ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 5, pp. 1001–1007. © Pleiades Publishing, Ltd., 2011.
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Construction Materials Based on Reinforced Thermoplastics

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Received December 1, 2009

Abstract—The properties of thermoplastic polymers intended for decorative-structural, structural, and special applications are described. These materials are in full compliance with the domestic (AP-25) and international (FAR-25) fire safety requirements.

DOI: 10.1134/S1070363211050318

In recent years great attention has been paid to development of new construction materials (CM) based on thermoplastics reinforced with continuous fibers [1–3].

Thermoplastic composite materials (TCM) have the following advantages over traditional CM based on thermosetting (epoxy) resins:

(a) Operational: 20–40 percent higher impact resistance and resistance to local damages; high water resistance and resistance to water erosion; chemical stability, including resistance to aviation fuels and oils; fire resistance, reduced smoke formation and toxicity; and maintainability (easy to weld);

(b) Technological: the possibility of molding of parts at metallurgical equipment (stamping, pressure forming, and rolling); a short (10–60 min) molding cycle; the possibility of defective products re-molding; the material utilization ratio reaching 95%; and an unlimited storage life of the prepreg.

The disadvantages of TCM are a high processing temperatures (200–400°C) and difficulties in laying-up of the prepreg with no tackiness.

The technology for manufacturing of parts from polymer CM reinforced with continuous fibers is traditional: first a semi-finished item is prepared, then a prepreg is produced, released, laid-up in a plastic bag, and molded into an item or a sheet.

However, such specific properties of thermoplastic binders as a high viscosity of solutions and melts, a high temperature of transition into the viscous flow state, the dependence of properties on the crystallinity degree and cooling rate, a low adhesion capability of many heat-resistant thermoplastics, and the fiberization and self-reinforcement capability introduce corrections in each of the above-listed steps.

Thermoplastic Binders for TCM

Any thermoplastics that can be processed for production of prepregs and molding of parts, including polyolefins, polycarbonates, polysulfones, and others, can be used as binders for composite materials [3, 4]. The creation of high-strength TCM became possible after the synthesis of "construction" thermoplastics (based on aromatic polyesters) characterized by strength and the elasticity modulus exceeding 60 and 2500 MPa, respectively.

The presence of phenolic rings in the chain of the thermoplastic polymer, as well as polyester and sulfur-containing groups increases its operational temperature and fire resistance, ensures its high processability, chemical stability, high specific strength, and reduced smoke formation during combustion [5].

By heat resistance and strength characteristics the developed thermoplastic binders are competitive with thermosetting materials, while in terms of impact resistance the former exceed the latter by factor of 4–10 (Table 1).

It is known that the maximum strength and service life of items made from CM are ensured if thermoplastic polymers, characterized by high strength and, at the same time, by tensile elongation of 8–12% within the boundaries of Hooke's law, are used as binders. Almost all new thermoplastic binders are in

Table 1. Properties of binders for composite materials

Thermoplastics	Trade mark	Density, kg m^{-3}	Glass-transition temperature, °C	Tensile strength, MPa	Impact resilience, kJ m^{-2}	Water absorption, %
Liquid-crystal polymers	Vectra A-950	1400	–	126	30–50	0.02
Polyamideimide	Torlon 4203	1420	280	195	–	0.12–0.33
Polyetheretherketone	Victrex PEEK 150 G	1300	143	150	50	0.25
Polyetherimide	Ultem 1000	1270	215–220	105	80	0.25
Polyethersulfone	Victrex 200 P	1370	230	86	80	0.43
Polyphenylene sulfide	Fortron	1360	90	80	–	0.01
Polyphenylene-sulfone, poliarilen-sulfone	Radel A-400	1290	285	72	–	1.8
Polysulfone	Udel P-1700	1240	180–190	70	100	0.02
Epoxy resins	–	1300	–	50	5–10	–
Bismaleimide	–	1300	–	80	–	0.4

compliance with this requirement, which has made it possible for developers in Great Britain, the United States, Germany, and Japan to obtain TCM characterized by higher crack resistance and strength.

Composites based on polyetheretherketone (PEEK) and liquid-crystal polymers (LCP) can successfully compete with CM based on epoxy and bismaleimide binders in production of airframe and engine load-bearing parts.

