NEW AFFORDABLE REINFORCED SULFIDE/SULFONE THERMOPLASTIC FOR HIGH-PERFORMANCE APPLICATIONS

D.R. Meyer, P. Carnevale, H.E.N. Bersee
Faculty of Aerospace Engineering, Delft University of Technology,
Kluyverweg 1, 2629 HS Delft, The Netherlands
D.R.Meyer@Tudelft.nl, H.E.N.Bersee@Tudelft.nl

SUMMARY

A new affordable reinforced composite with a poly (phenylene sulfide sulfone) matrix, presenting high mechanical and thermal resistance properties, is introduced in this paper. Mechanical, thermal and chemical characterizations, as well as microscopy analyses measurements, have been achieved.

INTRODUCTION

High performance reinforced thermoplastic composites have become an increasing interest by the aerospace industry for structural applications in modern aircraft [1], with the goal of reducing weight and saving fuel consumption. Indeed, in the recent years, the application of reinforced thermoplastic composites has considerably increased: thus, composite materials make up 25% of the total weight of the A380's airframe (extensively in wings, fuselage sections, tail surfaces and doors).

Since composites based on continuous carbon fibres embedded in high performance thermoplastic polymers were commercially introduced in the early 1980s, advanced thermoplastic matrix composites have been among the most attractive materials in the aerospace industry and other high-performance applications. Their common advantages include not only those of polymer matrix composites, such as high-specific modulus and strength, but also characteristics that thermoplastics offer as matrices, namely unlimited shelf life, recyclability, cost effective processing and excellent toughness [2].

The use of thermoplastics for structural applications in aircraft leads to the use of high performance polymers, such as poly (ether ether ketone) (PEEK), poly (phenylene sulfide) (PPS), or poly (ether imide) (PEI). The use of current applied reinforced thermoplastic composites is very limited because materials with higher mechanical and physical properties are needed. Indeed, current high performance thermoplastic polymers are only used in secondary or semi-structural aircraft components such as ribs. The reason for the reluctance to incorporate thermoplastic composites into primary aircraft structures is the performance/cost ratio in comparison to metals and thermoset composites. Despite offering cost advantages over thermoset composites, due to the processing characteristics of thermoplastics, material costs are still relatively high and

the mechanical temperature resistance is below what is required (e.g. PPS). Indeed, during an aircraft flight, temperature cycles may lead to conformational changes in the polymer matrix and cause thermal transitions which greatly affect the practical applications. Meyer et al. [3] pointed out that in a structural application, substantial loss of mechanical properties occurs for any thermoplastic composite material beyond the glass transition point of the matrix material, as the matrix passes from an elastic to a thermo-viscoelastic phase. The crystalline regions in the polymer can still carry a load above the T_g but most structural applications are concerned with the initial loss of mechanical properties. Matrix influence can therefore not be ignored.

In the recent years, aircraft manufacturers have requirements for new continuous fibre reinforced thermoplastic composites with significantly improved performance/costs ratio for new applications in aircraft structure. This is the main reason why it is desirable to introduce a thermoplastic onto the market which has a high glass transition temperature, improved mechanical properties and high temperature and chemical resistances, which would make it suitable for aircraft applications. As aromatic sulfone-containing polymers, such as PSU, PPSU or PES, are known as high-performance polymers [4], attention was focused on the poly (phenylene sulfide sulfone) (PPSS) with the repeating structural unit $-(-p-C_6H_4-S-C_6H_4-SO_2-p-)-$. References to this polymer are mostly limited to either the patents or commercial trade literature [5-7]. PPSS is described as an amorphous polymer with Tg around 212-217°C [5, 7]. Like other poly (arylene sulfide)s polymers, PPSS is an engineering thermoplastic with commercial potential for film, fibre, molding and composite application, and the highly stable chemical bonds of its molecular structure gives a remarkable degree of molecular stability toward both thermal degradation and chemical reactivity [6, 7].

The aim of the study is to fully determine the mechanical performances of the unreinforced PPSS thermoplastic (temperature, chemical and humidity resistance) and the carbon fibre reinforced PPSS composite (elastic and flexural moduli) to compare its properties to other thermoplastics currently used in aircraft structural parts.

