DEVELOPMENT OF COST-EFFECTIVE THERMOPLASTIC COMPOSITES FOR ADVANCED AIRFRAME STRUCTURES

T. Kroöß, M. Gurka, V. Dück, U. Breuer

1 Institut für Verbundwerkstoffe GmbH, Erwin-Schrödinger-Straße, Building 58, D-67663 Kaiserslautern, Germany
Email: tim.krooss@ivw.uni-kl.de, martin.gurka@ivw.uni-kl.de, dueck@rhrk.uni-kl.de, ulf.breuer@ivw.uni-kl.de
web page: http://www.ivw.uni-kl.de/

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ABSTRACT

Carbon fiber reinforced composites are of great importance for primary structures in airplanes. They provide excellent mechanical properties combined with a superior lightweight potential and contribute to fuel reduction, less emissions and maintenance benefits. Today, epoxy resins are dominating the market for structural airframe applications. Thermoplastic polymers offer advantages, such as out-of-autoclave processing, thermoforming in short cycle times and automated welding for joining. Polyetheretherketone (PEEK), being the best performing candidate, is relatively expensive compared to qualified epoxy prepreg materials. Polyphenylensulfid (PPS) is more cost attractive, but its thermal and mechanical performance is lower than PEEK. Innovative polymer blends are therefore a promising approach to combine specific chemical and thermo-mechanical properties of different polymers while significantly reducing material cost.

This investigation aims at the development of thermoplastic PPS-PESU blends with properties comparable to PEEK. The focus is set on the improvement of thermo-mechanical properties as well as on chemical resistance. To investigate the combination of the specific properties of PPS and PESU in the resulting blends, selective experiments on the morphology formation are made in order to define a suitable processing window. Injection molded samples with a PESU amount of up to 50 wt.-% dispersed in the PPS matrix are characterized by means of dynamic-mechanical thermal analysis (DMTA), tensile testing and chemical resistivity experiments in methylethylketone (MEK). The results demonstrate a promising combination of the advantageous properties of the individual polymers: The excellent thermal stability of the dispersed PESU and the high chemical resistance of the PPS matrix. Up to a temperature of approx. 220 °C the blends show superior mechanical properties compared to PEEK. In the next step optimized blend formulation for the use in carbon fiber reinforced composites will be defined and films will be extruded. These films can be used for a film stacking process with carbon fiber textiles in order to verify superior composite properties.

INTRODUCTION

Thermoset resin systems are dominating composite applications of load carrying primary airframe structures of modern civil aircraft (B787, A350XWB). Thermoset carbon prepregs are typically processed to shells and covers by means of automated tape laying of fiber placement machines and autoclave cured at a temperature of 180 °C for several hours. The share of high performance thermoplastic composites within airframe structures, however, is still relatively small, although these materials offer the potential of very short cycle time processing [1]. Meanwhile the performance/price-relationship of some thermoplastics has improved. Thermoplastic applications include polycarbonates (PC), polyamides (PA), polyphenylene sulfides (PPS), polyetherimides (PI) and polyetheretherketones (PEEK) [2], but only PEEK and PPS are preferred for primary structure applications. PEEK/carbon-fiber materials can demonstrate remarkable weight savings compared to aluminum alloys [3, 4]. Additionally, the excellent chemical resistance and good high temperature performance makes PEEK very attractive for airframe structures. However, PEEK is not only the best performing thermoplastic polymer but the most expensive as well. The price of virgin PEEK can exceed 150 $/kg, thus
drastically elevating the manufacturing cost of composites [2]. Therefore, the development of thermoplastic alternatives has to be considered.

The current investigation aims at the development of a thermoplastic blend as a potential substitute for PEEK in fiber reinforced composites. The properties to be compared to a selected type of PEEK are the mechanical and thermo-mechanical behavior as well as the chemical resistance of the blend against methylethylketone (MEK). The polymers selected for blending are polyphenylene sulfide (PPS) and polyethersulfone (PESU) which in former studies were found to be poorly or only partly miscible [5, 6]. The generation of a dispersion of PESU in a PPS matrix is targeted. PPS has an excellent chemical resistance and a high tensile modulus. PESU is well known for its thermal resistance and high ductility at high strength. The blends analyzed in this study shall deliver possible matrix materials for carbon fiber reinforced composites out of thermoforming or film stacking processes. The main specifications to be met by the generated blends are:

- Good chemical resistance towards liquid media provided by a PPS matrix or a co-continuous morphology,
- thermal stability comparable to PEEK within the typical operating temperature range,
- maximum mechanical strength and modulus in relation to the neat polymers.

