

Multifunctional Composites

Reinforcing Materials. The combination of modern nanofillers with conventional glass fibers is paving the way to multifunctional composites with outstanding electrical and mechanical properties. The following article demonstrates this in tests with a polypropylene matrix.

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Multifunctional thermoplastic polymer composites combining electrical conductivity with good mechanical properties are suitable for a wide range of applications in many branches of engineering (e.g. for dissipation of static charges, electrostatic painting processes, and electromagnetic shielding). The potential of carbon nanotubes (CNTs) as a functional filler to impart electrical conductivity to both thermosetting and thermoplastic polymers is well known and is being utilized. But their potential – because of their exceptionally high elastic modulus (up to 1 TPa) – to improve the mechanical properties of thermoplastic composites, in particular, has not so far been exploited. The main reasons for this are the tendency of individual CNTs to agglomerate and form CNT clumps and their largely chemically inert surface that prevents effective bonding to the polymer matrix. In recent years, there have been many attempts to chemically modify the surface of CNTs to make them compatible with different thermoplastic polymers. But these functionalizations have the disadvantage of damaging the structure of the CNTs, which can lead to both length shortening and loss of electrical conductivity, so running counter to the two target properties of electrical conductivity and improved mechanical properties.

In comparison with the most commonly used functional filler for electrical conductivity – carbon black – CNTs have

the great advantage of being effective at significantly lower filler contents in the range of just a few percent by weight and so to embrittle the composite far less.

Polypropylene (PP) continues to be a popular commodity material, which is valued for its good mechanical properties and relatively low price. However, because of the respective surface properties of CNTs and the PP melt, PP is very unsuitable for uniform dispersion of CNTs in the matrix. This adversely affects both the electrical conductivity and mechanical properties of PP-CNT composites. Various compounding additives have improved the dispersion of CNTs and shifted the percolation threshold – the filler loading at which the composite becomes conductive – to lower filler contents (down to 0.4 % in PP). However, these measures did not achieve a substantial improvement in the mechanical properties of the composites.

PP glass fiber (GF) composites are used in many sectors on account of their impressive price/performance ratio. To attain the goal of electrically conductive composites with high mechanical property values at a moderate cost, it would therefore seem a promising approach to develop composites with a filler/reinforcing material mix of CNTs and glass fibers.

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Abbreviation	Meaning
PP	polypropylene
Px	peroxide
C2.5	2.5 wt.-% CNTs
G20	20 wt.-% glass fibers

Table 1. Test specimen designations used in the graphs

Materials and Processing

In the study reported here, a PP of the R352-08R type from Dow Deutschland Inc., Schwalbach, Germany, was used as the matrix material. The CNTs came from Nanocyl S.A., Sambreville, Belgium, (multiwalled CNTs, type NC 7000) and the glass fibers from European Owens Corning Fiberglas SPRL, Brussels, Belgium (type 968/968A). The additive used to improve dispersion of the CNTs was the organic peroxide Peroxan Bec from Pergan GmbH, Bocholt, Germany. The test specimen designations in the graphs are explained in **Table 1**.

The materials were compounded on a Leistritz ZSE 27HP-52D co-rotating twin-screw extruder with an L/D ratio of 52 from Leistritz AG, Nuremberg, Germany. First of all, PP-CNT composite materials with 2.5 % CNT content were produced. Then the glass fibers were fed in via a side port.

The composite materials were injection molded into test specimens (ISO 527-1 and ISO 179-1/1eA) on an Engel ES 200/60 HL ST injection molding machine from Engel Austria GmbH, Schwertberg, Austria, and their mechanical properties were tested. Other test specimens were compression molded from pellets into test specimens measur-

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ing $60 \times 10 \times 1 \text{ mm}^3$ on a Collins P 200 P/M laboratory press from Dr. Collin GmbH, Ebersberg, Germany. The electrical properties of both types of test specimen were tested.

