

THE INFLUENCE OF SEVERAL FILLERS ON THE THERMO-CHEMICAL AND MECHANICAL PROPERTIES OF HIGH PERFORMANCE THERMOPLASTIC POLYMERS

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Abstract

The objectives of this work were to evaluate the influence of several fillers (Expanded Graphite, Fumed Silica and Calcium carbonate) on the thermo-chemical and mechanical properties of high performance thermoplastic polymers (Polyether ketone ketone and Polyphenylene sulfide) to use as matrices in fiber reinforced composite panels. The analysis showed Expanded Graphite was the best performance filler. The fiber reinforced composite panels were realized by film stacking with two types of carbon fiber fabric (unidirectional and plain weave fabric). The properties of the composite panels were evaluated by Dynamic-mechanical analysis, Differential scanning calorimetry, Flexural and Tension tests and Thermographic analysis. The mechanical performances improved in the composite panels realized with developed new matrices.

1. Introduction

Continuous fiber reinforced thermoplastic composites are increasingly applied in aircraft structures. These high-performance thermoplastic matrices need processing at high temperatures; therefore, thermal residual stresses arise due to the mismatch in the coefficients of thermal expansion between the fibers and thermoplastic matrix. Since residual stresses are inherently present in virtually all composite materials and influence the properties of the composite structures significantly, it is of utmost importance that the residual thermal stresses are taken into account and controlled, when they cannot be suppressed, in the manufacturing processes. As well the elevated costs of high performance thermoplastic composites depend on the price of raw materials and on the high temperatures of manufacturing processes (elevated energetic costs), so a neat cost reduction is achievable reducing one or both factors. The objectives of this work were to evaluate the influence of several fillers on the thermo-chemical and mechanical properties of selected high performance thermoplastic polymers (Polyether ketone ketone, PEKK, and Polyphenylene sulfide, PPS) to use as matrices in fiber reinforced composite panels.

The thermoplastic nanocomposites have been developed, in order to realize systems with crystallization kinetics controlled by heterogeneous nucleation, activated by nanoparticles and to get the matrix crystallization process independent from cooling rate of the manufacturing process

2. Experimental section

2.1 Materials

The PPS, code Fortron 0320P0, was purchased by Ticona (Sulzbach, Germany). The PEKK, codes OXPEKK D, has been provided by ARKEMA (Colombes, France). Calcium carbonate (primary particle average size = $[90 \pm 15 \text{ nm}]$, PLCACOU- 25g) and fumed silica (primary particle average size = $[7 - 14 \text{ nm}]$, PLSiOF- 25g) were purchased by PlasmaChem (Berlin, Germany). Expanded graphite (primary particle average size $< 65 \mu\text{m}$, TG-741) was supplied by GrafTech International (Anmoore, WV, USA). The PEKK in pellets were provided by Arkema (Colombes Cedex, France): a semicrystalline grade coded OXPEKK D, melting temperature= $332 \text{ }^\circ\text{C}$ and glass transition temperature= $157 \text{ }^\circ\text{C}$.

As composite reinforcements were used two carbon fiber texture: Hexcel G0814, High Strength Carbon Fabric, 3K Plain Wave and Hexcel G1157, D 1300, Unidirectional

2.2 Preparation of Nanocomposites and fiber reinforced composite panels

Nanocomposites were prepared, loading PPS and PEKK matrices with three different fillers and in particular loaded Expanded Graphite (EG), Fumed Silica (SiO_2) and Calcium Carbonate (CaCO_3) at several concentration (0,1 – 0,5 – 1 – 2 %wt).

The PPS nanocomposites were prepared, dispersing nanoparticles in ethanol through ultrasonication for 60 min at 10 watt, subsequently the sonicated solution was poured in a becker containing polymer powder. The becker was heated till complete ethanol evaporation (magnetically stirred). The polymer with nanoparticles deposited onto grain surface was dried in a vacuum oven at $90 \text{ }^\circ\text{C}$ for 12 hours.

The PEKK nanocomposites were prepared via melt compounding by DSM twin screw mini-extruder (screw speed of 70 rpm, a mixing time of 5 min and a temperature of 330°C). The matrix was dried using a vacuum oven at $130 \text{ }^\circ\text{C}$ for 2 h before processing to minimize the effects of moisture.