EXPERIMENTAL

A. Polymer analysis

PPS and PPSS polymers were provided by Chevron Phillips Chemicals International NV, Belgium, as fine powders. These unreinforced materials were characterized by Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA) to understand their thermal behaviours. DSC measurements were performed with PerkinElmer Pyris Saphhire DSC thermal analysis equipment, fitted with a cooler system using liquid nitrogen. It was calibrated with an indium standard and operated at a gas rate of 10 ml/min under nitrogen atmosphere. The cooling/heating rate of DSC measurements was 10°C/min. Flexural and tensile DMA tests were performed on PerkinElmer Pyris Diamond DMA equipment fitted with a cooler system and mounted with a flexural or tensile set-up depending of the tests. The heating rate was 2.5°C/min for the flexural DMA measurements and 5°C/min for the tensile ones. The tests were performed with a 5μm amplitude at 1 Hz and a force of 2000mN. TGA measurements were conducted using PerkinElmer Pyris Diamond TG/DTA thermal analysis equipment with a heating rate of 10°C/min under nitrogen atmosphere.

Three points bending tests were performed on both polymers to measure their temperature, chemical and humidity resistance. Specimens were prepared by using a mould with the desired size of the specimens (3.4mm x 10mm x 60mm). The mould, with the powder placed in, was positioned in 1000 kN JOOS press, and when the desired temperature was reached, a pressure of 25 bars was applied for 2 minutes before cooling down at a rate of 10°C/min until room temperature. Flexural tests were performed according to the ASTM D790-07 procedure at a span to depth ratio of 14:1 with a 1 mm/min crosshead speed, and were conducted on a MTS 10 kN elastomer test system. For each test an average of five specimens for each polymer is presented.

To measure the temperature resistance, Thermotron FR-1-CH-LN2 environmental chamber was fitted to the testing machine to achieve the desired range of testing temperature. Temperature controller MTS 409.80 inside the circulating air oven chamber allowed a value within 1°C of the set value. The testing temperatures were from 20°C (i.e. room temperature) to above the glass transition of each thermoplastic (i.e. 85°C for PPS and 215°C for PPSS). After the chamber is heated to testing temperature, the temperature was held for 30 minutes to allow uniform temperature within the specimen, and then the testing was able to be conducted.

The chemical resistance of both polymers was measured by placing specimens in different solvents (e.g. sulfuric acid, chloroform…) for one week, according to the ASTM D543-06 procedure. The effect of humidity was also measured on both polymers, by placing specimens in an oven at different temperatures (range from 23°C to 90°C) for 40 hours and at a humidity rate of 80%, according to the procedure outlined in ASTM D618-05. In both chemical and humid tests, the residual flexural modulus of each specimen was measured and was compared to the reference specimen.

B. Composite preparation and testing

Materials are provided by TenCate Advanced Composite, The Netherlands, as 5H woven carbon PPSS prepregs and 5H woven carbon PPS semipregs. The laminates were manufactured using 1000 kN JOOS press. Meyer et al. [8] have determined the process to obtain PPSS laminates by thermopressing with high mechanical properties. PPS thermopressing process used is the one advised by TenCate Advanced Composite [9]. After producing the different composite plates, a non-destructive evaluation of the quality of the laminates was done by ultrasonic single through transmission inspection to check the quality. The instrument used for the inspection was an automated C-scanner produced by Midas Inc. of dimensions 3m by 1.5m using water probes as coupling media.

Mechanical testing was performed to determine the mechanical performance of PPS and PPSS reinforced materials. Flexural tests were conducted on Zwick 20 kN testing system, according to the procedure outlined in ASTM D7264-07 standard with a 1 mm/min crosshead speed and a span to depth ratio of 32:1. The size of the specimens was 13mm x 170mm and the thickness was 4.1mm (14 layers thick). Tensile tests were performed on Zwick 250 kN testing system, according to ASTM D3039-00 procedure. The testing parameters used were 2 mm/min loading rate and 50 mm for the gauge length. An extensometer was fitted to the specimen to provide accurate measurement of the materials elastic modulus. The specimens' thickness was 2.4 mm – 8 layers – and their size was 25 mm wide and 250 mm long. Tabs were glued on the specimen edges

for successful conduct of the tests. For all the tests, an average of five specimens for each composite is presented.

