

# Rheokinetic Investigations on CFRAI Matrix

FLORIN TACHE, ANICUTA STOICA, MARTA STROESCU, TANASE DOBRE

University Politehnica of Bucharest, Chemical Engineering Dept., 313 Splaiul Independentei, 060042, Bucharest, Romania

*The paper focuses on rheokinetic investigations on matrix of a new composite material. A simple, yet effective, experimental method has been employed to measure several parameters that can help, by resin viscosity measurements, in finding resin kinetic hardening parameters. As it is shown by one of our papers [1,3,4] CFRAI (Carbon Fibers Reinforced Aluminum) is a new hybrid composite under development. It has unique and promising properties, with foreseeable excellent results in applications requiring a reliable, yet light, reinforcement material that can also withstand powerful thermal shocks.*

*Keywords: rheokinetic model, composite material, carbon fibers, bullet-proof material*

Composites are considered to be heterogeneous and anisotropic materials obtained by the macroscopic combination of two or more phases that have a separation interface or inter-phase and which synergistically cooperate, leading to the final properties of the whole composite material [2].

CFRAI (Carbon Fibers Reinforced Aluminum) is made of an aluminum-epoxy matrix reinforced with carbon fibers. Even from the early stages of a composite material development, its final destination must be considered. Aspects like what kind of loads will act on the composite structure, their order of magnitude, etc., have to be taken into account and thoroughly examined. The material considered herein is supposed to withstand the impact of small-dimension high-velocity objects and to have a good behavior in the event of an explosion in its vicinity. Envisaged applications of the new material vary from sports articles and common goods to ballistic protection systems, bomb-proof containers and space vehicles outer hulls.

The hybrid composite has shown good results so far [1], thus encouraging further investigations, development and enhancement of the material. The first samples produced after our technology at the laboratory level [3] shown that these have a very low density, high specific strength and present the ability to stop a 9 mm caliber bullet. While mechanical tests like tensile strength, mechanical shock and ballistic tests have already been performed, producing good results, and some of these are still under way, attention is now paid to rheokinetic investigations on the matrix of CFRAI.

In brief, CFRAI is a hybrid composite, being made of a mixed aluminum-epoxy matrix, reinforced with carbon fibers. Several prototype samples have been produced in the laboratory so far, constantly increasing the composite properties in time. First samples had only 5 carbon fibers layers, while latest ones have 10 and 14 layers, possess a very low density (around  $1.65 \text{ g/cm}^3$ ), good tensile strength (best value recorded yet is  $319 \text{ MPa}$ ), an even better specific tensile strength ( $190.603 \times 10^3 \text{ N} \cdot \text{m} / \text{kg}$ ) ( and the ability to stop a 9 mm caliber bullet. Some details concerning the material testing and its structure are presented in the images shown in figures 1. This paper focuses on dynamic of reticulation of the resin used for CFRAI manufacturing. For that a simple but effective experimental method has been employed to measure several parameters that can help to determine the resin hardening kinetic by means of resin viscosity measurements.

## Modeling of binder hardening.

Knowing the hardening kinetic of the resin is important for the curing process. With respect to this problem, an experimental method is proposed here, that allows the identification of resin hardening parameters by means of dynamic measurements of resin viscosity. This experimental method considers one drop of a mixture from epoxy resin and hardener deposited on a point from a glass surface inclined at an  $\alpha$  angle with respect to the horizontal plane; the drop begins to flow along the inclined surface in a film having the width equal to the drop diameter; during the flow, in the liquid resin takes place their crosslinking and, consequently, the liquid viscosity increases; when gel time of reticulation is attained, the flow stops. The particularization of one model based on the transport phenomena equation [5] to this film flowing case reveals that it contains the following relationships:

-Navier Stokes equation for unsteady state in x direction of flow:

$$\frac{\partial w_x}{\partial \tau} + w_x \frac{\partial w_x}{\partial x} = g \sin \alpha + \left( \frac{\eta}{\rho} \right) \left( \frac{\partial^2 w_x}{\partial x^2} + \frac{\partial^2 w_x}{\partial y^2} \right) \quad (1)$$

-univocity conditions for film flow:

$$\tau = 0, x \geq 0, 0 \leq y \leq \delta_r, w_x = 0; \quad (2)$$

$$\tau > 0, x > 0, y = 0, w_x = 0, \frac{\partial^2 w_x}{\partial y^2} = 0 \quad \tau > 0, x > 0, y = \delta_r, \frac{\partial w_x}{\partial y} = 0 \quad (3)$$

-the constitutive equations of the x axis Newtonian flowing fluid:

$$\tau_{yx} = -\eta \frac{\partial w_x}{\partial y} \quad (4)$$

-the dependency of fluid flowing viscosity on the resin reticulation degree:

$$\eta = f(\eta_0, c_{r0}, X) \quad (5)$$

-the expression given the kinetic of resin reticulation dynamics:

$$\frac{dX}{d\tau} = g(c_{r0}, c_{r0}, X) \quad (6)$$

-the relationship showing the conservation of the drop mass:

$$m_0 = \rho l L \delta_r \quad (7)$$

If a homogeneous polymerization process is considered (the reticulation can be assumed as one-phase polymerization), then the medium viscosity  $\eta$  can be

