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PSP RESINS AND THEIR APPLICATIONS AS HEAT AND FIRE RESISTANT MATRICES

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Abstract

PSP resins form a unique class of heat resistant resins which are now developed on an industrial scale by SNPE. They are obtained by a condensation reaction between aromatic dialdehydes and methylpyridines. They are viscous or semi-solid oligomers, soluble in usual solvent, hot melt processable, and can be cured between 200 and 250°C. Their main characteristic is a high heat resistance and easy processability. Their ability to give rise to composite materials with good mechanical behaviour especially at high temperatures (250°C and above) is used in some of their applications : graphite and glass reinforced structural parts, glass reinforced plastic radomes for use up to 450°C, fire resistant protections, and many high temperature applications.

Introduction

Resin matrices have to reach a high level of thermal resistance in order to maintain high specific properties of fiber reinforced parts where elevated temperature capability is required, like in supersonic aircrafts, missiles, engines, with the ever critical humidity and fire resistance.

At the present time, it is well known that the best epoxy systems are limited to 130-150°C use under wet conditions. With the addition type polyimides such as PMR 15 and LARC 160, the solvent and by-product problems met with the previous systems have been significantly reduced, but they need a sophisticated curing cycle (dwelling time, 317°C cure). Recently, bismaleimide resin systems have been developed by several prepreggers, allowing the fabrication of void free laminates and moldings with curing at 180-200°C and post curing 10-20 hours at 240-250°C. They exhibit good flame resistance and excellent properties, but limited to 250°C.

The PSP (for polystyrylpyridine) resins, are heat-resistant matrices which can be cured at 200°C, exhibit excellent hot wet mechanical properties and thermal ageing up to 200-250°C, superior flame resistance, and when post cured at 250°C, provide thermal resistance up to 400°C. The applications of these features to the field of aerospace industry are the production of prepregs and fabrication of laminated structural parts, manufacturing of radomes, molding of compounds. Other processing techniques, such as filament winding, are under study.

General description of the PSP matrix

Synthesis and cure

PSP (polystyrylpyridine) resins, discovered by ONERA Materials Department[1], twelve years ago, then developed by SNPE for industrial production and use [2][3], represent a new family of heterocyclic aromatic polymers obtained by condensation of aromatic aldehydes with di- or trimethylpyridines. Their composition can be best described as a poly (methylpyridylene-vinylidene-phenylene) structure (see fig. 1).

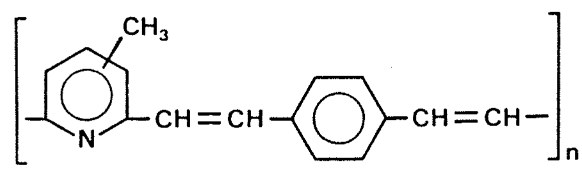

Fig. 1 - Structure of PSP resins

The chemical process is simple, fast, easy to control, and the raw materials are non exotic industrial compounds. So PSP resins, specially when compared to other heat resistant resins, can be considered as low cost matrices. The prepolymers are soluble in polar aprotic solvents (DMF, NMP) and usual chlorinated hydrocarbons, and the grades selected by SNPE for impregnation are totally soluble in common low boiling solvents such as methylethyl ketone.

As thermosetting resins, they cure between 200 and 250°C, by a chemical mechanism which has not yet been completely identified.
ONERA has proved recently that crosslinking occurs, at least partially, by an addition reaction of methyl groups onto the double bonds (see fig. 1) without generating volatiles. Such a mechanism is the reason why molded parts with a very low void content are easily produced.

Commercially available resins

Condensation can be tailored to specific applications, but 4 resins are currently in production scale : PSP 6022 M is a low viscosity solution with 75% resin content in methyl ethyl ketone, designed for solvent based impregnation of tapes and clothes. PSP 6022 P is a non solvent system, for hot melt applications filament winding and injection. PSP 6022 PL is the recently improved hot melt system with reduced pyridine-like smell and completely suitable for hot-melt prepregging. PSP 6022 PC is a powder of higher condensation level for injection or chopped fibers reinforced molding compounds.

Toxicity (skin and vapors) of PSP prepolymers and solution has been investigated and proved to be very low and acceptable for use.

Neat resin properties

Thermogravimetric analysis (see fig. 2) shows an excellent thermal resistance.

