INTRODUCTION

Nanoparticle reinforced interphases in fibrous polymer composites have attracted much interest [1-3]. Natural candidates for multifunctional reinforced interphases are carbon nanotubes (CNTs) due to their extraordinary mechanical and electrical properties.

More recently, Rausch et al. [4-6] reported on electrically conductive and mechanical improved interphases by utilizing CNT modified sizing systems (Fig. 1a) introduced during the glass fibre (GF) spinning. It was found that during mechanical loading already minor deformations within the percolated CNT network tend to influence the electrical resistivity and could be used to evaluate the structural health of the interphase and thus early warning of a composite part.

Fig. 1. Concept of CNT modified composite interphases for piezo-resistive health monitoring: a) As spun GF containing CNTs in the interface and b) CNT enriched interphase after composite consolidation

In the CNT sizing preparation aqueous dispersions are applied. An emulsifier and dispersing agent poly(ethylene glycol) (PEG) is used which interacts with the CNTs and the PP. Müller et al. [9] used PEG as a dispersion agent in MWCNT polyethylene (PE) nanocomposites and investigated the blend system in terms of morphology and electrical conductivity. Depending on the applied shear rate during melt mixing either the MWCNTs remained in

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the PEG phase or were pushed into the PE phase. For low shear rate manufacturing such as compression moulding of unidirectional composites it is likely that the CNTs remain in the PEG phase and might therefore be more sensitive to changes in thermal transitions of PEG rather than PP.

The main objective of this work is to investigate the influence of the temperature onto conductivity of CNT reinforced glass fibre interphases. Therefore, unidirectional GF/PP composites manufactured with conducting interphases are tested towards thermal expansion (TMA) and dynamic mechanical behaviour (DMA) during thermal loading. In order to distinguish between electrical resistivity changes arising from deformations or polymer transitions, also neat matrix samples and samples with sizing such as CNT/PP-Films without fibres are studied.

2 Experimental

2.1 Glass Fibre Spinning and Interface Modification

Two different types of GFs were spun at the Leibniz-Institut für Polymerforschung (IPF). Firstly, hybrid yarns consisting of continuous E-glass filaments and PP filaments (HG455FB, Borealis, Austria) were simultaneously spun and sized. This time, the same 3-aminopropyltriethoxyisilane (APS) and PP film former were used, but without CNTs. Detailed information on these hybrid yarns and the process can be found elsewhere [4]. Secondly, the preparation of the functional fibres, E-glass fibres with an average diameter of 17 µm were continuously spun and sized with an aqueous 1 wt% APS solution. In a subsequent process, the 120 tex filament yarns were coated with a CNT sizing using a horizontal/vertical padder type HVF in combination with a continuous coating system type KTF (both Werner Mathis AG, Switzerland). The CNT content within the sizing was systematically varied from 0.5 wt% CNTs relative to the solid content of the film former up to 5 wt%. For the sizing preparation, an aqueous dispersion of multi walled carbon nanotubes (Aquacyl IPFD, Nanocyl, Belgium) was poured into a PP film former (Aquacer 598, Byk, Germany) and stirred for several minutes. The required solid content of the sizing was achieved by adding deionised water and additional stirring. After the coating process, all fibre types were annealed in circulating air oven at 180 °C for 15 min.

2.2 Neat Matrix and CNT/PP-Film Preparation

The neat matrix was investigated using 2 mm and 4mm thick injection moulded plates with dimensions of 80 x 80 mm². The appropriate specimens were obtained by CNC milling of the plates. The same CNT sizing formulation used for the coating trials was applied for CNT/PP-Film preparation. The aqueous sizing dispersions were freeze dried at 0.001 mbar for 24 h. The dried sizing powders were then compression moulded at temperatures between 180 and 220 °C for annealing times between 1-15 min. The resulting films had a thickness of 0.5 mm and could be easily cut into appropriate size using a scalpel.

