

Plasma-modified graphene nanoplatelets and multiwalled carbon nanotubes as fillers for advanced rubber composites

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Abstract. In modern rubber industry, there still is a room for new fillers, which can improve the mechanical properties of the composites, or introduce a new function to the material. Modern fillers like carbon nanotubes or graphene nanoplatelets (GnP), are increasingly applied in advanced polymer composites technology. However, it might be hard to obtain a well dispersed system for such systems. The polymer matrix often exhibits higher surface free energy (SFE) level with the filler, which can cause problems with polymer-filler interphase adhesion. Filler particles are not wet properly by the polymer, and thus are easier to agglomerate. As a consequence, improvement in the mechanical properties is lower than expected. In this work, multi-walled carbon nanotubes (MWCNT) and GnP surface were modified with low-temperature plasma. Attempts were made to graft some functionalizing species on plasma-activated filler surface. The analysis of virgin and modified fillers' SFE was carried out. MWCNT and GnP rubber composites were produced, and ultimately, their morphology and mechanical properties were studied.

1. Introduction

Carbon materials are commonly used as fillers in rubber industry, and their major role is to improve the mechanical properties of the vulcanizates. Too low SFE of the filler can dramatically decrease the adhesion between filler and the polymer matrix, but on the other hand – too high SFE can intensify the agglomeration effect [1, 2]. The possibility of controlling the dispersive part of carbon filler's SFE is strongly limited, so the improvement can only be achieved via changing its polar part. Currently applied matrix – filler interphase compatibilization methods seem not to be effective in many cases, thus some attempts were made to adapt low-temperature plasma to filler surface modification [3, 4].

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Graphene and carbon nanotubes, since their structures were discovered, attracted much interest of many scientific groups from different sectors [5]. Due to their unique mechanical, electrical and thermal properties, they immediately became one of the most promising materials for advanced composites fillers [6]. Unfortunately it was quickly found, that there is a major problem with achieving a satisfactory dispersion in polymer matrix.

It seems that inactive, thin amorphous carbon layer on GnP and MWCNT surface, can significantly reduce expected polymer-filler interactions, which, along with agglomeration (especially talking about CNT which form strongly entangled micro-sized structures) can result in much lower mechanical properties of the composite than expected.

One of well-known chemical methods of surface layer activation is solvent treatment, with generation of covalently bonded acidic, amine or fluorine groups [7]. The process is effective, but unfortunately also has a few major disadvantages—e.g. reagent's harm on environment, and generation of dangerous solvent waste. Besides, more attempts were made for surface properties modification with alternative methods, such as low-temperature plasma treatment. The application of plasma techniques in polymer industry is very promising, especially due to environment protection issues – plasma treatment does not generate waste, is fast, and energetically advantageous process.

Low-temperature plasma can be observed as a discharge between electrodes of low-pressure reactor chamber. The discharge is maintained in a presence of a process gas, which, for example, can be Ar₂, O₂, H₂, N₂, acetylene, methane, or simply air. Depending on a type of gas by controlling the process parameters, plasma treatment can be used for cleaning of the material's surface (so called "micro-sandblasting"), or etching of some functional groups via material's reaction with ionized gas particles. For different material and purposes, a variety of generator frequencies can be applied – from kHz up to MHz. The process can be repeated, and the effect is stable for a few minutes up to months depending on the material (e.g. plasma activated polypropylene can be further processed after several weeks). The most important advantages of plasma technique can be pointed as follows: no solvents have to be used, explosion protection is not necessary, staff is not exposed to toxic chemicals, modified materials do not have to be dried, running costs are very low, and last but not least - all types of solid materials can be treated with plasma.

The process and general mechanism of MWCNT oxygen plasma activation were described. There are a few stages of modification, and their time depends on virgin MWCNT properties, as well as on applied plasma power. The modification stages can be described as follows:

- during the first few minutes of treatment, oxygen plasma activates the surface layer of the material, and the concentration of oxygen increases;
- as a consequence of ion and electron bombardment the amorphous carbon layer covering nanotubes loosens, and the material slightly expands;
- as the bombardment continues, amorphous layer is oxidized and removed—this process proceeds the proper modification of clean nanotubes;
- further process running provides etching of different oxygen groups to material's surface – mainly nanotubes edges and active centers where some structural defects are present (sp³ hybridization makes modification much easier than in the case of stable sp² structure).