Results

Rheology: An important consideration in incorporating nanoscale fillers in polymer melts is the change in viscosity of the melt. Because of the very large specific surface area of the fillers, melt viscosity generally rises very steeply. This is particularly true of compounding processes, where the aim is to break up agglomerates of nanoparticles to increase the specific surface area of the nanofillers. Current work on the dispersion of CNTs in thermoplastic melts has shown that a low matrix viscosity is advantageous for the dispersion of CNTs. To counter an excessively high viscosity increase, an organic peroxide was added to the composite in the present study. Its effect on melt viscosity can be seen in **Figure 1**. While the peroxide significantly reduces the viscosity of the PP on its own, it significantly increases viscosity on addition to the PP-CNT composite. This can be attributed to the better dispersion and correspondingly enlarged effective surface area of the CNTs (**Fig. 2**). The addition of 20 % glass fibers again increases viscosity significantly but the peroxide has an overall viscosity-lowering effect in the 2-filler system (CNTs + glass fibers).

The decrease in the viscosity of the matrix material achieved by the peroxide not only results in better dispersion of the CNTs but also reduces the specific energy input during compounding and hence energy costs. **Figure 3** shows thin sections of the composites containing 2.5 % CNTs

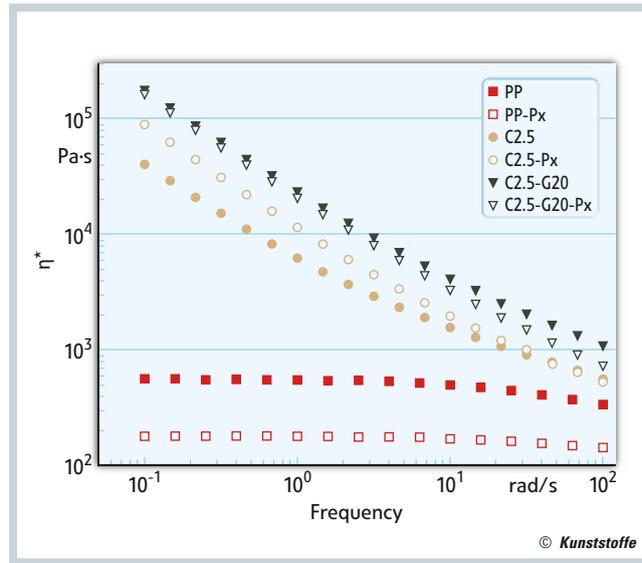


Fig. 1. Complex viscosities of the tested materials (figures: ICT)

without (left) and with (right) the addition of peroxide. Besides the reduction from 3.5 % to 3 % in the area of visible and therefore undispersed CNT agglomerates relative to the total observed surface area, a significant reduction in specific energy input (from 1.2 kWh/kg to 0.55 kWh/kg) was also noted.

Electrical Properties: **Figure 4** shows the volume resistivity of the composites. This was determined directly on extruded strands, injection molded specimens, and compression molded bars. Looking at the values for extruded strands, starting with the pure PP-CNT composite material, a significant reduction in volume resistivity can be seen with the use of peroxide, with the addition of glass fibers, and with the addition of both peroxide and glass fibers. Through the reduction in viscosity, the peroxide obviously achieves better deagglomeration of the CNTs, making more of them available to form the conductive network. The unexpected reduction in volume re-

sistivity when glass fibers are added to the PP-CNT composite can be attributed to better dispersion of the CNTs due to the double shearing of the material in two consecutive processing steps – production of the CNT composites and incorporation of the glass fibers in the CNT composite.

The test specimens produced by injection molding all show significantly higher volume resistivity values than the extruded strands. To simulate real-life conditions, the skin was not removed from the injection molded specimens before the electrical properties were tested. Directly on the surface, the flash has a filler-depleted layer with a higher electrical resistivity than the inside of the specimen. There is also the possibility that the CNTs are shortened because of the strong shear forces in the injection molding operation. The use of peroxide has no significant effect on resistivity. Through the addition of glass fibers, the resistivity value is slightly increased, as expected.

