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Mechanical performance of styrene-butadiene-rubber filled with carbon nanoparticles prepared by mechanical mixing

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ABSTRACT

Reinforcement of styrene-butadiene-rubber (SBR) was investigated using two different carbon blacks (CBs) with similar particle sizes, including highly structured CB and conventional CB, as well as multi-walled carbon nanotube (MWCNT) prepared by mechanical mixing. The attempts were made to examine reinforcing mechanism of these two different classes of carbon nanoparticles. Scanning electron microscopy and electrical conductivity measurement were used to investigate morphology. Tensile, cyclic tensile and stress relaxation analyses were performed. A modified Halpin–Tsai model based on the concept of an equivalent composite particle, consisting of rubber bound, occluded rubber and nanoparticle, was proposed. It was found that properties of CB filled SBR are significantly dominated by rubber shell and occluded rubber in which molecular mobility is strictly restricted. At low strains, these rubber constituents can contribute in hydrodynamic effects, leading to higher elastic modulus. However, at higher strains, they contribute in stress hardening resulting in higher elongation at break and higher tensile strength. These elastomeric regions can also influence stress relaxation behaviors of CB filled rubber. For SBR/MWCNT, the extremely great inherent mechanical properties of nanotube along with its big aspect ratio were postulated to be responsible for the reinforcement while their interfacial interaction was not so efficient.

1. Introduction

Pristine polymers are rarely suitable for demanding applications in engineering components so as a significant deal of attempts has been made to improve their physical and mechanical properties by incorporation of appropriate reinforcing materials [1]. Various reinforcing materials with broad diversities in the shape and properties, ranging from simple spherical inorganic fillers to high performance synthetic fibers, have been examined in this regard for a long time. In recent years, parallel to the progression of the nanoscience and nanotechnology in the past few decades, polymer composites reinforced with nanoparticles have opened new opportunities for the academia and industry to obtain high performance materials, thanks to the unique mechanical and physical properties of nanoparticles as well as their distinctive nanostructures. These promising opportunities are always traded off with high cost of nanoparticles and great challenging task for their processing with the polymeric matrices, restricting their widespread practical applications [2,3]. Thus, prior to the use of a specific nanoparticle in an industry, its suitability in terms of performance, processing and cost should be examined with respect to available conventional fillers.

The reinforcing mechanisms of soft polymers like elastomers with rigid particles are greatly different compared to glassy plastic materials. In the elastomeric materials, hydrodynamic effects are the first level of reinforcement which can be achieved by inclusion of rigid particles with either micro or nanosizes [1,4,5]. The reinforcement mechanisms associated to the rigid particles in the higher levels can be dominated by particle–elastomer chains and particle–particle interactions as well as particles networking within the elastomeric matrices. The successes in the elastomer reinforcement is greatly dependent on the capabilities of the reinforcing particles to fulfill all of these reinforcing mechanisms. Thus various characteristics of the reinforcing particles such as their inherent mechanical properties, size and shape, structure and surface chemistry could play critical role in the final properties of filled elastomers.

Carbon black (CB) is a kind of nanoscale filler that has been widely used in the rubber industry for more than a century [6]. Such a long lasting usage of CB owes largely to its unique structural characteristics and surface activity, creating excellent interaction with rubber macromolecules, as well as its low price. Actually, the primary particles of CBs, which are spherical in nature, are strongly bonded together through physical and chemical interactions lead-

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ing to highly branched clusters, so called aggregates [7], whose size stand below 100 nm. High surface activity of CB enables the formation of very thin layer of immobilized elastomer chains, i.e. 2–3 nm [8,9], on the outer surface of CB which shows always a glassy behavior followed by some sticky layer with stiffer properties compared with matrix rubber [8,10]. Additionally, the cluster structure of aggregates makes possible the occlusion of a part of elastomer chains within the aggregates which is shielded from the macroscopic deformation caused by the CB aggregate. Therefore, the CB reinforcement may be considered as a composite rigid particle consisting of CB, bound rubber and occluded rubber [10]. Such a unique structural characteristic often amplifies the hydrodynamic effect on the rubber reinforcement [5].

In recent years, a great deal of researches has been conducted to introduce new efficient alternatives for the CB, however, a few reinforcements such as silica [11–13] and clay [14–19] have attracted the attentions in rubber industry. Currently, the attempts are still offered to examine much stronger nanomaterials like carbon nanotube (CNT) for the rubber reinforcement. This nanomaterial with a Young's modulus and strength of ~1 TPa and 50–500 GPa [20–23], respectively, is known to be the strongest material recognized in the earth. Additionally, its unique tubular geometry with an aspect ratio of more than 1000 makes it promising in the polymer composites. However, to achieve full potential benefits of CNTs in the polymer composites, the uniform distribution of CNT bundles and strong interfacial interactions are also the significant pre-requisites in obtaining the polymer/nanoparticle composite. It has been shown that the incorporation of a few percent of CNT in rubber matrix, e.g. less than 10 phr, using solution mixing method leads to significant improvement in the mechanical properties, e.g. as high as 10-fold and 2-fold in modulus and strength, respectively [24–28], as well as low filler networking concentration (percolation threshold), e.g. as low as 2 phr [24,29,30]. However, solution mixing method is not practically attractive for industrial scale productions where the mechanical mixing method is often appreciated mainly due to the presence of cost effective as well as common equipment and facilitates.