2.2 GF-Composite Preparation and Electrical Resistance Measurements

For the preparation of the unidirectional composites, the CNT coated GF yarns were placed on a steel mandrel using conductive silver bond. During the next step, eight layers of nonconductive hybrid yarns were wound onto the mandrel in the direction of the CNT coated yarns.

Fig. 2. Expansion mode set up used during TMA experiments: a) Thermo couple, b) Cables for resistance measurement and c) CNT/PP film specimen

For hybrid yarn consolidation compression moulding (K207, Rucks GmbH, Germany) was applied. During the compression moulding, the temperature was increased up to the melting point of
the polymer (205 °C) then the pressure was increased up to the point where the glass fibres were fully wetted (1.4 MPa, 3 min).

Specimens with the dimension of 40 x 10 x 2 mm$^3$ (DMA) and 6 x 6 x 4 mm$^3$ (TMA) were cut from the plate using a diamond blade equipped circular saw. For the resistance measurement of the embedded GF yarn each specimen was equipped with electrical cables. In order to investigate the temperature and time dependent changes during thermo-mechanical loading a Keithley 2000 programmable electrometer in 2 wire setup and DC mode was used. The data acquisition at a sampling rate of one reading per second was realized using LabView software and a personal computer.

2.3 Thermal Analysis

Prior to the online electrical conductivity and thermal-mechanical measurements the neat polymer heat transitions such as melting, crystallization and glass transition were investigated by using the differential scanning calorimetry (DSC; Q2000 TA Instruments, USA) method. Two heating and one cooling run at 10 K/min were performed between -50 and 200 °C in nitrogen. The thermal degradation of the same materials was observed using thermogravimetric analyses (TGA; Q500 TA Instruments, USA) at a heating rate of 10 K/min in air atmosphere.

The thermal expansion and electrical resistance of the unidirectional composites was measured perpendicular and along the direction of the fibres by a thermomechanical analyzer (Q400 TA Instruments, USA; Fig. 2). The corresponding mechanical properties were obtained during dynamic mechanical analyses (Q800 TA Instruments, USA; Fig. 3) in the same temperature range. The single cantilever mode with a free gap length of 17.5 mm and a deflection frequency of 10 Hz was used. In order to minimize the temperature gradient within the specimen, the heating and cooling rate was set to 1 K/min.

3 Results and Discussion

3.1 Thermal Stability during Composite Manufacture

During the consolidation process of GF/PP composites sufficient amount of heat is required in order to melt the polymer and fully wet the fibres. The applied matrix and sizing systems must withstand these process temperatures in order to prevent depolymerisation which might yield to a reduction in physical properties. The degradation behaviour was studied by thermogravimetric analyses. From figure 4 and table 1 it is evident that the matrix polymer (HG455FB) entirely withstands the maximum processing temperature (MPT) of 205 °C.

Fig. 4. Thermogravimetric analyses for neat polymer, film former (Aquacer 598) and CNT dispersion (Aquacyl IPFDD) in air at a heating rate of 10 K/min.

Fig. 3. Test setup used during the single cantilever DMA measurements: a) Test specimen, b) Cables for resistance measurements and c) Test fixture mounted onto DMA.
The Aquacer 598 film former provides the least stability towards temperature for all applied polymers. At MPT a weight loss of 1.5 % occurs which is still feasible for the composite manufacture.

Tab. 1. Weight loss at annealing and processing temperatures

<table>
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<tr>
<th></th>
<th>160 °C</th>
<th>180 °C</th>
<th>205 °C</th>
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<tbody>
<tr>
<td>HG405FB</td>
<td>0.02</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>Aquacer 598</td>
<td>0.29</td>
<td>0.62</td>
<td>1.55</td>
</tr>
<tr>
<td>Aquacryl IPFDD</td>
<td>0.55</td>
<td>0.68</td>
<td>1.01</td>
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The degradation of the CNT dispersion differs from both others because it can be deduced into two individual stepwise processes. Beginning at 250 °C the dispersing agent starts to depolymerize followed by the CNTs at 450 °C.