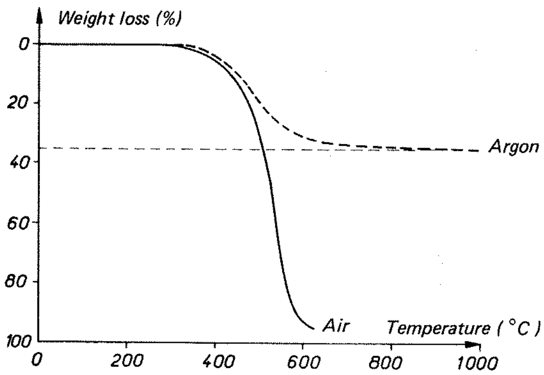

Fig. 2 - T.G.A. of PSP cured resin

Pyrolysis in non-oxydative atmosphere gives a high yield of about 65% at 1000°C of a char of good mechanical resistance. No glass transition temperature can be observed below 400°C.

Flammability resistance, as measured by L.O.I, the limiting oxygen concentration required to support flaming combustion, is 26% for neat resin.

Prepregs and laminated structural parts

Impregnation of continuous fibers is very easy by solvent (6022 M) or hot-melt (6022 PL) process, giving good tack and drape. Shelf life is typically 3 months at room temperature in sealed bags.

SNPE currently manufactures 12 inches graphite tapes, and carbon , glass and Kevlar cloth are available on request.

Curing of PSP 6022 laminates

Details of processing conditions may depend on the type of resin (M or PL), resin content, laying up configuration or equipment.

The typical autoclave curing schedule for 6022 M is described on figure 3.

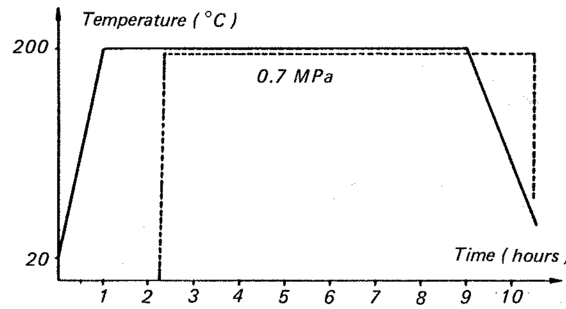

Fig. 3 - Autoclave cure cycle of PSP 6022 M

- heat from 20°C to 200° within 1 hour
- hold for 1 hour 15 minutes at 200°C
- apply 0.7 MPa at the rate of 0.1 MPa/mn
- hold for 8 hours at 200°C under 0.7 MPa
- cool down slowly to 50°C under pressure.

It is advised before starting, to apply full vacuum on the bag, to check it is leak proof, then to vent out vacuum or maintain a slight one.

Post-cure 4 to 16 hours at 250°C in oven, depending on high temperature requested.

The lay up in the vacuum bag is conventional for autoclave molding technology. A double sealant ring is advised, and although the cure temperature does not exceed 200°C, suitable bleeder cloth, sealants and vacuum bag are recommended.

Laminates properties

Thermomechanical properties (see TABLE 1)

At room temperature, PSP reinforced laminates exhibit the following mechanical properties :

Typical R.T. interlaminar shear strength (span to width ratio 5 : 1) is 90-100 MPa for unidirectional 6022 PSP/ carbon composites* and is only slightly affected by post-cure.

Cross-plied and fabric reinforced laminates are performing reasonably well before post-cure, but, as discussed below, suffer a drop of properties after prolonged post-curing.

At elevated temperatures, very high levels have been found up to 250°C without post-cure and up to 400°C when post-cured.

	NO POST-CURE		POST-CURE 16 hrs at 250°C					
Test temperature (15 mn soak)	20°C	250°C	20°C	150°C	250°C	300°C	320/330°C	400°C
Flexural strength (MPa)	1510	1100	1600	1400	1200	1100	1100	1100
" modulus (GPa)	105	91	110	110	120	106	112	116
Tensile strength (MPa)	1000	820	1000	1140	1100	1200	-	-
" modulus (GPa)	130	123	130	130	132	130	-	-
Interlaminar shear strength (MPa)	100	60	95	74	62	55	49	44

TABLE 1 : THERMOMECHANICAL PROPERTIES OF UNIDIRECTIONAL 6022 M/ CARBON Toray T300 : (fiber content : 60% vol.)

*All carbon fibers are epoxy sized, except otherwise mentioned.

