Innovative, carbon black-filled compounds and master-batches at the interface of the plastics and dye industries

Applications and benefits of Caparol NEFA MB masterbatches for thermoplastic elastomers – part 1

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Dispersive and distributive mixing processes are a major element in the manufacture of thermoplastic masterbatches and compounds. Continuously working twin-screw extruders and kneader systems are mainly used for compounding. A crucial restriction of these mixing machines is the limited dwell time of the components to be mixed. Caparol Industrial Solutions GmbH is a company that has specialised in the manufacture of primarily liquid and paste-form pigment and additive concentrates. Discontinuously working mixing and dispersion machines, such as roller mills, butterfly mixers or dissolvers are used in particular in the production of these concentrates.

This is where the electrically conductive carbon black compounds and masterbatches of the NEFA MB EL product group come into play. The combination of discontinuous mixers and twin-screw extruders can manufacture very highly filled, conductive performance concentrates on the basis of SEBS copolymers.

Compounds in the NEFA MB EL product group are characterised by specific electrical resistances less than one ohm-centimetre (measured according to DIN EN ISO 3915) with hardnesses in the range of Shore A 80 to Shore D 60 and elongations at break of more than 400 %. Used as a masterbatch, electrostatically dispersive properties can be achieved with NEFA MB-EL concentrations in TPVs, for example, from an adding concentration of just 25 %.

1 Introduction

Conventional thermoplastic polymer materials are electric insulators, because of their chemical structure. Various uses of plastics, for example in the field of electrical technology or explosion protection, however, require a discharge capacity or, to a limited extent, also a conductivity of plastics. For this, polymer materials are often modified with carbon-based additives such as carbon black or graphites. To ensure that a functional dissipative or conductive finish of the plastic is possible, a contacting network of the filler must form right through the material. This is also called the "percolation" of the filler. This is also the reason for the fact that an electrostatic discharge capacity with specific contact resistance in the area of less than 10^6 ohm-cm can only be reached very erratically from a particular filler concentration **(fig. 1).** The filler content needed to reach the percolation area depends considerably on the structure, form and size of the conductive fillers and also on the composition and morphology of the matrix polymers and the processing/manufacturing conditions. Once the percolation range has been exceeded, the specific resistance of a compound steadily decreases through increasing the filler content, since more and more conductive paths through the material can form. At the same time, with the increase in the filler content, more and more macromolecules are needed to wet the particle surfaces and are thus restricted in their freedom of movement. Consequently, an increasing filler content causes an increasing rigidity of the compound, causing a reduction in elasticity and ductility.

With thermoplastic elastomers in particular, this correlation presents a challenge when the requirement is to create systems with

Fig. 1: Resistivity of carbon filled compounds as function of the filler concentration