The conclusions of this work shall provide a basic knowledge for blend processing via film and melt-spinning extrusion for further investigations.

**METHOD & EXPERIMENTAL**

The experimental method applied in this study can be split up in three basic steps: The first step concentrated on the selection of suitable polymer grades fulfilling the requirements for an optimized morphology formation. This included preliminary work focusing on the measurement of rheological behavior of the considered polymer grades. Combinations of polymer grades for which the ratio of their viscosities is minimal should lead to reduced size distribution of the PESU within the blends [7, 8]. The rheological behavior of the polymers was then used to determine a potential processing window for blending during the injection molding process used for sample manufacturing. Shear rates and temperatures were selected to optimally reduce the viscosity ratio. Based on existing literature [9, 10] theoretical calculations were performed to give a first hint of the minimum amount of PESU to be added to the PPS resulting in phase inversion which changes the morphology of the resulting blend. Applying this method, it was possible to estimate the maximum amount of PESU in the blends while maintaining dispersion in a PPS matrix.

The second step of the experimental method was the processing of compounds by means of the injection molding process according to the rheological characterization. This process was chosen to directly manufacture dog bone samples for mechanical testing without an additional thermal process. Through variation of parameter settings, different shear rates were investigated to analyze their influence on the morphology formation. PESU amounts from 15 wt.-% up to 50 wt.-% were chosen and, furthermore, the addition of a compatibilizer was investigated. The dog bones were also used to prepare samples for dynamic-mechanical thermal analysis (DMTA).

In the third step of this study further analysis focused on the interpretation of morphology profiles via Scanning Electron Microscopy (SEM) and the evaluation of morphology efficiency through media resistance experiments. Therefore, selected samples of the processed compounds as well as neat PEEK and PPS samples were aged in methylethylketone (MEK) for 7 days at room temperature. Subsequently, the samples were tested in the DMTA. To further outline the potential of the developed blends different samples were tempered, targeting at cross-link reactions of the PPS.
Rheology

The capillary rheometer, a Rheotester 500 from Göttfert (Germany) was used to measure the viscosity of three Fortron PPS grades from Ticona and two Ultrason PESU grades from BASF. The shear rates applied at temperatures between 330 °C and 360 °C were set in the range of 10 to 400/s. A capillary with a diameter of 1 mm was used for the experiments. The generated viscosity curves and the calculation of viscosity ratios enabled the selection of processing temperature as well as best suited polymer grades. Targeting a minimal viscosity ratio between the participating polymers, the Fortron PPS 0320 and Ultrason PESU E1010 were chosen for further experiments. The manufacturers’ data is listed in Table 1 below.

Table 1: Manufacturers’ data of selected material grades.

<table>
<thead>
<tr>
<th></th>
<th>PEEK</th>
<th>PPS</th>
<th>PESU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength [MPa]</td>
<td>100</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Young’s Modulus [MPa]</td>
<td>3700</td>
<td>4200</td>
<td>2700</td>
</tr>
<tr>
<td>Strain at break [%]</td>
<td>40</td>
<td>8</td>
<td>&gt;25</td>
</tr>
<tr>
<td>Glass transition temperature (T_g) [°C]</td>
<td>143</td>
<td>90</td>
<td>220</td>
</tr>
<tr>
<td>Melting temperature (T_m) [°C]</td>
<td>340</td>
<td>280</td>
<td>-</td>
</tr>
<tr>
<td>Density [g/cm^3]</td>
<td>1.30</td>
<td>1.35</td>
<td>1.37</td>
</tr>
</tbody>
</table>

On the basis of the viscosity ratios of these grades the calculation of the minimum PESU portion necessary for a phase inversion was possible. Two simple approaches from Miles & Zurek and Ho et al were taken into account (Formulas 1 and 2):

Miles & Zurek [9]

\[
\frac{\Phi_1}{\Phi_2} = \frac{\eta_1(\dot{\gamma})}{\eta_2(\dot{\gamma})}
\]

(1)

Ho et al. [10]

\[
\frac{\Phi_1}{\Phi_2} = 1.22 \left( \frac{\eta_1(\dot{\gamma})}{\eta_2(\dot{\gamma})} \right)^{0.29}
\]

(2)

In these equations \(\Phi_i\) represent the polymer portions of PPS and PESU, \(\eta_i\) are the viscosities of the single components as a function of applied shear rates \(\dot{\gamma}\) at constant temperature. From the calculation of phase inversion points the definition of compositions to be processed was examined. The variance of results from these two approaches outlined that a precise prediction of morphological change on the basis of viscosity ratios is difficult. However, they delivered precursors which helped to rapidly define relevant compositions for the development of new blends without extensive extrusion trials and analytical effort. It is important to note that existent data do neither consider effects of coalescence and droplet breakup nor the exact relation to shear rates in the production process.

