Non-marking solid tires with graphene nanotubes: high mechanical strength and conductivity in compliance with international standards

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Abstract

New safety regulations related to electrostatic protection are being developed to keep pace with the increasing automation of industrial facilities and the growing automotive industry. Single wall carbon nanotubes (SWCNTs) were studied as a prospective additive to improve electrical conductive properties of rubber compounds used for non-marking anti-static solid tires. A ready-to-use masterbatch containing primary SWCNTs dispersed in a polymer-based carrier was used. The study was conducted with a standard non-marking solid tire NR/BR-based formulation filled with mineral filler by introducing the SWCNT-based masterbatch at different stages in the production sequence to see which would achieve the best performance. Another anti-static additive widely used in industrial applications was used as a reference to define the performance differences. The main finding of the study is that 0.22 wt.% of SWCNTs in a rubber compound can maintain tensile properties before and after heat aging, improve tear resistance, and provide electrical onductivity at the required anti-static level, without a negative influence on other properties, while also retaining the color and the non-marking effect.

Introduction

There are number of standards related to regulations on tires in the field of electrical properties – International Standard ISO 16392 Electrical Resistance — Test Methods to Measure the Electrical Resistance of Tyres on a Test Rig, Wirtschaftsverband der deutschen Kautschukindustrie e.V. (W.d.K) 110 Measurement of the Electrical Resistance of Tyres, ASTM F 1971 – Standard Test Method for Electrical Resistance of Tires Under Load On the Test Bench, etc. These requirements regulate and ensure ESD protection to remove static electricity from the surface of a tire when it occurs at high speed and to prevent its accumulation in the long run. In some application areas, a normal tires that are required to be anti-static are considered to be capable of safely dissipating electrical charge if the resistance measured does not exceed 1010 Ω But there are a number of specific cases, such as when the tire used in potentially explosive areas, that are strictly regulated by the ATEX Products Directive 2014/34/EU and EN 1755 – Industrial trucks – safety requirements and verification – Supplementary requirements for operation in potentially explosive atmospheres. According to EN 1755, the outer material of castors and wheels should have a maximum surface resistance of 109 Ω It is a well-known fact that most tire formulations contain carbon black and can easily achieve the requirements for being anti-static, but this is not the case with non-marking solid tires. The current article is dedicated to the study of using graphene nanotubes (also referred as single wall carbon nanotubes) as an alternative solution to provide the required conductive properties as well as maintain color and basic formulation properties of non-marking solid tires. It has been acknowledged by both scientists and manufacturer communities that graphene nanotubes are one of the most advanced additives for improving almost all materials used in our daily life. When applied in rubber compounds, they enhance mechanical performance while also imparting conductivity. The key to achieving this previously unobtainable combination of properties is graphene nanotubes' extremely low working dosage.

Conductive additives: balancing of consistent conductivity with mechanical performance Various types of inorganic nanofillers has proven to be an efficient way to enhance the mechanical and electrical properties of rubbers. Carbon black and silica are widely used in commercially produced rubbers, including rubbers for tires.

It is well known that the shape of the nanofiller affects the critical concentration required to create a connected network of filler (the percolation threshold): the higher the aspect ratio of the nanoparticle, the lower the percolation threshold. That is why using 2D and 1D carbon nanofillers (i.e. graphene sheets and carbon nanotubes) in rubbers has attracted the attention of numerous research groups in academic institutions and in industrial companies. Single wall carbon nanotubes (SWCNTs) are characterized by the smallest possible diameter of less than 2 nm and are of particular interest [3].

One fairly new conductive additive that has recently entered the polymer market is multi wall carbon nanotubes (MWCNTs). However, MWCNTs are not able to fully meet manufacturers' needs for stable levels of conductivity and easier compounding, as well as for suitable mechanical properties and softness requirements. To be effective in the host material, the required concentration of thick and short MWCNTs is tens or even hundreds of times higher than that of long and thin SWCNTs.