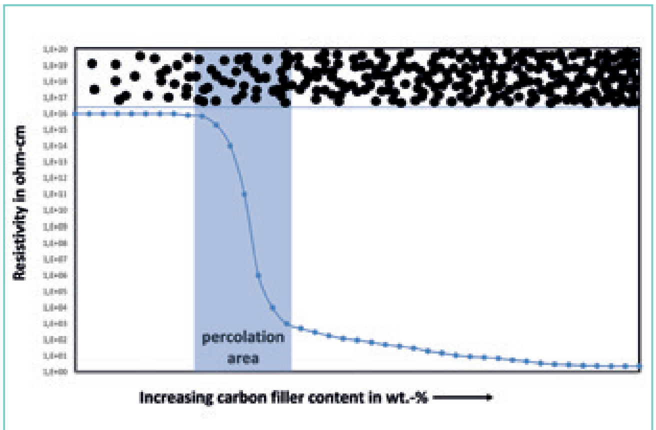

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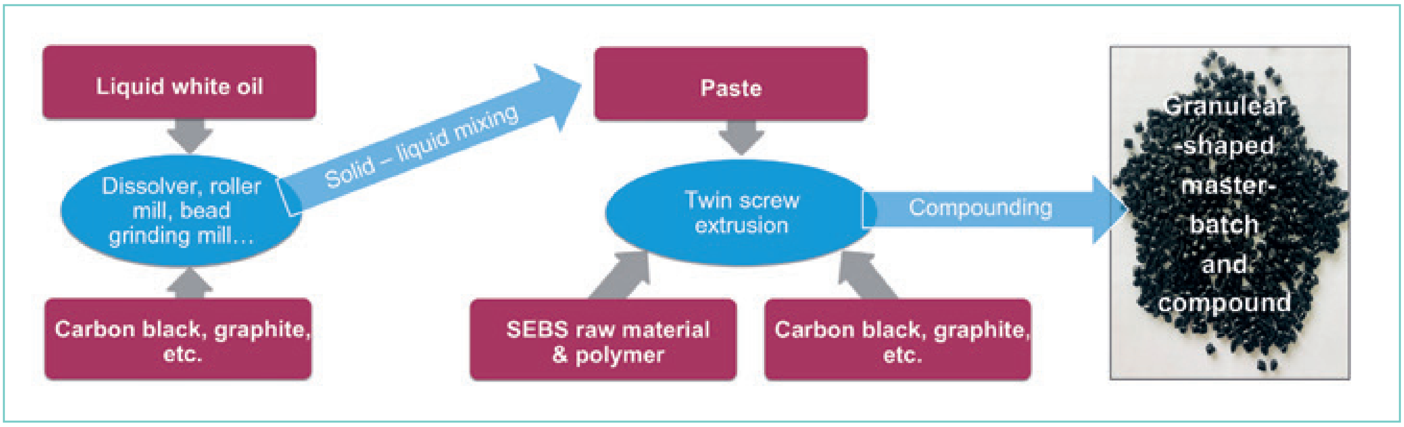
Fig. 2: Innovative processing route for highly conductive NEFA MB Masterbatches



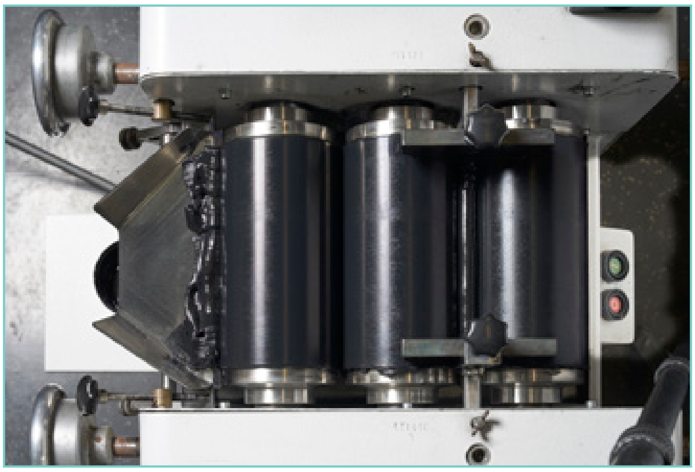
very low specific resistances. The high filler concentrations needed for this would considerably limit the mobility of the elastic phases, making it difficult to produce soft and elastic TPEs that also have low specific resistances in the range of less than 5 ohm-cm.

2 The manufacturing makes the difference

In this situation, the carbon black compounds and masterbatches developed and produced by Caparol Industrial Solutions GmbH represent an interesting addition and expansion of commercially available products in this area. The conventional way to create carbon black compounds is to compound individual or several polymers together with functional fillers. For this, twin-screw extruders or continuously working kneader systems are generally used. A limiting factor of these continuously working systems is the limited dwell time of the components in the mixing phases especially when it comes to the filler's important dispersing and wetting processes. This is where the special manufacturing process of NEFA MB EL compounds comes in. Unlike other classic compounds, NEFA MB EL products are manufactured in two separate process stages **(fig. 2)**.

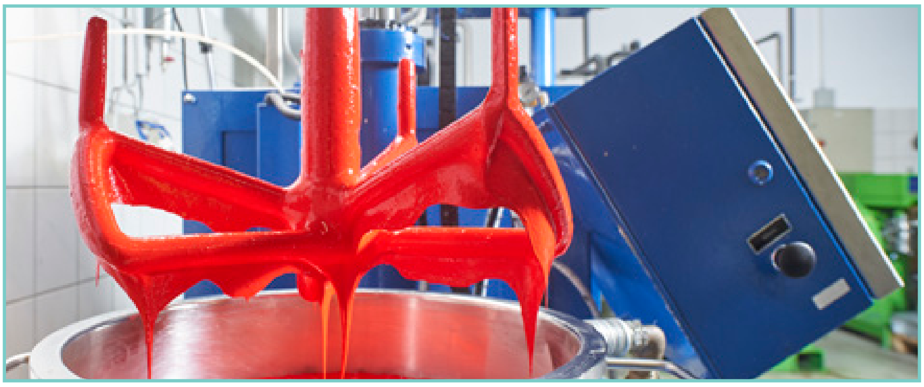
Firstly, the carbon black or another conductive filler is processed together with white oil into a paste in a classic solid-liquid dispersion process. White oil is a conventional component of SEBS compounds. Normally, triple-roller mills or butterfly mixers are used for this **(figs. 3, 4)**. In this dispersion stage, which is independent of dwell time, the conductive filler is very finely distributed in the white oil. In addition, the filler

Fig. 3: Laboratory triple-roller mill



is effectively wetted by the white oil. In a second process step, the paste is processed together with the other compound components such as SEBS, an additional quantity of conductive filler and other polymers if applicable in a twin-screw extruder into the finished compound granulate. Because

Fig. 4: Butterfly mixer



of the preliminary dispersion and pre-wetting of the carbon black with white oil, the carbon black can be worked into the polymer matrix and distributed better and more effectively during compounding. In addition, because of the pre-wetting, larger quantities of filler can be integrated into the matrix in comparison with the single-stage manufacturing process.