Comparison testing with polyimides

PSP 6022 and PMR 15 were compared on unidirectional laminates with carbon Toray T300 (epoxy-sized) and Celion 6000 (polyimide sized) fibers (See TABLE 3).

As observed earlier, epoxy sizing is to be preferred for PSP matrix, while P.I. sizing is chosen for PMR resins.

At temperatures higher than 320-350°C, PSP matrix performs better than PMR 15.

Test temperature (15 mn soak)		20°C	316°C	371°C
Toray T300 fiber (epoxy-sized)				
Flexural strength (MPa)	PSP	1440	860	1210
	PMR	1620	932	(*)
" modulus (GPa)	PSP	100	106	109
	PMR	109	115	(*)
I.L.S.S (MPa)	PSP	102	47	49
	PMR	116	49	(*)
Celion 6000 (P.I sized)				
I.L.S.S (MPa)	PSP	76	38	50
	PMR	108	50	(*)

(*) Unable to bear load

Glass fiber composites show good thermomechanical behaviour. (See TABLE 3).

TABLE 2 : COMPARISON TESTING OF PSP 6022
(Post-cure 16 hrs at 200°C)
AND POLYIMIDE PMR 15
(Post-cure 16 hrs at 317°C)

Test temperature (°C)	20	150	200	250	300
Flexural strength (MPa)	500	470	440	390	340
" modulus (GPa)	26	27.2	25	24.8	24.8
I.L.S.S (Mpa)	39	38	38	35	31

TABLE 3 : PSP 6022/GLASS FIBER COMPOSITES
Fiber content : 65% vol.
E-Glass cloth 181-type, TF 910
sizing (4 hrs 200°C + 2 hrs 250°C)

Thermal aging of laminates

Measurements have been made on test samples, in air at 250°C with undirectional carbon T300 reinforced PSP 6022. (See TABLE 4). Retention of 80% shear strength at 20°C and 250°C is maintained after 1000 hrs at 250°C.

Time at 250°C (hrs)		0	250	500	1000	1500
Flexural strength (MPa)	20°C	1400	1100	-	1000	-
	250°C	1300	1200	-	1000	-
" modulus (GPa)	20°C	107	93	-	89	-
	250°C	105	95	-	103	-
I.L.S.S (MPa)	20°C	85	84	79	62	60
	250°C	64	65	63	56	40

TABLE 4 : THERMAL AGING IN AIR AT 250°C
(POST-CURED)

Moisture resistance

There is only a slight loss of interlaminar shear strength of carbon laminates at 200°C after 1000 hours in boiling water. The moisture pick-up is less than 1% (instead of 2-4% for epoxies), depending on the relative humidity and generally increased by post-curing.

Flammability properties

They have been demonstrated on various reinforcements, and have been previously reported[2][3].

Resistance to combustion has been determined by L.O.I (ASTM D2863-70 or AFNOR T51-071) on 60% vol. fabric laminates. They are about 40% with Kevlar, 70% with graphite, 100% with E glass, to be compared with 25% for epoxy graphite composites.

The smoke generating properties have been determined in a NBS chamber[3] and a similar apparatus with a radiant heating of 25 W/cm^2.

As shown in table 5, glass and carbon reinforced PSP 6022 give outstanding low smoke emission in both flaming and non-flaming conditions, and in a vertical or horizontal fixture.

Flaming*		Thickness	Vertical F	Vertical NF	Horizontal F	Horizontal NF
Glass E fabric-181 sizing A1100	NO PC	0.8 mm	21.0	13.0	7.0	1.2
	PC	"	15.0	4.5	1.1	1.1
Carbon T300 fabric satin 5	PC	1.0 mm	17.0	1.4	0.7	3.0
Kevlar 49 fabric-181	PC	1.0 mm	105.0	101.0	32.0	48.0
		3.0 mm	231.0	318.0	163.0	172.0

TABLE 5 : SMOKE MAXIMUM SPECIFIC OPTICAL DENSITY OF PSP 6022 REINFORCED LAMINATES
Fiber content : 60-65 % vol.

* F : with pilot flame ignition. NF : without.

The toxicity of smoke gases from glass/PSP composites have been found particularly low.

On the other hand, protection against high temperature flames has been evaluated by exposure of glass fabric reinforced PSP to a plasma gun (1800-3000°C), when PSP matrix appeared more efficient than other resins.

HIGH TEMPERATURE REINFORCED PSP RADOMES MANUFACTURED BY INJECTION

A molding technique, which consists in injecting the molten resin within a reinforcing material previously installed in an airtight molding device, and curing under pressure, has been used by ONERA(4)(5) in the production of prototype heat resistant glass-reinforced radomes.

