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HIGH PERFORMANCE THERMOPLASTICS: A REVIEW OF NEAT RESIN AND COMPOSITE PROPERTIES

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ABSTRACT

A review was made of the principal thermoplastics used to fabricate high performance composites. Neat resin tensile and fracture toughness properties, glass transition temperatures (T_g), crystalline melt temperatures (T_m) and approximate processing conditions are presented. Mechanical properties of carbon fiber composites made from many of these thermoplastics are given, including flexural, longitudinal tensile, transverse tensile and in-plane shear properties as well as short beam shear and compressive strengths and interlaminar fracture toughness. Attractive features and problems involved in the use of thermoplastics as matrices for high performance composites are discussed.

INTRODUCTION

The purpose of this paper is to give a timely review of the

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properties of the principal candidate thermoplastic (TP) resins that either have been studied as composite matrices or are currently undergoing detailed experimental/developmental evaluation as matrices. This review is especially appropriate at this time because of the heavy emphasis being placed on the development and application of TPs as matrices for fiber reinforced composites on advanced Air Force weapons systems such as the Advanced Tactical Fighter (ATF).

The reader should note that the data included in this paper were obtained from a large number of sources, mostly materials suppliers. Variations in test methods from source to source are inevitable. There is no guarantee that ASTM procedures were employed. No attempt was made to normalize composites data to constant fiber volume fraction. Mechanical properties of a parti-

cular composite matrix will vary with fiber type and within a fiber type the date that fiber was produced. Problems with resin reproducibility, consistency, and processability also cause property variations as new materials mature in their development from experimental to commercial products. Consequently, the reader should bear these caveats in mind in using this data. Care and sound judgment should be exercised in making comparisons between materials.

GENERAL FEATURES OF THERMOPLASTIC MATRICES

Three of the most attractive features offered by TPs as composite matrices are listed in Table I. The majority of applications involving aircraft structures demand that components have superior damage tolerance and delamination resistance. Most high performance TPs offer outstanding interlaminar fracture toughness and acceptable post-impact compression response.

They also offer an even bigger payoff: the potential of low cost manufacturing. By taking advantage of the inherent chemical nature of TP molecules to undergo thermally-induced flow, shaped articles can be fabricated at elevated temperatures by relative-

ly fast processing methods. Consequently, time is profitably exchanged for temperature. Prodigious and ambitious programs are underway throughout the industry to develop cost-effective processing technology for TP materials. This effort is partly catalyzed by progressive Air Force contractual activities.

Other attractive benefits of TP composites include indefinite prepreg life, ability in certain processes to correct a flawed part, and the ease with which TP resins can be quality controlled during their manufacture. The latter is due, in part, because of their less complex formulations and their inherent stability at ambient conditions.

The major problems facing TP composites are outlined in Table II. TP prepreg of the quality generally associated with standard 177°C cure epoxies is difficult to fabricate. Either hot/melt or solution methods have to be employed. Both have their problems. In the former, temperatures generally above 650°F have to be employed in order to achieve a melt viscosity sufficiently low to wet out 6,000-12,000 filament carbon fiber tow. Solution pre-pregging to produce uni-tape is not an advanced state-of-the-art process in industry because of the

heavy emphasis in the past with solventless epoxy coatings and the strict air quality standards now in force. Further, many solvents, especially aprotic organic liquids, are difficult to remove during prepreg B-staging or composite fabrication. Solvents also can offer fire, explosion and health hazards. These problems can lead to non-uniform prepreg that contains misaligned and wavy fibers, resin-rich and resin-poor areas, gaps, and poor fiber wetting. TP prepreg generally has very little drape, unless powder impregnated, and no tack, unless tackifiers, solvents, or plasticizers are added.

The processing of TP prepreg into shaped composite structure affords many problems which are listed in detail in Table II. One or more of these difficulties is always present regardless of the fabrication technique employed. Edge buckling, fiber misalignment, porosity, and part uniformity are also continuous problems in thermoforming TP composites.