The pellets of prepared nanocomposites were then hot-pressed to produce thin films using the hot press P300P Collin (Ebersberg, Germany). The optimized process parameters were heating at $330 \text{ }^\circ\text{C}$ for 5 mins and 50 bar, and cooling).

The composite panels (200x200x2 mm) with PPS/EG or PEKK/EG matrix and Carbon fiber texture were fabricated by hot press forming process (Film Stacking process).

2.3. Characterization techniques

Thermal properties of neat polymers and nanocomposites were investigated by means of differential scanning calorimeter (DSC model Q20, TA Instruments). The DSC experiments were performed with different cooling rate (5, 10, 20 and $50^\circ\text{C}/\text{min}$) and heating rate at $10 \text{ }^\circ\text{C}/\text{min}$, in order to compare the effects of cooling on crystallization. The investigated temperature range for PPS based samples was $0\text{-}330 \text{ }^\circ\text{C}$, while for PEKK was $0\text{-}370 \text{ }^\circ\text{C}$.

The thermogravimetric analysis (TGA) of composite formulations was conducted by TA Instruments Discovery TGA, in the range of temperature $40 \div 700^\circ\text{C}$ with a ramp rate of $20^\circ\text{C}/\text{min}$ in an air-filled environment.

Dynamic-mechanical measurements (DMA) were performed using a tensile mode at a constant frequency of 1Hz and over a range of temperatures from 40°C to 180°C for PPS matrix and from 40 to 240 °C for PEKK matrix. For each sample, heated at a rate of 5°/min, variation of viscoelastic parameters, such as storage modulus (E') and mechanical loss factor ($\tan \delta = E''/E'$), were recorded as a function of temperature.

The rheological analysis was carried out on loaded matrices (TA Instrument, Discovery HR2) to understand the behavior of viscosity with the temperature in order to optimize the manufacturing process of composite panels by film stacking.

Flexural and Tensile tests were run at RT on both nanocomposites (only matrices) and composite panels by employing an Instron Machine. Regarding the flexural test, three point bending tests were performed (ASTM D 790) with the support span of 25 mm and the cross-head speed fixed to 2,5 mm/min. The tensile (ASTM D 3039) were performed using a cross-head speed of 1,3 mm/min. The coupon dimensions were 190 x 20 mm.

The produced composite plates have been analyzed via NDT (Non Destructive Testing) by using Lock-In Thermography. The set-up in house is made up of an infrared camera SC5000 MW InSb by FLIR®, four 1KW halogen lamps and their related driving system.

In order to evaluate the interaction matrix/fibers an SEM analysis was performed by QUANTA 200F, FEI. To obtain fracture surfaces that reveal the matrix morphology and the fiber/matrix interactions, the samples were fractured transversely to the fiber direction. Again, morphological analysis has been carried out by LEICA – DMRXE Optical Microscopy. This study allowed to evaluate the fraction of composite material matrix/fiber in the panels and the arrangement of the fibers.

3. Results and discussion

3.1. Nanocomposite Matrices Analysis

3.1.1 Neat PPS and PPS nanocomposites

Thermal properties of neat and loaded PPS were studied with both DSC dynamic scan at different cooling rate and DSC isothermal scans followed by dynamic scan. The calorimetric analysis shows that the crystallization temperature of neat PPS decreases as the cooling rate increases from about 240 °C at 5 °C/min to 225 °C at 20 °C (Figure1a). Conversely, melting temperature of PPS is very weakly dependent upon cooling, but its value reduces of about 15 °C after annealing at 330 °C for 5 min. The glass transition (T_g) of PPS is unaffected by the cooling rate ranging between 5 and 20 °C, while a reduction of 10 °C was measured in the sample quenched soon after heating step at 330 °C of press moulding process (Figure1b).

Similarly to melting temperature, the melting enthalpy of neat PPS did not show any relevant dependence upon cooling rate but rather a decrease in samples annealed at 330 °C for 5 min (Figure1c); considering that the melting enthalpy of PPS perfect crystal is 77.22 J/g, thermal treatment (annealing) results in a reduction of about 10% in crystallinity degree (from 71% to 58%). This trend is probably caused by: 1) an extreme difference between the cooling rate of the as received PPS pellets production process (such as solution polymerization) and those used during DSC experiments or 2) the annealing process that could induce a chemical variation of PPS macromolecules.