\* email: flotasoft@yahoo.com

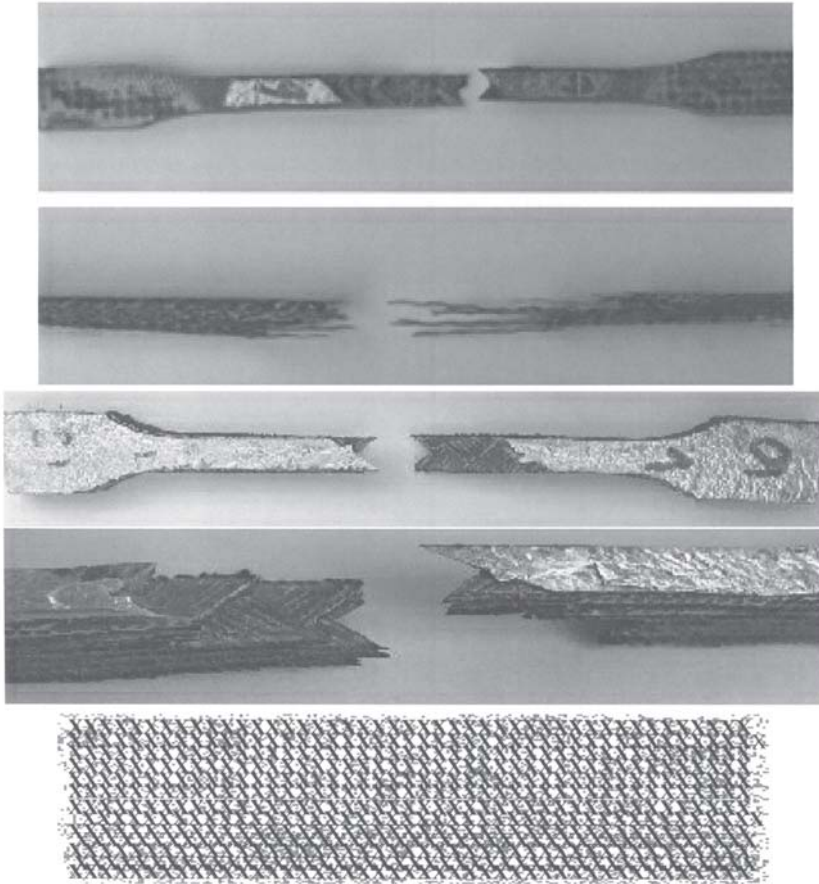


Fig. 1. Broken CFRAI tensile test specimens (up – 10 layers; down – 14 layers) and their structure details (charon fibres tissue (X) and Aluminium powder (:::) in reticulated resin)

considered to be a power law function of the number-averaged degree of polymerization  $N$  and of the dimensionless concentration of the reticulated polymer [6-8]. Relation (8) where  $K$ ,  $a$  and  $b$  are constant, shows this dependency.

$$\eta = KN^a \phi^b \quad (8)$$

This relationship was the starting point for deriving a rheokinetic model, i.e. a relationship for the viscosity increase during polymerization (reticulation) as a function of time or conversion. In fact, with the help of models for the chemical kinetics (see relation (6)),  $N$  and  $\phi$  can be expressed as a function of conversion ( $X$ ) and  $X$  as a function of time  $\tau$ . The derivation of the rheokinetic model is different for different kinds of polymerizations. If a kinetic similitude between reticulation and free radical polymerization is assumed, then the dimensionless concentration of the reticulated polymer and the basic resin conversion  $X$  are equal, as relation (9) shows; here,  $c_{r0}$  and  $c_r$  are the initial and current concentrations of the basic resin.

$$\phi = X = \frac{c_{r0} - c_r}{c_{r0}} \quad (9)$$

When considering the classical kinetics of homogeneous polymerization without chain transfer reactions, the following two relationships occur for  $N$  and  $X$ . It is known here that  $c_{i0}$  is the initial concentration of the initiator,  $f$  is the initiator efficiency,  $\tau$  is the time and  $k_i$ ,  $k_p$  and  $k_t$  are the rate constants of the initiation propagation and termination reaction.

$$N = \frac{c_{r0} X}{c_{h0} (1 - e^{-k_i \tau})} \quad (10)$$

$$\ln(1 - X) = \frac{2f^{1/2} k_p c_{h0}^{1/2}}{k_i^{1/2} k_t^{1/2}} (1 - e^{-k_i \tau}) \quad (11)$$

Substituting equation 9 and 10 into equation 8 [6,8], a rheokinetic model is derived for the dependence of the viscosity to the degree of conversion (reticulation).

$$\eta = KX^b \left( \frac{c_{r0} X}{c_{h0} (1 - e^{-k_i \tau})} \right)^a \quad (12)$$

Further substitution of (11) into (12) yielded relationship (13), where there is a dependency between viscosity and time.

$$\eta = \frac{Kc_{r0}^a}{c_{h0}^a (1 - e^{-k_i \tau})^a} \left( 1 - \exp \left( \frac{2f^{1/2} k_p c_{h0}^{1/2}}{k_i^{1/2} k_t^{1/2}} (1 - e^{-k_i \tau}) \right) \right)^{a+b} \quad (13)$$