3.2 Melting and Crystallisation Behaviour

Differential scanning calorimetry was carried out in order to obtain a qualitative picture of the melting and crystallization behaviour. Figure 5 shows the heat flow during 2nd heating for the matrix and sizing polymers, respectively. As expected, PEG is used as an emulsifier or dispersing agent for the CNTs (Aquacryl IPFDD) and the PP (Aquacer598) yielding to a melting peak above 30 °C. The PP motion within the film former results in a second melting peak at 155 °C.

The matrix polymer (HG455FB) shows an increased melting peak temperature of 162 °C. Film former Aquacer 598 consists of lower molecular weight PP ($M_w = 8.6 \times 10^4$) than the PP matrix polymers ($M_w = 16 \times 10^4$) which results in decreased peak melting temperatures as shown in Tab. 2.

During heating and cooling it was not possible to identify the glass transition temperatures ($T_g$). This is in accordance with other studies on highly crystalline polymers since only the amorphous phase possesses a $T_g$. The DMA measurements will provide reliable data on the glass transition in the following chapters.

Tab. 2. Melting and crystallization peak temperatures

<table>
<thead>
<tr>
<th></th>
<th>Polyethylene glycol</th>
<th>Polypropylene</th>
</tr>
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<tr>
<td></td>
<td>$T_{mPeak}$ [°C]</td>
<td>$T_{cPeak}$ [°C]</td>
</tr>
<tr>
<td>HG455FB</td>
<td>-</td>
<td>162</td>
</tr>
<tr>
<td>Aquacer598</td>
<td>31</td>
<td>155</td>
</tr>
<tr>
<td>Aquacer598 + 1wt% 15min</td>
<td>-3</td>
<td>156</td>
</tr>
<tr>
<td>Aquacryl IPFDD</td>
<td>-20/33</td>
<td>122</td>
</tr>
</tbody>
</table>

During cooling the Aquacer 598 film former begins to crystalize first, at a peak temperature of 121 °C (Tab. 2), followed by the HG455FB matrix polymer at 117 °C.

Fig. 5. Melting behaviour of PP matrix, individual sizing polymers and mixture of sizing polymers (Aquacer598 + 1wt% CNT) as applied during the coating process

Fig. 6. Crystallization behaviour of PP matrix and sizing polymers

The crystallisation for the PEG phase differs significantly between Aquacer 598 and Aquacryl
IPFDD (Fig. 6) which can be attributed to the molecular weight distribution. For Aquacryl IPFDD two distinctive peaks can be observed with corresponding peak temperatures of 30 and -29 °C, respectively. Both systems have in common that crystallisation and melting occur either slightly above or below room temperature. Therefore, varying the room temperatures can be used to switch from crystalline to amorphous and vice versa. As mentioned during the introduction, the conductivity of CNT networks is also sensitive towards crystallinity and should therefore change significantly by varying the ambient temperature.

Based on these findings of the Aquacer598 + Aquacryl IPFDD samples, the CNTs themself did not act as nucleation agents for the crystallization of PEG or PP. Filler contents up to 2 wt% of CNTs relative to the film former content were investigated at a cooling rate of 10 K/min.

### 3.3 Electrical Behaviour of CNT/PP Films

The effect of dynamic percolation in CNT/PP films was addressed by measuring the volume resistivity of compression moulded films processed at different annealing times. It was observed that for increasing CNT contents the electrical volume resistivity is decreased (Tab. 3).

<table>
<thead>
<tr>
<th>CNT filler content [wt%]</th>
<th>Annealing [min]</th>
<th>Volume Resistivity [Ω cm]</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>19.70</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>22.42</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>62.15</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>65.24</td>
</tr>
</tbody>
</table>

Increasing the annealing time did not show to have a significant influence on the volume conductivity as it was observed by Alig [6-7]. Therefore, annealing for 1 min at processing conditions seems feasible for reaching the equilibrium of dynamic percolation.

