

THERMO-MECHANICAL STIFFNESS AND MEDIA RESISTANCE OF ENDLESS CARBON FIBER COMPOSITES WITH POLYPHENYLENE SULFIDE (PPS)/POLYETHER SULFONE (PES) BLEND MATRICES

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Abstract

The development of high performance thermoplastic blends based on Polyphenylene sulfide (PPS) and high glass transition (T_g) Polyether sulfone (PES) was investigated in former studies [1–5] in terms of mechanical and thermomechanical properties with the aim to improve brittleness and thermal stability compared to neat PPS. As a continuation of this work in the current report the effectiveness of special property thermoplastic PPS/PES blends in endless carbon fibre composites was focused. Main target was the evaluation of the unique components properties for being the thermo-mechanical stiffness as well as media resistance of the blends in their derived endless carbon fibre composites. Therefore, different compositions with up to 50 wt.-% PES were produced in a film extrusion process and subsequently stacked and consolidated with carbon fibre fabrics. The influence of phase to phase interactions was investigated by the addition of PES-OH groups in reference samples. Dynamic mechanical thermal analysis (DMTA) was then examined in a temperature range of 70-150 °C to evaluate the transfer of thermal stability of the PES phase into the composite blend samples. Additionally, samples were stored in methylethylketone (MEK) for 300 h and subsequently tested similarly to investigate the residual storage and loss moduli. Results showed that both the transfer of high- T_g -PES(U) thermal stability as well as partially maintaining the media resistance of the PPS component, thanks to its protective role as major continuous phase, was successful. For the higher temperature range from 100 °C the storage modulus of blend samples was significantly improved. MEK aging further lead to a drop of storage modulus for non-compatibilized samples, indicating strong influence of morphological features and fiber/matrix adhesion. The quantification of PES spheres in polished and selectively etched cross sections, indicated that for high PES fractions narrow distributions of spheres are favorable regarding the overall chemical resistance and thermal stability. For low PES fractions the width of sphere's distribution seemed to be less relevant. Instead an improved fiber matrix adhesion, provided by the compatibilizing PES-OH groups, was assumed to have greater influence on the stiffness than the presence of added PES-fraction itself.

1. Introduction

Structural parts in the automotive and aircraft sector are more and more made of composite materials. Meanwhile, carbon fibre reinforced thermoplastics are used as well thanks to their inherent advantages compared to thermoset based composites: Fast processing, meltability, impact toughness, etc. However, even the high performing thermoplastic polymers used for composites exhibit weaknesses that limit their application or favour the use of more complicated and expensive alternative materials. Already in the last decades of the past century polymer blending became an interesting alternative for 'a lack of properties' of single polymers. The idea was to combine the different attributes of two or

more polymers and define a new mixture of properties. For high performance polymer blends some successful examples exist [1,2]. Unfortunately, the majority of polymers are immiscible [3] which means that meta- or instable heterogeneous mixtures are formed. This fact limits the degree of property transfer. Nevertheless, several investigations focused on immiscible polymer blends [4,5] and some even made it into industrial production [6]. No attention is paid so far to immiscible thermoplastic polymer blends in endless carbon fibre composites. But especially in the high-end application sectors property improvements and cost reductions play vital roles.

Polyphenylene sulfide (PPS) is known for its high stiffness, tensile strength, thermal stability and resistance towards chemicals. However, the glass transition temperature of PPS is moderate compared to other high temperature polymers such as Polyether etherketone (PEEK).

Polyethersulfone (PES) as an amorphous high performance thermoplastic polymer exhibits a high glass transition temperature above 220 °C and excellent thermal stability. Blends of PPS and PES were therefore investigated intensively in the past [7–11], but not considered for endless fibre composite's structures so far. A successful transfer of PES' properties to PPS/PES composites would mean a potential increase of the application range of conventional PPS parts.