Finally, the time-dependent properties of most TP composites need to be fully characterized so that creep and fatigue problems will not become a Pandora's box.

PRINCIPAL HIGH PERFORMANCE THERMOPLASTICS

Sixteen principal thermoplastics considered as candidates to fabricate high performance composites are shown in Table III along with their supplier, T_g, T_m (for semi-crystalline polymers), and approximate maximum processing temperature. The first five are polyarylene ether or sulfide polymers, three of which are semicrystalline. The next three are amide or amideimide compositions, followed by four polyimides. Three polysulfones and one polyester complete the list. All except the J-polymer are heavily aromatic in character.

The dominant chemical structure of all polymers except the five latest compositions (APC-HTX, PXM 8505, PAS-2, Torlon AIX638, and Avimid K-III) are known. In these eleven systems, the chemical flexibilizing groups between phenyl rings in the backbone include isopropylidene, carbonyl, oxygen, sulfur, and sulfone.

It is notable that the average dry T_g value of the polyimides and polyamideimides is higher than the average T_g from any other polymer class. Three of the five latest compositions are polyarylene ethers or sulfides and have much higher T_g values than their

predecessors (e.g., APC-HTX vs. PEEK, PAS-2 vs. PPS). The Tg values were increased in order to afford improved wet 177°C properties for ATF applications. Most of the polyarylene ethers and polyimides are candidate 177°C/AFT resins. J-Polymer's Tg is too low. Torlon C is too difficult to process and the three polysulfones are too moisture and solvent sensitive.

Processing temperatures for all 16 polymers are extremely high and range from 329° to 420°C. Processing pressures range from 100 to 300 psi for conventional press moldings while processing times vary from 1 to 13 hours. Most TPs use short cycles; Avimid K-III requires a much longer cure because chain growth occurs with the evolution of condensation volatiles (and residual solvent).

NEAT RESIN PROPERTIES

Table IV lists the tensile and fracture toughness properties of 14 of the principal TPs shown in Table III. Values for APC-HTX were not available and J-Polymer was omitted because of its low Tg. Although tensile strengths are extremely notch sensitive, most of the newer polyarylene ethers, polysulfides and polyimides have very respectable

values in the range from 14 to 17 Ksi.

Tensile moduli should be above 450 Ksi to achieve acceptable composite compression strengths. The polysulfones fall way below this value; PXM 8505 and Torlon AIX638 appear to be marginal; most of the polyimides are well above it. The high value for PISO₂ stands out and helps explain why some of the PISO₂ composite strengths are outstanding. The Xydar SRT-300 is a liquid crystalline polyester whose tensile properties are outstanding, as would be expected for an ordered molecule. In this case, the high value might not translate into high composite compression strength; resin compression modulus might be a better indicator.

Neat resin fracture energies (G_{IC}) between 5 and 10 in-lb/in² should give composites with acceptable interlaminar fracture toughness. Values above 10 in-lb/in², while excellent, are overkill and should not be obtained at the expense of some other property such as hot/wet strength or modulus. All the values listed in Table IV are either acceptable or excellent. Notched Izod impact strengths have not been correlated with composite interlaminar fracture toughness.

COMPOSITE PROPERTIES

Of the original 16 TPs listed in Table III, composite properties were obtained for 10 and are given in Tables V and VI. Flexure strengths above 250 Ksi are excellent; only Udel P-1700 and PPS fall substantially below this value, the latter probably because of either poor fiber-resin adhesion or fiber damage. Flexure moduli listed in Table V are very good; values should generally be in the 16-19 Msi range.

Short beam shear strengths generally should be above 14 Ksi, where most 177°C cure epoxies fall. The values listed in Table V are acceptable but not outstanding and suggest premature failures on the compressive side of the specimen. The lower than desired compressive strengths tend to substantiate this. Room temperature compressive strengths for 177°C cure epoxies average well above 210 Ksi. Compressive strengths for all the TPs except one are below 165 Ksi. Yet the resin moduli for these same materials, in all cases except Udel P-1700, are sufficiently high (450 to 667 Ksi; Table IV) that one would predict their composite compression strengths to be above 200 Ksi.