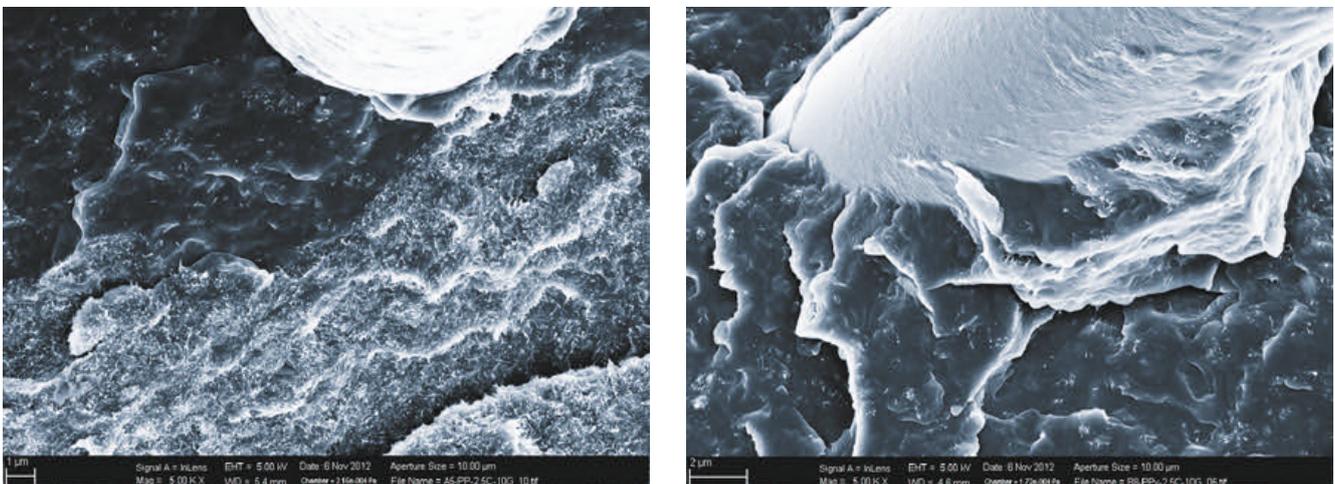


Fig. 2. Typical morphology of the PP-CNT-GF composites without peroxide (left) and with peroxide (right)