Equations 12 and 13 make it possible [6,8] to give a complete description of the change in the viscosity of reacting media during free radical polymerization if the kinetic constants are known. This is only partially true, because the influence of the shear rate on the viscosity, which is important for non-newtonian media, is not taken into account. Another problem lies in the fact that the kinetic constant of the propagation reaction may change during the polymerization because of self-acceleration of the rate of polymerization (gel effect or Trommsdorff effect, which can appear at appreciable conversion level [9]). So at moderate conversion level, the kinetic constants could be assumed to be invariable, and equation (13) could be

simplified expanding  $(1 - e^{-k_i \tau})$  and  $\left( 1 - \exp \left( \frac{2f^{1/2} k_p c_{h0}^{1/2}}{k_i^{1/2} k_t^{1/2}} (1 - e^{-k_i \tau}) \right) \right)^{a+b}$  into power series up to linear terms. Results are in relation (14), rewritten as (15) with the aim to show the effect of initial concentration of reticulation initiator (hardening agent) and of time on the reticulating resin viscosity

$$\eta = \frac{Kc_{r0}^{3/2a+b} c_{h0}^{(b-a)/2} f^{(a+b)/2} k_p^{(a+b)} k_t^{(b-a)/2}}{k_i^{(a+b)}} \tau^b \quad (14)$$

$$\eta = Ac_{h0}^{(b-a)/2} \tau^b \quad (15)$$

Moreover, relation (14) can be used to show the temperature and time influence on the reticulating resin viscosity. For that, a particularization of the Arrhenius expression for the constants of reactions rate  $k_r$ ,  $k_p$  and  $k_t$  is performed, with results in relation (16), rewritten as (17) by coupling some constants and factors in  $B$  and  $C$ .

$$\eta = \frac{Kc_{r0}^{3/2a+b} c_{h0}^{(b-a)/2} f^{(a+b)/2} k_{p0}^{(a+b)} k_{t0}^{(b-a)/2}}{k_{t0}^{(a+b)}} \tau^b \exp\left(-\frac{(a+b)E_p + (b-a)/2E_t - (a+b)E_t}{RT}\right) \quad (16)$$

$$\eta = Bc_{h0}^{(b-a)/2} \tau^b \exp\left(-\frac{C}{RT}\right) \quad (17)$$

If resin reticulation is treated as a polycondensation process with a single monomer, then one must accept that the binding of non reticulated polymer chains is a bimolecular process. So reticulation kinetic of basic polymer chains follows the kinetics given by relation (18).

$$-\frac{dc_r}{d\tau} = k_{pc}c_r^2 \quad (18)$$

Using the integral state of this kinetics relation, and the definition of  $X$  and  $N$ , expressions (19), (20) and (21) are obtained. Building rheokinetics relation corresponding to this reticulation model is in the result of dependency  $\eta = f(N, X)$ .

$$c_r = \frac{c_{r0}}{1 + c_{r0}k_{pc}\tau} \quad (19)$$

$$X = 1 - \frac{1}{1 + c_{r0}k_{pc}\tau} \quad (20)$$

$$N = \frac{1}{1 - X} = 1 + c_{r0}k_{pc}\tau \quad (21)$$

In the case of polymerization by polycondensation, there are strong motives in literature [8, 10-11] that sustain the dependency of medium viscosity only to the polymerization degree. Moreover, this dependency obeys a power law as in relation (22).

$$\eta = KN^\alpha \quad (22)$$

The coupling of (21) and (22) is in relation (23), that yields the time dependency of reticulating resin as power law dependency, which is somewhat different referring to relation (15).

$$\eta = K(1 + c_{r0}k_{pc}\tau)^\alpha \quad (23)$$

If one accepts that  $\alpha$  depends on reticulating polymer concentration in the basic solution, then there are literature considerations [12] which show for  $\alpha$  a value of 1 under a critical polymer concentration and 3.4 over that. Particularization of relation (23) for time moment  $\tau = 0$  finds relation (24). Temperature influence on the reticulating media appears by considering the dependence of initial viscosity and of polymerization reaction constant with temperature. Results are in relation (25), where an exponential dependence of basic polymerization reaction constant to hardening species concentration has been supplementary introduced.

$$\eta = \eta_0(1 + c_{r0}k_{pc}\tau)^\alpha \quad (24)$$

$$\eta = \eta_0\left(1 + c_{r0}k_{pc00} \exp(\beta c_{h0}) \exp\left(-\frac{\gamma}{RT}\right)\tau\right)^\alpha \exp(-\delta T) \quad (25)$$

For the resins currently used for electronic or other packaging by their reticulation (Epiphen RE6513N resin),  $c_{r0}k_{pc00}$  is unknown and consequently it can be replaced as  $D$  parameter.

$$\eta = \eta_0\left(1 + D \exp(\beta c_{h0}) \exp\left(-\frac{\gamma}{RT}\right)\tau\right)^\alpha \exp(-\delta T) \quad (26)$$

So time and temperature evolution of a reticulating resin viscosity is a complex process which depends on four (relation 17) or five (relation 26) parameters. It is important to show that the temperature of reticulating media, when the process is not temperature-controlled, varies due to reaction heat generation. For the experiment with falling drop on an inclined plane surface, geometric conditions show that the flowing surface temperature is practically equal with the flowing resin temperature. Looking to the model of the flowing drops on the inclined surface, it appears that the flowing equation will be used to obtain an estimation of time evolution of the hardening resin. It is considered that, for a small time interval (with report to resin gel time), the resin drop flows in a steady state evolution. Moreover, the  $x$  axis velocity is near to constant and so from (1) and (3) relation (27) is obtained. This relation can be integrated after  $y$  from 0 to  $\delta_r$ , with results in (28).