Despite the similarity in names, multi wall carbon nanotubes and single wall carbon nanotubes – two allotropes of carbon – have hardly anything in common, and thus they impart a number of very different properties. While MWCNTs feature many tubes with decreasing diameter that are coiled inside each other, SWCNTs can be thought of as an extremely thin rolled up sheet of graphene, and thus they are widely referred to as graphene nanotubes. Being an excellent conductor similar to copper and 100 times stronger than steel, graphene nanotubes gain traction starting from a loading of just 0.01%. Even such an ultra-low concentration is enough to enable conductivity without a negative effect on the material's mechanical properties or viscosity.

Currently, graphene nanotubes are the most innovative additive that facilitates efficiency, durability, and affordability in solid tires, particularly for colored or non-marking applications where anti-static or conductive properties are required for tires to dissipate the static charge.

To impart conductive properties to white filler-based rubbers, conductive fillers need to be added during the compounding process. There are not many additives which can reach the desired level of electrical conductivity without affecting the color. Depending on the particular application, it could be copper powder, silver- and nickel-coated graphite, copper or aluminum – while these do provide the required conductive properties, adding them also leads to a number of negative trade-offs in flexibility, elasticity and high price.

For conventional polymer-based additives which are more commonly used due to their low price, the high working dosages required result in a number of drawbacks in the rubber's mechanical properties and a reduced cycle life of the final products. These shortcomings severely restrict the potential range of non-marking solid tire applications. Furthermore, conventional polymer-based additives are normally humidity-dependent and subject to migration, so the rubber's properties are not stable because of migration of the additive to the surface and release during the cycle life.

Historically, there have been several technical barriers that have prevented the mass application of graphene nanotubes in various industries, including elastomers. The main challenge was related to the difficulty in achieving uniform and homogeneous dispersion of nanotubes in the material matrix and in preventing further agglomeration. However, recent materials technology advances have enabled easy-handling nanotube concentrates that are compatible with industry-standard formulations and manufacturing processes, without requiring any specific changes or additional tools.

This article investigates the effect of graphene nanotubes on the electrical and mechanical properties of a non-marking solid tire compound in comparison with a conventional commercially available additive that is widely used in industrial applications to implement electrical conductive properties to rubber compounds without discoloration.

Experimental part

Materials

The current study investigates rubber mixtures based on a standard solid tire formulation – a blend of NR/BR and mineral filler (silica). Commercially available TUBALL™ graphene nanotubes (OCSiAl), with a diameter of 1.6±0.4 nm, were used. The Raman spectroscopy (532 nm laser) G/D ratio peaks varied in the range 70–100, indicating a very low concentration of defects. The type of TUBALL™ applied contains 14–15% of catalyst impurities (metallic iron and iron carbides), which are covered by graphite-like shells. The contents of nanotubes in the material is above 85% by weight (on a dry basis). The TEM micrographs in Figure 1 show that the untreated nanotubes form the entangled mesh of bundles with thickness varying from 10 to 50 nm [4].