Injection Molding

The injection molding machine used was an Arburg Allrounder 320S 500-150, injection speeds differed from 10 to 80 mm/s. Accompanying higher amounts of PESU, the difficulty of forming fine droplet dispersion rises and the necessity of compatibilizers grows due to viscosity differences [14]. Thus, a PESU grade with a hydroxyl group [15] was added to investigate its influence on the formation of a droplet dispersion or co-continuous morphology, respectively. At least 10 samples of
each composition were molded and used for the mechanical and thermo-mechanical analysis. Based on the preliminary conclusions of first experiments a third injection speed of 50 mm/s was set for one composition.

**Analysis and Testing**

The central issue of this work focused on the morphology formation of the blends and the derived blend properties. Thus, Scanning Electron Microscopy (SEM) was used to determine the representative influences of processing conditions on the blends’ structures. All samples were first quenched in liquid nitrogen and cryo-fractured to obtain plane and non-deformed cross section surfaces. The molded dog bone samples were also directly used for quasistatic tensile tests examined on a Zwick/Roell testing machine according to DIN EN ISO 527-1. The initial force was set at 10 N, testing speed was 1 mm/min. For all compositions the thermo-mechanical behavior was analyzed on a GABO Eplexor within a temperature sweep test starting at an initial temperature of 45 °C up to 245 °C with a heating rate of 2.5 K. The testing frequency was determined at 3 Hz, maximum strain amounted to 1.5 % with a 0.1 % dynamic portion. All DMTA experiments were carried out according to DIN EN ISO 6721-1. At least 3 samples were tested for each composition. The evaluation of morphological effectiveness was examined in media resistance experiments according to EN ISO 175. Selected samples were aged for 7 days at room temperature. After additional drying a comparison of the specimens was realized in further DMTA experiments. In the same manner tempered samples were tested. The tempering process was defined at 250 °C for 7 days [16-18].

**Material Compositions**

Table 2 shows the average phase inversion points that were calculated based on the approaches of Miles & Zurek and Ho et al for the chosen polymer grades.

**Table 2: Minimum phase inversion portions of Fortron PPS 0320 and Ultrason PESU E1010.**

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Avg. minimum PESU portion for phase inversion [vol.-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ho et al</td>
</tr>
<tr>
<td>330</td>
<td>34.5</td>
</tr>
<tr>
<td>340</td>
<td>35.6</td>
</tr>
<tr>
<td>350</td>
<td>35.4</td>
</tr>
<tr>
<td>360</td>
<td>35.6</td>
</tr>
</tbody>
</table>

The calculations of both approaches show nearly no dependency on the applied temperatures. This correlation also applied to the viscosity ratios of the polymers. However, two different regions were identified by the values: Following the approach of Ho et al the earliest phase inversion will occur with a PESU portion of approx. 35 vol.-%, while the second approach predicts the switch to a PPS matrix at 18 – 20 vol.-% and more. Based on these results the compositions to be processed were determined, as shown in Table 3.

The defined compositions were rounded to full weight percentages. Besides the PPS reference three non-compatibilized compositions were processed: With a PESU portion of 15 wt.-% blend 1 shall represent a morphology before the inversion (b. i.), the second and third composition with 30 wt.-% and 40 wt.-% PESU represent blends after the inversion (a. i.), theoretically calculated by the approaches of Miles & Zurek and Ho et al, respectively. Additionally, two compatibilized compositions with high amounts of PESU were processed to analyze a potential shift of inversion (s. i.).
Table 3: Blend compositions determined for injection molding process.

<table>
<thead>
<tr>
<th>No</th>
<th>Composition character</th>
<th>PPS (wt-% // vol-%)</th>
<th>PESU (wt-% // vol-%)</th>
<th>Compatibilizer (wt-% // vol-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100-0-0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>85-15-0 (b. i.)</td>
<td>85 // 85.49</td>
<td>15 // 14.51</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>70-30-0 (a. i.)</td>
<td>70 // 70.41</td>
<td>30 // 29.59</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>60-40-0 (a. i.)</td>
<td>60 // 60.35</td>
<td>40 // 39.65</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>60-37-3 (s. i.)</td>
<td>60 // 60.35</td>
<td>37 // 36.67</td>
<td>3 // 2.98</td>
</tr>
<tr>
<td>6</td>
<td>50-47-3 (s. i.)</td>
<td>50 // 50.29</td>
<td>47 // 46.73</td>
<td>3 // 2.98</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

SEM Observation

Figures 1 to 5 below show the developed compositions with their morphological characteristics, classified by the amount of PESU and the applied injection speeds within the injection molding process.