The property of PSP resin which makes this technique easier than with other types of thermostable resins such as polyimides, is its low viscosity and still low reactivity at injection temperature (150-180°C).

The advantage of this technique is a simpler fabrication of low porosity parts with preset thicknesses, while obviating the need for an intermediate preimpregnation stage.

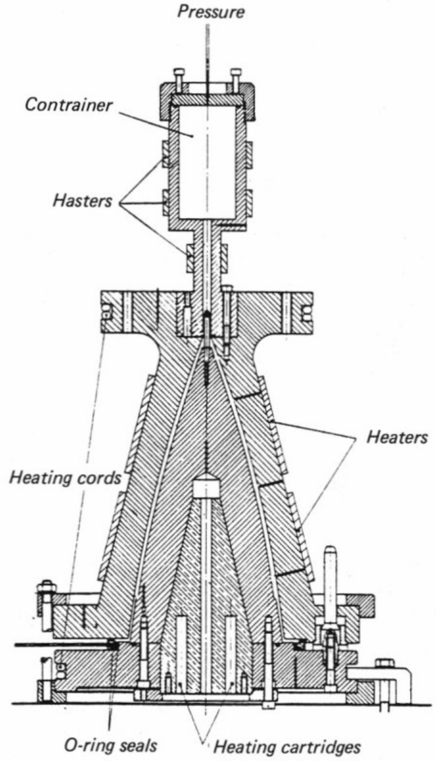

Fig. 4 - Mold used for Glass/PSP radomes

The mold used (see fig. 4) is very similar to a classical one, using, as reinforcement material, axisymmetric woven preforms, the shape of which follows exactly the shape of the radome to be fabricated. The only modifications are related to the adjunction of an autonomous heating system capable of maintaining an homogeneous temperature over the whole molding zone, and of a tightness device allowing curing under pressure (1.5 MPa maximum). The whole molding device is presented on figure 5.

As far as dielectric performance are concerned the radomes obtained are both homogeneous and reproducible and lead to low distortion and transmission loss rates.

Typical mechanical and dielectric data on flat small coupons obtained by the same technique are listed in table 6.

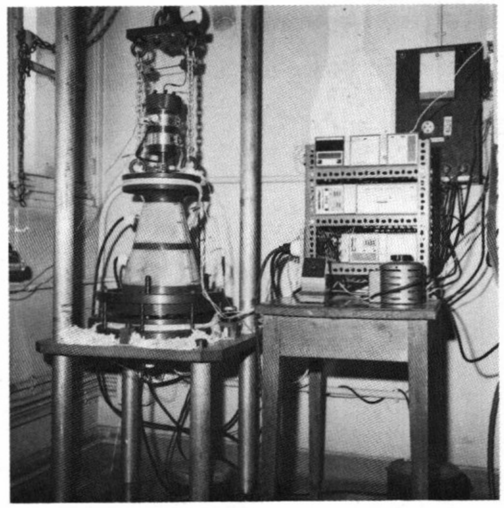

Fig. 5 - Molding device

Test temperature (°C)	20	250	300	350	400
Flexural strength (MPa)	310	240	190	195	-
Dielectric constant	4.33	4.45	4.48	4.48	4.30
Loss factor x 10^2	1.05	1.64	1.23	1.34	1.4

TABLE 6 : THERMOMECHANICAL AND DIELECTRIC PROPERTIES OF INJECTION MOLDED, E-GLASS FABRIC REINFORCED PSP (Fiber content : 45% vol.)

They demonstrate the stability of mechanical and physical properties of the resin up to 350-400°C, for relatively long durations (corresponding to the stabilization time of the testing temperature, about 15 minutes).

The glass PSP material thus appears very interesting as component of high speed missile radomes, the PSP resin being in itself perfectly adapted to the injection molding technique.

MOLDING COMPOUNDS

SNPE develops molding compounds with chopped fibers (6 mm length) of glass (35 % volume) or graphite (22% volume). The compressor cycle is 260°C, 20 MPa for 20-30 minutes and post-cure 8 hours at 250°C.

The intrinsic flexural strength (see fig. 6-a) and modulus (fig. 6-b) are higher than that of corresponding polyimides compounds above 200°C and the thermal aging resistance is excellent (over 1000 hours) at intermediate temperatures (235°C) decreasing for long periods above 250°C.

