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Film Binders for the RFI Technology

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Abstract—Main principles of the RFI technology are described. Technological requirements for film binders are determined. The properties of the produced polymer co-composite materials are presented.

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The vigorous growth in 2000s of the share of polymer composite materials (PCMs) in civil aircraft designs (Boeing 787, Airbus A380, etc.) has made possible rapid progress in decreasing their weight and enhancing reliability and service life. However, this made quite urgent the problem of lowering the cost of PCM constructions which were always more costly that analogous metal parts. The high cost of PCM parts is largely explained by the fact that they are most commonly fabricated by a labor- and power-consuming autoclave technology, as well as by a high cost of equipment. Therefore, over the past years the major aircraft design companies like EADS and Boeing have put much effort in the development of autoclaveless PCM production technologies.

Resin film infusion (RFI) is one of such technologies. This technology consists in the impregnation with a binder of a preformed dry filler pack (so-called preform), and, therewith, the binder which is an elastic film is applied on top of a matrix and then covered with a preform. This allows the filler to be impregnated in a transverse rather than longitudinal direction, like in the resin transfer molding (RTM) technology. Thus, the way for the binder to pass during infusion gets much shorter, which decreases the threat of appearance of uninfused areas and poses lower, than in the RTM technology, requirements to binder rheology. Moreover, the RFI technology allows one to use 3D-reinforced fillers, which, on the one hand, improves impact characteristics of composites and also abandon use of higher cost binders with a high fracture viscosity and on the other hand, makes less labor-consuming laying-up workpieces. Moreover, the RFI technology no longer involves such a high-cost procedure as prepreg formation, which, along with the above-mentioned advantages allows, according to foreign estimates, decreases the cost of the workpiece formation process by 20–25%.

The RFI technology imposes certain requirements on the binder. Thus, the binder film should exhibit a necessary contact adhesion to allow fixing on the matrix but should not be too adhesive. The binder film should be elastic enough to allow one to lay-up double-curvature workpieces. The binder rheology should ensure that the shape of a workpiece laid-up on the matrix is sufficiently stable (no blender spreading over the matrix surface is allowed). It is quite important that the binder viscosity and its persistence time allow a high-quality impregnation of thick-wall workpieces. Thus, one of the key issue in the development of binders of this technology is to choose properly their rheologic characteristics.

As known [1], the RTM process and its RFI version is basев on the law of Darcy who was the first to reveal, in the middle of XIX century, a correlation between filtration rate and pressure under laminar flow and a constant filter thickness. In honor of this scientist, the permeability coefficient of porous structures (sands, ceramics, as well as fibrous reinforcing structures like fabrics, felts, batts, etc) was called after Darcy. Tendler [2, 3], as well as one of the authors of this paper [5] showed that this law nicely fits the experimental data obtained on the fabrication of variously shaped workpieces on the basis of glass fillers.

According to the Darcy's law, the impregnation time can be calculated [3] by formula (1):

$$\tau = \frac{m\mu L^2}{2K\Delta P}, \quad (1)$$

where τ is the impregnation time, s; m, reinforcing filler porosity, unit fractions; μ, viscosity, cP; L, length of a specimen to be impregnated, cm; ΔP, pressure drop across the binder, kgf cm^{-2}; and K, permeability coefficient, darcy.

As seen from formula (1), the impregnation rate depends on filtration characteristics of the filler, including the permeability coefficient and porosity, as well as binder viscosity. Furthermore, the impregnation time is directly to the squared binder flow length and inversely related to the pressure drop. Permeability is transmission of fluid under pressure. The permeability coefficient is generally determined experimentally [4] and calculation by Eq. (2):

$$K = \frac{Q\mu L}{A\Delta P}, \quad (2)$$

where Q is the fluid volume flow rate, cm^3 s^{-1}; A, cross-section of a specimen to be impregnated, cm^2; ΔP, pressure drop of the fluid, kgf cm^{-2}; μ, viscosity of the experimental fluid, cP; and L, flow length in the specimen impregnation direction, cm.