Microscopy analysis was also performed on the fracture region of the specimens to see the influence of the resin on the formation of cracks between the layers. The analyses of the samples were achieved in both weft and wrap directions of the carbon fibres through visual inspection using Leica DMLM microscope 10X with CCD camera.

RESULTS AND DISCUSSION

A. Temperature resistance measurements

Thermal properties of PPS and PPSS were examined by DSC and TGA analyses, the values of corresponding properties are listed in Table 1. DSC measurement results are in agreement with those found in literature [5,7,10]. The value of glass transition temperature of PPSS polymer seems to indicate that a low molecular weight PPSS was analyzed, around 1500 g/mol [10]. Indeed, a low molecular weight will lead to short polymer chains and few cross-linking between the polymer chains can occur in the matrix, lowering the glass transition. The marked increase of glass transition temperature passing from PPS to PPSS (about 110°C) is due to the presence of the rigid sulfone group in the polymer structure [11].

The initial degradation temperature T_i, the maximum degradation rate temperature T_{max}, the final weight lost temperature T_f and the char yield at 700°C are determined from the TGA curves. The results from this measurement are comparable with those obtained by Liu for PPSS of different molecular weights [10]. PPSS TGA curve corresponds to a single-stage decomposition reaction, in agreement with literature [10,12]. As seen from Table 1, TGA measurements show that PPSS is quite thermally stable up to about 450°C, and begins to degrade around 40°C below PPS degradation temperature. The presence of the sulfone group in the polymer chain leads to a lower degradation temperature. The hypothesis is that half of the polymer chain of PPSS is already oxidized, so the kinetics of attack towards the sulfide groups is faster compared to PPS, which has twice the sulfide groups to be attacked.

B. Mechanical characterization of the unreinforced materials

As visible from the DMA results in Figure 1, PPSS curve shows a main transition in correlation with the glass transition temperature, at about 205°C and a second transition at about -100°C. These results are consistent with those reported by Liu [10]. The transition at -100°C is defined as the γ transition and is associated with chain motions

Table 1: Thermal properties of PPS and PPSS

	T_g (°C)	T_m (°C)	Delta H (J/g)	Crystallinity (%)
PPSS	206.5	-	-	-
PPS	89.4	282	45.6	59.6

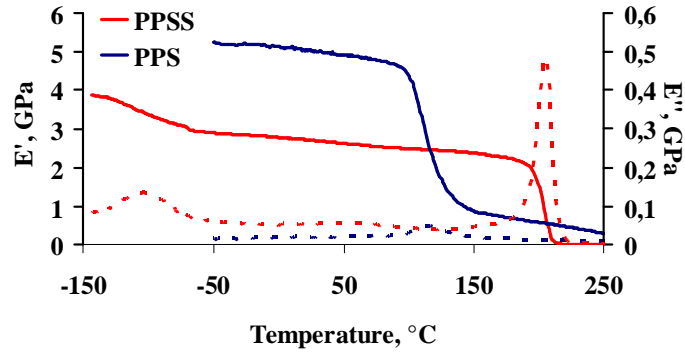|	T_i (°C)	T_{max} (°C)	T_f (°C)	Char yield at 700°C (wt. %)
PPSS	452	495	545	39
PPS	496	505	575	45

Figure 1: Storage modulus (E') (continuous lines) and loss modulus (E") (dot lines) for PPSS and PPS tensile DMA measurements at 1 Hz

involving the sulfone group, as suggested by Fried and al. for as concerns the relaxation processes in bisphenol-A-polysulphone [13].

Table 2 synthesizes the results obtained for PPSS and PPS from the tensile and flexural dynamic mechanical analysis. The glass transition area appears shifted towards higher temperature values in the tensile DMA tests, compared to the values for the flexural DMA. This is actually due to the different heating rates used for the tests. The heat transfer from the furnace to the sample, in fact, is not instantaneous but depends on conduction, convection and radiation within the DMA instrument. There is bound to be a thermal lag between different parts of the instrument and the higher the heating rate, the greater this lag is. The result is a shift of the glass transition temperature towards higher temperatures with increasing heating rate.

