Monitoring the Processing Temperature of the Polymeric Matrix Composite Materials

GHEORGHE AMZA[1], MARINELA MARINESCU[1], ANGELA MORARU[1], CATALIN GHEORGHE AMZA[1]*, NICOLAE NEGUT[2], GINA STOICA[1]

[1] University Politehnica of Bucharest, 313 Splaiul Independenþei, 060042, Bucharest, Roamania

[1] University Politehnica of Timisoare, 1 Mihai Viteazul Blvd., 300222, Timisoara, Romania

This paper presents a monitoring methodology of the processing temperature for the polymeric composite materials. An experimental stand was realized consisting of a computer with an acquisition card and the LabVIEW software that allows the real time monitoring of the composite materials temperature during the processing through the aid of a new heat sensor LM 335Z. This digital sensor had proved to be more efficient than the classical thermo-couplings. Using the LabVIEW software, a virtual instrument called "Virtual Thermometer" was created. This virtual instrument has the same functions as a real instrument, but with a much more complexity as well as the possibility of real time measuring, save, analysis and presentation of the collected data.

Keywords: monitoring, polymeric composites, virtual instrument

The most used advanced composite materials are realized from the thermo-rigid or thermo-plastic polymeric matrix that is reinforced with fibers of various lengths and nature. The quality of the part obtained this way is directly influenced by the curing time, temperature and pressure [8]. This is why, the understanding of the reticulation process is very important through the design of an optimum curing cycle and the selection of a corresponding process monitoring method [3, 4]. All this factors are the framework of obtaining superior quality composites.

In order to optimize the processing of these composites one must find the key elements during the manufacturing process through proper monitoring of this process. Thus, one must realize that composite matrix properties are dependent of the thermokinetic and chemio-rheologic of the selected polymer. The variation of the chemio-rheological properties such as the degree of reticulation and viscosity, are determined by the parameters of the processing cycle: pressure, temperature, reticulation time, etc. [14, 11].

If one assumes that the heat generation speed during reticulation is proportional with the speed of the reticulation reaction [7, 10], then the hardening degree α, of the resin can be defined as:

$$\alpha = \frac{H(t)}{H_R} \qquad (1)$$

where $H(t)$ is the developed heat (per mass unit of the composite), from the beginning of the reaction until moment "t" and H_R is the total reaction heat per mass unit of the composite during reticulation.

The reaction heat can be expressed as follows:

$$H_R = \frac{\rho_r}{\rho_{sfp}} v_r H_r \qquad (2)$$

where:

ρ_r is the resin density;

ρ_{sfp} - the impregnated pre-form density;

v_f - the volumetric fraction of the resin;

H_r is the total reaction heat per mass unit of the resin.

H_r can e determined from the resulting data of the differential scanning calorimetry (DSC) of several pure resin samples.

For an unhardened resin, α is zero and for a reticulated resin, α is almost an unit. Equation (1) transforms into:

$$H = \frac{d\alpha}{dt} H_R \qquad (3)$$

where: ratio *da/dt* is defined as reaction or reticulation speed. For a thermo-rigid resin, the reticulation speed depends on the temperature and the degree of reticulation [13,14]. In the case of composite materials with matrix made of epoxy resins that use amines as hardener, the typical expression of the reticulation speed *da/dt* is:

$$\frac{d\alpha}{dt} = \left(k_1 + k_2\alpha^m\right)\left(1-\alpha\right)^n \qquad (4)$$

where: k_1 and k_2 are the speed constants, and m and n are the kinetic exponents. The sum $(m+n)$ refers to the level of the general reaction. Temperature dependence of the speed constants is given by the Arrhenius-type formulas:

$$k_1 = A_1 \exp\left[\frac{-E_1}{RT}\right]; \quad k_2 = A_2 \exp\left[\frac{-E_2}{RT}\right]; \qquad (5)$$

where:

A_1 ºi A_2 are pre-exponential Arrhenius factors,

E_1 and E_2 are the Arrhenius activation energies, and R is the gas constant.

Experimental part

In order to monitor the processing parameters of the intelligent composite materials with polymeric matrix (temperature, pressure, viscosity, degree of reticulation, etc.) an experimental stand was designed and implemented. Its scheme is presented in Figure 1. It comprises the following: load amplifier, power amplifier, computer with acquisition card LabVIEW, processing installation of the composite material in which the vibrating probe and temperature sensors were embedded.