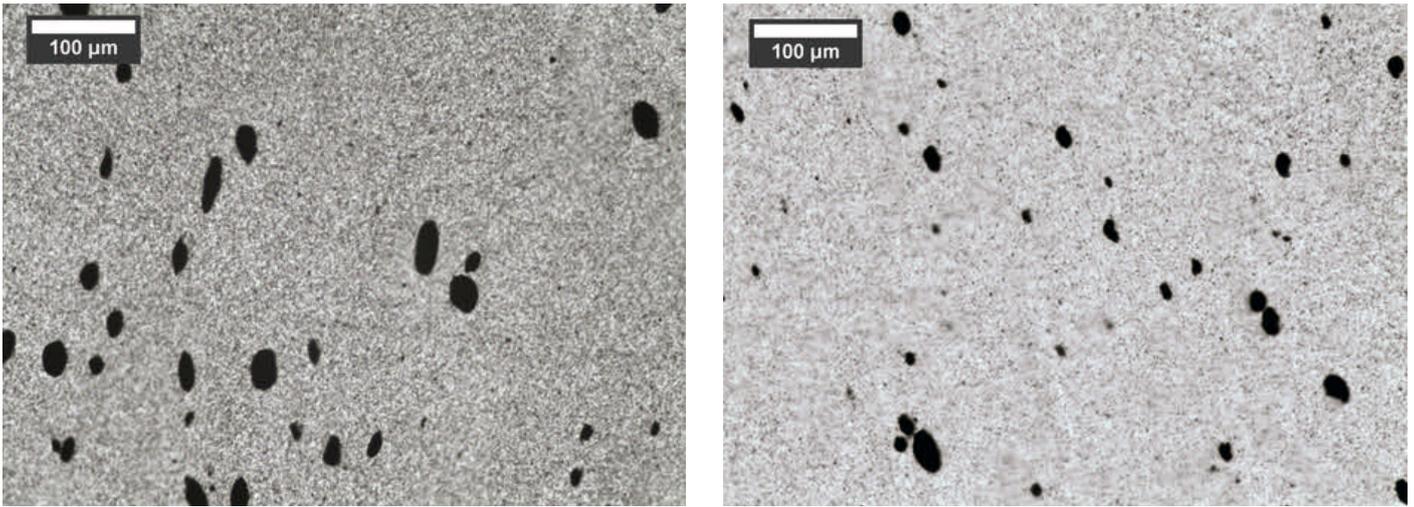


Fig. 3. Micrographs showing thin sections of the PP-CNT composites (2.5 % CNTs) without (left) and with (right) peroxide

Virtually all the compression molded materials show the lowest resistivity values. Compression molding offers the dispersed CNTs the best conditions for forming a conductive network, thanks to the very long cooling times and low shear. Any negative influence by the glass fibers is scarcely perceptible.

Mechanical Properties: The elastic modulus of the materials is increased by around 30 % through the addition of 2.5 % CNTs, and by about 380 % through the addition of 20 % glass fibers. The combination of the two fillers leads to an increase in the elastic modulus that is slightly greater than the sum

of the two individual effects. The chain-shortening effect of the peroxide is reflected in a slight decrease in the elastic modulus of all the composite materials as compared with the peroxide-free variants.

The maximum stresses follow the same pattern as the elastic moduli. A 2.5 % addition of CNTs achieves a slight increase of about 16 %, while with 20 % glass fibers, the maximum stress goes up by about 160 %, and with a combination of the two by about 200 %. Here again, the differences between the peroxide-containing and peroxide-free composites are small.

An interesting picture emerges in the case of notched impact strength. First of all, there is a very significant increase with the addition of only 2.5 % CNTs. 20 % glass fibers increases the notched impact strength more than 2.5 % CNTs. The combination of the two produces the best values, according to the familiar pattern. While the use of peroxide reduces notched impact strength in the case of PP on its own and the PP-CNT composite, this value is increased in the case of the

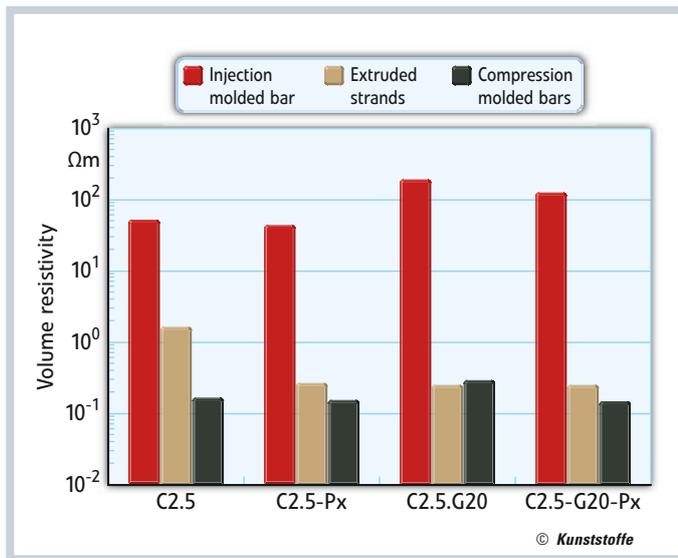


Fig. 4. Volume resistivities of the tested composites as a function of the method of processing