Permeability is measured in "darcy" units. One darcy relates the permeability of a material in which the pressure drop of 1 atm maintains the volume flow rate of 1 cm^3 s^{-1} at the viscosity of 1 cP through a cube with the edge length of 1 cm. Thus, in the SI system, 1D = 9.87×10^{-13} m^2 ≈ 10^{-12} m^2.

The permeability of a porous medium in laboratory conditions is determined by directly measuring the volume flow rate a fluid oa a definite viscosity through a unit surface area of the medium and the pressure gradient maintaining this flow, and calculating the permeability coefficient by Eq. (2).

To develop rheological requirements to binders for the RFI technology, we first of all determined permeability coefficients K for the following fillers: a unidirectional carbon fiber tape (brand T700SC 12, Toray Ind.) and an equal-strength fabric of Toho Tenax-E HTA 5131 200 tex f 3000 t0 carbon fiber fabric (article 3692, Porcher Ind.). The characteristics of these carbon fillers, as well as the measured permeability coefficient K at the pack porosity of 0.42 are listed in Table 1.

Further on, using the resulting K values and Eq. (1), we determined the time required to impregnate the filler pack with varied viscosity binders under a vacuum. Therewith, the flow length L in the impregnation direction (in our case, specimen thickness) was taken to be equal to 1–10 mm. The impregnation time for this filler pack was limited by 60–80 min. As a result, we obtained binder viscosity characteristics for the chosen fillers (Table 2).

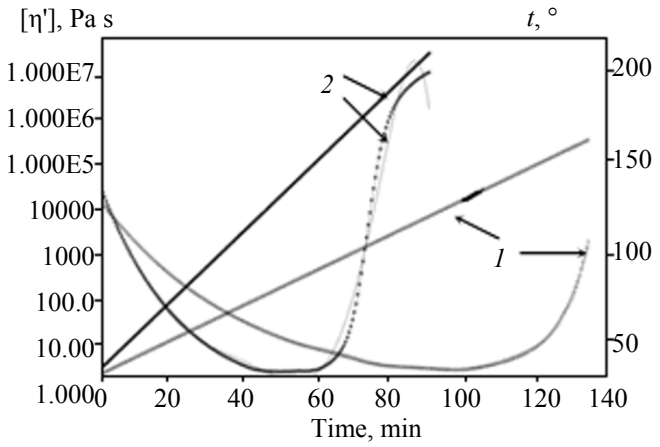
As seen from Table 2, the unidirectional filler has quite a low permeability coefficient, a very low-

Table 1. Characteristics of carbon fillers

Filler brand	Fiber brand	Weave type	Surface density, g/m^2	Fiber diameter, μm	Permeability coefficient K, D
Porcher 3692	Toho Tenax-E HTA 5131 200 tex f 3000 t0	Serge	204	7	8.6×10^{-2}
Toray T700SC	Toray T700SC 12k	–	199	7	5.8×10^{-4}

Table 2. Viscosity of binders for selected fillers

Filler Brand	Permeability coefficient K, D	Impregnated pack thickness, mm	Impregnation time, min	Binder viscosity, Pa s
Porcher 3692	8.6×10^{-2}	1	77.6	170
		5	79.9	7
		10	77.6	1.7
Toray T700SC	5.8×10^{-4}	1	71.0	0.4
		5	88.7	0.02
		10	–	–



Temperature dynamics of binder viscosity, heating rate (*1*) 1 and (*2*) 2°C/min. measurements were performed at an EXTA Instruments AR 2000 rheometer.

viscosity binder is required to impregnate even 1 mm of the binder. In this connection the use of unidirectional fillers for fabrication of PCM articles by the RFI technology under vacuum is quite limited.

The resulting data allowed us to formulate the principal rheological requirements to binders for the RFI process: viscosity at the impregnation temperature ≤ 2 Pa s, time for viscosity rise to 2 Pa s ≥ 60 min.

