

TECMAT

Thermal & Electrical Conductive Fibre and Plastic Materials



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TECMAT newsletter

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Project presentation

TECMAT aims to develop conductive compounds combining a high conductivity and improved processability in a wide range of processing techniques, including fiber extrusion, injection molding, film extrusion and thermoforming.

Polymers are good insulators, which means that to achieve a certain level of conductivity, it is necessary to apply a high concentration of conductive additives. These additives form clusters in the polymer matrix, the size of which depends on the polarity and viscosity of the polymer. In order to establish electrical conduction, these clusters must be connected. The minimum concentration of additive required to make connections and eventually form a network (and consequently induce conduction) is called the percolation concentration (Fig.1). However, the addition of a high concentration of conductive additives is typically accompanied by a huge increase in viscosity, which greatly affects the processability of the polymers during the production process.

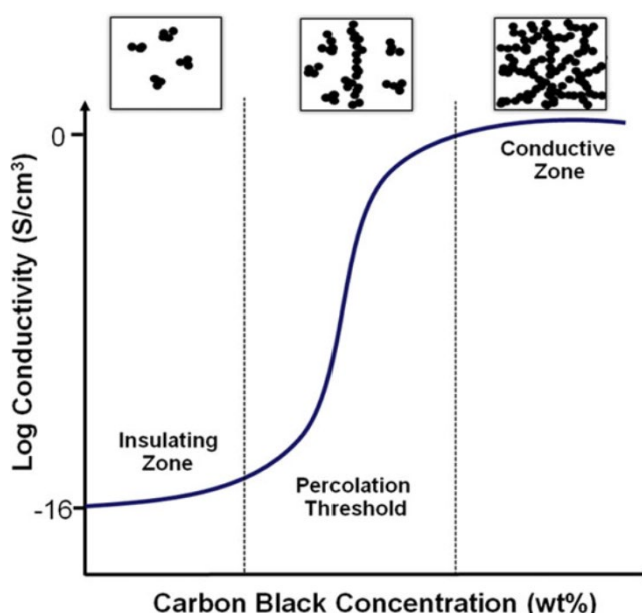


Fig.1: Schematic representation of the carbon black concentration in relation to conductivity, to illustrate the concept of percolation concentration.

This project strives to increase the processability of conductive formulations by means of blends composed of two incompatible polymers. The conductive additives are added to the phase with the lowest mass percentage in the blend. This would lead to a double percolation, whereby a certain level of conductivity can still be achieved, even though a lower concentration of conductive additive is used. Double percolation can be achieved if the dispersed phase creates microfibrils that form a conductive network. An additional advantage is that a higher processability can be achieved by selecting an appropriate matrix polymer and applying a lower total concentration of conductive additive in the blend. Choosing the most suitable matrix polymer (with appropriate viscosity) will ensure easier processing, as in principle there is only a significant increase in viscosity of the phase containing the additives. The TECMAT two-phase system thus tries to combine good conductivity (through double percolation) with better processability than traditional single-phase systems (because the viscosity of the matrix polymer is hardly influenced by the additives).

The materials, especially the components of the blends and suitable additives, were selected in cooperation with the advisory group, by means of a questionnaire. In addition, the survey was also used to determine the preferred production processes, the desired conductivity range and the intended applications. The results revealed that PP, PA6 and PET, and Carbon black (CB) and Carbon nanotubes (CNT) were considered the most interesting as polymer matrix and conductive fillers, respectively. Upon further deliberation with the project partners, PP and PA6 were selected as non-compatible polymers for the two-phase system, combined with CB and/or CNTs for the conductivity.

Our German project partners (Fraunhofer ICT and SKZ) started exploring different possibilities to produce a variety of conductive compounds from PP/PA6 blends. Different parameters (blend ratio, dilution of the dispersed phase, the use of a PP or a PA6 masterbatch, the concentration of conductive additive, etc.) are being investigated. In parallel, Centexbel started to process dry blends into filaments, to compare with the compounds produced by our partners. In this newsletter we will elaborate on the filament extrusion trials of the selected dry blends.

Filament extrusion

Two PA6/CB compounds (containing 35% and 45% CB, respectively) were blended with PP, the matrix polymer, in different ratios, namely 90/10, 80/20 and 70/30. The blends were processed into monofilaments using a spinning die with round holes. These trials showed that a 70/30 blend was difficult to process (unstable extrusion, rough filaments as a result). Moreover, a very high resistivity was measured after stretching the filaments. In order to improve processing and obtain smoother filaments, a compatibiliser was added, with success. Unfortunately, the positive effect on processing was accompanied by an enormous loss of conductivity, even for the unstretched filaments. As illustrated in Fig.2 using electron microscopy images (SEM), the addition of the compatibiliser led to a much better mixing of the PA6 phase in the PP phase. However, this also means that the conductive additives are distributed throughout the entire matrix, instead of just in the PA6 phase, which causes a large drop in conductivity. Consequently, it is no longer considered a double percolation, as this requires 2 incompatible phases.