Three-point bending tests were performed on PPSS and PPS polymer specimens. The flexural properties of PPSS and PPS samples were obtained by tests carried out at environment humidity and temperature conditions. PPSS was found to have a 3.17 GPa flexural modulus and 160MPa flexural strength, whereas PPS flexural modulus was 3.89GPa and its strength 163MPa. The results obtained for PPSS are in agreement with those found by Tamada and al. who reported a flexural modulus of 3.03GPa and a flexural strength of 145MPa for PPSS [14]. The flexural properties of PPS appear higher than those reported in the Technical Data of Cetex PPS from TenCate which indicates a 3.725GPa flexural modulus and a 125MPa flexural strength [9].

Table 2: Flexural and tensile DMA results for PPSS and PPS polymers at 1Hz

	Flexural DMA			
	E' at 25°C, GPa	E" at 25°C, GPa	T at tan δ_{max}, °C	T at E"$_{max}$, °C
PPSS	2.95	0.06	201.7	189.4
PPS	3.55	0.84	103.9	97.1

	Tensile DMA			
	E' at 25°C, GPa	E" at 25°C, GPa	T at tan δ_{max}, °C	T at E"$_{max}$, °C
PPSS	3.00	0.06	214.9	205.7
PPS	5.03	0.19	131.7	114.0

The effect of the temperature on PPSS flexural properties is also measured and is compared to the elastic modulus E' obtained from a PPSS and PPS bending DMA curve obtained at a frequency of 1Hz (Figure 2). It can easily be seen that the flexural modulus of PPSS decreases continuously until 190°C (i.e. 20°C below Tg), before a complete loss of the flexural modulus occurs in a small range of temperatures in the glass transition range area, between 190°C and 200°C. At 210°C, no residual flexural modulus is left. In comparison, PPS flexural modulus is dropping at the glass transition temperature and then the flexural modulus continues to decrease with a slower slope, which is due to the crystal parts present in PPS structure which keep some strength in the specimen. A perfect correlation between the flexural tests at high temperatures and the DMA bending tests is observed for both PPSS and PPS curves, as visible in the graphs in Figure 2. The bending measurement can by consequence also be used to determine the onset value of the polymer glass transition.

C. Humidity and chemical resistance of PPSS polymer

The percent humidity absorption and the residual flexural modulus of PPSS and PPS after conditioning at different temperatures at 80% humidity are presenting in Figure 3. According to these humidity resistance tests, PPSS shows a much higher absorption of humidity compared to PPS and, consequently, a marked degradation of the mechanical properties already at a temperature of 40°C. Its maximum humidity absorption is of about 0.5% at 50°C – 70°C. PPS shows only a slight increase of the humidity absorption from the 0.02% at 23°C to the 0.08% at 90°C.
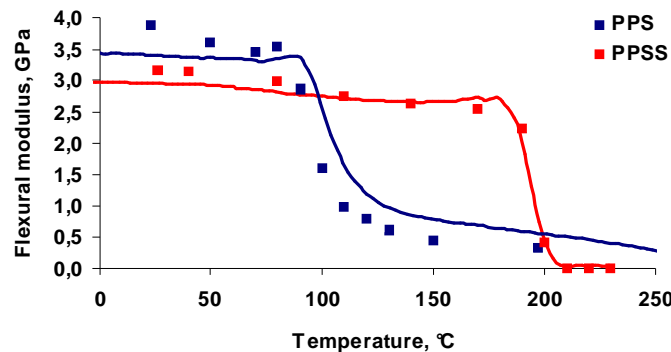