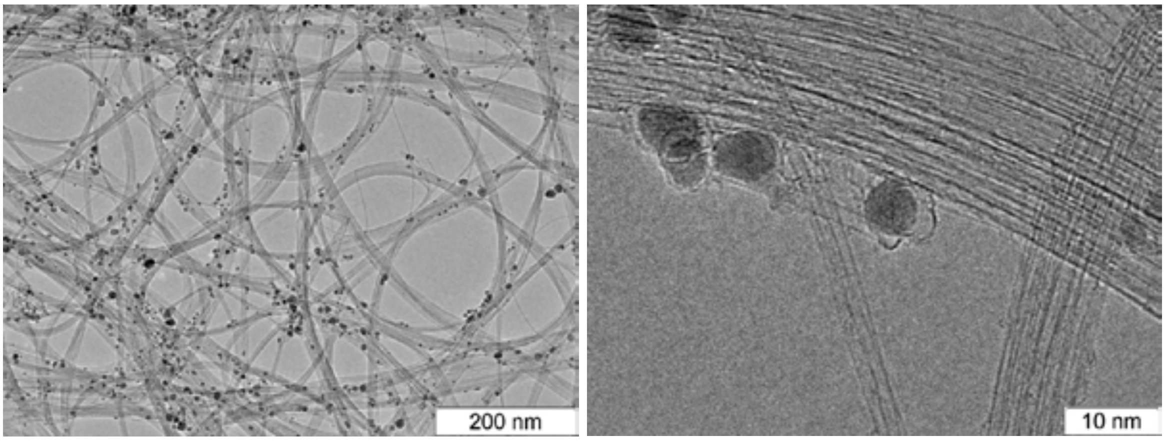

Figure 1. TEM micrographs of TUBALL™ nanotubes; batch 01RW02.N1.299 was used in the study.

Dispersing the graphene nanotubes requires the bundles to be split. Therefore TUBALL™ MATRIX 618 beta, a predispersed concentrate containing 10% of nanotubes in an ether-based plasticizer [5], was used in this study. As an additional comparison, a commercially available anti-static plasticizer based on fatty alkyl ether of polyethylene glycol, Rhenosin® RC 200 (LANXESS Deutschland GmbH), was used.

Formulation and mixing

A Banbury 1.6L internal mixer and a two-roll rubber mill (10 inch roll diameter) were used for compounding

Several ways of introducing the TUBALL™ MATRIX 618 beta were tested: at the 1st stage together with the second part of filler; at the 2nd stage into the internal mixer; into the two-roll mill together with curing agents after compounding at internal mixer. The best performance was achieved with the latter two mixing options – introducing the TUBALL™ MATRIX 618 beta into the two-roll mill at the end of compounding, and into internal mixer at the end of the mixing stage.

Testing procedures and data

Electrical properties were tested by the four-point method according to ASTM D991 and ASTM D257. Mechanical properties were studied according to ASTM

Table 1. Examples of the recipes of rubber compounds.

Composition and feeding stages			Reference compound	6.9 wt.% RC 200	2 wt.% TUBALL™ MATRIX 618 beta
Feeding stage	Raw material	Brand	phr	phr	phr
Stage 1	Natural rubber	CV 60	85.0	85.0	85.0
	Butadiene rubber	BR9000	15.0	15.0	15.0
	Naphthenic oil	KN4010	5.0	5.0	5.0
	Silica	Z-155	50.0	50.0	50.0
	Silane TESPT	SI-69	4.0	4.0	4.0
	Stearic acid	SA1801	2.0	2.0	2.0
	Zinc oxide	Active ZnO	5.0	5.0	5.0
Stage 2	Plasticizer	RC 200		12.5	–
	Sulfur	S-80	1.0	1.0	1.0
	TBzTD		0.5	0.5	0.5
	CBS		2.0	2.0	2.0
	TUBALL™ MATRIX 618 beta				3.9
Total, phr			169.5	182.0	173.4

standards D412, D624, D5963 and D2240. Heat aging was performed according to ASTM D573 (5 days, at 85°C).

Results

Electrical resistivity

Electrical resistivity measurement results are shown in Table 2. Before testing the resistivity, the surface of the unaged samples was treated with ethanol to remove the plasticizer which could bleed out to surface.

Table 2. Electrical resistivity of the compounds.

Sample	ASTM D 991		ASTM D 257		Surface resistivity meter
	Volume resistivity, Ω·cm	Deviation	Volume resistivity, Ω·cm	Deviation	Resistivity, Ω/sq
Before heat aging					
Reference compound	R out of range (too high)	–	1×10^{14}	4×10^{10}	10^{13}
RC 200	R out of range (too high)	–	2×10^{11}	3×10^{10}	10^{10}
TUBALL™ MATRIX 618 beta	**2×10^{2}**	1×10^{1}	**R out of range (too low)**	–	**10^{6}**
After heat aging (non treated sample)					
RC 200	R out of range (too high)	–	1×10^{12}	7×10^{10}	10^{13}
TUBALL™ MATRIX 618 beta	**5×10^{2}**	3×10^{2}	**R out of range (too low)**	–	**10^{6}**
After heat aging (sample surface treated with ethanol)					
RC 200	R out of range (too high)	–	1×10^{12}	7×10^{10}	10^{13}
TUBALL™ MATRIX 618 beta	**4×10^{3}**	2×10^{2}	**4×10^{7}**	**3×10^{7}**	**10^{7}**
Electrical resistivity (four-probe method) – ASTM D 991					
Electrical resistivity (two-probe method) – ASTM D 257					
Heat aging – ASTM D573					