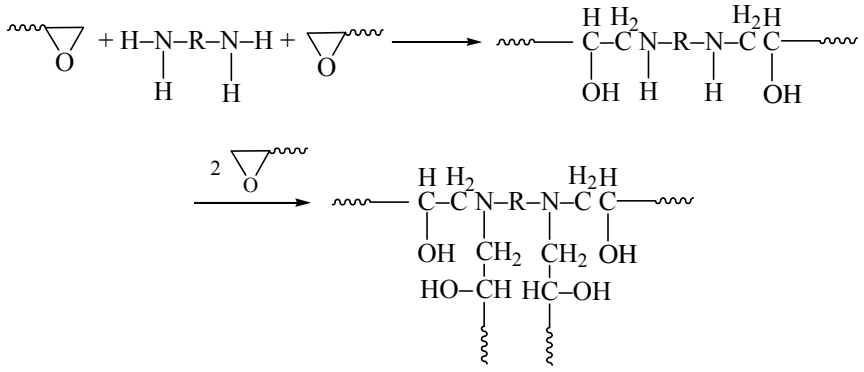
Along with specific rheological properties, in developing film binders we also had to take into account that the modern state of performance characteristics of construction materials could not be reached using traditional epoxy binders. The binder to be developed was envisioned to form during curing a high-strength polymer matrix with the following parameters: tensile stress $\sigma_t \geq 90$ MPa, working temperature $T_w \geq 120$°C, and relative breaking elongation $\varepsilon_b \geq 3\%$. Binders with such characteristics allow one to take a maximum advantage of the strength of reinforcing fibers used today for fabrication of PCM constructions.

As film binders we considered melt-type systems of epoxy oligomers doped with thermoplastic low-molecular polymers soluble in the resin by elevated temperatures but forming a separate phase on cooling. As a result, the binder converts into a strong and an elastic gel. Binders of this type have a high cohesion energy ensuring a high film strength and a fairly low adhesion which allows the film to be laid-up without damage. Heating of such gels destroys physical structural bonds, and the composite collapses, which leads to a jumpwise viscosity drop to 0.4731.5 Pa s, which is sufficient for high-quality impregnation of the fibrous filler pack.

We tested different types of polymers and chose a number of film-forming polymers capable of imparting to binders the required performance characteristics not appreciably deteriorating the construction properties of matrices (primarily thermal stability and strength at working temperatures). Good characteristics were shown by low-molecular polyoxyethers, polyarylenes, polyarylates, and polyvinylformal. Their doping imparts to the system the entire set of required performance characteristics.

To develop melt-type epoxy binders with enhanced performance characteristics, we combined epoxy oligomers with enhanced specific functionality with a difunctional epoxy oligomer. Amine curing agents favor formation of tightly cross-linked thermally stable matrices and impart to the polymer the required performance and physic-chemical characteristics.

The curing of epoxy oligomers with amine curing agents occurs by the following scheme:



Preliminary tests revealed the best strength and thermal stability characteristics in epoxy resins cured with an aromatic amine curing agent; according to DSC, active reaction with the chosen epoxy resin initiates at 120°C. Therewith, the gel collapse point for the used film-forming polymers is no higher than 80°C (see the figure), which provides a sufficiently broad temperature range for impregnation of matrices with binders without essential viscosity rise due to chemical cross-linking.

The obtained binder and the carbon fabric (article 3692, Porcher Ind.) were used to prepare a PCM sample by oven vacuum molding, after which we assessed physicomechanical properties of the resulting material.

Testing a 2-mm thick plastic sample (density of 1.53 g cm^{-3}) showed that its bulk porosity is < 1%, and the interlaminar shear strength is 58 MPa.

At present, in view of the great promise of this direction, the RIAM proceeds with R&D on materials and technologies of their production on the basis of the developed binder and on a binder with a maximum working temperature of 170°C for the RFI technology.

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