Figure 2: Evolution of PPSS and PPS flexural modulus in function of the temperature, in comparison with their related elastic modulus E' from DMA measurement at 1Hz
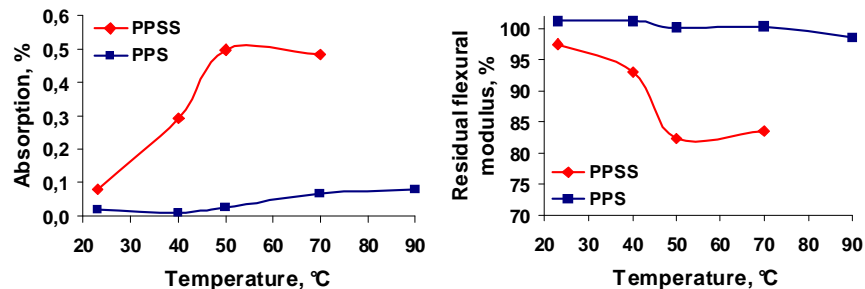

Figure 3: Humidity resistance of PPSS compared to PPS, with the percent humidity absorption and the flexural residual stress at different temperatures

Table 3: PPSS and PPS chemical resistance

Solvents		Chemical resistance, %	
		PPSS	PPS
Acids	Chloridric acid 30%	100	96.83
	Sulfuric acid 98%	0[a]	96.74
Salts	Sodium hydroxide 10%	96.18	93.92
Bases	Sodium hydroxide	100	98.11
	Ammonia	95.66	95.12
Ketones	Acetone	91.88	92.20
Alcohols	Methanol	98.25	88.17
	Ethanol	88.70	96.07
	Propan-1-ol	99.86	100
	Propan-2-ol	87.85	96.98
	Glycerol 99%	93.12	99.48
Halomethanes	Chloroform	0[a]	90.66
	Dichloromethane	58.99	89.89
	Diiodomethane	86.30	87.96
Halobenzenes	1,2 Dichlorobenzene	84.18	99.49
	1,2,3 Trichlorobenzene	87.84	96.07

[a] Specimens were dissolved in the solvent and therefore could not be tested

The lower humidity resistance of PPSS can be explained by the presence of the sulfone group. Both the sulfone and the sulfide groups, in fact, will attract water, forming hydrogen bonds with it. Being the electronegativity of the oxygen atom (3.5) higher than that of the sulphur atom (2.5), it will attract more water molecules, giving higher water absorption values.

Table 3 summarizes the results of the bending tests carried out on PPSS and PPS specimens after one week of conditioning, as described in the experimental part. Being PPSS an amorphous polymer, it shows, as a general tendency, a lower chemical resistance compared to PPS, which is semi-crystalline. Semi-crystalline polymers, in fact, tend to display a higher solvent resistance due to the facts that the densely packed spherulites in the crystalline region impede the diffusion of the solvent into the polymer and that the crystallinity prevents dissolution of the entire molecule structure.

PPSS resistance to acids is much lower than that of PPS. Its resistance to acid, furthermore, appears to decrease with the increase in the dielectric constant of the solvent. Going from Chloridric acid (4.60) to Sulphuric acid (100), the chemical resistance of PPSS decreases from 100% to 0%. PPSS appears in fact to be totally degraded in Sulphuric acid. This dielectric constant gives direct information on the relative static permittivity which is a relative measure of the polarity of the solvent under given conditions. By consequence, a polar solvent will be more attracted to atoms with high electronegativity, like the Oxygen atom present in PPSS. That is why PPSS is more chemical resistant to Chloridric acid than Sulphuric Acid.

PPSS chemical resistance to alcohols, except methanol, is slightly lower than that of PPS. It can be seen with the results that with a solvent which has a long molecular structure, the resistance of the polymer is higher. In fact, a molecule with long structural chain has a bigger free volume and so has more problems to diffuse easily through the

polymer chains. That is why Propan-1-ol or Glycerol has less effect on the polymer structure than Ethanol.

Contrary to what stated by Liu [10], PPSS appears to be soluble in Chloroform. Its chemical resistance to every solvent from the halogen group, except Diiodomethane, is much lower than that of PPS. PPSS appears indeed to have a chemical resistance to Dichloromethane and Diiodomethane lower than 60% and 90%. The effect of the halogen solvent is depending mainly on which halogen atom is present in the solvent molecule. As the electronegativity decrease from Chlorine (Cl) to Iodine (I), it is not surprising to see an increase of PPSS chemical resistance when exposed to Dichloromethane to Diiodomethane. Also, as Chloroform has three Chlorine atoms in its structure, it is chemically stronger than Dichloromethane which has only two Chlorine atoms. That is why PPSS is dissolved by Chloroform and not by Dichloromethane. Furthermore, the size of the solvent molecule is also important as seen before with the alcohol solvents: a bigger molecule will have less effect on the polymer structure, as it can less easily diffuse through the polymer chains. That explains that the different Chlorobenzenes have less effect on the polymer structure than the smaller molecules which also posses Chlorine atoms in their structure.