$$\rho g \sin \alpha = \frac{d\tau_{yx}}{dy} \quad (27)$$

$$\tau_{yx} = \rho g \delta_r \sin \alpha \quad (28)$$

Coupling expression (28) of  $\tau_{yx}$  with Newton law in expression (3), where the  $y$  gradient velocity is considered  $w_x / \delta_r$ , produces relation (29) which shows how to find the liquid resin viscosity (by measuring film length evolution in time, there is  $w_x$  versus time and consequently, by relation (29),  $\eta$  versus time).

$$\eta = \frac{g}{w_x} \rho \delta_r^2 \sin \alpha \quad (29)$$

This method of flow on the inclined plane has been used to identify the rheological behaviour of liquid, suspensions or poly-phase systems without internal reaction [13,14]. The extension of this method to identify parameters of rheokinetics models characterizing the reticulation of some resins is the basic aim of this paper, with Epiphen RE6513N reticulation being the particular analyzed case.

## Experimental part

### Materials

The materials were used in their commercial state. The commercial resin Epiphen RE6513N has the basic resin as bisphenol - epichlorhidine polycondensate epoxy. Near to more specific additives it contains Aluminium powder, with 20  $\mu\text{m}$  mean particle diameter, at 20% concentration level. The very good wetability of carbon fibres tissues used in composite near to its low viscosity has the criteria for their selection as basic materials for composite manufacturing. The hardener Epiphen DE 7513 contains benzyl - dimethyl - amine as active component.

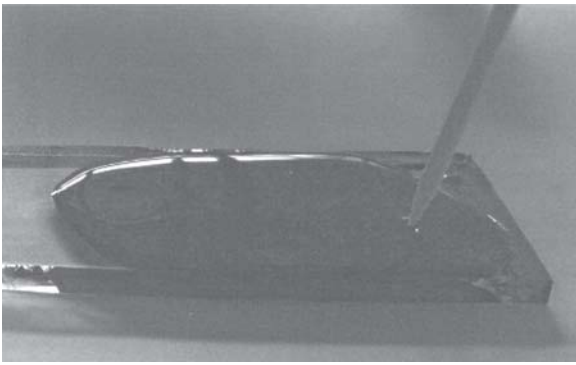


Fig. 2. Measuring gel time at 28°C

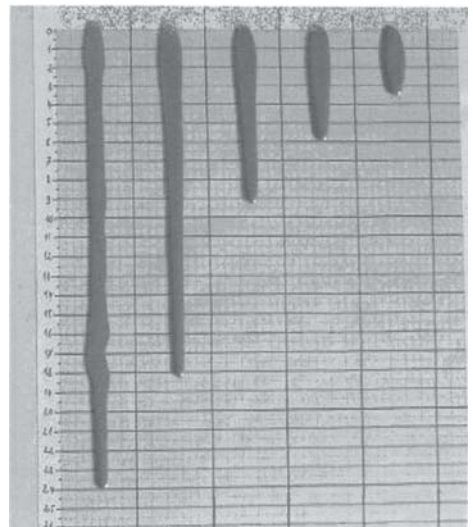
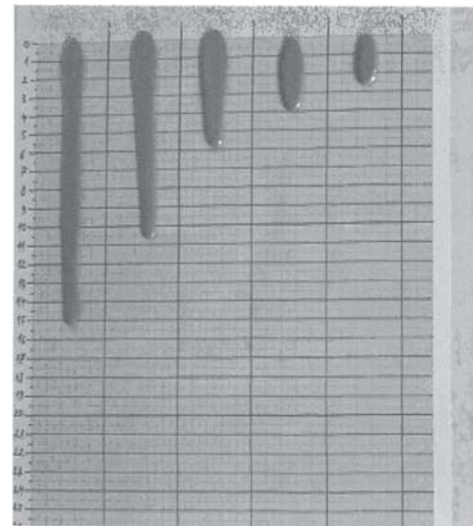


Fig. 5. Next day photos of both glasses (fluid completely cured at 28°C) 20 degrees tilt angle (left) and 30 degrees tilt angle (right)

Sample 1, 0 min      Sample 2, 20 min

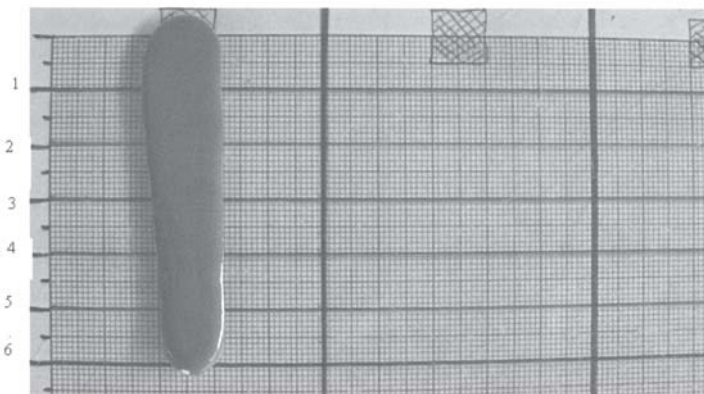


Fig. 3. A 0.5 mL resin-hardener mixture drop flowing, at 28°C, on a 20-degree tilted glass