MISCELLANEOUS PROCESSES

An exploratory evaluation study of filament winding with graphite and Kevlar has been led by French companies and has to be widened for new fabrications.

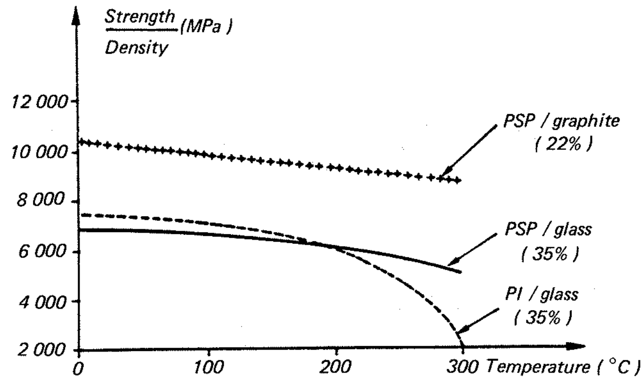

Fig. 6.a - Intrinsic flexural strength of PSP compounds

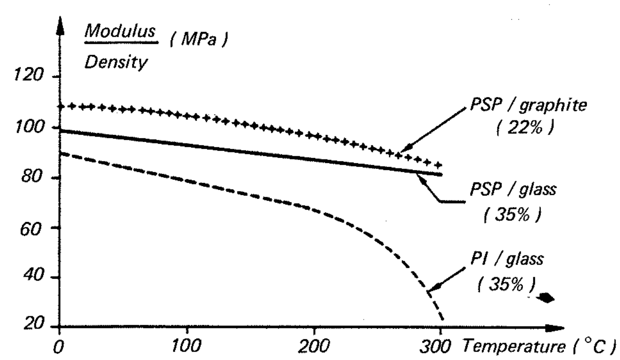

Fig. 6.b - Intrinsic flexural modulus of PSP compounds

SNPE is studying pultrusion of graphite fibers with PSP resins. Thermomechanical properties are not much lower at elevated temperatures than from autoclave laminates. Flame resistance and low smoke toxicity have been confirmed.

NEWLY IMPROVED PSP MATRICES

Increased cross-plied laminates performances

It has been pointed out that cross-plied composites, when post-cured at elevated temperatures to ensure high temperature mechanical properties, suffer a loss of room temperature performance, together with the extension of microcraks.

A modification of one of the raw components of the PSP synthesis has been achieved to bring an increased toughness to the polymerised network. This new family of PSP (PSP 7022) is now in an advanced development stage.

It has been compared on carbon fabric laminates to PSP 6022 M (see TABLE 7).

I L S S (MPa)	NO POST-CURE	POST-CURE (16 hrs 250°C)	
Testing temperature	20°C	20°C	250°C
Fabric/PSP 6022 M	57	33	36
Fabric/PSP 7022	67	52	40

TABLE 7 : IMPROVED CROSS-PLIED PERFORMANCE (CARBON FABRIC) OF PSP 7022
Fiber content : 50-60% vol.

The new resin is much less brittle after post-cure and remains efficient, at least up to the investigated temperature of 250°C. At this temperature, the thermal ageing of composites is similar to 6022 M systems (250 hours).

From that viewpoint, another modified system (HSP resin) at the moment under study, has been shown to extend retention of the ILSS of cross-plied carbon composite from 250 hrs to 1000 hrs at 250°C, actually at the same somewhat low level as that of post-cured PSP laminates (35 MPa at 20° and 250°C).

Increased reactivity

As mentioned before, the hardening rate of PSP becomes important at about 200°C. This relatively low reactivity, which allows the injection molding method, would be usefully increased for many applications where molding conditions contribute significantly to the cost of the part. A program is being developed to shorten gelation times and reduce curing time and temperature.

SUMMARY

The PSP matrices are easy to synthetize, comparatively low-cost resins, available on production scale with tailored viscosity according to the technique of application (solvent, hot-melt, powder). It can be cured at the acceptable temperature of 200°C, with post-cure at 220-250°C for higher temperature resistance.

The matrix main features are high thermomechanical behaviour and good thermal aging retention up to 250°C. At higher temperatures (300-400°C), the PSP systems exhibit outstanding thermomechanical properties for short periods of time, much higher than the best polyimides. These properties, together with excellent moisture and flame resistance, lead to many processes and applications in the field of aerospace industry.

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