The thermal properties of nanocomposites were investigated and compared to those of a neat PPS film produced with the same moulding processing of nanocomposite films, because thermal properties are evidently influenced by processing. Glass transition temperature of PPS nanocomposites presents a modest variation with all nanoparticle contents and types (Figure 2a *Glass transition*). It is a measure of macromolecules mobility and can be influenced by nanoparticles strongly interacting with macromolecules or by degree of crystallinity as shown

in Figure 1. The weak Tg variation indicates that the selected nanoparticles do not have a strong interface interaction with hosting polymer and could promote crystalline nucleation, as reported in the following.

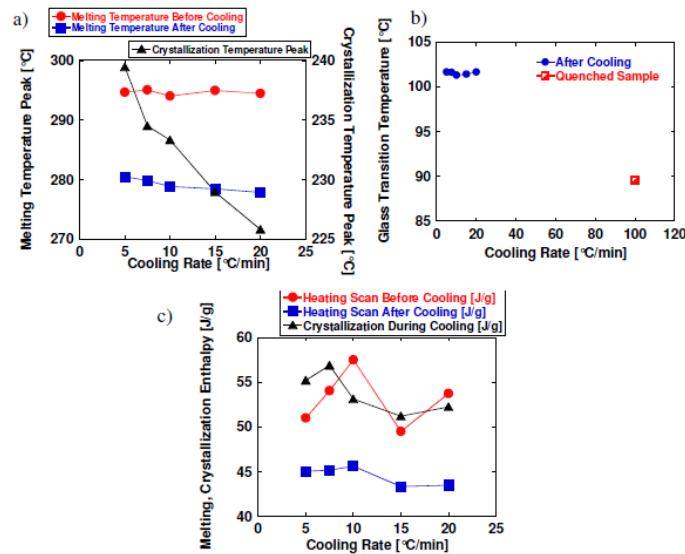


Figure 1: Thermal properties of neat PPS as function of cooling rate: a) melting and crystallization temperatures (note that with the term ‘before cooling’ is intended the value of the as-received sample before melting and subsequent cooling; it was reported for comparison); b) glass transition temperature; c) melting and crystallization enthalpy.

The crystallization temperature of PPS nanocomposite reinforced with EG increases with the filler content for the three investigated cooling rates (Figure 2a *Crystallization temperature*) with a shift of about 8-10 °C at 1.0% concentration. Nanocomposites filled with round shaped particles present an increment not higher than 2-3 °C (Figure 2b and c).

Melting temperature of all nanocomposites is almost unaffected by nanoparticle content (Figure 2); conversely, melting enthalpy nanocomposites increases with respect to neat PPS. In particular, the addition of EG results in an increase of about 8-10 J/g starting from 0.1% concentration (equivalent to 10% increment of crystallinity degree) as illustrated in Figure 2a. Melting enthalpy of PPS filled with fumed silica and calcium carbonate presents an increment lower than that of PPS containing EG. These differences could be due the degree of dispersion of nanoparticles into PPS matrix or to different surface properties of nanoparticles.

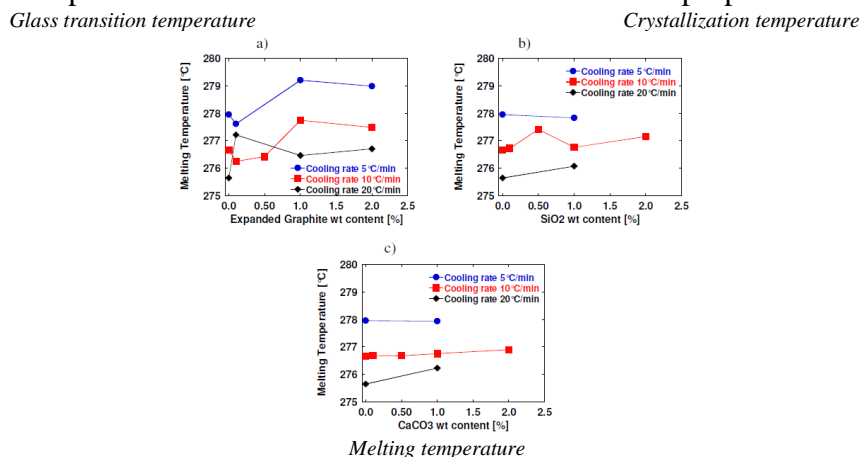


Figure 2: Thermal properties of PPS nanocomposites as function of both cooling rate and filler content: a) nanocomposite reinforced with EG; b) SiO₂, c) CaCO₃.