Some works consider oxygen plasma treatment as a simple, quick and cheap method for MWCNT cleaning—an inactive, amorphous carbon layer is eliminated in this way. In this work, attempts to modify the commercial GnP and MWCNT were made to obtain improved filler dispersion in elastomer matrix, which was expected after the increasing of filler's SFE values. To achieve a homogenously modified powdery filler, samples were treated in a rotating reactor chamber. Based on previous experience, the process was carried out only in a discharge power of 100 W [8].

2. Experimental

2.1. Materials

The materials treated and used as fillers for rubber composites were:

- GnP Grade 4-Research grade, (CheapTubes, USA)
- MWCNT, purity wt. 95%, (CheapTubes, USA)

As an elastomer matrix, a styrene-butadiene rubber (KER 1500, Synthos S.A., Polska) was used.

2.2. Composites production

Rubber mixes were prepared with a Brabender Plasticorder laboratory micro mixer (Brabender, Germany), operated with 45 rpm, for 30 min. Their composition is presented in table 1. The only one variable was the type of modified mineral filler.

Table 1. Composition of the rubber compounds studied.

Component	Quantity[phr]
SBR (KER 1500)	100
Carbon Black N550	40
MWCNT/GnP	10
ZnO	3,5
Stearine	1
Polnox (antioxidant)	2
TMTD (tetramethyl thiuram disulfide)	0,2
TBBS (N-tert-butyl-2-benzothiazole sulfenamide)	1,4
S	1

2.3. Modification of fillers

Fillers studied were modified with a Zepto plasma reactor (Diener, Germany). The reactor was operated with the frequency of 40 kHz and the maximum discharge power of 100 W. Two different system set-ups were used – one for simple filler activation, and the other for activation, followed by transportation of the modifying agent vapours to the reactor chamber.

Carbon fillers were subject to the oxygen plasma treatment during various time. Efficiency of process gas flow was 20 - 60 cm³/min, and the pressure in the reactor chamber was maintained at 30-80 Pa. Symbols of the modified fillers were as follows:

- CNT₀/GnP₀ – virgin material
- CNT₁/ GnP₁ - 16 min. oxygen plasma treatment
- CNT₂/ GnP₂ - 32 min. oxygen plasma treatment
- CNT₃/ GnP₃ – 48 min. oxygen plasma treatment
- CNT₄/ GnP₄ - 64 min. oxygen plasma treatment

3. Methods

3.1. Tensiometric measurements of SFE

Effectiveness of the modification is represented by changes in the filler's SFE and its components – polar and dispersive. SFE was examined with a K100 MKII tensiometer (KRÜSS GmbH, Germany). Contact angle was determined using polar (water, methanol, ethanol) and non-polar (n-hexane, n-heptane) solvents. SFE and its components were calculated by the method proposed by Owens-Wendt-Rabel-Kaelble [9].

3.2. Micromorphology of fillers

Micromorphology of the filler was studied with an AURIGA (Zeiss, Germany) scanning electron microscope (SEM). Secondary electron signal (SE) was used for surface imaging. Accelerating voltage of the electron beam was set to 10 keV.

3.3. Mechanical properties of elastomer composites

Mechanical properties of the vulcanizates studied were determined with a Zwick 1435 universal mechanical testing machine (Germany). Tests were carried out on “dumbbell” shape, 1.5 mm thick and 4 mm width specimens, according to PN-ISO 37:1998 standard. The following properties of the materials were determined: elongation at break (Eb), stress at elongation of 100% (SE100), 200% (SE200), 300% (SE300) and tensile strength (TS).

3.4. Micromechanical properties of composites

Mechanical properties of the surface layer of the samples were determined with a NanoTest 600 instrument (MicroMaterials Ltd., UK) – figure 1. The Berkovich diamond penetrated the sample with a normal load of $P = 0.5$ mN, applying loading/unloading rate of $dP/dt = 0.01$ mN/s, in 20 different points of the surface. All the experiments were run under the controlled conditions of temperature ($T = 23^{\pm 2}$ °C) and relative humidity ($60^{\pm 5}$ %).