Fiber Fillers for TCM

In development of TCM for construction purposes the same high-strength fiber fillers are used for TCM reinforcement as in production of CM based on thermosetting binders, including carbon, glass, basalt, polymer, and metallic fillers, in the form of thread waste, ribbons, yarns, or cloth [1, 2].

Operational properties of CM are determined by characteristics of the matrix, reinforcing fibers, and interfacial (boundary) layer between them [1, 4]. Unlike thermosetting binders, thermoplastic binders are chemically inert and their melt viscosity is 1–2 orders higher. As a result, the filler is not wetted with polymer melts. Therefore, in development of TCM it is necessary to use intermediate layers, finishing agents or modifying additives, in order to reduce the viscosity of melts of thermoplastic binders without changing their glass transition temperature. Apart from the finishing agents, the intermediate layers can be formed by solutions of oligomers and polymers, including low-concentration solutions of the binder itself. Application of such solutions provides high-quality wetting of the fibers with the thermoplastic binder, which in turn results in an increase in compression strength of, for instance, thermoplastic organoplastics and carbon fiber reinforced plastics by a factor of 1.5–2.0 and 3.0–3.5, respectively.

Operational and technological properties of TCM depend not only on the composition of the finishing agents and modifying additives, but also on their application technology.

TCM Production Technology

Thermoplastic composite materials are heterogeneous systems consisting of the thermoplastic polymer matrix reinforced with high-strength high-modulus fibers of the filler (carbon, glass, polymer etc.).

There are many methods of matching thermoplastic matrices with continuous fillers. The most wide-spread technologies are as follows [1, 6, 7]:

– *Solution technology*: double or triple impregnation of the filler with a dilute solution of the binder;

– *Melt technology*: application of the binding powder on the fabric filler with further melting of the binder in the thermal chamber and indentation of the binder into the filler with the use of a special tool;

– *Electron-ion technology*: precipitation of the charged binding powder on the filler due to the

Table 2. Impact of intermediate layers on TCM properties

Binder	Fiber filler	Intermediate layer, wt %	Compression strength, MPa
Polycarbonate	56313 SVM	–	160–180
Polycarbonate	Same	Polycarbonate 5–7	190–210
Polycarbonate	Same	Epoxy oligomer 10–15	190–210
Polysulfone	ELUR-0.1P carbon fiber	–	200–300
Polysulfone	Same	Polysulfone 5–7	750–800
Polysulfone	Same	Epoxy oligomer 5–7	750–800

electrostatic attraction and further melting of the binder;

– *Film technology*: alternation of the filler and the film binder;

– *Fiber technology*: combination of reinforcing and fused thermoplastic fibers in the semi-finished item.

Among the above-listed methods only the solution and the fiber technologies provide high-quality impregnation of the filler with the binder and ensure a high level of CM mechanical properties. However, application of solvents requires the use of bulky and expensive recuperating units and the impregnation is performed in 2–3 stages.

The resulting prepreg is almost unworkable because of its hardness. Moreover, many thermoplastic binders, e.g. polyphenylene sulfide (PPS), are insoluble or only soluble in concentrated acids (LCP and PEEK). Therefore, the solution technology is unlikely to become a wide-spread method of TCM production.

The fiber technology makes it possible to obtain prepregs with any filler. However, not all thermoplastics are prone to fiberization: for example, it is impossible to produce fibers with the required level of physical, mechanical, and textile properties from amorphous thermoplastics.

Low mechanical properties of TCM produced on the basis of various combination techniques are associated with low quality impregnation of the filler with the high-viscosity melt of the binder (with the exception of the solution technology). Subsequent pressing of the plastic has almost no effect on the level of impregnation of the filler with the binder: the fibers remain dry and are not bonded together. Regardless of the combination technique applied, the strength characteristics of the produced TCM will be similar to the properties of TCM manufactured on the basis of the solution technology only in case before matching with the binder the filler is treated with a finishing agent or impregnated with an intermediate layer (Table 2).

The detected trend is of great practical importance as, depending on the physical state, the nature of the binder, and the type of the filler, it is possible to select an economically and technologically efficient combination technique without reducing the operational properties of the plastic. The resulting prepregs have an almost unlimited storage life.

Technology of TCM Processing

It is possible to mold parts from thermoplastic prepregs applying the same traditional technology that is used for CM based on thermosetting binders. This technology involves the use of autoclaves, winding at a rate of 30 m/min, pultrusion etc. The most efficient way to process TCM from a semi-finished product (sheet) is through pressure forming, stamping, and rolling at high-capacity metallurgical equipment. According to this technological process the industrial consumers should receive sheets of the required thickness and have no need for chemical sections for preparation of binders, impregnation of fillers, and molding of sheets at their plants, as well as for cold storage chambers for prepregs.