This suggests that poor fiber alignment and poor fiber-resin

interfacial adhesion may be playing a destructive role in compression response. The low transverse strengths in all cases except PEEK-APC-2, which is known to have excellent fiber-resin interfacial adhesion, indicates that the remaining TPs have an interface problem. Transverse tensile strengths for epoxies are generally above 8-10 Ksi and they exhibit excellent interfacial adhesion.

It also seems possible that in some cases fiber damage due to harsh prepreg fabrication might be the culprit. The generally poor longitudinal tensile strengths, which are a fiber dominated property, seem to suggest poor fiber alignment and/or fiber damage. Values above 280-300 Ksi are obtained with 177°C cure epoxies.

Interlaminar fracture toughness (G_{IC}) values for all the TP composites are excellent as expected, based on neat resin fracture toughness. Values between 4 and 6 in-lb/in² are good and should afford acceptable post-impact compression strengths.

THERMOSETS VERSUS THERMOPLASTICS

Table VII summarizes the trade-off in properties between thermosets and TPs as composite matrices.

177°C Cure epoxies and bismaleimides can be considered thermosets for purposes of this comparison. In this paper, most of the listed properties have been discussed in terms of the advantages and deficiencies of TPs; it is felt TPs have to overcome certain disadvantages. On the other hand, it should be noted that the thermosets have very few disadvantages and, even then, most of those are acceptable and can be dealt with. The one key element that dominates the trade-off list and can tip the balance to TPs is that of fabrication costs. However, the potential for low cost manufacturing of TPs remains to be demonstrated.

CHALLENGES

Utilization of TP composites will raise some of the same performance concerns inherent in toughened thermosets, except the problems could be exacerbated by a higher anticipated use temperature. These concerns include fatigue and creep response and load-rate sensitivity, especially at elevated temperatures and at high stress levels. No long-term environmental exposure experience even with small coupons has been obtained, especially in the presence of corrosive fluids under load. The effects of large built-in residual stresses generated by higher

processing temperatures need to be understood, especially in larger structures containing cut-outs, cavities and built-up areas. Very little flight experience even with TP secondary structure exists to gauge either durability or maintenance requirements, let alone damage tolerance. The newer TP materials are generally more costly than current generation epoxies and bismaleimides. Extensive use of composites will be tempered by costs and cost/performance trade-offs. The total performance characterization of these promising "new-improved" composite matrices (toughened thermosets as well as TPs) is incomplete and new, untried materials will be introduced with caution.

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TABLE I

**ATTRACTIVE FEATURES OFFERED BY THERMOPLASTICS
AS COMPOSITE MATRICES**

- **POTENTIAL OF LOW COST MANUFACTURING**
 - INDEFINITE PREPREG STABILITY
 - THERMOFORMING OF FLAT SHEET STOCK
 - REPROCESSING TO CORRECT FLAWS
 - FAST PROCESSING CYCLE
- **HIGH TOUGHNESS (DAMAGE TOLERANCE)**
- **EASY QUALITY CONTROL**

TABLE II

PROBLEMS TO RESOLVE WITH THERMOPLASTIC COMPOSITE MATRICES

- **QUALITY PREPREG**
 - DIFFICULT TO MAKE
 - FIBER WETTING
 - NON-UNIFORMITY
 - NO TACK
 - NO DRAPE (UNLESS POWDER IMPREGNATED)
 - PROPER SIZING
- **PROCESSING PROBLEMS**
 - LAY-UP WITH BOARDY PREPREG
 - COST OF TOOLING
 - BAGGING MATERIALS
 - HIGH TEMPERATURES
 - MODERATE TO HIGH PRESSURES
- **UNKNOWN FATIGUE PERFORMANCE**
- **UNKNOWN CREEP BEHAVIOR**
- **SOLVENT SENSITIVITY (EXCEPT SEMI-CRYSTALLINE POLYMERS)**
- **CONTROL OF MORPHOLOGY WITH SEMI-CRYSTALLINE POLYMERS**