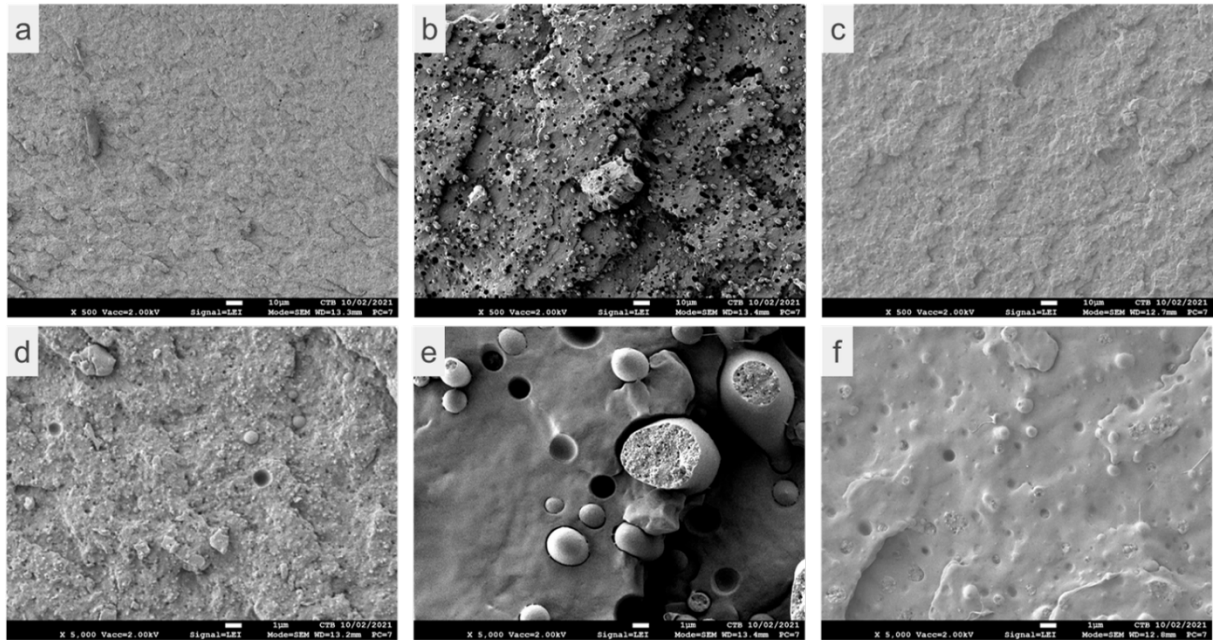


Fig.2: SEM: a-c: 500 x magnification and d-f: 5000 x magnification of the unstretched monofilaments of (from left to right) the PA6/CB-compound, the 70/30-blend of PP and the PA6/CB-compound, and the same blend with the addition of 5% compatibilizer, respectively.

The loss of conductivity upon drawing also led us to suspect that the microfibrils formed are pulled apart when the monofilaments are stretched. To further investigate this, monofilaments of a 90/10 PP/PA6 blend (without conductive additives) were produced. Again, the addition of a compatibiliser was necessary to ensure stable extrusion, but, as in the previous experiments, this led to the formation of a single phase (see Fig.3 b/e and c/f). The SEM images of the filaments without compatibilizer indeed show that microfibrils were already formed before drawing and that this was the case both in the blends without and in the blends with conductive additives (see Fig.2 b/e and Fig.3 a/d).