The temperature dependency of a PP/CNT film was studied using the dynamic mechanical analysis (DMA) and the thermomechanical analysis (TMA). Fig. 7 reveals that the CNT/PP films possess only an individual T	extsubscript{g} of -22 °C which is far below what is expected for neat PP. However, it is near the properties of neat PEG. This result highlights that the PP/CNT films are miscible blend systems of low molecular PP and PEG, reinforced with CNTs.

![Fig. 7. Dynamic mechanical (DMA) and thermomechanical (TMA) behaviour of a CNT/PP film](image)

The ability to withstand temperature is crucially determined by the T	extsubscript{g} and the degree of crystallinity. As it was observed during the DSC investigations melting of the PEG begins at 15 °C. At this temperature a significant increase in the dimension change signal as well as position signal of the cantilever beam occurs which approves the DSC findings. Unfortunately, it is not possible to increase the temperature further without irreversible changes of the morphology of the CNT/PP film. Therefore, it is not possible to perform cyclic DMA measurements above 15 °C without getting problems with the cantilever beam deformation during measuring.

![Fig. 8. Electrical response upon temperature during thermomechanical analysis for a CNT/PP film](image)
Although cyclic TMA measurements do not bear as much mechanical load on the PP/CNT film as DMA ones, there is an irreversible dimension change during the first heating run shown in Fig. 8. As expected, the film expands upon heating but reaches a maximum at 40 °C. Until the end of the first heating run the film contracts due to the molten PEG phase. In this temperature region PP does not melt as shown during the DSC measurements but becomes softer and residual stresses can relax. The relaxation during the first heating explains why the expansion and contraction upon heating and cooling is reproducible for the consecutive runs and differ significantly from the first heating (Fig. 8 and 9).

Upon the 2nd heating run the dimension change is significantly increased in the temperature region between 15 and 40 °C which corresponds to the melting region of PEG identified by DSC measurements (Fig 9). The specific density of a crystalline structure is lower than for an amorphous one thus the dimension change increases when crystals start to melt. Vice versa the dimension change is decreased when passing the crystallization region between 20 and -10 °C. The dimension change signal fulfills a hysteresis in the temperature region above the crystallization. Below the crystallization temperature heating and cooling yield to the same dimension change.

As mentioned initially, the electrical resistance is believed to be affected by melting and crystallization. Fig. 10 shows the electrical resistance change during heating and cooling. In principle, increasing the temperature tends to decrease the electrical resistance. Upon heating a steep increase in electrical resistance occurs which corresponds to the temperature region where dimension change indicated melting. Above the PEG melting temperature the electrical resistance starts to decrease as expected. This is of particular interest since the melting of the PEG can be identified by the electrical resistance signal.

![Fig. 9. Melting and crystallization of PEG phase within a CNT/PP film](image)

Upon cooling the electrical resistance fulfils the same hysteresis as previously observed during the dimension change measurement. Again, the hysteresis ends when the crystallisation comes to an end and below 0 °C both signals are identical. The crystallisation can be identified by the electrical resistance as well as melting by a steep increasing in the resistance upon cooling.

### 3.4 Electrical Behaviour of multifunctional CNT modified interphases in unidirectional GF composites

The interphases occupy only a very small volume in fibrous composites, as illustrated in Fig. 1. The majority of the composites' volume consists of the matrix and the glass fibres. Therefore, it is likely that thermomechanical properties of unidirectional GF/PP composites differ from CNT/PP films (interphase).
The storage and loss modulus for the GF/PP composite, matrix (HG455FB) and CNT/PP film upon heating are shown in Fig. 11 and Fig. 12, respectively. The lowest modulus and glass transition temperature shows the CNT/PP film followed by the neat matrix. The storage modulus perpendicular to the fibres (GF/PP 90°) is significantly lower than along the fibres (GF/PP 0°), as expected. Upon heating distinctive transitions reflected by the changes of storage and loss modulus slope can be identified (Fig. 11, dotted black lines). For the GF/PP composites these changes in the modulus slope are distinguished by the matrix rather than the interfaces.