sample 1    sample 2    sample 3    sample 4    sample 5

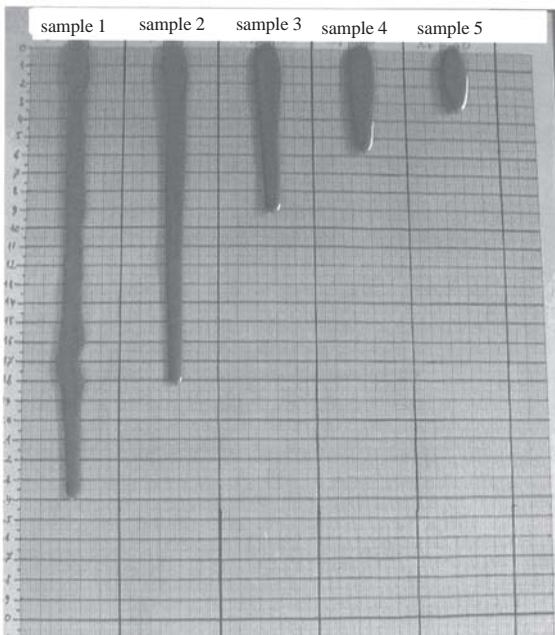


Fig. 4. Drops flowing at 28°C on 30-degree tilted glass, as they appear at 120 min after curing process started

#### Experimental procedure and plant

The resin – hardener mixture (Epiphen RE6513N - Epiphen DE 7513) has been prepared, in the appropriate proportions and also used when making CFRAI samples. Small quantities, in the amount of 0.5 mL, were dropped at 20-min intervals on two different glass beds, one tilted at 20 degrees, the other at 30 degrees with respect to the horizontal plane. After every 20 min, the distance traveled on the glass by the respective resin drop was recorded,

along with the thickness of the fluid film in the area. Gel time was also measured to be of around 90 min (fig. 2). So the latest sample poured on the glasses was 80 min after the resin – hardener mixing took place, thus ensuring that the fluid would still flow onto the tilted glasses.

To obtain the basic experimental device, a cube with 0.2 m basic dimension, made of transparent plastic sheets, was cut along the diagonal plane. For each part, a new cutting has been made with the purpose to displace the diagonal plane from 45 to 30 and 20 degrees, respectively. Water resistant milimetric paper was put below the glasses, which represents the drops film flowing surface, before those sticking with one processed cube part. Under the inclined surface there is water of constant temperature from a thermostat. In figure 3, one can see how a 0.5 mL resin-hardener mixture drop actually flows, to 28°C, on a tilted glass (20 degrees inclination in this case). Figures on the left of the image mark centimeters, while millimeters are directly visible on the white-blue paper underneath the glass. Drops were poured on the glass at 20 min intervals with a graded syringe. While the first drop flows on the glass, the curing process taking place in the same time, the fluid for the next drops already started to cure inside the syringe, so the following drop, 20 min away from the previous one, is poured on the glass after it had already flowed on the glass should not be reached, nor surpassed, by the following drop, fact demonstrated by the experimental measurements and which can be easily

**Table 1**  
MEASURED PARAMETERS OF RESIN FLOW ON THE 20-DEGREE TILTED GLASS

Distances and thickness in mm vs. time (min) for resin flow at 28 C on 20 degree inclined surface						
Measured parameter	Time of measurement	Time of sample put on glass				
		0	20	40	60	80
thickness	20	0.42				
distance		13.40				
thickness	40	0.60	0.68			
distance		15.10	9.80			
thickness	60	0.32	0.58	0.96		
distance		15.40	10.80	5.70		
thickness	80	0.32	0.42	1.00	1.30	
distance		15.40	10.80	6.00	4.00	
thickness	100	0.32	0.42	1.00	1.22	1.68
distance		15.40	10.80	6.00	4.10	1.80
thickness	120	0.32	0.42	1.00	1.22	1.70
distance		15.40	10.80	6.00	4.10	1.90

**Table 2**  
MEASURED PARAMETERS OF RESIN FLOW ON THE 30-DEGREE TILTED GLASS

Distances and thickness in mm vs time (min) for resin flow at 28 C on 30 degree inclined surface						
Measured parameter	Time of measurement	Time of sample put on glass				
		0	20	40	60	80
thickness	20	0.33				
distance		19.60				
thickness	40	0.41	0.70			
distance		23.40	16.30			
thickness	60	0.31	0.61	1.00		
distance		24.00	18.10	8.80		
thickness	80	0.30	0.42	0.59	1.20	
distance		24.10	18.30	9.35	5.85	
thickness	100	0.30	0.42	0.59	1.00	1.50
distance		24.10	18.30	9.35	6.00	3.50
thickness	120	0.30	0.42	0.59	1.00	1.55
distance		24.10	18.30	9.35	6.00	3.60

**Table 3**  
COMPUTED FLOW RATES ON 20-DEGREE TILTED GLASS

Flowing velocity (mm/min) vs. time (min) on 20 degree inclined surface						
Time of measurement	Time of sample put on glass					
	0	20	40	60	80	
20	0.67000					
40	0.08500	0.49000				
60	0.01500	0.05000	0.28500			
80	0.00000	0.00000	0.01500	0.20000		
100	0.00000	0.00000	0.00000	0.00500	0.09000	
120	0.00000	0.00000	0.00000	0.00000	0.00500	

**Table 4**  
COMPUTED VISCOSITIES ON 20-DEGREE TILTED GLASS

Resin viscosity (Pa.s) vs. time (min) for flow at 28 C on 20 degree inclined surface						
Time of measurement	Time of sample put on glass					
	0	20	40	60	80	
20	0.022813					
40	0.366975	0.081766				
60	0.591509	0.582960	0.280189			
80			5.776457	0.732166		
100				25.793036	2.717245	
120						50.081883

observed in figure 4. One can observe the almost-linear variation of the travelled distances, which can be seen in a picture showing both glasses (20 and 30-degree inclination), taken the next day, when the resin – hardener mixture was completely cured. Details are in figures 5.