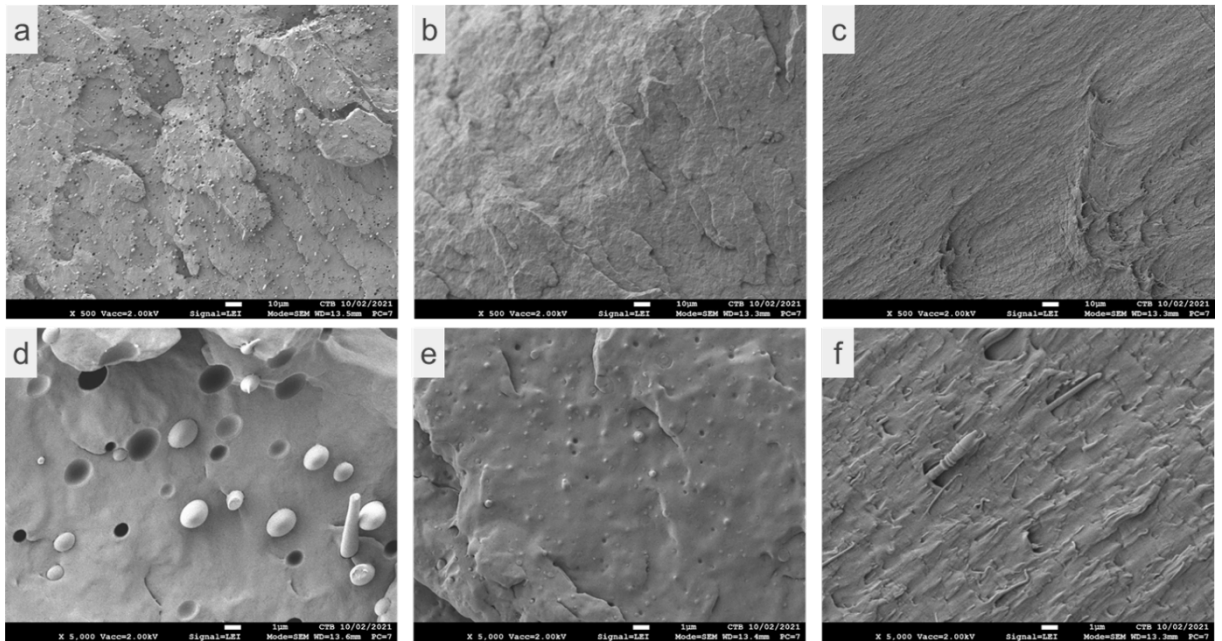


Fig.3: SEM: a-c: 500 x magnification and d-f: 5000 x magnification of the unstretched monofilaments of (from left to right) the 90/10 PP/PA6-blend and the blend with the addition of 3 and 5% compatibilizer, respectively

Considering the difficulties experienced while processing the incompatible PP/PA6 blends, it was decided to switch the spinneret from a round filament die to a narrow tape die. With this die, PP/PA6 blends with ratio 90/10, 70/30 and even 50/50 were successfully processed, without the addition of a compatibilizer and with higher draw ratios. In addition, the flatness of the tapes provides a great advantage in measuring the resistivity and in visualising the microfibrils via SEM. Tapes are easier to cryogenically break than round monofilaments, especially for stretched filaments, allowing the cross-section to be better studied. Moreover, tapes also enable visualization via SEM of a longitudinal section. This makes it possible to check whether the microfibrils form a continuous network, which is necessary to guarantee double percolation and, consequently, good conductivity, when conductive additives are added. The SEM images in Fig.4 show that the 90/10 and 70/30 blends of PP and PA6 already formed microfibrils before drawing, whereas the 50/50 blend rather led to co-continuous phases.

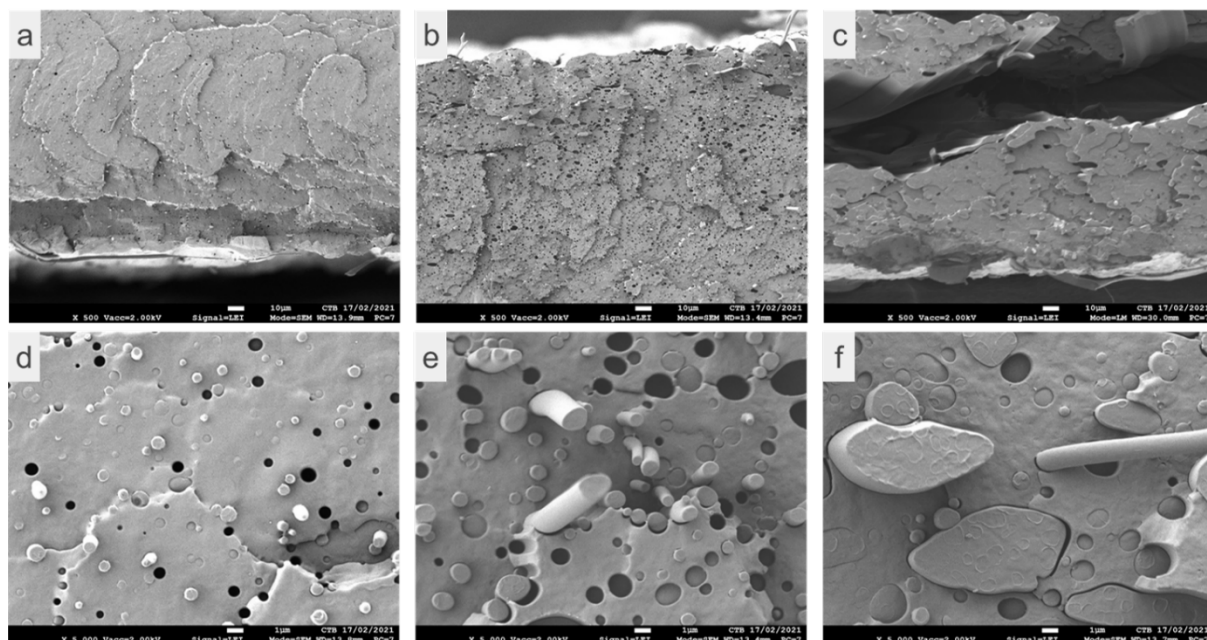


Fig.4: SEM: a-c: 500 x magnification and d-f: 5000 x magnification of the unstretched tapes of (from left to right) the 90/10-, the 70/30-, and the 50/50-PP/PA6 blends.