The first transition occurs above $T_g$ (-2 °C) due to the increased chain mobility of the polymer followed by a second one around 50 °C. Since PP melting takes place at higher temperatures and the matrix is free of PEG which melts at temperatures above 30 °C the second transition might be due to annealing at room temperature. For a better understanding of the second transition cyclic TMA measurements on the neat polymer and the GF/PP composites were performed (Fig. 13-16). During the first heating run thermal relaxations occur in the matrix PP and the GF/PP composites as shown in Fig. 13 and Fig. 15, respectively within the temperature region of the second transition.
During the consecutive cyclic runs no thermal relaxations can be observed (Fig. 14 and Fig. 16). In contrast to other engineering thermoplastics PP has a \( T_g \) (~2 °C) significantly below room temperature. In general, relaxation and recrystallization takes place above the \( T_g \). Therefore, keeping PP at room temperature will equilibrate/optimise its structure (annealing). The temperature stability of this effect is limited. Heating above annealing temperature will erase this effect yielding to dimensional relaxation and a reduction in storage modulus (Fig. 18).

The effect of the mismatch of thermal expansion between fibre and matrix on to the dimensional change of GF/PP composites is shown in Fig. 16. It differs significantly from the dimensional change of the neat matrix (Fig. 14). Along the x-direction (fibre) the thermal expansion is much lower than in both other directions (z and y) which are controlled by the thermal expansion of the matrix. This mismatch is likely to produce additional strains in the interphase.

Fig. 17 shows the electrical resistance of the composites with CNT modified GF interphases during cyclic heating and cooling. Similar to the CNT/PP films increasing the temperature tends to decrease the resistance while decreasing the temperature tends to increase the resistance.

Below ~20 °C the electrical resistance upon heating and cooling is identical (Fig.18). Above ~20 °C
electrical resistance and storage modulus perform a hysteresis similar to the one which was observed for the CNT/PP films. In contrast to the CNT/PP films neither the beginning nor the end correspond to the onset of melting or offset of crystallization for PP or PEG. Upon heating the electrical resistance changes almost linear with increasing temperature and reaches lowest resistance values near 80 °C. For higher temperatures the resistance starts to increase. During cooling the resistance decreases until 60 °C than it increases almost linear with the temperature until -50 °C.

The thermal relaxation which was observed during the first heating run in DMA and TMA is also evident in the electrical resistance signal (Fig.19). Instead of further decreasing the electrical resistance begins to increase from 40 °C and reaches a maximum at 50 °C. Upon further increasing the temperature the electrical resistance and the modulus signal go back to their baseline signal. This founding emphasizes that thermal relaxations in unidirectional GF/PP can be detected by electrical resistance monitoring within CNT modified interphases

4 Conclusions

The piezo-resistive behaviour of CNT/PP films upon thermomechanical loading was determined to detect melting and crystallization of the dispersing agent containing PEG phase within the film. For a deeper understanding of the electrical resistance changes occurring upon melting and crystallization it is necessary to investigate the morphology of the CNT/PP/PEG blend system and how it develops with temperature.

For unidirectional GF/PP composites with CNT modified interphases thermal relaxation was detected by the electrical resistance. It was shown that the PEG melting and crystallization do not tend to influence the electrical resistance of the interphase although it primarily consists of the same material as the CNT/PP film. For a better understanding how the thermal expansion and the interdiffusion between sizing and matrix affects the electrical resistance further investigation is underway.

5 Acknowledgements

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References