2. Method And Experimental

2.1 Targets and Method

The method applied in this investigation focused on the characterization of film stacked carbon fibre composites containing different matrix compositions of high performance PPS and PES grades. Main target was the evaluation of thermal stability of these immiscible polymer blend composites as well as their resistance towards technical media. It is known from former studies [1–5] that the temperature dependent stiffness (storage modulus) of PES is being transferred to PPS/PES blends and that it follows the rule of mixture below the glass transitions of both components. Important aspects for the evaluation of property transfer in composite samples were the crystallisation, the fibre volume contents and the formation of morphologies of the immiscible blend partners in the different compositions. Film stacked composite samples with high fibre volume contents were processed and analysed. Untreated samples were investigated qualitatively regarding their degree of crystallisation and subsequently tested in dynamic mechanical thermal analysis (DMTA). Chemical resistance of samples was evaluated by DMTA measurements after treatment with Methyl ethyl ketone (MEK). Finally the quantification of matrix morphologies was targeted to correlate structure and performance. A selective etching procedure with Dimethylacetamide (DMAc) was examined to remove the dispersed PES phase, followed by Scanning Electron Microscopy (SEM) imaging and quantitative (residual) pore analysis.

2.2 Materials and Processing

The selected PPS grade was a *PPS Fortron 0320* from *Ticona*, the *PES Ultrason E1010* grade was provided by *BASF, Germany*. Additionally, a compatibilizing *PES Ultrason E2020 P SR Micro* grade with OH-modification was added to each composition to evaluate the influence on the morphology formation and its impact on the chemical resistance. Compositions and naming of all blend films as well as the fibre volume contents of composite samples are listed in table 1.

PPS/PES blends with and without the PES-OH grade were extruded in a film extrusion process on a cast film device. Extrusion temperatures averaged between 345 °C and 360 °C in the different sections.

Table 1: PPS/PES blend film compositions processed in cast film extrusion and fiber volume amounts of PPS, PES and PPS/PES carbon composites.

Films				Composites	
Identifier	PPS [Wt.-%]	PES [Wt.-%]	PES-OH [Wt.-%]	Identifier	Fibre content [Vol.-%]
PPS	100	-	-	<i>PPS CF</i>	62.2
85-15-0	85	15	-	<i>85-15 CF</i>	60.9
85-12-3	85	12	3	<i>85-12-3 CF</i>	61.9
50-50	50	50	-	<i>50-50 CF</i>	63.4
50-45-5	50	45	5	<i>50-45-5 CF</i>	63.1
PES	-	100	-	<i>PES CF</i>	60.4

For the film stacking a standard high tenacity *Toray T300B* carbon fibre satin weave 4/1 textile with an aerial weight of 270 g/m² and 3000 fibres per roving was used. All samples were stacked with 8 textile layers and 4-7 film layers depending on film thickness. Processing temperature was set at 340 °C for 1 h. The fibre volume amounts were calculated from optical analysis of polished cross sections. Pores and voids were found to amount less than 1 %.

2.3 Differential Scanning Calorimetry

Melting and crystallization behaviour of the composite samples was investigated by DSC measurements. Initial temperature was set to 70°C. Samples were heated up to 300 °C. Heating and cooling rate was 10 K/Min. Investigation of process dependent crystallization of the composite samples focused on qualitative analysis such as the determination of post-crystallisation- and miscibility-phenomena.

2.4 Dynamic Mechanical Thermal Analysis

Determination of the thermo-mechanical stiffness was examined in a 3-point-bending set-up with a *Gabo Eplexor, Germany* DMTA device. Temperature range was set at 70-150 °C. Test frequency was 10 Hz. Measurements were examined force regulated with 120 N static and 30 N dynamic forces.

2.5 Selective Etching And Quantification

Quantification of the immiscible blend morphologies was realized by polishing of sample's cross sections with subsequent selective etching of the PES phase. DMAc was used to remove the PES phase from the cross sections. Documentation of sample's weight loss evidenced that PPS was not affected by this procedure. Etched surfaces were statistically imaged with the SEM. Of each composition two samples were prepared from which seven pictures were taken with an area of 85x64 µm at a magnification of 3500. Quantification of the PES phase residual pores was achieved by computer-assisted *analySIS docu* software by *Olympus Soft Imaging Solutions GmbH, Germany* of these SEM images.

3. Results and Discussion

3.1 Crystallization

The crystallinity of PPS is known to significantly influence its mechanical and thermo-mechanical properties. Former investigations revealed only poor miscibility of PPS with PES in non-reinforced blends. Analysis of PPS/PES carbon composite crystallinity and miscibility-phenomena was examined

by DSC measurements after composite processing. Figure 1 shows representative 1st heating and 1st cooling graphs of the different blend composite samples.