The measurements of resin flowing dynamics at a constant temperature were recorded into a triangle-like matrix, each matrix element being a vector with two components:

- a measured value for the traveled distance on the glass (lower cell number);
- a measured value representing the thickness of the fluid film in the area of the travelled distance.

Both values are expressed in millimeters and measurements were taken from 20 to 20 min. These experimentally – measured parameters were of great help in calculating several values of the fluid viscosity during the curing process. For working temperature of 28°C, details are presented in tables 1 and 2.

*Data processing and rheokinetic models parameters identification*

The experiment described for 28°C as working temperature was repeated when the surface of the drops film flow has the temperature of 18 and 38°C, respectively. Thus, some basic measurements exist, allowing one to obtain a matrix showing time and temperature dependency of the hardening resin. This matrix serves for rheokinetic

**Table 5**  
COMPUTED FLOW RATES ON 30-DEGREE TILTED GLASS

Resin velocity (mm/min) vs. time for flow at 28 C on 30 degrees inclined surface					
Time of measurement	Time of sample put on glass				
	0	20	40	60	80
20	0.98000				
40	0.19000	0.81500			
60	0.03000	0.09000	0.44000		
80	0.00500	0.01000	0.02750	0.29250	
100	0.00000	0.00000	0.00000	0.00750	0.17500
120	0.00000	0.00000	0.00000	0.00000	0.00500

**Table 6**  
COMPUTED VISCOSITIES ON 30-DEGREE TILTED GLASS

Resin viscosity (Pa.s) vs. time (min) for flow at 28 C on 30 degrees inclined surface					
Time of measurement	Time of sample put on glass				
	0	20	40	60	80
20	0.014076				
40	0.112069	0.076157			
60	0.405764	0.523707	0.287885		
80	2.280046	2.234445	1.603402	0.623602	
100				16.889231	1.628604
120					60.864565

model parameters identification. Rheokinetic models (17) and (26) are here used by relation (30) and (31), respectively, as experiments are available at only one value of the hardening agent concentration  $c_{ho}$ .

$$\eta = B' \tau^b \exp\left(-\frac{C}{RT}\right) \quad (30)$$

$$\eta = \eta_{00} \left(1 + D' \exp\left(-\frac{\gamma}{RT}\right) \tau\right)^\alpha \exp(-\delta T) \quad (31)$$

Turning now to data processing, the following algorithm has been proposed:

- a) select working temperature (ex. 28°C);
- b) for flow on the inclined plane of 20 degree use, for each sample, the measurement  $L_x$  vs.  $\tau$  (distance vs. time) and  $\delta_x$  vs.  $\tau$  (thickness vs. time) to obtain:
  - b<sub>1</sub>) the dependency  $w_x$  vs.  $\tau$  (table 3);
  - b<sub>2</sub>) the dependency  $\eta_x$  vs.  $\tau$  (table 4);
- c) repeat step b for the flow on inclined plane at 30 degrees (tables 5 and 6);
- d) for matrix of dependency  $\eta$  vs.  $\tau$  obtained at b and c, introduce a media rule (at the same time the characteristic resin viscosity is the mean value of samples viscosities (table 7);
- e) compute the mean value of viscosities obtained, at the same time, for flow on 20 and 30-degree inclined planes, accepting the independency of viscosity vs. stress (table 7), otherwise try to find this dependency and use the viscosities mean value by this dependency;

Matrix of experimental data	Identified parameters model (30)	Identified parameters model (31)
$\eta := \begin{pmatrix} 0.014 & 0.015 & 0.091 & 0.21 & 0.87 & 3.14 \\ 0.012 & 0.018 & 0.162 & 0.45 & 2.442 & 11.935 \\ 0.008 & 0.38 & 0.49 & 1.21 & 6.99 & 34.41 \end{pmatrix}$	$B' = 177,7$ $b = 1.43$ $C = 9.39 \cdot 10^7$	$D = 0.019$ $\gamma = 8.821 \cdot 10^6$ $\alpha = 1.639$ $\delta = 0.054$

**Table 7**  
MEAN VISCOSITIES (PA.S) VS. TIME FOR FLOW AT 28°C

Plane angle	20 min	40 min	60 min	80 min	100 min
20 degrees	0.022	0.229	0.481	3.0	14.62
30 degrees	0.014	0.0945	0.42	1.684	9.25
mean	0.018	0.162	0.45	2.442	11.935

f) fill in the matrix showing time and temperature dependency, the line corresponding to the selected temperature;

g) repeat steps b to f for other working temperatures;

h) use the matrix showing time and temperature dependency to plot the time dependency of the hardening resin viscosity having the temperature as graphic parameter;

i) minimize the functional

$$\Phi(B', b, C) = \sum_j \sum_i \left( \eta_{ij} - B' \tau_i^b \exp\left(-\frac{C}{RT_j}\right) \right)^2$$

for identification of  $B'$ ,  $b$ ,  $C$  from relation model (30);

j) minimize the functional

$$\Phi(D', \gamma, \alpha, \delta) = \sum_j \sum_i \left( \eta_{ij} - \eta_{00} \left(1 + D' \exp\left(-\frac{\gamma}{RT_j}\right) \tau_i \right)^\alpha \exp(-\delta T_j) \right)^2$$

for identification of  $D'$ ,  $\gamma$ ,  $\alpha$ ,  $\delta$  from relation model (31).