4. Results

4.1. MWCNT surface layer modification

The tensiometric analysis revealed (table 2), that a virgin material was oxidized. Sixteen minutes' modification of MWCNT caused the significant decrease in SFE polar part, what stays in conformity with second and third stage of cleaning process described by Xu [10]. Extending the plasma treatment time to 32 minutes causes very significant SFE value increase, which is connected with the sudden change of its polar part from 13.3 up to 54.5 mJ/m². Longer modification brings almost no effect on SFE and its parts – the total value stays at the level of 73 mJ/m² after 48 minutes, and 75.6 mJ/m² after 64 minutes.

Sample (oxygen plasma treatment time)	SFE [mJ/m ²]	polar part [mJ/m ²]	dispersive part [mJ/m ²]
MWCNT ₀	39.3	18.2	21.2
MWCNT ₁ (16 min.)	31.6	18.3	13.3
MWCNT ₂ (32 min.)	72.9	18.4	54.5
MWCNT ₃ (48 min.)	73.3	18.3	55.0
MWCNT ₄ (64 min.)	33.6	18.0	15.6

Table 2. Total SFE of vulcanizates containing MWCNT with its components (L – total surface free energy, Ld – dispersive part, Lp – polar part).

For GnP, there is a lack of information on plasma treatment in the literature, as rather mono- and double- layer structures are investigated [11, 12]. In this case, the situation is completely different – although the process was also carried out for time up to 64 minutes, the obtained maximum SFE value was 30 mJ/m², with a polar part changing from 4.7 for virgin material, to 12.7 mJ/m² for 64 minutes

Table 3. Results of the analysis of total SFE of vulcanizates containing graphene with its components (L – total surface free energy, Ld – dispersive part, Lp – polar part).

Sample (oxygen plasma treatment time)	SFE [mJ/m ²]	polar part [mJ/m ²]	dispersive part [mJ/m ²]
GnP ₀	22.9	4.7	18.2
GnP ₁ (16 min.)	24.2	5.9	18.3
GnP ₂ (32 min.)	22.8	4.5	18.3
GnP ₃ (48 min.)	26.1	7.7	18.4
GnP ₄ (64 min.)	30.0	12.7	17.3

treatment (table 3). It seems that also for GnP, some equilibrium of oxidation and amorphous carbon layer elimination can be observed, as SFE values for particular treatment time vary from 4.5 to 7.7 mJ/m² before the adequate surface oxidation starts (between 48 and 64 minutes). It also has to be underlined, that also in case of commercial GnP, the virgin material demonstrates the presence of oxides layer (polar part of SFE – 4.7 mJ/m²).

It is easily seen that the modified nanotubes form a bit different structures from virgin material (figures 1A and 1B). Plasma-treated agglomerates seem to be loosened, what is confirmed by micrographs (figures 1C and 1D), where a lot of “molten” edges, and shorter nanotubes are visible. The loosened structure may be achieved due to the amorphous phase elimination stage during MWCNT plasma modification. It seems that in a consequence of long-time oxygen plasma treatment, some of MWCNT tend to break and form shorter structures. Such phenomena can be reflected by better filler distribution in polymer matrix, and ultimately better mechanical properties of a composite.

