1 Introduction

The increasing demand for eco-friendly, high efficient automobiles led to the introduction of new materials. Due to their specific properties such as high toughness, fatigue resistance, chemical resistance and an unlimited shelf life fiber-reinforced composites gain more and more importance within the automotive industry. Especially thermoplastic endless fiber-reinforced composites, so called organic sheets, offer great potential in structural and semi-structural applications. However, when it comes to exterior applications tremendous efforts have to be made to meet the industries requirements, e.g. on the appearance of components. The online varnishing of composite components together with the body in white is a promising way to achieve color matching parts in an economical and ecological process. As the varnishing process is based on an electrostatic deposition process, the intrinsic isolating polymer composites have to be modified with conductive filler to reach a minimum electrical conductivity of $10^{-4}$ S/m [1]. Within the last years a vast number of polymers, both thermoplastic and thermoset, have been modified with carbon nanotubes [2]. But even as the electrical conductivity of many polymers has been increased there are only single applications on the market which use the benefits of incorporated CNT [3]. However, one of the main challenges when working with nano materials is to evenly distribute and disperse the particles within the matrix systems.

2 Experimental

As nano sized filler material both carbon black and carbon nanotubes were used. As carbon nanotubes Baytubes C 150P and Baytubes C 70P from Bayer MaterialScience AG and for carbon black Printex XE2 from Evonik Degussa GmbH were used. These particles were selectively incorporated into semi-crystalline polyamide 6, polyamide 6.6 from BASF SE and amorphous polycarbonate (Makrolon 2408) from Bayer MaterialScience AG, respectively. The incorporation was done using the twin screw extrusion process. After the dispersion of the CNT/carbon black into the polymers, the melt was calendered into polymer films with a mean thickness of 100 µm, which together with the fiber-reinforcement are the base products for endless fiber-reinforced composites (organic sheets). Organic sheets were manufactured using the film stacking process where alternating layers of polymer and reinforcement build up the composite laminate. A twill 2x2 glass fabric with an areal weight of 300 g/m² was used as reinforcement. The process temperature and pressure were set to 280°C and 25 bar for both the polyamides and the polycarbonate.

The electrical conductivities of the films as well as the organic sheets were measured in dependence on DIN EN ISO 3915, which is a four point measuring technique. To guarantee a proper contact between the electrodes and the specimens the contact areas were brushed with a silver paste to achieve a low contact resistance. If the electrical conductivity is below $10^{-5}$ S/m the conductivity was measured using a 8009 Resistivity Fixture (ring electrodes with 60 mm diameter) equipped with a Keithley electrometer model 6517A designed for high resistivity samples according to DIN VDE 0303, which was developed for isolating materials. The results shown are mean values of at least 5 measurements.

3 Results

3.1 Electrical conductivities for unreinforced polymers
The influence of different CNT contents in both semi-crystalline and amorphous polymers on the electrical conductivity was compared by manufacturing concentration series with a varying CNT content for polyamide 6, polyamide 6.6 and polycarbonate. Polyamide 6 was modified with 3, 5 and 7 wt.-% Baytubes C 150P, while the concentration series for polyamide 6.6 was made with 1, 3, 5 and 7 wt.-% Baytubes C 150P. In Fig. 1 it can be seen that for both polymers a CNT content of 3 wt.-% is not sufficient to build up a percolated network within the polymer as no electrical conductivity could be measured using the four-point measurement method. While the maximum measured electrical conductivity is in good agreement with the literature the percolation thresholds are higher in the systems investigated here [4].

To compare the level of conductivity for Baytubes C 70P polycarbonate was manufactured with 4 and 8 wt.-% carbon black Printex XE2, respectively. The systems with 1 wt.-% Baytubes C 70P and 4 wt.-% Printex XE2 could not be measured and therefore had not developed a percolation network. The electrical conductivity for 5 wt.-% Baytubes C 70P is in the range of $10^0$ S/m and about two orders of magnitude higher than the benchmark system with 8 wt.-% Printex XE2 (see Fig. 2). In general the gained conductivities for polycarbonate are in good agreement with the literature [5-8].

3.2 Electrical conductivities for endless fiber-reinforced composites

All tested polymers were further processed into endless fiber-reinforced composites with an non-conductive glass-fiber reinforcement, which takes no part in the overall electrical conductivity. Thus an influence of the reinforcement could be excluded. When processing the polymer films to organic sheets processing times vary from 15 minutes up to 2 hours depending on the used process, which was either a static press process or a continuous compression molding process. Common to all processes is a remelting of the polymer for several minutes. As almost nor shear forces are applied to the systems, a reorganisation of the particle network is possible. This leads to stronger percolation networks which increases the electrical conductivity. Fig. 3 shows the electrical conductivities for the polyamide based organic sheets. A general increase in electrical conductivity compared to the unreinforced polymers is measurable. It also can be seen that all formerly non-electrically conductive systems are now electrically conductive. This might be an indicator for reagglomeration processes within the polymer-CNT compound.

A similar behavior is visible for polycarbonate based organic sheets. An increase of one order of magnitude for the system with 5 wt.-% C 70P is comparable to the increase for polyamide systems. However, the carbon black reinforced polycarbonate with 8 wt.-% Printex XE2 showed an increase of almost three orders of magnitude in electrical conductivity.

As an electrical conductivity may just be needed as a functional layer e.g. high conductivity on the surface and isolating behavior in the core, a study with varying laminate layout was performed. As base material polycarbonate with 5 wt.-% CNT was chosen, as it has a guaranteed percolated CNT network. The CNT content was linearly increased from the outer layers towards the core of the organic sheets with a minimum of one PC/CNT layers on each surface. Fig. 5 shows the electrical conductivities for different laminate structures. The volume conductivity increases about 13 orders of magnitude compared to neat polycarbonate systems. Two layers of CNT-doped polycarbonate, one on each side of the organic sheet, is sufficient enough to increase the volume conductivity to a level of $10^0$ S/m. A further increase of conductive polymer films increased the electrical conductivity of the whole system (see Fig. 6). The increase itself follows a linear equation as the conductivity paths for electrons increase linearly with the linear addition of CNT to the system.

4. Summary

The influence of incorporating different nanoparticles (CNT and carbon black) into neat thermoplastics and endless fiber-reinforced composites on the electrical conductivity was examined. It could be shown that the incorporation of nanoparticles, in particular carbon black and carbon nanotubes, lead to a significant increase in electrical conductivity in polymer films as well as organic sheets. The electrical conductivity is dependent on various factors including the type and
amount of electrically conductive fillers and the used polymers. Amorphous polycarbonate showed higher conductivity values than the semi-crystalline polyamides. However, when further processing the polymer films into organic sheets reagglomeration of the nanofillers occur which leads to a general increase in electrical conductivity of about one order of magnitude for carbon nanotube systems. Furthermore, a study of the laminate structure revealed that a sufficient electrical conductivity can be established with very low amounts of conductive polymer film. A further increase of conductive polymer films increases the electrical conductivity and follows a linear equation.

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Fig. 1: Electrical conductivities of CNT modified polyamide 6 and polyamide 6.6 films

Fig. 2: Electrical conductivity of nanoparticle modified polycarbonate films

Fig. 3: Electrical conductivities of CNT modified organic sheets made of polyamide 6 and polyamide 6.6

Fig. 4: Electrical conductivity of nanoparticle modified organic sheets
Fig. 5. Electrical conductivity of CNT modified organic sheets with a varying laminate build-up

Fig. 6. Linear dependency of electrical conductivity of CNT modified organic sheets with an increasing CNT content

3 References