In this way, electrically conductive compounds with outstanding properties, characterised in particular by very high filler concentrations, are created. In this way, it is possible, for example, to incorporate special conductivity carbon blacks with specific surfaces of over 1,000 m^2/g with up to 30 % by weight into the NEFA MB EL compounds. With conven-

Fig. 5: Stress-strain-behavior of NEFA MB EL 23381

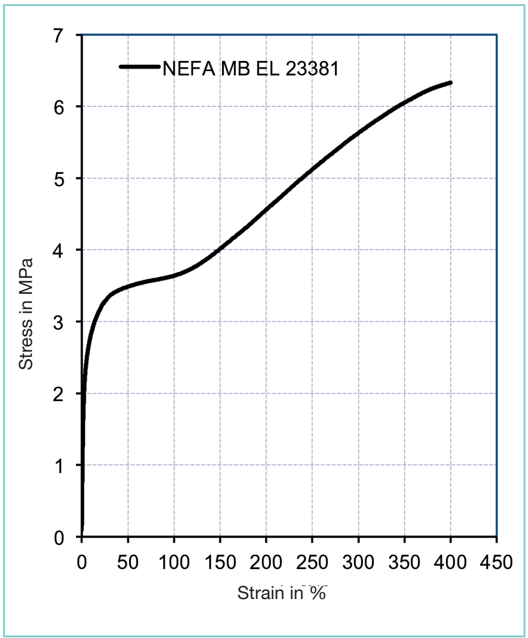


Fig. 6: Stress-strain-behavior of TPU A80 and a compound with NEFA MB EL 23381

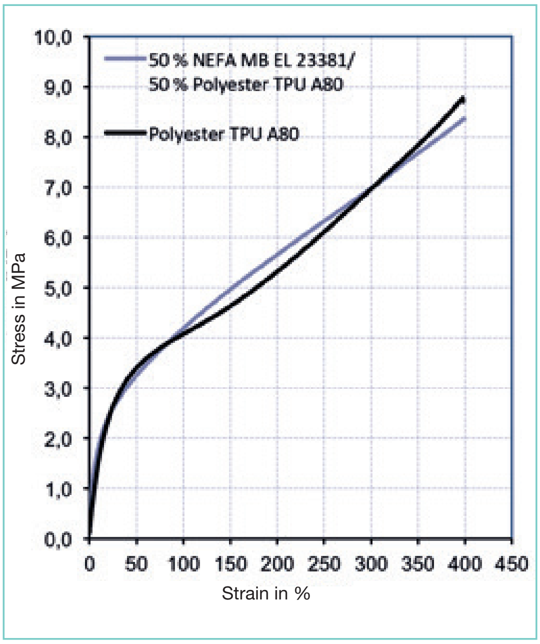
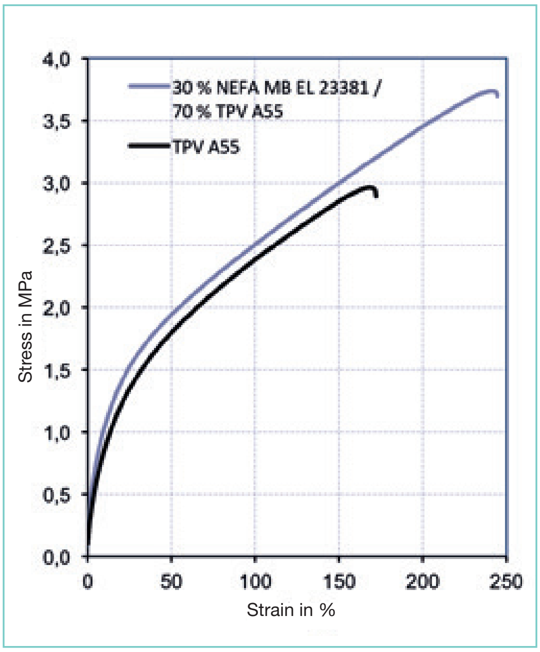


Fig. 7: Stress-strain-behavior of TPV A55 and a compound with NEFA MB EL 23381



tional technical carbon blacks with specific surfaces in the range of 20 – 200 m²/g, fill levels of up to 60 % by weight are possible.

