketyl.

### 2.2. Synthesis of polybutadiene-graft-polyperfluoroarene

PB-g-PPFS was synthesized by our previously reported route [30,31] using a constant 2:1 M ratio of PFS to PB repeat units. The temperature and the amount of initiator were varied to obtain different lengths of the PPFS grafts. In a custom-made round bottom flask sealed with a valve attached through a high vacuum joint, a THF solution of PB (1.2 g, 23 mmol butadiene groups) was deoxygenated by 5 freeze-evacuate-thaw routines. The mixture was stirred overnight at  $50^\circ\text{C}$  in a  $\text{N}_2$  atmosphere to fully dissolve PB. Benzoyl peroxide (0.55 g, 2.3 mmol) and PFS (8.8 g, 45 mmol) were added to the PB soln. at room temperature, and the solution was again deoxygenated by 5 freeze-evacuate-thaw routines. After stirring at  $60^\circ\text{C}$  under a 1 mm Hg vacuum for 48 h, the graft copolymerization was terminated by opening the flask to air after cooling it to  $0^\circ\text{C}$ . In order to prevent oxidative crosslinking of the isolated PB-based graft copolymer, the polymerization solution was precipitated into a solution of BHT (1% w/v) in methanol (500 mL) saturated with  $\text{N}_2$ . The resulting white solid (7.3 g, 73% yield) contained PB-g-PPFS graft copolymer ( $M_n = 398$  kDa,  $\bar{D} = 1.63$ ), PPFS homopolymer ( $M_n = 8.52$  kDa), and a negligible quantity of unreacted PB homopolymer. This mixture of PB-g-PPFS and PPFS

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