Fig. 1: Representative SEM images of PPS/PESU 85/15 blends processed at 10 mm/s (a) and 80 mm/s (b).

Fig. 2: Representative SEM image of PPS/PESU 70/30 blends processed at 10 mm/s.
Based on the SEM observations the following facts can be concluded: Despite a suboptimal viscosity ratio a general fine dispersion of 15 wt.-% and 30 wt.-% PESU in the PPS was possible, leading to a quasi-homogeneous morphology (Fig. 1a and 2). A higher injection speed obviously supports coalescence and agglomeration as can be seen in Fig. 1b. The inversion from a PPS matrix towards a PESU or co-continuous matrix occurred at 40 wt.-% (Fig. 3) which is closer to the prognostic value of Ho et al. The spherical lines divide several levels of sub- and sub-sub-inclusions, indicating a switch from a matrix/phase to a co-continuous system. By addition of the compatibilizer this phenomenon is significantly inhibited (Fig. 4). The last composition in Figure 5 with 47 wt.-% PESU shows the sophisticated inversion of the PPS matrix which is also suppressed by the presence of the third phase, the PESU grade with a hydroxyl group (Fig. 5a). Fig. 5b shows a representative
cryo-fractured surface of composition 5 injection molded at a speed of 50 mm/s. This sample indicates the importance of adequate process parameters: The morphology was identified to be more homogeneous and better dispersed compared to samples processed at low and high injection speed.

Characteristic compositions could be identified in which the blends’ morphologies experience significant changes. Hence, mechanical, thermo-mechanical and chemical properties of the molded samples should vary related to the specific morphology types.

**Mechanical Testing**

As shown in Fig. 6 the addition of PESU first reduced the tensile strength of blend 1A and 1B significantly compared to the neat PPS samples. However, especially a higher injection speed or shear rate shows a negative influence on the mechanical properties for this composition and neat PPS as well. With higher amounts of PESU the tensile strength continuously rose and also the variation was reduced, as can be seen from the compositions 2, 3 and 4. Contrary to blend 1A and 1B the increase of injection speed did not lead to a decrease in tensile strength until a portion of 50 wt.-% PESU was reached. The highest PESU fraction was realized with blends of composition 6. For these samples 3 wt.-% of the PESU grade with a hydroxyl group was added to 47 wt.-% PESU E1010.

Since the phase portions of both polymers are similar for these compositions, it must be considered that the point of phase inversion has already been reached. The influences of shearing (injection speed) thus led to a drop of mechanical properties and a higher variation respectively. Coalescence of the PESU droplets was more likely and led to a mixed morphology with inhomogeneous areas. This inhomogeneity caused higher variation of mechanical values. The adjustment of injection speed to 50 mm/s (Blend 6C) reduced the variance to a minimum. The development of the Young’s modulus can be summarized as follows: The addition of PESU continuously reduced the modulus, although this trend was slightly inhibited by the presence of PESU with the hydroxyl group. The highest modulus was observed for composition 2 while the tensile strength only reached approx. 70 MPa. A slight increase of modulus was measured for blends 5A and 5B with a majority portion of PPS.

![Fig. 6: Mechanical properties of injection molded blend compositions.](image)
comparison of these compositions with high and low amounts of PESU is of interest for the thermo-mechanical behavior as well as for the resistance towards liquid media.

**Dynamic Mechanical Thermal Analysis (DMTA)**

Within the DMTA testing all compositions processed at an injection speed of 10 mm/s were considered. Regarding the thermo-mechanical behavior, the developed blends show a clear dependency on the PESU portion (Fig. 7). The storage modulus $E'$ of all blends is illustrated over the temperatures from 45 °C up to 245 °C. The better modulus of PPS led to a recognizable advantage of blend 2A at lower temperatures with a modulus of more than 2700 MPa. Once heated above the glass transition point of PPS (90 °C) the storage modulus dropped to a significantly lower level for each composition. The glass transition temperature of the PESU portion (220 °C) limited the relevant stability of the blends. However, the presence of PESU led to a plateau of $E'$ at high temperatures. All blends with a PESU portion of 30 wt.-% and more show a storage modulus of several hundred MPa, composition 6A delivered a constant $E'$ of more than 1000 MPa. Since the PEEK samples delivered high moduli up to the $T_g$ at approx. 145 °C it can be constituted as superior in this region. Comparing the high temperature properties it can be concluded that all blends show higher values from 160 °C to approx. 220 °C. In this region blend 6A delivered a storage modulus outmatching PEEK by a factor of more than 2.5. The presence of PESU significantly elevated the thermal stability of all blends while lowering the modulus at moderate temperatures.

