

# Styrene-butadiene rubber/graphene nanocomposites: Effect of co-milling with cyclic butylene-terephthalate

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**Abstract.** Graphene nanoplatelets (GnP) reinforced styrene-butadiene rubber (SBR) nanocomposites were produced by two different methods. For reference purpose carbon black (CB) reinforced formulations served. In the first method the components were mixed on a two roll open mill directly. In the second method, GnP was subjected to milling in an attritor mill together with cyclic butylene-terephthalate oligomer (CBT) powder prior to the mixing on two roll mill. Samples were cured in a hot press. The rubber sheets were characterized by tensile and tear tests, and their fracture surfaces inspected in scanning electron microscopy (SEM). Results showed that GnP outperformed CB with respect to reinforcing effect. Previous co-milling of GnP with CBT caused a slight decrease in mechanical properties. SEM images proved, that the co-milling process did not affect significantly the dispersion of GnP, its particles were shredded into smaller pieces, which caused the slight decrease in the mechanical properties.

## Introduction

Research to explore possibilities of rubber reinforcement by various fillers is dating back to the beginning of rubber industry. The role of fillers became particularly emphatic with the appearance of synthetic rubbers (such as SBR), because most of their properties are poor in their raw, unfilled state. It was discovered in the early years, that mechanical and wear properties of rubbers can greatly be improved by adding carbon black (CB) to the mixture. Note that CB can be considered as a nanofiller, because the average particle size of CBs is in nanometer scale [1-3].

In the past two decades novel allotropes of carbon was discovered, such as graphene and single- or multiwalled carbon nanotubes (SWCNT and MWCNT). Due to their extraordinary mechanical, physical, electrical and thermal properties they became objects of strong interest [3, 4]. Their outstanding specific surface area accompanied by excellent mechanical properties and the potential presence of reactive or functional groups makes them ideal for preparation of composite structures. The reason why they did not become widely used is linked with the difficulty of adequate dispersion of these fillers. This dispersion problem arises from the anisotropy of particles (wide, closely stacked layers, or very thin fibrous structure, which can form a heavily entangled network of nanotubes) along with the Van der Waals interactions acting between them. To increase the dispersion of carbonaceous nanofillers is a key issue of nanocomposites' production [5].

Cyclic butylene terephthalate oligomer (CBT) is a cyclic compound, its rings are composed of 2-7 monomer units. The melting temperature of CBT ranges from 120 to 160°C. In the presence of a suitable catalyst it can be polymerized into polybutylene-terephthalate (PBT). Due to the difference in the average molecular weight and crystallinity compared to the traditional polycondensation PBT, the ring-opening polymerized version is denoted by pCBT in the literature. The very low melt viscosity (0.02 Pas at 190°C) makes CBT particularly suitable as in situ polymerizable matrix

material for composites. Furthermore it can be used as a processing aid to improve the processability of a broad range of thermoplastic resins. Flow properties can be significantly improved by adding only a few wt.% of CBT and it hardly affects other properties of the material [6]. Previous studies showed that rubber/CBT hybrids have outstanding mechanical and wear properties, so CBT seems to be able to act as an active filler in rubbers [6-8]. Another noteworthy work demonstrated, that using CBT powder and high-energy ball milling (HEBM) the strongly entangled MWCNT agglomerates can be efficiently broken up, and well dispersed MWCNT reinforced nanocomposites can be prepared [9].

Based on the above mentioned properties and results the goal of this work was to investigate the effect of graphene nanoplatelets (GnP) and CBT for the properties of sulphur-cured styrene-butadiene rubber (SBR). Attempt was also made to check whether or not a preliminary co-milling of GnP with CBT is beneficial.

### Materials and Testing

As matrix material Plioflex 1502 SBR was used with 23.5 wt.% bound styrene content supplied by Goodyear Chemical (Akron, Ohio, USA). The activator, antioxidant and curing agents were commercially available materials. Cyclic butylene-terephthalate oligomer, grade CBT100 (without polymerization catalyst), was provided by Cyclic Corporation (Schwarzheide, Germany) in a powder form. Carbon black was a commercial grade high abrasion furnace (HAF) N330 CB. Graphene nanoplatelets powder was xGnP H grade, supplied by XG Sciences Inc. (Lansing, Michigan, USA). CBT-GnP dry blends were milled in a Union Process 01HD laboratory attritor (Union Process Inc., Akron Ohio, USA) for 3x10 minutes with 600 rpm. The weight of the steel balls was 1000 g and the balls were 5 mm in diameter. A schematic illustration of the attritor is given in Fig. 1.