With respect to working temperature of 28°C, the application of proposed algorithm appears in tables 3 to 7. Figure 6, where experimental data processed by the algorithm is presented, shows the dependency of resin hardening viscosities vs. time with temperature as graphic parameter. Based on these data, a classical soft has been used for model parameters identification with respect to functional  $\Phi(B', b, C)$  or  $\Phi(D', \gamma, \alpha, \delta)$ . Table 8 concentrates experimental data showing resin viscosity dependence on time and temperature and the identification results of the unknown parameters of models (30) and (31). Results are transposed into relations (32) and (33). Due to the

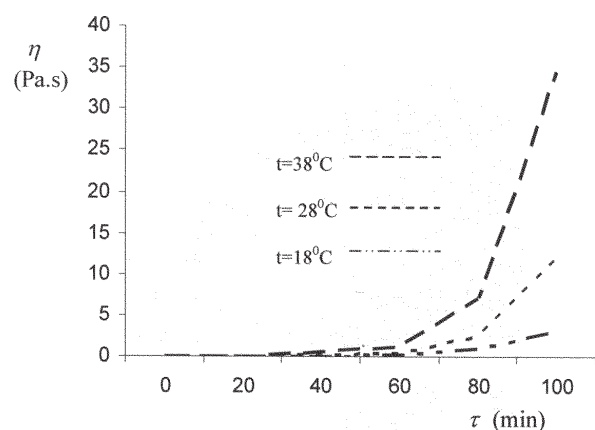


Fig. 6. Viscosity of hardening resin vs. time and temperature

**Table 8**  
EXPERIMENTAL MATRIX OF  $\eta(\tau, t)$  AND IDENTIFIED PARAMETERS OF MODELS (30) AND (31)

procedure used in parameters identification models, these relations are reliable.

$$\eta = 171.7 \tau^{1.43} \exp\left(-\frac{9.39 \cdot 10^7}{R(273+t)}\right) \quad (32)$$

$$\eta = 0.008 \left(1 + 0.019 \exp\left(-\frac{8.82 \cdot 10^6}{R(273+t)}\right)\tau\right)^{1.63} \exp(-0.054(273+t)) \quad (33)$$

## Results and discussions

In selecting of hardening diagram (time temperature evolution for this manufacture phase) of CFRAI composites, the detailed known of the binder hardening (in the presented case, Epiphen RE6513N (28% Al powder with  $d_p < 20 \mu\text{m}$ ) with Epiphen DE 7513 hardener at 0.1 level of volumetric ratio) is of great importance. With an inadequate hardening diagram, mechanical properties of CFRAI composites can be strongly affected. The rheokinetic model, which has been theoretically derived and practically particularized by means of experimental data, shows that near the ratio of resin / hardener, temperature and time determine the increase of the viscosity of the hardening resin. Both considered models show that the hardening resin viscosity depends on time upon a power law with a power between 1.43 – 1.63 (1.43 for model (32) and 1.63 in model (33)). That is in compliance with some published data on some other polymerization cases [15,16]. The dual effect of temperature on the viscosity of the hardening resin is observed only by model (33), in which the term  $\exp(-0.054(273+t))$  shows that the resin, as a liquid, decreases its viscosity when the temperature increases, whereas the terms  $0.019 \exp(-\frac{8.82 \cdot 10^6}{RT})$  as a global reticulation reaction constant, demonstrates the increase of reaction rate and, consequently, the increase of hardening resin viscosity.

The comparison between the effects given by these terms on viscosity dynamics shows that the first term can be neglected. This observation finds out model (32). Both models yield that resin reticulation is an exothermic process having activation energy around of  $10^7 \text{ J/kmol}$  when the process is assumed as a polycondensation reaction, and close to  $10^8 \text{ J/kmol}$  if it is observed as a radicalic polymerization.

First of all, the paper importance consists in experimental and modeling (including data processing algorithm) particularization of flow on an inclined plane surface in order to analyze the hardening of a resin. Despite of several critical aspects ((a) it is difficult to accept steady state flow for long time interval, (b) the film thickness is not constant over it width, (c) solvent evaporation from falling film is neglected, (d) reporting of extreme kinetic models of reticulation, etc.) the presented analysis procedure of the resin hardening, has some major advantage: I) it can be used for many resin cases; II) it uses a very simple experimental device; III) it has a simple data processing procedure; IV) it can be further developed in order to cover coherently most of the critical aspects.

## Conclusions

During the development and manufacturing of CFRAI composites, there has been a need to appeal to various theoretical measures mainly known by more experimental-oriented investigations. The basic guideline here is obtaining a composite having the capacity to support very strong pointy and localized mechanical loads (explosion, ballistic impact, controlled impact etc.). Some

results, reported in figures 1 to 4, sustain that this objective has been attained. In CFRAI manufacturing, the hardening diagram, which shows how temperature regime of the composite pressed system changes with time, is of high importance for material quality. The use of a rheokinetic model characterizing the resin hardening helps developing that diagram.