The success of CNTs in rubber industry can be expected wherever they offer higher performance compared to CBs as industrially efficient reinforcement. Therefore, most of the researches have been focused on the comparative investigation on the reinforcing efficiency of conventional CBs versus that of CNTs [31–33]. All of these works suggested that CNTs exhibit higher mechanical improvement in the final rubber product compared with conventional CBs filled rubbers obtained by a given mixing method. In these studies, the structural influence of the CBs has not been taken into account, while it is well known that the final properties of CB filled rubber is highly dependent on the microstructure and specific surface area of CB aggregates [34–38]. Highly structured CBs (HSCBs) consist of a great number of primary particles with highly branched clusters exhibiting high surface area towards rubber macromolecules [7,39]. Such CBs are expected to offer great reinforcing efficiency with rubber. Recently, Li et al. [40] compared the influence of HSCB with conventional CBs on the cure characteristics and mechanical properties of ethylene propylene diene monomer rubber (EPDM). They concluded that higher surface area of HSCB makes some additional physical crosslinking between the rubber and the fillers, leading to enhanced mechanical properties such as hardness, tensile strength and tensile modulus. Knite et al. [41] observed that polyisoprene rubber reinforced by HSCB shows higher reversibility in change of electrical resistivity at large stretches vis-a-vis multi-walled CNT (MWCNT) filled polymer.

In this work, we investigated the influence of a super conductive CB (SCCB) and carboxylated multi-walled CNT on the mechanical performance of styrene-butadiene rubber (SBR). The SCCB used in this investigation was highly structured filler with a very high specific surface area. A conventional CB, i.e. N330, with a normal specific surface area but with the same particle size of SCCB was also used to acquire a better understanding about the role of structure (specific surface area) of the CB aggregates on the mechanical performance. Mechanical mixing method was used to prepare the rubber compounds. This work enables one to obtain an insight concerning the effectiveness of stronger nature as well as elongated shape of MWCNT, and the structure (specific surface area) of CBs on the property enhancement of filled SBR obtained by much appreciated mixing method, i.e. mechanical mixing method.

Table 1
Characteristics of CBs and MWCNT used in this study (taken from manufacturers).

Reinforcement	Mean particle size (nm)	Specific surface (m^2/g)	DBP (ml/100 g)
MWCNT[a]	10–20 (outer diameter)	200	–
XE2B[b]	30	1000	420
N330[b]	30	80	102

[a] The density was taken to be 1.68 g/cm^3 [42,43].
[b] The density is assumed to be 1.8 g/cm^3.

2. Experimental

2.1. Materials

The rubber material used in this research was SBR 1502 produced by Bandar Imam Petrochemical Co. (Iran). MWCNT-COOH (TNMC3, COOH content 2 wt%, purity > 95%, length 10–30 μm, inner diameter 5–10 nm, outer diameter 10–20 nm) was supplied by Timesnano, China. SCCB (Printex® XE2B) was donated by Evonik Degussa, and N330 CB was obtained by Iran Carbon Co. Table 1 summarizes the characteristics of the nanofillers.

2.2. Preparation

Table 2 exhibits the formulation of pristine SBR vulcanizate and the SBR vulcanizates filled with different nanoparticles with various concentrations ranging between 2.5 and 12.5 phr. All the samples were compounded using a traditional two roll mill. At first, SBR was masticated to obtain a soft rubber gum and then the curing agents and the nanoparticles were gradually added to the masticated rubber followed by a further mixing to attain a uniform mixture. Eventually, the compounds were compression molded in a sheet form with a thickness of 2 mm at 145 °C and the pressure of 150 bars for an optimum period, i.e. 40–50 min according to their relevant cure rheometeric curve. The samples were then post cured at 145 °C for 1 h.

2.3. Characterization

Field emission scanning electron microscopy (FESEM) images were used to characterize dispersion of fillers in the SBR. These

Table 2
Recipe of the compounds.

Materials	Part per hundred rubber (phr)
SBR	100
Sulfur	1.2
Accelerator (TBBS)	1.3
Stearic acid	2
Zinc oxide	5
Anti oxidant	1
reinforcement[a]	0, 2.5, 5, 7.5, 10 or 12.5

[a] The nanofiller is either MWCNT, CB-XE2B or CB-N330.