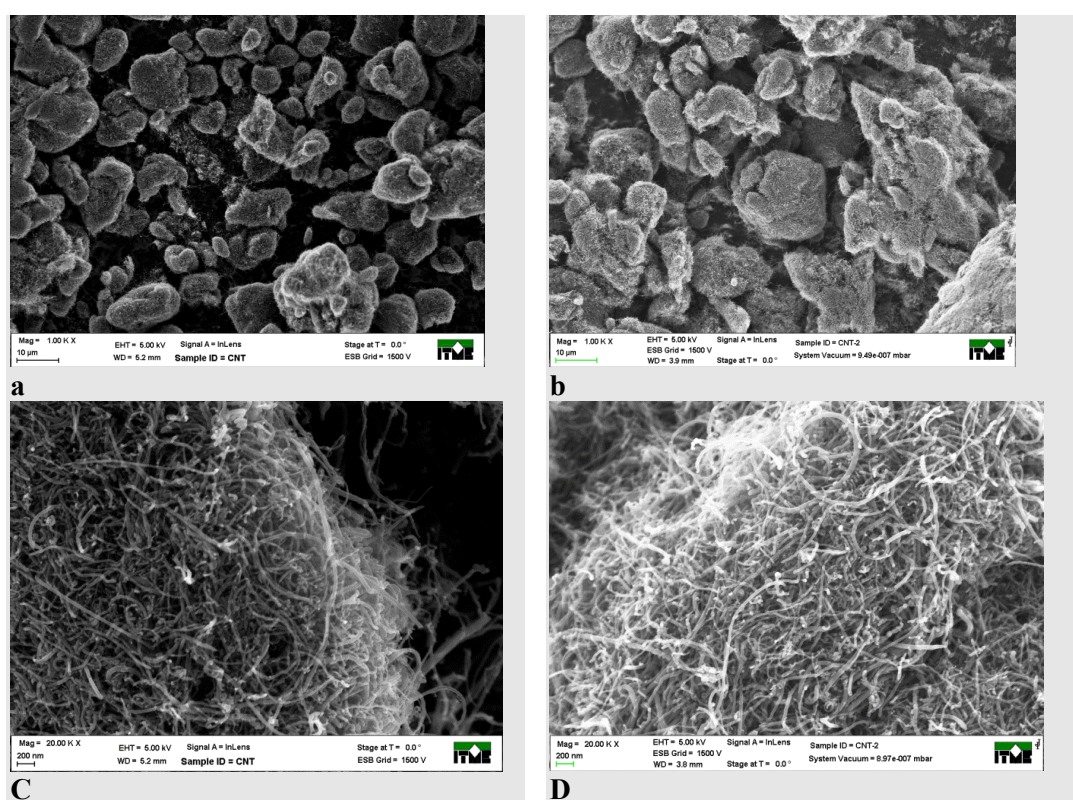


Figure 1. Morphology of carbon nanotubes studied: A, C,— not modified MWCNT, B, D,— modified MWCNT.

Results of SFE analysis for GnP suggested, that its mechanism is completely different from that for MWCNT. GnP surface, probably very stable, almost free of structure defects, is much harder to modify compared with carbon nanotubes. Relatively small changes in SFE values are reflected by SEM analysis – only slight differences can be observed between virgin and plasma treated GnP – for modified materials, some delayered graphene galleries were observed, whereas such structures were not found for virgin samples (figure 2).

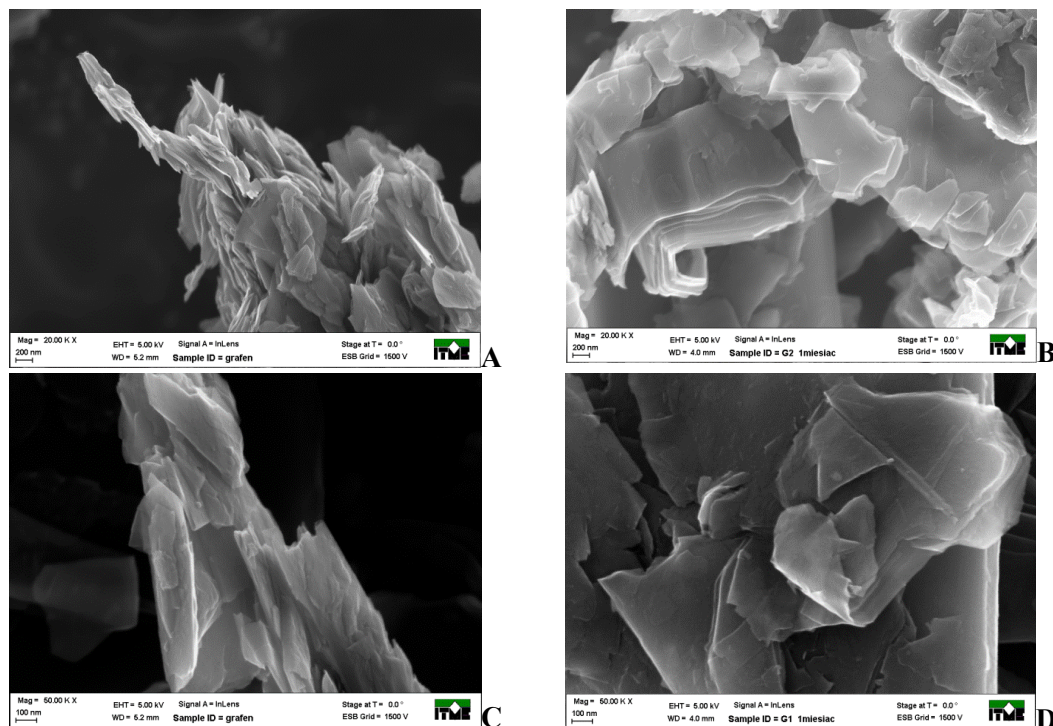


Figure 2. Morphology of graphene samples studied: A, C – not modified graphene, B, D – modified graphene.