Influence of the viscosity ratio

Through a brief literature review, it became clear that the viscosity ratio of both polymers is the determining factor for the formation of microfibrils before or after drawing. The theory, presented in Fig.5, states that a high viscosity matrix gives rise to a smaller dispersed phase, where fine microfibrils are already formed right after extrusion. Stretching these filaments would then lead to fracture of the fibrils and thus loss of conductivity. The ideal scenario is to use a low-viscosity matrix, in which the dispersed phase forms larger droplets that, by stretching, extend into a network of microfibrils and thus ultimately lead to a higher conductivity.¹

As described above, the processing of the 90/10 and 70/30 PP/PA6 blends without conductive additives led to the formation of microfibrils before drawing. Thus, drawing of these filaments resulted in an increase of the resistivity or a decrease of the conductivity. In order to validate the proposed theory with our blends, several PP grades with different MFI (3, 15 and 25 respectively) were selected.

¹ A. Soroudi, M. Skrifvars, J. Appl. Polym. Sci., 2011, 119, 2800-2807.

Moreover, to include an even larger variety of different viscosity ratios between the 2 polymers, it was decided to test 2 different CNT/PA6 masterbatches in combination with the 3 different PP-grades. The ultimate goal was to select the best combination in terms of processability and conductivity. This time, a CNT masterbatch (in PA6) was chosen as second phase, because the same conductivity level as with CB can be achieved with lower concentrations, due to the higher aspect ratio (largest dimension compared to the smallest dimension) of CNT compared to CB. Variations in different extrusion parameters (such as extrusion temperature, throughput, oven temperature, take-up speed and draw ratio) will be tested. The first results of these tests will be presented at the next advisory group meeting.

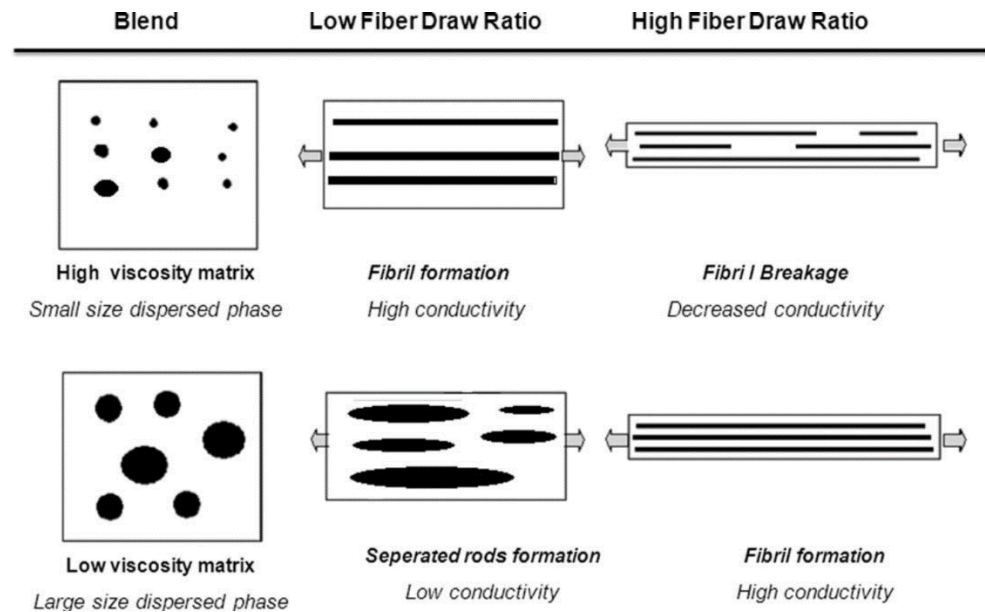


Fig.5: Schematic representation of the change in morphology and conductivity in relation to the viscosity and drawing of the blends.¹

Save the date!

The Guidance Committee will be organized on **22 september 2021** (morning) at **VKC** (Etienne Sabbelaan 49, 8500 Kortrijk). The first results of the influence of the viscosity ratio on the electrical properties will be presented. In addition, the analyses of the compounding trials, performed by the German partners, will be explained.