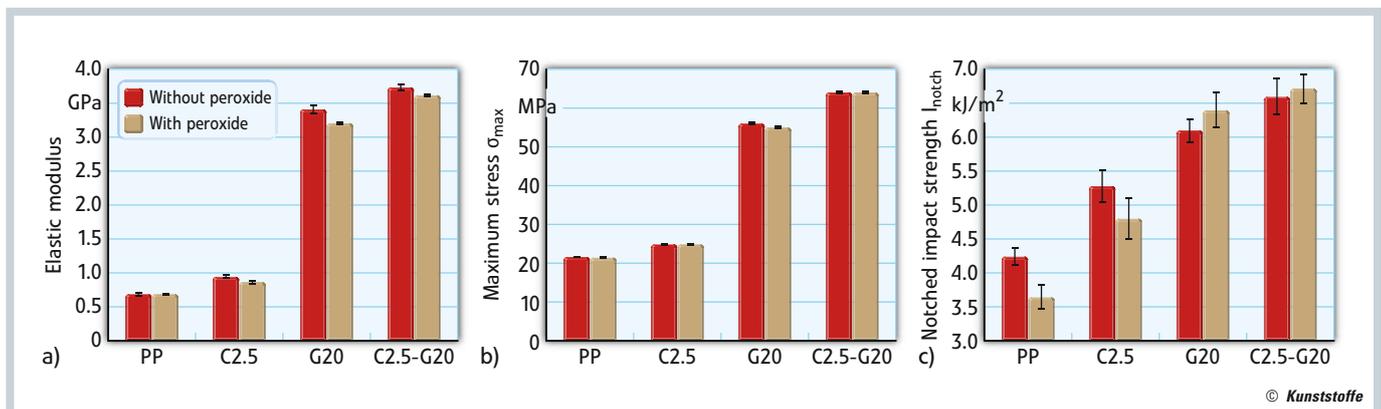


Fig. 5. Mechanical properties of the composites

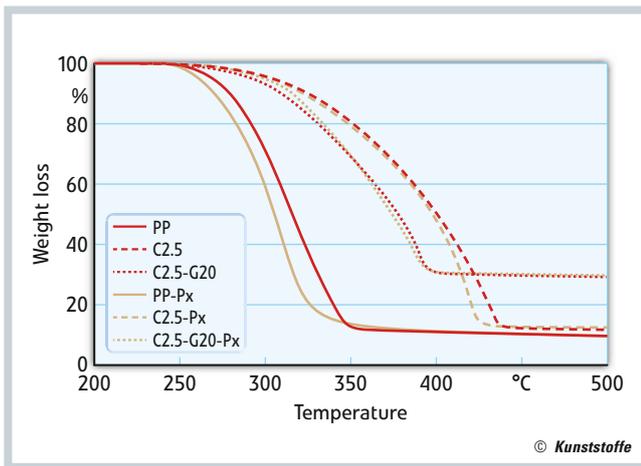


Fig. 6. Thermal properties of the composites

two composites with a combination of CNTs and glass fibers (Fig. 5).

Thermal Properties: Figure 6 shows the results of thermogravimetric measurements (TGA) on composites in air. The use of peroxide reduces the thermal stability of the PP slightly due to shortening of the polymer chains, while the addition of 2.5 % CNTs increases the thermal stability of the PP-CNT composites considerably as compared with PP alone. In the 2-filler system (CNTs + glass fibers), thermal stability drops somewhat as compared with the composites with CNTs alone but is still significantly higher than in the case of the matrices alone. In view of the minimal differences between the peroxide-free and peroxide-containing

composites, it was concluded that there was no systematic effect of the peroxide on the thermal stability of the composites.

The increase in the thermal stability of the composites containing CNTs can be attributed to the radical-intercepting action of the CNTs described in the literature, which delays oxidative decomposition of the polymer matrix. This is particularly important in terms of the increased processing stability of CNT composites.

Conclusion

In the reported study, it was shown that skilful combination of glass fibers with

CNTs as fillers makes it possible to produce multifunctional composites with an excellent property profile. The properties resulting from the addition of both types of filler, such as mechanical stability and electrical conductivity, can be combined with virtually no mutually adverse effect. The negative influence of peroxide used as a processing aid on the thermal stability of the matrix material PP is very much more than compensated by the CNTs. At the same time, the peroxide enables the specific energy input during compounding to be reduced by 50 %. ■

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