4.2. Mechanical properties of composites

The results of mechanical properties of the composites are consistent with SEM observations and SFE analysis. In case of MWCNT, plasma modification causes significant increase of composite tensile strength. For virgin samples, the obtained value was 7.2 MPa, 12 MPa for 16 min. modification, 15.2 MPa for 32 min. modification, and approximately 18 MPa for 48 min. and 64 min. treatment (table 4). The results of mechanical test confirmed that plasma treatment positively affects the composite tensile strength, probably due to improved filler dispersion in polymer matrix.

Table 4. Mechanical properties of elastomer composites filled with carbon nanotubes.

	SBR/CNT ₀	SBR/CNT ₁	SBR/CNT ₂	SBR/CNT ₃	SBR/CNT ₄
SE ₁₀₀ , MPa	2.3	4.1	4.5	4.6	4.7
SE ₂₀₀ , MPa	4.2	8.5	9.9	9.4	8.8
SE ₃₀₀ , MPa	5.9	8.9	14.7	13.6	13.8
TS, MPa	7.2	12	15.2	17.9	18.3
E _b , %	366	312	310	393	361

Such an effect was not observed for GnP containing composites (table 5). The vulcanizates with a modified filler showed lower tensile strength compared with the virgin sample, and only the 64 min. GnP treated sample presented similar parameters to virgin samples. However, what is interesting is Sample SBR/GnP₁, where significant increase of elongation at break was observed. Probably short modification makes the graphene galleries loosened, enabling the relative movement of structures in this way during material stretching.

4.3. Micromechanical properties of composites surface layer

The composites microhardness reaches the maximum value for samples containing 32 min. treated filler, and it doesn't depend on the filler type (table 6). The extension of a modification time to 48 or

64 min. is reflected by significant microhardness decrease. Plastic deformation of the composites is inversely proportional to the microhardness values.

Table 5. Mechanical properties of elastomer composites filled with grapheme.

	SBR/GnP ₀	SBR/GnP ₁	SBR/GnP ₂	SBR/GnP ₃	SBR/GnP ₄
SE ₁₀₀ , MPa	4.2	2.8	3.7	3.3	4.5
SE ₂₀₀ , MPa	9.2	6.7	8.5	7.5	9.8
SE ₃₀₀ , MPa	13.3	10.4	12.7	11.2	14.3
TS, MPa	19.3	17	16.1	15.6	20.5
E _b , %	413	469	374	418	435

Table 6. Micromechanical properties of the surface layer of the composites studied.

	Microhardness, MPa	Plastic deformation, μm
SBR/CNT ₀	2,6 \pm 0,1	2,9 \pm 0,3
SBR/CNT ₁	3,1 \pm 0,1	2,6 \pm 0,2
SBR/CNT ₂	4,5 \pm 0,1	2,2 \pm 0,2
SBR/CNT ₃	3,3 \pm 0,1	2,4 \pm 0,2
SBR/CNT ₄	2,2 \pm 0,1	3,1 \pm 0,3
SBR/grafen ₀	3,2 \pm 0,1	2,6 \pm 0,4
SBR/grafen ₁	4,1 \pm 0,1	2,3 \pm 0,2
SBR/grafen ₂	5,7 \pm 0,1	1,9 \pm 0,1
SBR/grafen ₃	3,1 \pm 0,1	2,6 \pm 0,2
SBR/grafen ₄	2,3 \pm 0,1	3,1 \pm 0,5

5. Conclusion

The plasma modification effect strongly depends on a filler type and character, which is confirmed by SFE measurements and mechanical tests. The oxygen plasma activation seems to be reasonable only for MWCNT, as in this case process causes a significant SFE increase reflected by the increased mechanical performance of the composite. During plasma treatment MWCNT, agglomerates tend to expand and form loosened structures, what probably makes the dispersion better. The micromechanical tests have shown some similar tendency for MWCNT and GnP. The measurement indicates that different phenomena are present - visible at micro- and nano-level, and negligible when the composite is tested in a macro-scale.

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