**Figure 1.** Schematic build-up of the attritor

Preparation of the rubber blends were carried out on a laboratory two roll mill (Labtech Scientific LRM-SC-110, Labtech Engineering Co., Ltd., Samut Prakarn, Thailand), friction was set to 1.3, the temperatures of the front and back rotor were 70°C and 50°C, respectively. The compositions of the samples are listed in Table 1.

## Mixtures

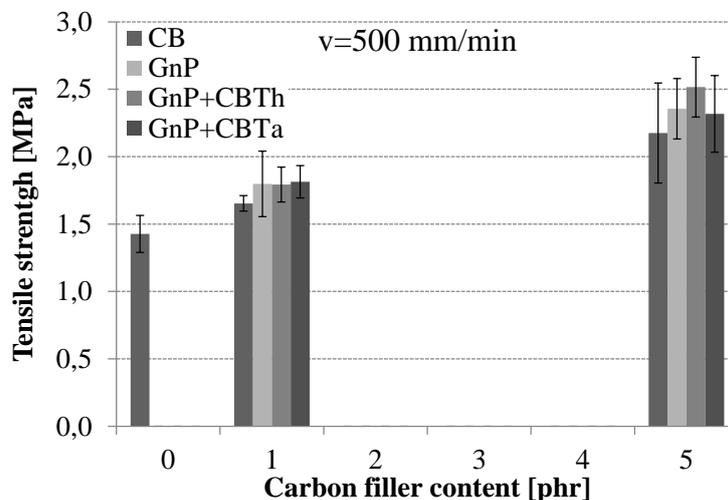
		Sample No.								Samples		
		1	2	3	4	5	6	7	8	9	Sample No.	Abbreviation
<b>SBR 1502</b> <b>ZnO</b> <b>Stearic acid</b> <b>TMQ</b> <b>CBS</b> <b>Sulphur</b> <b>N330 CB</b> <b>CBT100</b> <b>xGnP H</b>	<b>[phr]</b>	100								1	Reference	
		5								2	CB	
		1								3		
		1								4	GnP	
		1								5		
		2								6	GnP+CBTh	
		0	1	5	0					7		
		0				4	20	4	20	8	GnP+CBTa	
		0			1	5	1	5	1	5		9

**Table 1.** Recipes of the sample, and their abbreviation. Designations: TMQ - 2,2,4-trimethyl-1,2-dihydroquinoline CBS - Cyclohexyl-2-benzothazolesulfenamide phr- part per hundred part rubber

The samples were cured in a Collin Teach-Line Platen Press 200E laboratory press (Dr. Collin GmbH, Edersberg, Germany) at 170°C for 20 min with 2 MPa pressure producing sheets with ca. 2 mm thickness. Specimens (DIN 53504 Type 1 for tensile and ASTM D624 Type C for tear tests) were punched from the sheets. Tensile and tear tests were performed on a Zwick Z250 universal testing machine equipped with a 20 kN load cell (Zwick GmbH & Co. KG, Ulm, Germany) with a crosshead speed of 500 mm/min at room temperature.