A simple experimental procedure coupled with an adequate mathematical model has the possibility to give all the information characterizing the resin hardening dynamics. For the Epiphen RE6513N – Epiphen DE 7513 systems, two rheokinetic models have been considered. Both models show that the system viscosity depends upon time to the power between 1.45 – 1.75. Temperature affects the system viscosity, especially, according Arrhenius law for exothermic homogeneous processes. Depending on considered polymerization kinetics, average activation energy of the accepted reactions has been identified.

## Symbols

$w$  - flow velocity  
 $x$  - coordinate along fluid flow  
 $y$  - coordinate normal to flow  
 $g$  - gravitational acceleration  
 $c$  - concentration  
 $X$  - conversion of reticulating species  
 $l$  - width of flowing film  
 $L$  - length of flowing film  
 $m$  - drop mass  
 $K$  - onstant in relation (8) and (22)  
 $N$  - polymerization degree  
 $k$  - reaction rate constant  
 $f$  - initiator efficiency  
 $a$  - constant power in relation (8)  
 $b$  - constant power in relation (8)  
 $A$  - constant in relation (15) derived from (14)  
 $B$  - constant in relation (17) derived from (16)  
 $C$  - constant in relation (17) derived from (16)  
 $D$  - constant in relation (26) derived from (25)  
 $B'$  - constant in relation (30)  
 $D'$  - constant in relation (31)

## Greek Symbols

$\tau$  - time or stress tensor in relation (27)  
 $\eta$  - viscosity  
 $\rho$  - density  
 $\alpha$  - inclined plane surface angle or constant in relation (22)  
 $\delta$  - film thickness or constant in relation (25)  
 $\gamma$  - constant in relation (25)

## Subscripts

$x$  - flow direction  
 $r$  - basic reticulating species and resin film in (2) and (7)  
 $ro$  - initial basic reticulating species  
 $i$  - initiation  
 $p$  - propagation  
 $t$  - termination  
 $ho$  - initial hardening species  
 $pc$  - polycondensation  
 $yx$  - stress tensor pane and direction

*Acknowledgements:* This work was performed within CNCSIS grants, codes TD-13/2007 and ID -1031/2007.

## References

1. TACHE, F., STANCIU, V., CHICIUDEAN, T.G., TOMA, A.C., STOICA, A., DOBRE, T., Statistical Risks in High Performance Nano-Composites Technology for Space Structures, The 57<sup>th</sup> International Astronautical

- Congress, Valencia, Spain, October 2006 (IAC-06-C2.8.04), IAC 2006 DVD Proceedings, 2006
2. ZGURA, GH., MOGA, V., Bazele proiectării materialelor compozite (Basics of Composite Materials Design), Editura Bren, Bucuresti, 1999
  3. TACHE, F., DOBRE, T., CHIRILUS, A. A., Optimization and Modeling of CFRPI Properties and Manufacturing Technology, The 59<sup>th</sup> International Astronautical Congress, Glasgow, October 2008, (IAC-08-C2.1.5), IAC 2008 DVD Proceedings, 2008
  4. \*\*\* [http://en.wikipedia.org/wiki/Plain\\_weave](http://en.wikipedia.org/wiki/Plain_weave), Plain weave – Wikipedia, 2008
  5. DOBRE, T., SANCHEZ, J.M., Chemical Engineering –Modelling, Simulation and Similitude, Chap. III, 35-48, Wiley VCH, 2007
  6. MALKIN, A. Ya., KULICHIKHIN S. G., Rheokinetics, Hiithig & Wepf, Heidelberg, Germany, 1996
  7. CIOFFI, M., HOFFMANN, A. C., JANSSEN, L. P. B., Polym. Eng. Sci, **41**, 2001, p.595
  8. MALKIN, A. Ya., KULICHIKHI, S. G., EMEL'YANO, D. N., SMETANINA. I. ., RYABOKON, N. V., Polymer, **25**, 1984, p.778
  9. CIOFFI, M., Rheokinetics – Ph D Thesis, Rijksuniversiteit, Groningen 2002, ISBN 90-367-1657-8, p 38
  10. MALKIN, A.YA., Polym. Eng. Sci., **20**, 1980, p.1035
  11. MALKIN, A.YA., NESYN, G.V., ILYUSNIKOV, A.V., MANZHAI, V.N., J. Rheology, **44**, 2000, p.371
  12. A.KH. BULAI, V.N. KLYUCHNIKOV, YA.G. URMAN, I.YA. SLONIM, L.M. BOLOTINA, VA. KOZHINA, M.M. GOL'DER, S.G. KULICHIKHIN, V.P. BEGHISHEV, A.YA. MALKIN, Polymer, **28**, 1987, p.1349
  13. MØLLER, P. C. F., MEWIS, J., DANIEL, B., Soft Mater, **2**, 2006, p.274
  14. CHANSON, H., COUSSOT, P., JARNY, S., TOCQUER, L., A study of dam break wave of thixotropic fluid: Bentonite surges down an inclined plane, University of Queensland Department of Civil Engineering, Report 54/04, 2004, ISBN 1864997710, p.47
  15. YEMELYANOV, D.N., SMETANINA, I.YE., VINOGRADOV, G., Rheol. Acta, **21**, 1982, p. 280
  16. MALKIN, A.YA., NESYN, G.V., ILYUSNIKOV, A.V., MANZHAI, V.N., J. Rheology, **44**, 2000, p.371

---

Manuscript received: 20.10.2009