3 Carbon black compounds and masterbatches with outstanding properties

Because of the high specific loading with conductive fillers, NEFA MB EL compounds are characterised by very low specific surface and contact resistances in the range of 0.5 – 5 ohm-cm. The products can also be used very effectively as masterbatches to equip polymer materials with a permanent electrostatic discharge capacity. Unlike established carbon black-based masterbatches, NEFA MB EL compounds, however, are still very elastic and ductile despite the high carbon black concentration. This is due in particular to the improved dispersal of the conductive filler. The masterbatch systems are therefore particularly suitable for the modification of thermoplastic elastomers. Due to the chain structure of the styrene-butadiene-styrene block copolymers, the masterbatches are basically compatible with styrene-based TPS and thermoplastic elastomers on an olefin basis (TPO or TPV). But thermoplastic elastomers with a higher polarity such as TPC, TPA or TPU can also be modified very effectively with NEFA MB EL compounds.

Figure 5 and **table 1** show the stress-strain behaviour and some characteristic measurement values of a typical compound variant, NEFA MB EL 23381. The material has a conductive carbon black level of 26 % by weight with a specific BET surface of the carbon black of 1,000 m²/g. In relation to the high carbon black fill level, NEFA MB EL 23381 shows an extraordinary degree of elasticity and ductility. Particular mention should be made of the low surface resistance of the compound of less than 2 ohm with an elongation at break of more than 400 %. This means that NEFA MB EL compounds should no longer be regarded just as classic antistatic plastic mixes. Instead, the compounds can also take on functional tasks relating, for example, to the transmission of low electrical capacities or switching currents.

Figures 6–7 and **table 1** show, using stress-strain diagrams and a number of specific characteristic values, examples of the use of NEFA MB EL 23381 as a masterbatch for the electrostatic equipping of other TPE materials. Both in TPV A55 and in polyester-based TPU A80, the SEBS-based masterbatch can be integrated without further additives. With addition concentrations of 30–50 % by weight, an electrostatic equipment of the thermoplastic elastomers can be achieved, which is typically characterised above the surface resistance in a range less than 1,000 ohm. In particular, the mechanical properties and the hardness of the mixtures are only influenced to a minor extent despite the carbon black-based electrostatic additives. This is a major advantage of NEFA MB EL masterbatches.

4 Summary

The combination of various mixing and dispersion techniques at the interface between the dyes and plastics industries create synergies that produce special masterbatches and compounds. If very high filling levels with outstanding dispersion quality are the focus of a masterbatch or compound application, the process for manufacturing the NEFA MB EL products is an innovative solution for

Tab. 1: Specific measured values for TPV and TPU and compounds with NEFA MB EL

Properties	NEFA MB EL 23381	Polyester TPU A80	50 % NEFA MB EL 23381 in Polyester TPU A80	TPV A55	30 % NEFA MB EL 23381 in TPV A55
Surface resistivity in Ohm	1.9	$> 10^{12}$	250	$> 10^{12}$	80
Hardness in Shore A	85	78	76	56	64
Stress, 50 % strain in MPa	3.49	3.38	3.22	1.79	1.94
Stress, 300 % strain in MPa	5.63	6.94	6.97	/	/

product development. The examples presented are only intended to provide a glimpse of the possibilities of NEFA MB EL compounds. Through the careful selection and combination of conductive filler and also of the basic raw materials such as SEBS, polymers and white oil, a very broad range of mechanical, rheological and electrical properties of the materials and masterbatches can be created. The focus of the compounds, however, is always on multi-stage manufacturing technology that makes a special filler dispersion possible.

About the company

Caparol Industrial Solutions GmbH (CIS), with its production plant in Grimma-Nerchau, Germany, is a subsidiary of DAW SE, Ober-Ramstadt. CIS develops and produces high-quality dyeing and additive concentrates, such as tints, industrial dye pastes and masterbatches for a range of applications. In addition to its outstanding pigmentation expertise, the dispersion of solids in liquid and paste-form carrier systems is the core competence of CIS. DAW SE is the largest private manufacturer of building paints and thermal insulation in Europe. In 2018, the company, which has a workforce of around 5,800 people, achieved total revenues of EUR 1.4 billion. Internationally, the company is represented in more than 40 countries and has 25 production locations worldwide.

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Following the Call for Parts and Components in September, the first entries for the 20th SPE Automotive Award have already been received. Until 15 January 2021, innovative vehicle components and parts made of plastic can still be submitted in the categories Body Interior, Body Exterior, Power Train, New Mobility, Electronical/Optical Part, Chassis Unit/Structural Component and Enabler Technology. Further information is available at www.automotiveaward.de.

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