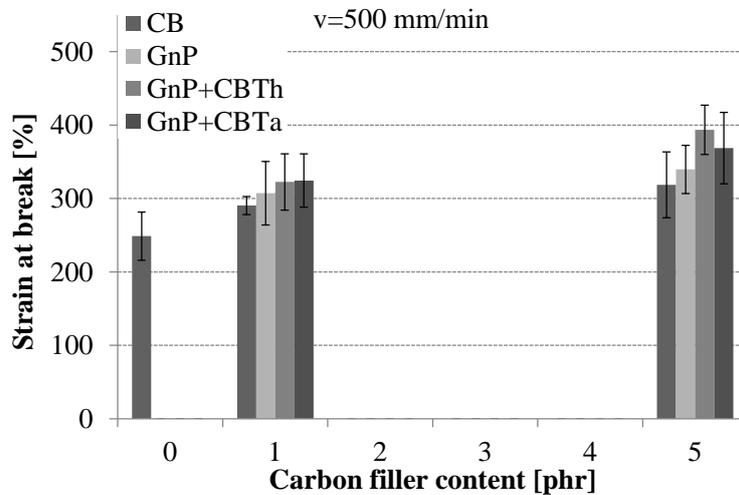
## Results and Discussion

**Mechanical characterizations.** Fig. 2-4 shows the tensile strength, strain at break and modulus (M-100, stress at 100% strain) values of the composites as a function of the filler (CB and GnP) content. GnP+CBTa represents the previously milled sample, GnP+CBTh samples were mixed only on the two roll mill. It can be seen, that GnP has superior reinforcing effect than CB even at lower filler content. Tensile strength was affected negatively by the milling process. CBT itself has a reinforcing effect in SBR. Recall that the reinforcing effect of CBT was already presented earlier by us [6].



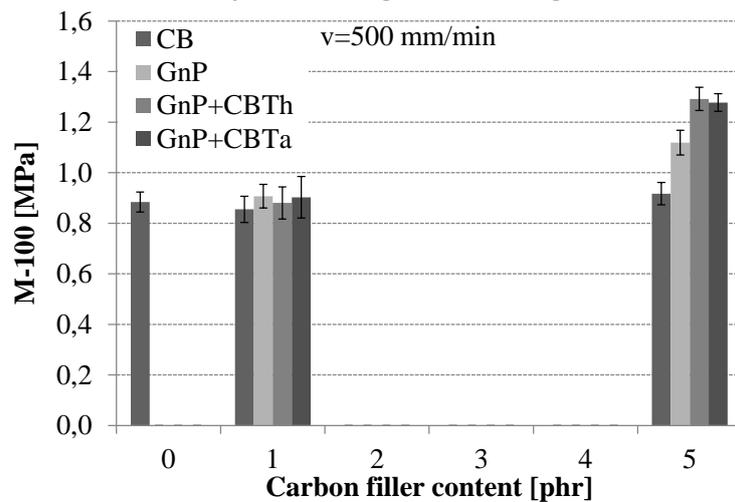
**Figure 2.** Tensile strength values as a function of filler (CB or GnP) content

Similar tendency can be noted for the strain at break values. At lower filler contents the difference between the effects of fillers and co-milled and non-milled GnP-CBT systems are less notable. However, at higher filling it can be seen that non-milled GnP-CBT improves the strain at break compared to the sample with co-milled GnP-CBT.



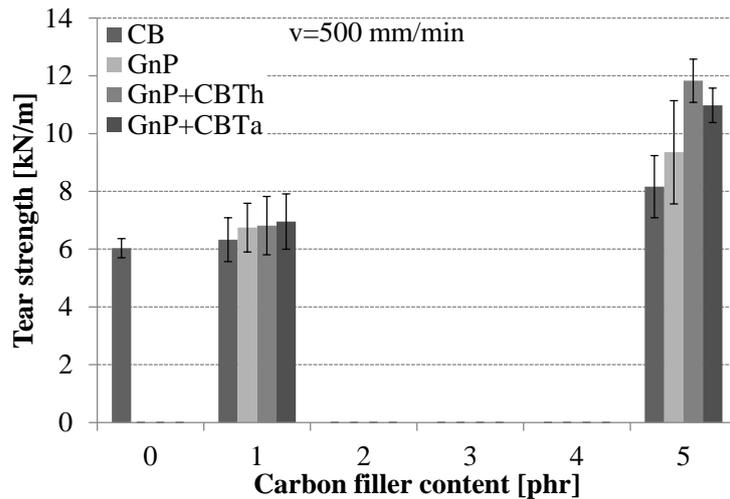
**Figure 3.** Strain at break values as a function of filler (CB or GnP) content

Analyzing the M-100 values of the composites containing 5 phr carbon filler content, it can be concluded, that the difference caused by the milling is increasing with increasing filler content.