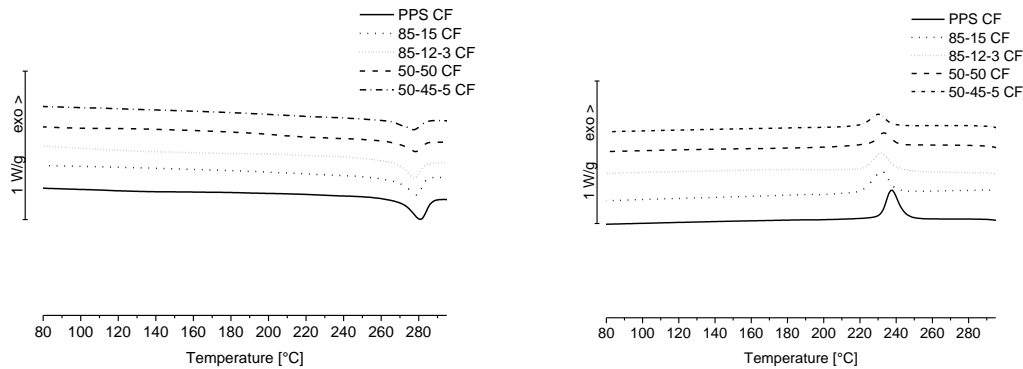


Figure 1: Comparison of DSC graphs of neat PPS and PPS/PES blend composites, left: 1st heating, right: 1st cooling.

Heating curves indicated that composite processing lead to complete crystallization of the present PPS phase since no post-crystallization peak was detected. Shifts were recognized regarding the melting range of PPS. A slight dependency of the melting range from the present PES phase can be assumed. Cooling curves additionally revealed that crystal growth is only slightly affected by the PES fractions. Further, no difference in crystallisation or melting behaviour was recognized for compatibilized samples. From former studies it is known that crystal growth of PPS can be hindered by the presence of a second phase [7].

3.2 Dynamic Mechanical Thermal Analysis

The glass transition temperature of *Fortron* PPS was given by the supplier to be at 90 °C approx. It was assumed that below 90 °C storage moduli of composite samples should depend only of the PES fraction present. However, figure 2 shows different behaviour for the compatibilized compositions.

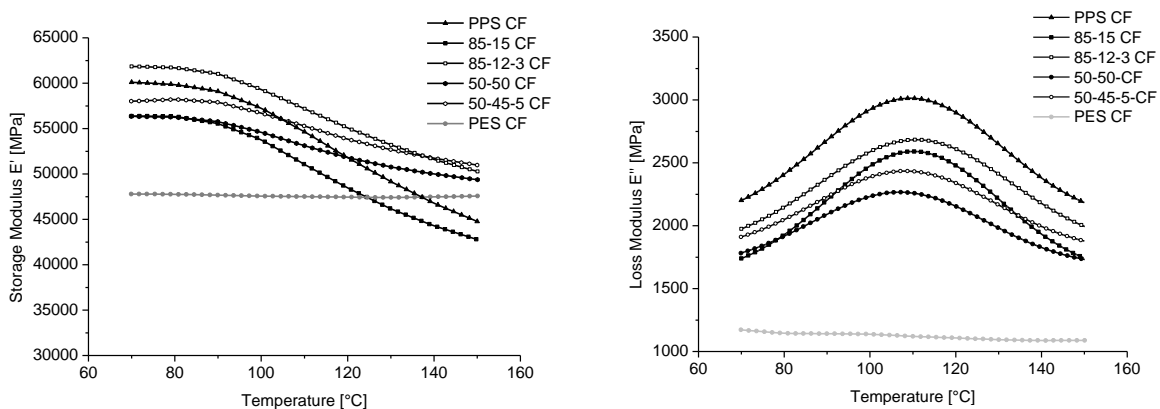


Figure 2: Comparison of temperature dependent behavior of neat PPS and PPS/PES blend composites, left: storage moduli, right: loss moduli.

