



## Macromolecular Nanotechnology

## Multifunctional multilayer graphene/elastomer nanocomposites



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## ABSTRACT

Elastomers are usually reinforced and employed in different applications. Various different nanoparticles, including layered silicates, carbon nanotubes, and expanded graphite, are currently being used as nanofiller. Multilayer Graphene (MLG) is proposed as promising nanofiller to improve the functional properties of Chlorine-Isobutylene-Isoprene Rubber (CIIR), Nitrile-Butadiene Rubber (NBR), Natural Rubber (NR) and Styrene-Butadiene Rubber (SBR) at low concentrations. MLG is constituted by only approximately 10 graphene sheets. Nanocomposites with extremely low MLG content (3 phr) showed evident improvement in rheological, mechanical and curing properties. The Young's modulus of the nanocomposites increased more than twice in comparison with the unfilled rubbers. MLG also improved the weathering resistance of the different rubbers. The nanocomposites conserved their initial mechanical properties against weathering exposure.

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## 1. Introduction

Elastomers are usually compounded with reinforcing fillers like carbon black (CB) and silica to improve their mechanical properties such as elastic modulus, hardness, tear resistance, abrasion resistance and gas barrier properties. High concentrations (more than 50 phr) of conventional filler are required to obtain the desired properties of the final rubber composites [1–3].

In recent years, several nanoparticles have been proposed to achieve the required properties with low filler loading. The most commonly used nanoparticles are layered silicates [4,5], spherical nanosilica [6], carbon nanotubes [7,8] and bio-nanofillers [9]. The discovery of graphene [10] with its combination of extraordinary properties and ability to be dispersed in various polymer matrices has created a new candidate among polymer nanocomposites [11–13]. Graphene is an atomically thick, two-dimensional (2-D) sheet composed of sp<sup>2</sup> carbon atoms arranged in a honeycomb structure [14,15].

Beyond the reinforcement effect, graphene improves the weathering stability of the elastomeric matrix. The interaction between UV and oxidative agents can degrade the elastomers through multi-step photo-oxidation [16]. Photo-oxidation includes radical formations and oxidative reactions that result in elastomeric chain scission [17]. Carbon particles absorb UV [18,19] and act as radical [20] scavengers, inhibiting polymer degradation. In the presence of impurities, as in NR, photo-oxidation can also produce new covalent bonds between the polymeric chains [21].

In this study, Multilayer Graphene (MLG) with a BET of 250 m<sup>2</sup>/g is proposed as promising novel nanofiller. BET is an extremely powerful measure to characterize the degree of exfoliation of graphene sheets and thus the real number of layers in graphene stacks [22,23]. Since a single graphene sheet has a surface area of up to 2600 m<sup>2</sup>/g, the MLG used is constituted by only approximately 10 graphene sheets. MLG is produced by a modified Hummer method which includes the oxidation

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and the thermal exfoliation of graphite. It has recently become commercially available at a reasonable price. In literature, materials with lower BET (80–200 m<sup>2</sup>/g) and thus stacks with more than 15 sheets are often referred to as graphene. Nevertheless, we would like to systemize our denotation: graphene (less than 7 layers), MLG (7–15 layers) and expanded graphite (15–75 layers) [24].

The nanocomposites were prepared by pre-mixing MLG with the different rubbers by an ultrasonically-assisted solution mixing procedure followed by two-roll milling [25]. The effect of the MLG was evaluated on 4 of the most popular rubbers: Chlorine-Isobutylene-Isoprene Rubber (CIIR), Nitrile-Butadiene Rubber (NBR), Natural Rubber (NR) and Styrene-Butadiene Rubber (SBR). CIIR is the chlorinated form of Isobutylene Isoprene Rubber, often shortened to “Butyl Rubber”. Due to its air impermeability, CIIR is today’s most important material for the inner linings of tubeless tires [26]. NBR is a synthetic rubber copolymer of acrylonitrile and butadiene. Its physical and chemical properties depend on the ratio of the two monomers. NBR is found in several applications, for instance in non-latex gloves, automotive transmission belts and seals [27]. NR originates from the “*Hevea Brasiliensis*” tree and is a mixture of cis-1,4-polyisoprene (94–95%) fat acids and protein. Natural rubber is used extensively in many applications and products, such as tires, gloves, toy balloons, condoms and boots [28]. SBR is a synthetic rubber copolymer of styrene and butadiene. The ratio of the monomers influences the properties of the rubber. This elastomer is widely used in tires (especially in the tread), shoe heels and soles [29].