Analyzing the Dynamic Mechanical Analysis, the inclusion of graphite deals to an increase of the storage modulus both in the glass and in the rubbery regions. This positive trend seems to be monotonous with the nanoparticles percentage and may be explained mainly assuming the occurrence of phenomena usually revealed in similar nanostructured formulations such as nucleating effects of dispersed nanofiller (Figure 3a).

The Flexural modulus increases with the addition of EG and it reaches his maximum value with 1wt% EG (Figure 3). At this concentration, instead, the flexural strength of the nanocomposites decreased compared with neat polymer. Presumably, this is due to the poor interaction between EG and polymer matrix, and stress concentrations resulting from the aggregation or agglomeration of the EG in the polymer matrix.

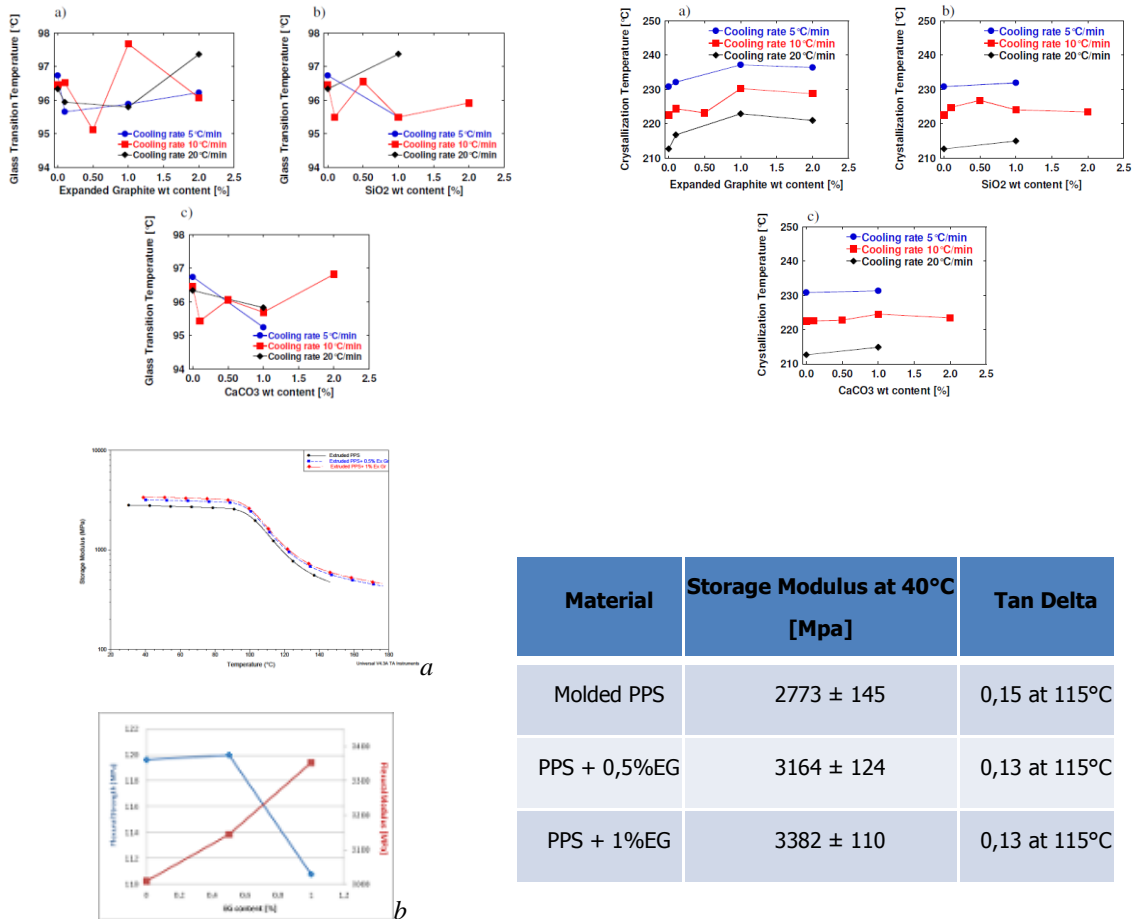


Figure 3: Loss Factor ($Tan \delta$) and flexural test of neat PPS and PPS based nanocomposite containing 0.5 and 1.0 wt% of EG

3.1.2 Neat PEKK and PEKK nanocomposites

The calorimetric analysis of the PEKK nanocomposites shows that the melting temperature is weakly dependent upon nanofiller content. The melting Enthalpy of PEKK nanocomposites reinforced with EG increases with the filler percentage, with a shift of about 5 J/g at 1.0%wt concentration (Figure 4a). Instead, nanocomposites filled with round shaped particles (SiO_2 and $CaCO_3$), are weakly influenced by the nanofiller content. The Glass transition temperature is slightly influenced with the filler content (Figure 4c). This result indicates that the selected nanoparticles do not have a strong interface interaction with hosting polymer and could promote crystalline nucleation. The crystallization temperature increases strongly with the introduction of EG. In particular it reaches his maximum value with 1%wt EG and at 20°C/min cooling rate (Figure 4d). The other nanocomposites, instead, don't seem to be