It should be noted that for TCM processing it is necessary either to retrofit the existing equipment or to develop new machinery. Such well-known companies as ICI (Great Britain), Bayer (Germany), and others are engaged in development of this special-purpose equipment for TCM processing abroad.

The equipment intended for TCM processing should envisage preheating of the prepreg for softening purposes; welding of each subsequent layer to the previous one during laying-up; high molding temperatures (200–450°C) and pressures (100–400 MPa);

Table 3. Properties of organoplastics and glass fiber reinforced plastics based on thermoplastic binders[a]

Parameter	TCM composition (filler-binder)								
	Glass fiber					Kevlar-49			
	PA-6	PPS	PES	PEI	PEEK	PC	PPS	PSN	PA-6.6/ EPON 826
Filler content, vol %	33	55	20	50	20	50	55	50	55
Density, kg m^{-3}	1580	1850	1510	1800	1440	1350	1400	1340	–
Compression strength, MPa	634	790	126	370	137	416	700	371	600–700
Elongation at rupture, %	–	1–2	3	1–3	3	–	1–2	1.4	–
Modulus of rupture, MPa	–	–	6020	21000	6860	28400	30000–33000	31700	–
Bending strength, MPa	–	96.5	–	–	–	284	300	317	640/620
Rupture strength, MPa	620	450	–	440	–	200	210	230	270/276
Shear strength, MPa	41	–	–	–	–	–	–	27	58/53
Manufacturer	–	Phillips Petroleum Company	ICI	General Electric	ICI	–	Phillips Petroleum Company	–	–

[a] The samples are obtained through impregnation of Kevlar-49 yarns with the binding melt.

Table 4. Properties of unidirectional plastics based on thermoplastic and epoxy binders

Parameter	Thermoplastic binders[a]							Epoxy binders	
	PC	PSN	PES	PEI	PPS	PEEK	K-polymer-armide	3501-06	5208
Filler content, vol %	–		45–55	55	55–60	62–68	55–62	60	65.4
Rupture strength, MPa	–	–	1020	–	1170 (1380)	2130	(793)	2130	1830
Elongation at rupture, %	1.25	1.45	1.4	–	0.8	1.45	–	1.5	–
Tensile modulus, 10^{-3} MPa	105	112	86	110	125	134	–	148	147
Bending strength, MPa	1370	1560	1100	1400	(1170) 147	1800–2100	1440	–	1800
Bending modulus, MPa	–	–	90	105	100–124	121	126	–	126
Compression strength, MPa	–	–	810	–	690	1100–1200	–	1350	1300
Shear strength, MPa	65	75	84	94	77	105	112(63)	127	90–110
Manufacturer	–	–	IRKHA	IRKHA	Phillips Chemical, Petrolium Company	ICI	DuPont	ICI	Narkho

[a] PC and PSN are reinforced with Toho fiber, the other binders with Hercules AS-4 fiber.

and cooling of the molded part (blank part) under pressure at a certain rate.

Properties of Plastics Based on TCM

The main physical and mechanical properties of foreign glass and carbon fiber reinforced plastics, and organoplastics based on modern construction thermoplastic binders in comparison with epoxy-based plastics are given in Tables 3 and 4. It is demonstrated that the strength characteristics of the plastics are largely defined by the nature of the filler and the technology of the plastic production.

Table 5. Mechanical properties of unidirectional carbon fiber reinforced plastics

Matrix	Fiber type[a]	Strength, MPa				E_v, GPa	$d_{\pm}$[b], %
		σ_v^+	σ_v^-	$\sigma_v^{\pm}$	τ_{shear}		
Epoxy resin	AS4	1932–2130	1200–1400	50–60	–	120–130	0.6
	T-300	1200–1600	1000–1200	–	50–90	–	0.4
Polysulfone	AS4	1330	1200	60	–	129	0.9
	Tcho TA-7	1300	–	70	65	112	–
Polyethersulfone	T-300	1000–1300	800–900	–	75	110	–
Polyetherimide	AS4	–	825	–	94	135	–
Polyphenylene sulfide	AS4	1600	655	31.7	69	135	–
Polyetheretherketone	AS4 (APC-2)	2130	1000–1100	80	106	134	1.0
	T-300	1500	1000	–	117	–	–

[a] Carbon fiber content of 50–60 vol %. [b] ($d_{\pm}$) relative elongation.