The storage modulus of neat PPS samples averaged around 60 GPa in the temperature range from 70 to 90 °C. A drop of storage modulus for all samples was recognized beginning at approx. 90 °C. Initial

stiffness of 85-15 CF and 50-50-CF averaged at only 56 GPa. 50-45-5 CF revealed higher stiffness of approx. 58 GPa in this temperature range. Neat PPS CF exhibited a storage modulus of 60 GPa. The 85-12-3 CF composite samples instead exhibited higher storage moduli of around 62 GPa. At higher temperatures, compositions with 15 wt.-% PES revealed a stronger drop in modulus than samples with 50 wt.-% PES. The slope of the high temperature plateaus of these blend samples seemed independent of the initial stiffness. Interestingly, the compatibilized compositions showed higher stiffness over the whole temperature range than their non-compatible counterparts. The neat PES curve served as a reference and showed the unaffected stiffness in the whole temperature range of the test. The graphs of loss moduli revealed that all compositions exhibited a maximum at approx. 105-110 °C independent of the PES weight fraction. In this temperature range the PPS stiffness was maximally decreasing and undermatched the blend compositions.

These results showed that firstly, the lower temperature regions were dominated by the PPS phase in the blend composite samples. Secondly, the independency of loss modulus maxima from the PES fractions underlined the immiscibility of PPS and PES. Thirdly, it can be assumed that the addition of the PES-OH grade influenced the stiffness in the whole temperature range. This effect may be achieved by an improvement of the polymer/polymer phase interactions or by an improvement of the fibre matrix adhesion.

The investigation of morphology effectiveness regarding the chemical resistance of blend composites was realized by MEK treatment and subsequent DMTA testing. Figure 3 illustrates the dependency of resulting storage and loss moduli from the temperature.

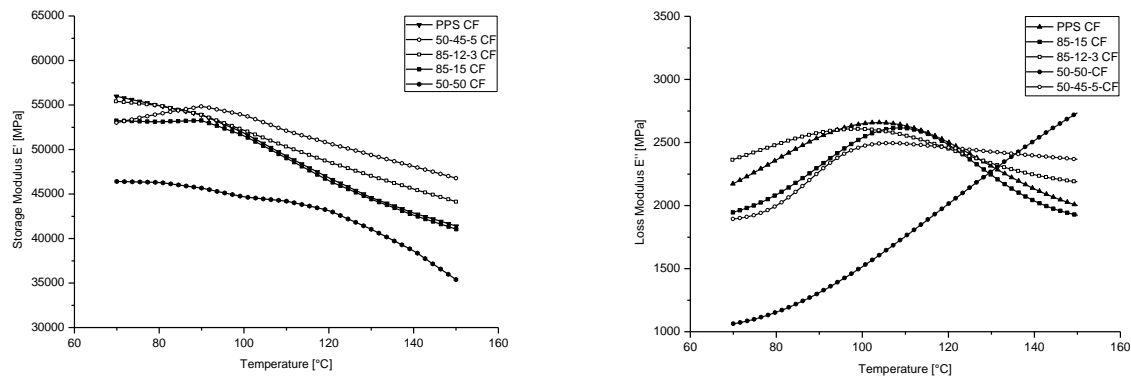


Figure 3: Comparison of temperature dependent behaviour of neat PPS and PPS/PES blend composites after MEK treatment, left: storage moduli, right: loss moduli.

Due to the solubility of PES in MEK neat PES CF samples could not be tested. All samples, including neat PPS CF, showed a significant drop of initial storage modulus. The highest loss of stiffness was recognized for the 50-50 CF samples: Neither the expected initial stiffness nor the high temperature plateau of the untreated samples was reproduced. Neat PPS and 85-12-3 CF samples matched at approx. 56 GPa regarding their initial stiffness. The storage modulus of PPS then dropped at higher temperatures as already observed for untreated samples. Samples of 85-12-3 CF partially kept a higher stiffness in the upper temperature regions. The 50-45-5 CF blend composites revealed higher thermal stability but at significantly lower level compared to untreated samples. The initial storage modulus instead increased at the beginning, indicating that pores have occurred during the MEK treatment. The non-compatible 85-15 CF composites showed identical behaviour as the neat PPS CF. The graphs of loss moduli underlined the above observations.

From these results it can be assumed that the temperature dependent behaviour of MEK treated blend composites was strongly affected by the presence of the compatibilizing PES-OH grade and, as

expectd, of the PES fraction in the samples. Further, the drop of PPS CF storage modulus indicated that the fibre matrix strength may was reduced by the MEK treatment.