influenced by the filler content. The experimental results show that the EG acts as nucleating agent. In fact, both the shifts of the crystallization peaks and the decreases of the degree of supercooling in PEKK with EG are evidence of the nucleating effect of the graphite. In conclusion, the calorimetric analysis shows that the best nanocomposites are: PEKK + 1%wt EG and PEKK + 2%wt EG. So, those two kinds of nanocomposites were hot pressed to carry out the DMA and the Mechanical test.

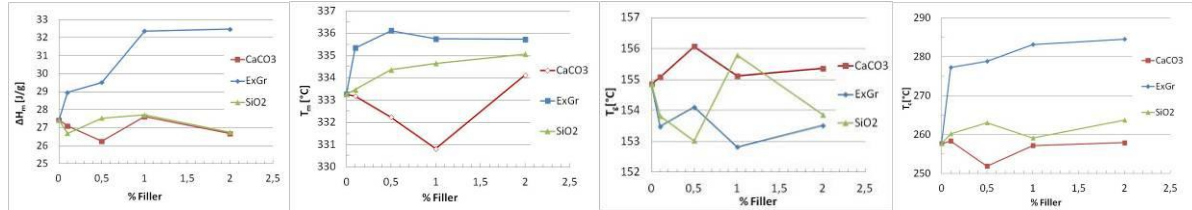
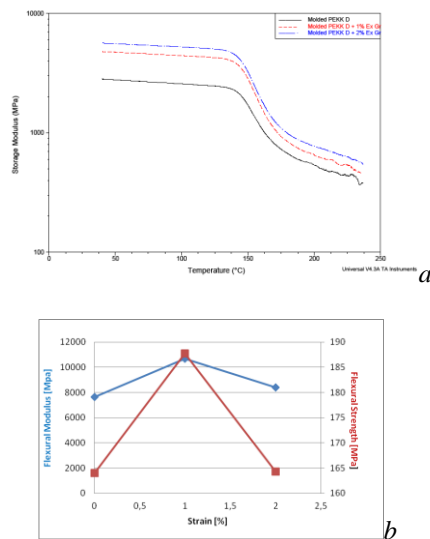


Figure 4: Melting Enthalpy (a), Melting Temperature (b), Tg (c) and Crystallization Temperature and of PEKK nanocomposites as function of filler content: EG; SiO₂ and CaCO₃

The storage modulus increases both in the glass and in the rubbery regions with the inclusion of graphite (Figure 5a). This trend seems to be monotonous with the nanoparticles percentage. In terms of Tan δ, there is a slight influence on the signal consequent to the graphite inclusions. The peaks of tan delta slightly decreases with 2.0%wt of EG. The improvement of the storage modulus can be attributed to the already cited nucleating effect of dispersed phase and to the interactions occurring at the graphite-matrix interphase. The Flexural strength of the nanocomposites increases of about 15% with 1wt% EG addition, while it has the same value as the neat PEKK with the addition of 2wt% EG (Figure 5b). Also the Flexural modulus reaches the maximum value with 1wt% of EG and it increases of about 35% compared to the pure PEKK D. So the nanocomposites with 1%wt EG show the best mechanical performance.