By properties thermoplastic CM based on polysulfone (PSN), polycarbonate (PC), and polyethersulfone (PES) are superior to traditional CM based on epoxy resins or are close to them, as in the case of CM based on polyetheretherketone (PEEK), polyphenylene sulfide (PS) etc.

It should be noted that a significant share of published works on TCM are advertising materials, which neither describe the methods of the filler preparation before impregnation with the binder, nor specify the additives reducing the thermoplastics viscosity, nor indicate the technological parameters for production of the prepreg and the sheet. Therefore, the parameters figures given in various sources are quite different.

For instance, carbon fiber reinforced plastic based on PPS is characterized by the rupture strength and bending strength of 1170–1380 MPa and 1170–1470 MPa, respectively (Table 3).

Among the developed carbon-filled TCM it is necessary to pay special attention to carbon fiber reinforced plastics based on PEEK characterized by high strength, hardness, chemical stability, fire resistance, and low creep. On the basis of PEEK and carbon fibers the British Company ICI developed APC-1 and APC-2 materials, containing 52 and 61 vol % of fibers, respectively. These materials were objects of research for a great number of works [1, 8, 9]. It was demonstrated that the high values of the physical and mechanical properties of APC-2 carbon fiber reinforced plastic were achieved after solution of the following problems:

– Reduction in viscosity of the binder melt through its modification and selection of molecular weight;

– Reduction in PEEK crystallization rate;

– Application of finishing layers;

– Use of continuous fillers of the given density;

– Elaboration of the technology of impregnating the carbon filler with binder melt (the melt temperature, pressure, impregnation period, and cooling rate).

The solution of these problems made it possible for ICI developers to abandon APC-1 and put forward APC-2 plastic. APC-2 is competitive with the epoxy-based carbon fiber reinforced plastic in terms of strength, while its fracture toughness, fire resistance, atmospheric resistance, and chemical stability are much higher. The advantages of APC-2 carbon fiber reinforced plastic can be seen most evidently in stretching of specimen with the orientation of ±45° or in the transversal direction (Table 5). The only parameter by which APC-2 is inferior to the epoxy-based carbon fiber reinforced plastic is tensile strength, which is associated with a higher curvature of the fibers resulting from their shift during impregnation with high-viscosity PEEK melt under pressure.

By strength characteristics, thermoplastic carbon fiber reinforced plastics based on amorphous polymers are slightly inferior to APC-2 plastic with the crystalline binder. It is explained by a higher viscosity of the melt and its hindered penetration into the interfiber space of the filler.

Russian researchers have also performed works on development of thermoplastic CM, the properties of

Table 6. Properties of domestic thermoplastic CM

Parameter	KTMS-1[a]	KTMS-2[a]	KTM-1-1[a]	KTMU-1[b]
Density, kg m^{-3}	1580–1600	1580	1330	1450–1480
Water absorption, %, 1 s	0.1	0.18	–	0.09
Tensile strength, MPa, min	400	400	650	1000
Bending strength, MPa, min	540	350	410	–
Impact resilience, kJ m^{-2}, min	140	95–125	250	60[c]

[a] Tests performed by T.F. Izotova. [b] Tests performed by D.N. Perfilova. [c] Notched specimen.

Table 7. Application of TCM in aerospace engineering

Aircraft type	Application examples	Binder	Filler
Cargo and passenger aircrafts	Interior elements and components of seats, air-conditioning systems, wall and floor sandwich panels	PEI, PPS, and PEEK	Glass fiber and kevlar
	Windshield frame, antenna dome, and parts of the empennage, fuselage, and wings	PEEK, LCP, PES, and PPS	Hybrid and carbon fiber
Helicopters	Hatch panels, engine cones, fuselage, fin endings, weapon compartment doors, front gearbox cones, and the helicopter rotor	PES, PPS, and PEEK	Carbon, glass, and polymer fibers
Fighter aircrafts	Stiffening ribs, wing skins, hatch covers, nervures, and stringers	PEEK, PPS, LCP, and fusible polyimides	Carbon fiber
Spacecrafts	Walls of liquid hydrogen tanks, load-bearing parts, and frames of solar batteries	PEEK, PPS, LCP, and fusible polyimides	Carbon fiber
Tomahawk missiles	Wings, hatch panels, cones, nozzles, and the combustion chamber	PPS, PEEK, LCP, and PES	Kevlar and carbon fiber
Special equipment for all aircraft types	Cases of instruments and units, radio equipment cases, ballistic protection parts, and electromagnetic shielding screens	PSP, PES, PEEK, LCP, and PPS	Kevlar, carbon fiber, and glass fiber