D. Mechanical characterization of PPSS composite plates

Table 4 lists flexural and tensile properties of PPSS and PPS carbon reinforced composite, and also of PEEK and PEI for comparison. It can be seen that PPSS has similar tensile and flexural properties than PPS, except for its flexural strength which is lower. That is concordant with the properties found for the unreinforced materials, as PPS polymer showed higher flexural strength than PPSS. By comparison, PPSS mechanical properties are higher than PEI, which is also an amorphous polymer, and lower than PEEK, a very high performance thermoplastic.

To have a better understanding of the microscopy behaviour of PPSS composite, microscopic analyses were performed on the failure points (Figure 4). It can be seen on Figure 4b that a lot of micro-cracks are present in the different layers of PPS resin near the breaking point. These micro-cracks are only present in this area, not in the other parts of the specimen, and are induced during failure. The occurrence of these cracks can be due to the release of the residual stresses produced by the production of the laminate [3]. Parlevliet et al. [15] pointed out that for semi-crystalline thermoplastics, these residual stresses are due to densification upon crystallization, with crystals being of higher density than the amorphous phase. Consequently, when the failure occurs, the breaking energy propagates through the layers and the presence of these residual

Table 4: PPSS and PPS carbon reinforced flexural and tensile properties

	Flexural modulus, GPa	Flexural strength, MPa	Tensile modulus, GPa	Tensile strength, MPa
PPSS	64.6	825	63.5	820
PPS	63.7	928	61.9	815
PEEK[a]	68.4	1101	58.7	886
PEI[a]	60.3	910	53.4	697

[a] Data obtained in laboratory scale, using 5H woven carbon reinforcement
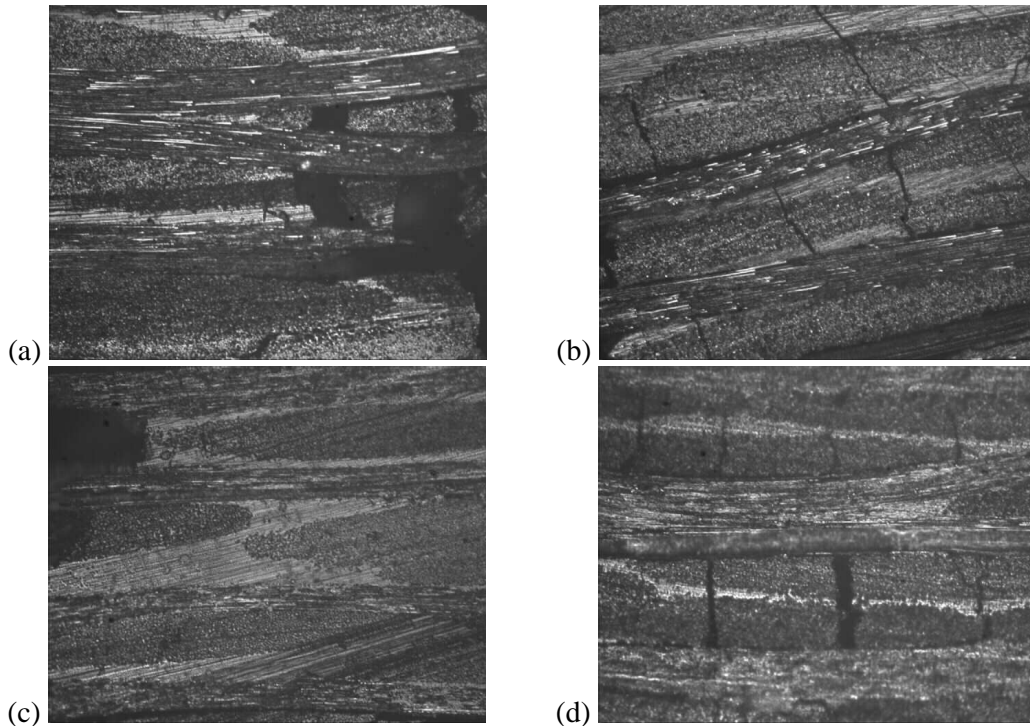
Figure 4: Microscopic analysis of PPSS (a), PPS (b), PEI (c) and PEEK(d) flexural failure cross-ply surfaces, weft direction, 10x