It was noticed that all samples containing Rhenosin® RC 200 had oil bleeding onto the surface after curing and heat aging. This probably occurred due to the high dosage of material (6.9% used, with the recommended maximum according to the technical datasheet being 10%).

Figure 1. A sample of rubber containing TUBALL™ MATRIX 618 beta having its volume resistivity measured according to ASTM D257.

Mechanical properties

Tensile and tear properties are shown in Table 3.

The mixtures, containing 0.22 wt.% graphene nanotubes (2.2 wt.% TUBALL™ MATRIX 618 beta), were prepared by the mixing sequences as briefly mentioned above. The current study found that the best performance was obtained when the nanotube concentrate was introduced at the 2nd stage into the internal mixer.

Table 3. Mechanical properties of the compounds.

Sample	M50, MPa	M100, MPa	M200, MPa	M300, MPa	M500, MPa	Tensile strength, MPa	Elongation at break, %	Tear strength, kN/m
Before heat aging								
Reference compound	1.0	1.9	5.1	10.1	21.3	22.1	502	44.7
RC 200	0.9	1.5	3.8	7.3	17.0	21.0	571	52.2
TUBALL™ MATRIX 618 beta	1.5	2.2	4.7	8.7	19.0	19.9	516	49.2
After heat aging								
RC 200	0.8	1.4	3.4	6.5	14.7	15.6	521	24.8
TUBALL™ MATRIX 618 beta	1.5	2.4	5.0	9.0	–	15.7	446	30.6
Tensile parameters – ASTM D412								
Tear parameters – ASTM D624								
Heat aging – ASTM D573								

It should be noted that, despite the tensile strength remaining unchanged with either additive, at small deformations graphene nanotubes increase the moduli at 50% and 100% and RC 200 has the opposite effect. At higher elongations, nanotubes showed slightly better results compared with RC 200, probably due to higher plasticizer content in the samples containing RC 200, which is evident on elongation data. Both of the additives have a positive effect on the tear strength of unaged samples.

After heat aging, a reinforcement effect from graphene nanotubes and a strong degradation effect on tensile modulus from RC 200 was evident (a performance difference ranging from 87% to 38% for M50–M300). Tear strength was maintained to at least 20% more with TUBALL™ MATRIX 618 beta than with RC 200.

Conclusions

This study has shown that even a minor amount (0.22 wt.%) of TUBALL™ graphene nanotubes can strongly increase electrical conductivity without the negative effects on mechanical properties which normally occurs with conventional conductive fillers. The effect on electrical conductive properties of 6.9 wt.% of the anti-static plasticizer is negligible and can not meet the requirements for dissipative tire properties. Higher dosages of plasticizer would result in an even worse effect on mechanical properties.

Introduction of 2.2 wt.% of TUBALL™ MATRIX 618 beta into a standard NR/BR and silica-filled solid tire formulation improves the moduli of the rubber, increases its tear strength and improves the stability of properties after heat aging compared with a conventional anti-static additive used as a reference.

Good dispersion and distribution of graphene nanotubes in rubber is crucial for achieving the desired enhancement. For two-stage, internal-mixer rubber compounding, introducing the TUBALL™ MATRIX 618 beta at the 2nd mixing stage was found to be optimal to achieve the targeted resistivity level and the best balance of mechanical improvements.

Adding the properly dispersed graphene nanotubes in TUBALL™ MATRIX 618 beta into rubber material provides consistent electrical conductive properties without migration of carrier onto the surface and that remain stable after heat aging. The low required dosage of the graphene nanotubes allows the color of the rubber to be maintained, without any carbon release, which is crucial for non-marking solid tires.

References

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