![Fig. 7: Storage moduli of injection molded blends, untreated.](image)

In Fig. 8 the mechanical thermal behavior of selected blends is visualized by the storage modulus after aging samples in methylethylketone (MEK) for 7 days at room temperature. By testing the media resistance, the effectiveness of blends’ morphologies could be quantified. The overall reference of the samples was neat PPS (composition 1). As expected and concluded from SEM imaging those samples with a fine and closed dispersion of PESU in a PPS matrix do not show a dramatic loss of the storage modulus (compositions 2 and 3), which was constituted at less than 7 % for a 15 wt.-% PESU portion and less than 10 % for a 30 wt.-% PESU portion up to 210 °C. At higher amounts of PESU the sensitivity of the blends towards the MEK became stronger. Blends 5 and 6 show a loss of $E'$ between
15% and 30% up to a temperature of 210 °C. Although fine dispersion with low PESU portions led to better resistance towards the MEK, the overall stability for injection molded samples was not verified thoroughly.

According to studies on the curing and crystallization behavior of PPS [16-18] four compositions were tempered at 250 °C for 7 days: Blend 2A with best chemical resistance and highest Young’s modulus, blends 3A and 5A with constant average mechanical and thermal properties as well as chemical resistance and blend 6A with highest storage modulus at elevated temperatures. The tempered samples were again analyzed in DMTA experiments under the same conditions (Fig. 9). As can be seen from Fig. 9 the tempered samples constitute significantly elevated storage moduli over the whole temperature range. At moderate temperatures below the T_g of PPS the increase of the storage modulus ranges from only 7% for composition 6A to approx. 15% for compositions 2A and 3A. While E’ of untempered samples decreased from approx. 95 °C (Fig. 7) the tempered blends show a shift of this drop to approx. 105 °C, indicating a shift of glass transition temperature through the tempering process. This drop is comparatively gentle between 130 °C and 220 °C and shows significantly higher values for all tested blends. The highest improvement in this region was realized for blend 2A with the highest PPS portion outmatching the uncured blend by more than 300%. Even with an increased PESU portion the improvement of thermal stability ranges from 65% to 114% for composition 3A and up to 60% for composition 6A. Blend 5A is improved by only 30% in average. However, in the region between 150 °C and 220 °C PEEK is clearly exceeded and at moderate temperatures the modulus of blend 2A shows comparable values. It is peculiar that above the T_g of PESU at 220 °C the tempered blends still show superior behavior. This phenomenon was clearly improved with higher PPS portions.
CONCLUSIONS

The results illustrate the high potential of the developed PPS/PESU blends. Through specific selection of polymer grades and adjustment of processing parameters it was possible to generate characteristic blends with diverse properties. It was shown that the mechanical properties as well as the thermal stability of the analyzed samples are influenced by the portions of both fractions. The mechanical testing showed that the modulus of PPS is reduced because of the more ductile PESU phase. However, the strength of blends with a higher PESU amount is comparable to the neat PPS samples. Variation of shearing rate or injection speed improved the variance. In a same manner the thermal stability could be identified to be adjusted by the PESU portion in the blends: Low amounts of PESU delivered better storage moduli up to approx. 90 °C while high PESU amounts significantly increased the stability at high temperatures. Especially the tempering of selected samples underlined the excellent high temperature resistance of the developed blends. The shift of glass transition temperature of the PPS and the potential cross-linking reactions significantly influenced the temperature region in which PEEK shows superior behavior. By the diverse behavior of the different compositions it could be illustrated that tailored properties can be generated through simple variation of polymer portions and effective compatibilization. The importance of adequate morphology formation was shown by media resistance experiments. Although the overall chemical resistance of the blends was not completely verified it became clear that morphological influence is significant. Thus, the manufacturing of samples within the injection molding process thus delivered important information about the possibilities of blending PPS and PESU.

Further investigations will focus on the transfer onto film and melt-spinning extrusion lines to improve and specifically adjust the morphological formation of developed blends. It is of great importance to narrow the adjustment of presented properties by means of standard extrusion technologies aiming at the reproducible in-situ tailoring of blends. Within this context the general performance of specialty blends as matrices for carbon and glass fiber reinforced composites will be
analyzed. The influence of tempering steps regarding the neat blends as well as composites has to be examined more closely in future studies.

REFERENCES