TABLE III

PRINCIPAL HIGH PERFORMANCE THERMOPLASTICS*

POLYMER	SUPPLIER	T_g , °C (T_m , °C)	PROCESSING TEMP., °C
POLYETHERETHERKETONE (PEEK)	ICI	143 (343)	-371
POLYARYLENE KETONE (APC-HTX)	ICI	205 (386)	-420
POLYARYLENE KETONE (PXM 8505)	AMOCO	265	--
POLYPHENYLENE SULFIDE (PPS, RYTON)	PHILLIPS PET.	90 (290)	-343
POLYARYLENE SULFIDE (PAS-2)	PHILLIPS PET.	215	-329
POLYARYLAMIDE (J-POLYMER)	DuPONT	-120 (279)	-343
POLYAMIDEIMIDE (TORLON C)	AMOCO	275	-350-400
POLYAMIDEIMIDE (TORLON AIX638/696)	AMOCO	243	-350
POLYETHERIMIDE (ULTEM 1000)	G. E.	217	-343
POLYIMIDE (AVIMID K-III)	DuPONT	251	-343-360
POLYIMIDE (LARC-TPI)	mitsui TOATSU	264 (275, 325**)	-350
POLYIMIDESULFONE (PISO ₂)	HIGH TECH SERVICES	273	-350
POLYSULFONE (UDEL P-1700)	AMOCO	190	-300
POLYARYLSULFONE (RADEL A400)	AMOCO	220	-330
POLYARYLETHERSULFONE (VICTREX 4100G)	ICI	230	-300
POLYESTER (XYDAR SRT-300)	DARTCO	350 (421)	-400

*DIFFERENT GRADES GENERALLY AVAILABLE; DATA FROM VARIOUS SOURCES

**SEMICRYSTALLINE POWDER FORM ONLY

TABLE IV
NEAT RESIN MECHANICAL AND FRACTURE TOUGHNESS PROPERTIES OF HIGH PERFORMANCE THERMOPLASTICS*

POLYMER	TENSILE PROPERTIES AT 25°C				FRACTURE ENERGY (G _{IC}), IN-LB/IN ^{3/2}	NOTCHED IZOD, FT. LB/IN
	STRENGTH (YIELD), KSI	MODULUS, KSI	STRAIN (BREAK), %			
POLYETHERETHERKETONE (PEEK)	14.5	-450	> 40	> 23	1.6	
POLYARYLENE KETONE (PXM 8505)	12.7	360	13	--	--	
POLYPHENYLENESULFIDE (PPS)	12.0	630	5	--	3.0	
POLYARYLENE SULFIDE (PAS-2)	14.5	470**	7.3	--	0.8	
POLYAMIDEIMIDE (TORLON C)	20.0	550	15	19.4	2.7	
POLYAMIDEIMIDE (TORLON PIX638/696)	13.0	400	30	20	--	
POLYETHERIMIDE (ULTEM 1000)	15.2	430	60	19	1.0	
POLYIMIDE (AVIMID K-111)	14.8	546	14	11	--	
POLYIMIDE (LARC-TPI)	17.3	540	4.8	--	--	
POLYIMIDESULFONE (PISO ₂)	9.1	719	1.3	8	--	
POLYSULFONE (UDEL P-1700)	10.2	360	> 50	14	1.2	
POLYARYLSULFONE (RADEL A400)	10.4	310	60	20	12	
POLYETHERSULFONE (VICTREX PES 4100G)	12.2	380**	> 40	11	1.6	
POLYESTER (XYDAR SRT-300)	20.0	2400	4.9	6.9	2.4	