Material	Storage Modulus at 40°C [Mpa]	Tan Delta
Molded PEKK D	2813 ± 145	0,27 at 160°C
PEKK D + 1%EG	4872 ± 173	0,28 at 162°C
PEKK D + 2%EG	5045 ± 125	0,25 at 160°C

Figure 5: Loss Factor (Tan δ) and flexural test of neat PEKK and PEKK based nanocomposite containing 0.5 and 1.0 wt% of EG

3.2. Fiber reinforced composite panel using the new loaded Matrices

According to results of the nanocomposites analysis, the PPS and PEKK nanocomposites loaded with 1%wt EG have been used to realize the composite panels by film stacking using two types of carbon fiber textile as reinforcement (Unidirectional and Plain Wave). A detailed characterization (rheological, morphological and thermal) of the first realized panels and of the new realized mold (designed and realized ad hoc) has allowed to optimize the film stacking process parameters, in terms of Temperature, pressure and time, as well as the treatment of the tools and the procedure for lamination.

The morphological analysis (SEM and optical) of the first panels showed a not good interaction matrix/fiber in the panels with loaded matrix, probably because of high viscosity of the matrix during the impregnation phase. Again the optical analysis has allowed to evaluate the tow percentage (fraction of composite material matrix/fiber) in the panels and a good arrangement of the fibers. These studies allowed to optimize the manufacturing process. As far as **mechanical properties** are concerned, the modulus is not effected by EG (about 46GPa) both in the PPS//PW and PPS //UD panels (Figure6). The max load and the ultimate tensile strength, instead, are higher in the PPS panels with Plain Weave texture, than in the PPS panels with Unidirectional texture (11 kN). The tensile modulus shows the same value in the PEKK//PW and in the PEKK+1%EG//PW panels (43 and 48 MPa respectively). In addition, the max load and ultimate tensile strength increase of about 40% in the PEKK//PW with graphite (Figure6).The PEKK panels with Plain weave texture show best properties compared to the PEKK panel with UD texture.

Sample	Modulus [MPa]	Max Load [kN]	Ultimate tensile stress [MPa]	Ultimate tensile strain %
PPS//PW	46000 ± 1925	15,97 ± 0,51	384,73± 11,01	1,53 ± 0,07
PPS+ 1%EG//PW	45543 ± 1512	16,39 ± 0,23	368,11 ± 9,86	1,55 ± 0,13
PPS//UD	46512 ± 3357	11,10 ± 2,52	335,18 ± 26,98	2,06 ± 0,08
PPS+1%EG//UD	46770 ± 660	11,62 ± 1,09	325,51 ± 28,74	1,67 ± 0,27
PEKK//PW	43246 ± 4494	16,90 ± 1,01	366,65 ± 26,92	1,33 ± 0,20
PEKK+ 1%EG//PW	48000 ± 2820	22,80 ± 0,58	526,61 ± 41,27	1,70 ± 0,13
PEKK//UD	24485 ± 671	10,53 ± 0,83	211,09 ± 7,50	1,12 ± 0,23

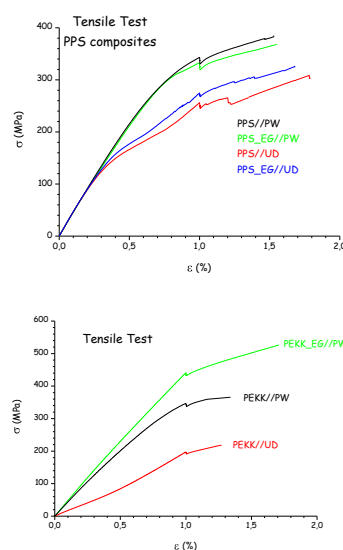
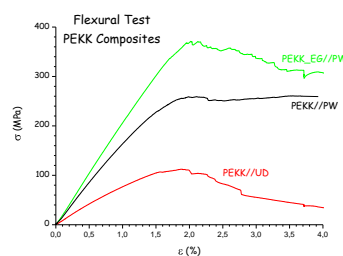