However, the performance of blend composites can not only be explained by differences in the fibre/matrix adhesion. Especially, the chemical resistance must have been influenced by the resulting morphology of these composites.

3.3 Morphology Quantification

The analysis of blend composites morphologies was realized by selective etching of the PES phase and subsequent quantification of the residual pores. Figure 4 shows polished and etched cross sections before and after the computer assisted quantification of residual pores.

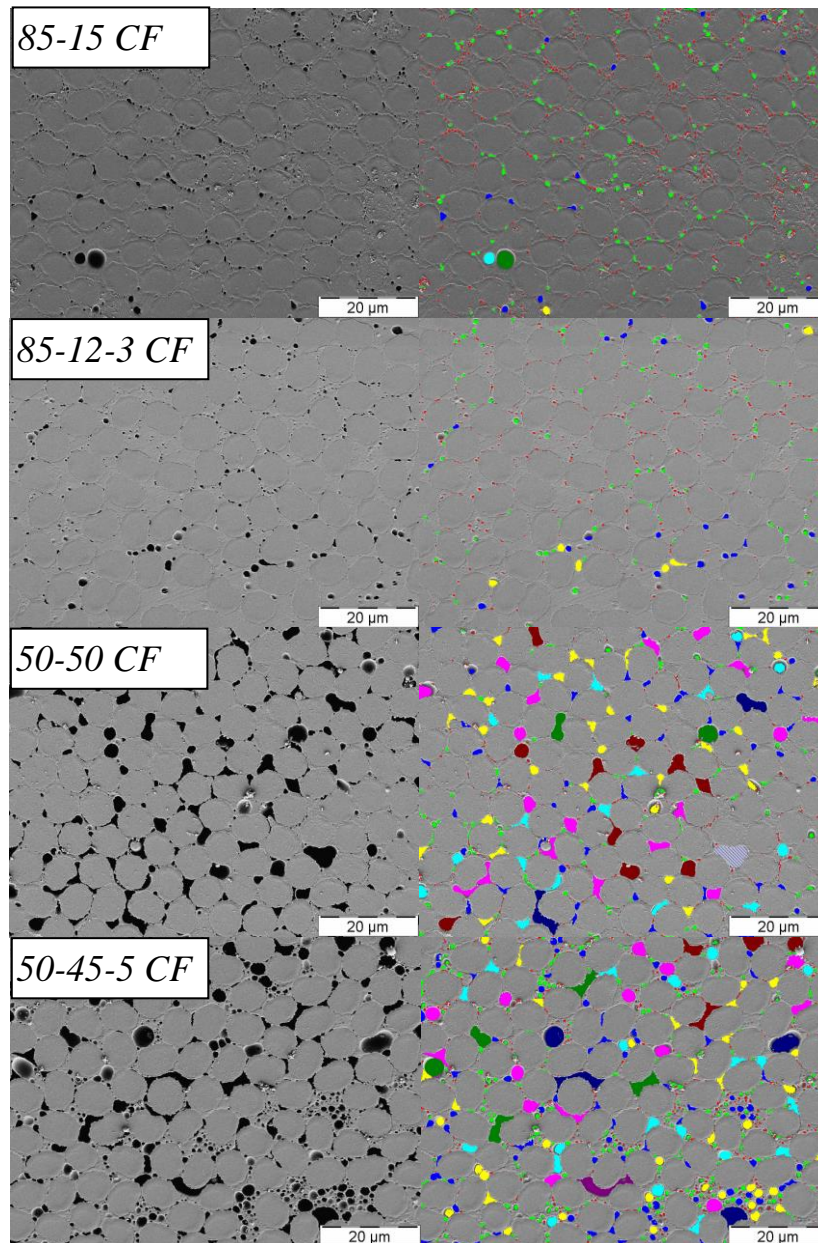


Figure 4: SEM images at magnification 3500 of polished and etched cross sections of PPS/PES blend composites, left: after selective etching with DMAc, right: after quantification of residual pores.

Observation of these SEM images revealed, as expected, that the number of residual pores increased with the PES weight fraction in the composites. Further, in the case of 50 wt.-% PES the addition of the PES-OH grade lead to a higher amount of small profiles in the composites. For 85-15 CF and 85-12-3 CF the differences were not that clear. In figure 5 the number of detected profiles is plotted as a function of profile's area for the different compositions.