stresses results of the formation of these micro-cracks for PPS laminates [3]. Similar results are found for semi-crystalline PEEK laminates, as seen in Figure 4d. These micro-cracks are not present in PPSS and PEI specimens (Figures 4a and 4c). As these polymers are amorphous thermoplastics, no crystals are formed during the cooling, in consequence of what no residual stresses are present in these laminates.

CONCLUSION

This paper has examined the properties of unreinforced PPSS, showing that this thermoplastic has similar mechanical properties compared to PPS, but lower chemical and humidity resistance, mainly because of its amorphous phase. The mechanical characterization pointed out that PPSS reinforced material has flexural and tensile properties compared to PPS. With PPSS high thermal properties, it places this thermoplastic as a serious candidate for composite manufacturing for applications with high temperature resistance needs, such as structural aircraft parts, but where chemical resistance is not a crucial aspect.

ACKNOWLEDGMENTS

REFERENCES

1. Herrmann A.S., Baisch P., Das "virtuelle Modell" zur CFK-Produkt und Prozessgestaltung, in conference proceedings of the DGLR Conference, Friedrichshafen, September 2005

2. Offringa A.R., "Thermoplastic composites - rapid processing applications", Composites Part A, 1996, 27A:329–36

3. Meyer D.R., Bersee H.E.N., Beukers A., *Temperature effect on reinforced thermoplastic composite properties for primary aircraft structure applications*, 49th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Schaumburg, IL, 2008

4. Harper C.A., Modern Plastics Handbook, Chapter 8 - Design of Plastic Products by J. R. Rotheiser, 2000

5. Seo K.H., Park L.S., Baek J.B., Brostow W., *Thermal behaviour of poly(phenylene sulfide) and its derivatives*, Polymer 1993, Vol. 34, Issue 12

6. Campbell R. W., U.S. Pat. 4,016,145 (to Phillips Petroleum Co.) (1977)

7. Yang J., Wang H.-D., Xu S.-X., Li G.-X., Huang Y.-J., *Study on Polymerization Conditions and Structure of Poly(phenylene Sulfide Sulfone)*, Journal of Polymer Research, pp 317–323, 2005

8. Meyer D.R., Carnevale P., Bersee H.E.N., Beukers A., *New affordable reinforced thermoplastic composite for structural aircraft applications*, 50th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Palm Springs, CA, 2009

9. TenCate Company

10. Liu Y., Synthesis and Characterization of New Phosphine oxide and Ketone Containing Poly(Arylene Sulfide Sulfone)s, Faculty of the Virginia Polytechnic Institute and State University, 1998

11. Young R. J. and Lovell P. A., Introduction to Polymers, second edition 1991

12. H. Wang, J. Yang, S. Long, X. Wang, Z. Yang, G. Li, *Studies on thermal degradation of poly (phenylene sulfide sulfone), Polymer Degradation and Stability*, 229-235, 2003

13. Fried J.R., Letton A. and Welsh W.J., *Secondary relaxation processes in bisphenol-a-polysulphone*, Polymer, 31, 6, 1990

14. Tamada H., Okita S., Kobayashi K., *Physical and mechanical properties and enthalpy relaxation behavior of Polyphenylenesulfidesulfone (PPSS)*, Polymer Journal, Vol. 25 No.4 339-346 1993

15. Parlevliet P.P., Bersee, H.E.N., Beukers A., *Residual stresses in thermoplastic composites – a study of the literature. Part III: effects of the thermal residual stresses, Composites: Part A*, 1581-1596, 2007