Figure 6: PEKK and PPS Composites - Tensile stress-strain curves overlay and main results

The flexural properties of PPS composite panels are not influenced by the presence of EG in the composites (Figure7). The flexural modulus and the max load are higher in the composites with Plain Weave texture compared to the unidirectional texture. Consequently the flexural strain is lower in the panels with plain weave compared to the panels with unidirectional texture. Regarding PEKK composite panels, the expanded graphite seems to lead a small increment (from 18000MPa to 23000MPa) of the flexural modulus and flexural stress at break in the composite with plain weave texture. The latter, moreover, shows higher flexural properties compared to the unidirectional composite panels. This characterization showed that the optimized process allowed to get composite panels with improved mechanical performances.

Sample	Flexural Modulus [MPa]	Flexural Stress at Break [MPa]	Flexural Strain at break [%]	Max Load [kN]
PPS//PW	20376 ± 600	290,03 ± 37,0	1,91 ± 0,38	0,36 ± 0,04
PPS+ 1%EG//PW	21572 ± 2763	279,12 ± 29,36	1,71 ± 0,15	0,39 ± 0,06
PPS//UD	10596 ± 3036	153,73 ± 37,96	3,05 ± 0,52	0,15 ± 0,04
PPS+1%EG//UD	1366 ± 1071	167,08 ± 6,12	2,25 ± 0,44	0,15 ± 0,01
PEKK//PW	17703 ±	0,47 ± 0,04	266,09 ± 23,07	3,19 ±



	2852			0,80
PEKK+	23960 ±	0,58 ± 0,04	381,88 ± 36,10	2,14 ±
1%EG//PW	2126			0,12
PEKK//UD	7383 ± 651	0,20 ± 0,03	123,59 ± 6,82	2,10 ± 0,21

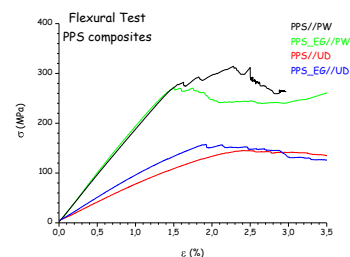


Figure 6: PEKK and PPS Composites – Flexural Test, curves overlay and main results

4. Conclusions

The carried out activities showed that for both PPS and PEKK thermoplastic matrices the best filler was Expanded Graphite at 1% wt. In particular, in the PEKK matrix, the EG has more influence on the mechanical properties (Flexural and Dynamical- mechanical test) of nanocomposites, while in the PPS matrix, the EG has more influence on thermal properties of the nanocomposites. In both matrices PPS and PEKK, the EG inclusion doesn't influence the melting temperature, while it leads an increment of crystallization temperature and a drop of degree of supercooling, very important thermal properties for the process and maintaining the high values of T_g. In both matrix PPS and PEKK, the EG inclusion leads an increment of flexural modulus and storage modulus. In the PPS matrix, the EG leads a slight decrease of Flexural strength, while in the PEKK matrix, the filler inclusion leads a slight increase of flexural strength.

The optimized process parameters allowed realizing composite panels with high crystallinity of the matrices and good mechanical properties of the composite panels.

In particular, in the PEKK composite the mechanical performances of the panels made with loaded matrices were higher than panels made with as prepared matrix, both in the flexural and tensile test.

Regarding the PPS composite panels, the improvement of the composite panels made with loaded matrix were in line with results of the nanocomposite (only loaded matrix).

Anyway, for both matrices the best carbon fibers textile was the Plain Wave one. Probably, the mechanical performances of the composite panels can be further improved using different types of carbon fiber textile, such as dry fibers, without binder.

Very interesting performed characterization was the residual stress analysis on the realized panels, in order to evaluate the residual stresses due to the significantly higher shrinkage of the matrix compared with the fibers.

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