which are given in Table 6. The level of development of domestic thermoplastic CM is comparable to the best foreign analogues with the exception of carbon-filled TCM, which is caused by the following reasons: unavailability of high-strength heat-resistant binders like PEEK or LCP and of carbon fibers with the strength of 4–7 GPa; insufficient knowledge of processes occurring on the filler-binder interface (problems of wetting, impregnation, and adhesion); and the absence of processing and research equipment with the molding elements temperature $T > 400°C$.

Application of TCM in Aerospace Engineering

Technological and operational advantages of thermoplastic CM draw attention of aircraft designers and manufacturing engineers. The first company whose experts started serious works with TCM was Boeing. Since the 1980s in cooperation with the Flight Dynamics Laboratory and the US Air Force Laboratory the company has carried out research works on thermoplastic carbon fiber reinforced plastics in order to find a substitution for epoxy-based plastics in manufacturing of low-loaded structures of the aircraft fuselage. Thus, parts of unmanned flying targets were manufactured on the basis of P-1700 polysulfone and later this material was used in US-14 aircraft elevator frame. The weight of such structure was 27% lower than the weight of the aluminum structure and the production costs were 20% less as well.

The analysis of published works allows us to assume that TCM will be used in manufacturing of interior elements and components of seats, air-conditioning systems, wall and floor sandwich panels, windshield frames, antenna domes, and parts of the empennage, fuselage, and wings of cargo and passenger aircrafts (PEEK, LCP, PES, and PPS with hybrid yarns and carbon fibers).

Stiffening ribs, wing skins, hatch covers, nervures, and stringers of fighter aircrafts are expected to be manufactured from PEEK, PPS, LCP, and thermoplastic polyimides with carbon fibers. It is also expected that TCM will be widely used in manufacturing of helicopter parts, including hatch panels, engine cones, empennage parts, weapon com-partment doors, the helicopter rotor etc.

The weight fraction of plastics and polymer composites in Airbus A340 aircraft family has increased from 7% in 1980 to 40% as a result of application of high-strength composites based on low-density construction thermoplastics in the aircraft load-bearing external parts and is likely to continue increasing.

It is also expected that almost 40 wt % of parts for Super Airbus A380, which can accommodate 550 passengers, will be made from composites with carbon fibers. In this connection an important role is given to Ticona Company (Kelsterbach, Frankfurt, Germany), the producer of Fortron 0214C1 PPS. This material serves as a binding agent for these extremely light and efficient composites used for production of the wing leading edge for Airbus A380.

The transition from aluminum to PPS-composites has made it possible to reduce the weight and change the airfoil of the wing leading edge. Instead of the five 5.5-meter aluminum sections of the wing edge, previously located between the fuselage and the engine, now it is possible to use two sections made of Celex glass-reinforced PPS, and the weight of these sections is 20% lower. Moreover, the traditional D-shaped leading edge has been replaced by a J-shaped edge with higher aerodynamic characteristics. This new shape makes it possible to place the electric, deicing, and other aircraft systems under the aircraft skin.

The elements of the wing leading edge are strengthened by stiffening ribs in the direction of the countercurrent air flow and, at the same time, they allow wing oscillations in the direction perpendicular to the air flow.

Polyphenylene sulfide is in compliance with all the major requirements of the aviation industry, including the necessary resistance to extreme temperatures, hardness, impact resilience, dimensional stability, and chemical stability. PPS retains permanent toughness, hardness, and dimensional stability within a temperature range from –40 to +250°C. Its intrinsic fire resistance is an essential safety factor. PPS-based composites are molded at 300°C and under high pressure from PPS films that are alternated with layers of fiber fillers. Separate parts are welded together in an autoclave in order to produce a durable sealed element, which makes it unnecessary to carry out labor-intensive assembly operations of drilling or riveting and ensures high strength and safety, at the same time saving time and money [10].

Table 7 shows possible fields of TCM application in aerospace engineering according to information from foreign companies.

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