A low content of MLG modifies the curing and improves the mechanical properties of all the elastomers: the Young’s modulus increases by almost 3 times. MLG also improved the weathering resistance of the tested rubbers.

## 2. Materials and methods

### 2.1. Materials

CIIR (Chlorobutyl 1240), NBR 2845 (Perbunan 2845 F) and SBR 2525 (Buna VSL 2525-0) were obtained from LANXESS Deutschland GmbH, Germany. NR (TSR-L) was supplied by Dan Tien, Vietnam. The chemical structures of the tested rubbers are showed in Fig. 1. The commercially available MLG (EXG R98 250) was produced on the pilot plant (2–5 kg batches) by Graphit Kropfmühl AG, Germany. Zinc oxide (Zincoxyd Activ), IPPD (Vulkanox 4010 NA/LG) and MBTS (Vulcacit DM/C-MG) were obtained from LANXESS Deutschland GmbH, Germany. CB660 (CXN660) was supplied by Orion Engineered Carbons GmbH, Germany. Stearic acid (Stearic acid pure) was produced by Applichem, Germany. Sulphur was obtained from Merck, Germany. Struktol (Struktol 40 MS Flakes) was supplied by Schill + Seilacher, Germany. Analytical-grade toluene was obtained from Fisher Chemical, Germany. Cumene and 2,2-azobisisobutyronitrile (AIBN) were supplied by Sigma Aldrich (USA).

### 2.2. Preparation of elastomers MLG nanocomposites

MLG was dispersed in a toluene/elastomer solution by sonication (3 h) using UPS 400S (Hielscher, Germany). Then the mixture was stirred for 2 h. The ratio elastomer:MLG was 7:1 and the concentration of MLG in the solution was 1 mg/mL. The masterbatch was obtained after evaporation of the solvent (60 °C, 150 mBar) using a rotary evaporator (Hei Vap Value, Hiedolph, Germany).

The elastomers and the other ingredients, in accordance with the formula given in Table 1, were mixed directly in a two-roll mill (Lab Walzwerk MT 6” × 13”, Rubicon, Germany). The rubbers were compounded in three stages. In the first

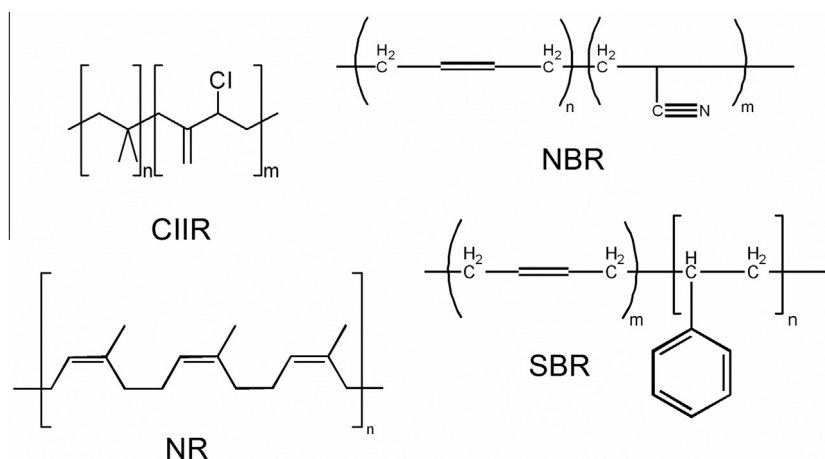


Fig. 1. Chemical structure of the tested rubbers.

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