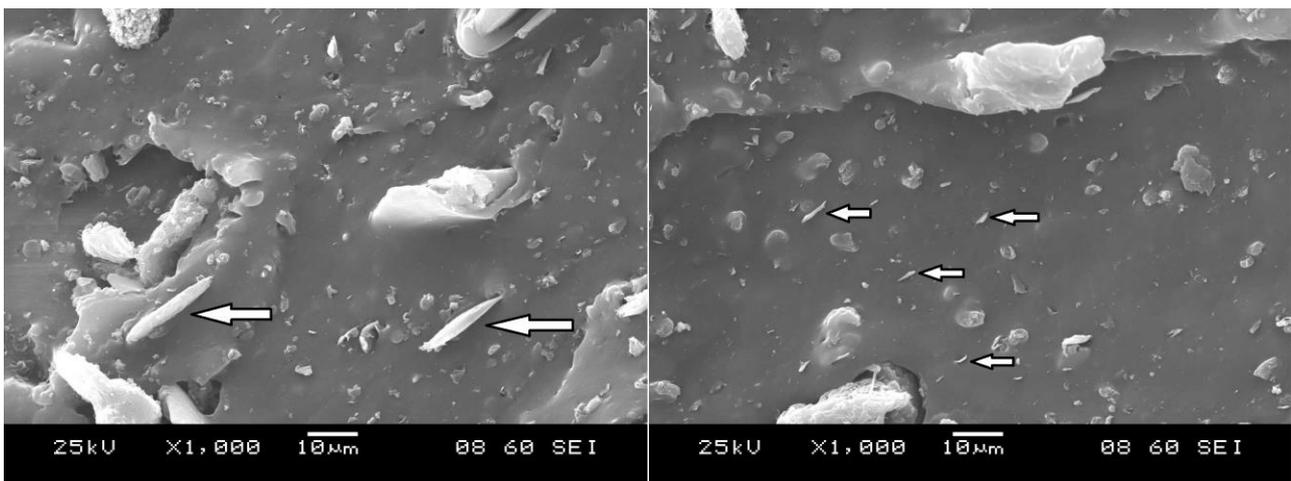
**Figure 4.** M-100 values as a function of filler (CB or GnP) content

Fig. 5 shows the tear strength values of the samples as a function of the filler (CB and GnP) content. Similarly to M-100, tear strength is only minimally affected by the fillers, if their content is only 1 phr. If the content is increased, a remarkable increment can be noticed, and the values of the non-milled samples were the highest.



**Figure 5.** Tear strength values as a function of filler (CB or GnP) content

**Morphology.** Fig. 6 shows the torn surface of a specimen after tear test. It can be clearly observed, that the GnPs were shredded during the milling. Not only their lateral (thickness), but also their longitudinal (width) dimensions were reduced. Note that the white arrows mark the GnPs. Consequently the dispersion of the GnP filler was improved. On the other hand, these smaller particles could not reinforce the rubber as effectively as the original larger ones.



**Figure 6.** SEM images taken from the torn surface of tear specimens (*GnP+CBT left, GnP+CBTa right*)

## Summary

The aim of this study was to investigate the effect of a previous milling of the nanofiller with a “carrier” powder on the dispersion of the nanofiller. This carrier in this case was a cyclic butylene terephthalate oligomer (CBT) in powder form GnP. Rubber samples were prepared by different methods: including a preliminary milling and without it. To compare the effects of GnP, carbon black (CB) filled samples were also produced. Tensile and tear tests showed, that GnP has a slightly stronger reinforcing effect compared to traditional CB. Incorporation of CBT alone also improved thermomechanical properties. SEM pictures showed, that the milling reduced the GnP particle size, thereby improving the dispersion of the platelets. This had, however, a negative effect on the mechanical properties. Nonetheless, the method introduced in this work is very promising for the production of rubber nanocomposites containing high filler contents. Next, co-milling with CBT will be adapted to disperse other nanofillers, such as carbon nanotubes (CNTs), silica in rubbers. Milling parameters, mostly the milling time is that parameter which should be optimized for better results.

## Acknowledgements

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