*TAKEN MOSTLY FROM PRODUCT LITERATURE

**FLEXURE MODULUS

TABLE V

MECHANICAL PROPERTIES OF HIGH PERFORMANCE THERMOPLASTIC/
UNIDIRECTIONAL CARBON FIBER COMPOSITES AT 25°C*

POLYMER	FIBER	FLEXURAL ST., Ksi	FLEXURAL MOD., Msi	SHORT BEAM SHEAR ST., Ksi	COMPRESSIVE ST., Ksi	6Ic, IN-LB/IN ²
PEEK (APC-2)	AS-4	273	19.4	15.2	150-160	10.7
APC-HTX	AS-4	257	19.0	12.0	164	12.7
PPS	AS-4	187	17.6	--	95	5.1
PAS-2	AS-4	241	16.0	--	130	--
TORLON C	C-3000	300	18.5	16.0	200	10.0
ULTEM 1000	AS-4	--	--	--	--	6.1
AVIMID K-III	IM-6	230	18.0	13.9	144	9.7
LARC-TPI	AS-4	285	14.1	13.8	--	4.8
PISO ₂ :LARC-TPI (2:1)	AS-4	300	18.8	18.4	--	7.0
UDEL P1700	AS	214	14.0	14.3	151	7.7

*FIBER VOLUME VARIES; DATA FROM VARIOUS SOURCES

TABLE VI

MECHANICAL PROPERTIES OF HIGH PERFORMANCE THERMOPLASTIC/
UNIDIRECTIONAL CARBON FIBER COMPOSITES AT 25°C*

POLYMER	FIBER	LONGITUDINAL TENSILE		TRANSVERSE TENSILE		IN-PLANE SHEAR	
		STRENGTH, KSI	MODULUS, MSI	STRENGTH, KSI	MODULUS, MSI	STRENGTH, KSI	MODULUS, MSI
PEEK (APC-2)	AS-4	309-356	19.4-20.5	11.9	1.3-1.5	--	0.74-0.91
APC-HTX	AS-4	--	19.7	--	--	--	--
PPS	AS-4	238	19.6	4.6	1.3	--	--
PAS-2	AS-4	194	21.0	5.5	--	--	--
TORLON C	C-3000	200	20.6	--	--	--	--
ULTEM 1000	T-300	--	19.7	--	1.2	--	0.71
AVIMID K-III	AS-4	--	--	7.0	1.5	17.3	0.6
LARC-TPI	AS-4	--	--	--	--	16.2	0.8
UDEL P1700	AS	193	18.7	8.6	1.0	--	--

*FIBER VOLUME VARIES; DATA FROM VARIOUS SOURCES

TABLE VII
TRADE-OFFS OF THERMOSETS VERSUS THERMOPLASTICS AS COMPOSITE MATRICES

<u>PROPERTY</u>	<u>THERMOSETS</u>	<u>THERMOPLASTICS</u>
FORMULATIONS	COMPLEX	SIMPLE
MELT VISCOSITY	VERY LOW	HIGH
FIBER IMPREGNATION	EASY	DIFFICULT
PREPREG TACK	GOOD	NONE
PREPREG DRAPE	GOOD	NONE TO FAIR
PREPREG STABILITY	POOR	EXCELLENT
PROCESSING CYCLE	LONG	SHORT TO LONG
PROCESSING TEMPERATURE/PRESSURE	LOW TO MODERATE	HIGH
FABRICATION COST	HIGH	LOW (POTENTIALLY)
MECHANICAL PROPERTIES	FAIR TO GOOD	FAIR TO GOOD
-54 TO 93°C, HOT/WET		
ENVIRONMENTAL DURABILITY	GOOD	UNKNOWN
SOLVENT RESISTANCE	EXCELLENT	POOR TO GOOD
DAMAGE TOLERANCE	POOR TO EXCELLENT	FAIR TO GOOD
DATA BASE	VERY LARGE	SMALL

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