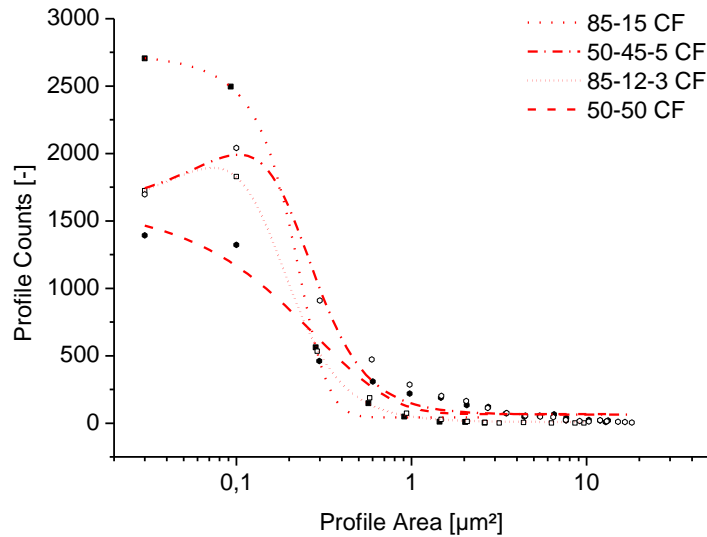


Figure 5: Number of counted profiles as a function of class average profile's size.

As assumed the profile size distribution of 50-50 CF samples was relatively coarse compared to its compatibilized counterpart. The small profile fractions were lower for this blend compared to the other compositions. The number of small profiles for 85-12-3 CF and 50-45-5 CF were almost equal. However, with its higher PES fraction the number of bigger profiles was higher in 50-45-5 CF. Finest distribution was observed for the 85-15 CF samples with significantly higher amount of smallest profile size of lower than 0.25 µm.

Table 2: Weight loss of composite samples after etching with DMAc.

Identifier	Weight loss [Wt.-%]
PPS CF	0.01937
85-15 CF	0.00341
85-12-3 CF	0.02872
50-50 CF	2.95024
50-45-5 CF	0.82282
PES CF	100

The etching procedure with DMAc was evaluated by sample's weight loss of each composition (table 2). While for neat PPS CF and the compositions with 15 wt.-% PES the weight loss was negligible, the 50 wt.-% PES compositions exhibited significant weight reductions. A good correlation of MEK treated DMTA results was observed for the 50-50 CF composites, since here the thermo-mechanical decline was most significant and so was the weight loss after etching. With greater number of bigger profiles, the contact surface to large PES volumes was increased. Hence, chemical resistance was reduced.

4. Summary

Immiscible thermoplastic PPS/PES blends were investigated regarding their morphological features and resulting thermomechanical properties in carbon composite samples. The PES fraction dependent morphologies lead to different thermomechanical and media dependent properties. With high PES fractions the storage modulus of carbon composites was improved significantly from 110 °C on. However, this thermal stability was strongly dependent of the distribution of PES spheres in the composite samples which was influenced by the addition of OH-bridges provided by a modified PES grade. Compatibilized samples exhibited better stiffness thanks to improved transfer of thermal stability. It was further assumed that an improvement of fiber/matrix adhesion was achieved by the compatibilizing PES-OH grade which further increased the level of storage moduli.

Differences in the morphological features could successfully be quantified by a selective etching procedure and were found to be the driving factors for the property development in composite samples: Fine distributions could provide better chemical resistance due to the protective role of the PPS phase and the reduced contact surface of big PES volumes; Compatibilizing OH-groups could improve the fineness of distribution when high a PES fraction was present, thus the chemical resistance was partially maintained.

We conclude that the mechanisms of morphology and property development in thermoplastic immiscible blend composites are influenced by the phase to phase and the phase to fiber behavior of molten polymers during the processing step. It is shown that property improvement of immiscible polymer blends can be transferred to endless carbon fiber composites. Hence, future work will focus the analysis of polymer melt's interface and the wetting behavior of polymer blends on the surfaces of carbon fibers. These aspects will enable the further description, modelling and improvement of thermoplastic blend composites.

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