* email: acatal@camis.pub.ro

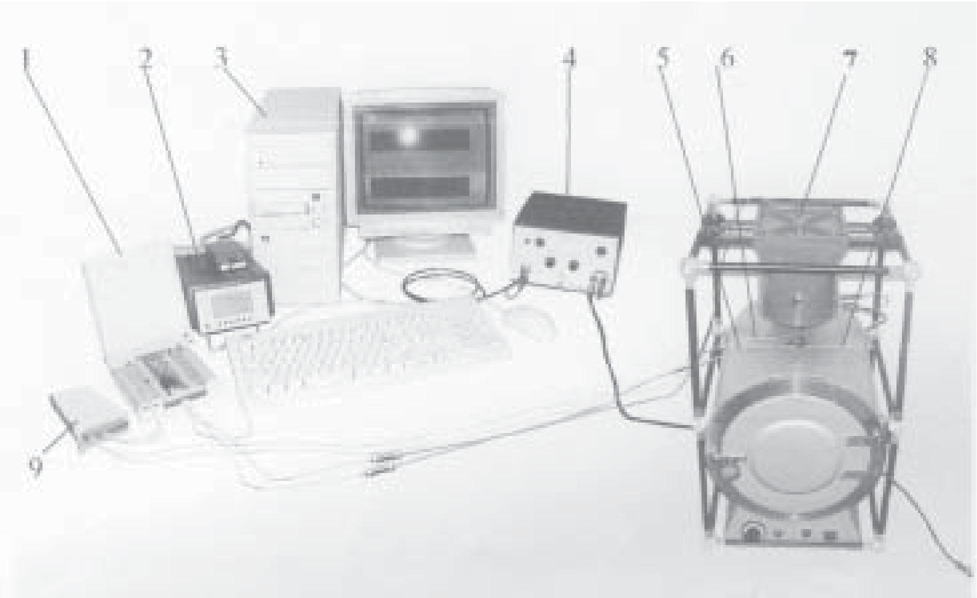

Fig. 1. Real time monitoring stand of the composite material with polymeric matrix processing: 1 – connectors box, 2 – charge amplifier, 3 – PC, 4 – power amplifier, 5- temperature sensor, 6 – thermo-coupling; 7 – electro-dynamic excitator, 8 – oven, 9 – amplification block

The stand was created on the idea of having a sensor with its functioning principle based on the mechanical impedance. The implementation of this experimental stand allowed the real time measurement of the viscoelastic properties of the thermoreactive polymeric resins and of composite materials with such a matrix, the determination of the dynamic mechanic characteristics of the studied composite structure and the determination of the processing degree of the composite material. The system thermically analyses the composite material in real time, giving information regarding the composite material temperature evolution during processing and spectral analysis (frequency analysis of the composite system studied). This gives information about the state of the composite material processing and time evolution of its mechanical properties.

During the reticulation process, the mechanical dynamical properties of the composite material are controlled mainly by two factors : temeprature and the degree of reticulation of the resin. Because temperature influences heavily the degree of reticulation, one of the most important parameter of the processing is is the treating temperature of the material [3,7].

For the monitoring of the temperature variation within the composite material during its processing at various temperatures, a new type of temperature sensor was proposed LM 335Z and a virtual instrument called “VI Thermometer” was created with the aid of LabVIEW. Virtual instrumentation programs allow the realization of virtual apparatus more efficient at low cost compared to real apparatus [2].

The virtual thermometer has the same functions as a real apparatus, but has a much higher complexity and the possibility of saving the data measurements. Thus, the instrument is capable of monitoring, acquisitioning and graphical representing temperature evolution during composite processing, independent on two channels that can be extended to 8 channels. The acquisition period and the number of acquisition per channel can be modified. The “VI Thermometer” can be used for temperature monitoring during the processing of any composite material with polymeric matrix or other nature.

The instrument frontal panel for temperature acquisition is presented in figure 2, and its block diagram in figure 3.

Results and discussions

The matrix of the studied composite material is made out of a epoxy resin of type DGEBA – Epilox T19-36 and its corresponding hardener in liquid state H 10-30. Both are produced by the German company Leuna-Hartze GmbH, and their characteristic are presented in Table 1. This resin-hardener system is a new one, improved by the producer

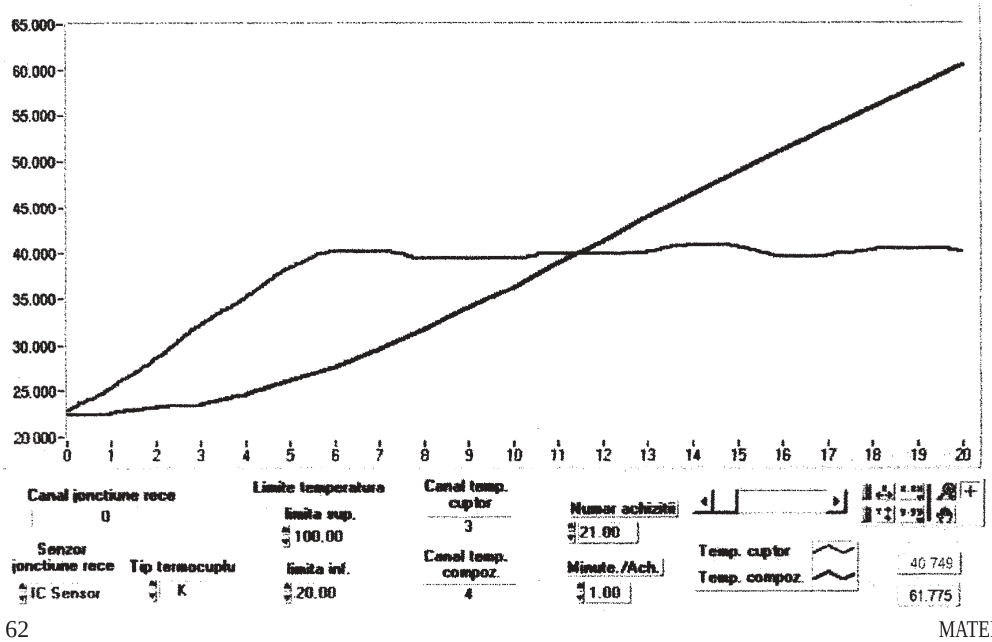

Fig. 2. Front panel of the virtual instrument for temperature acquisition

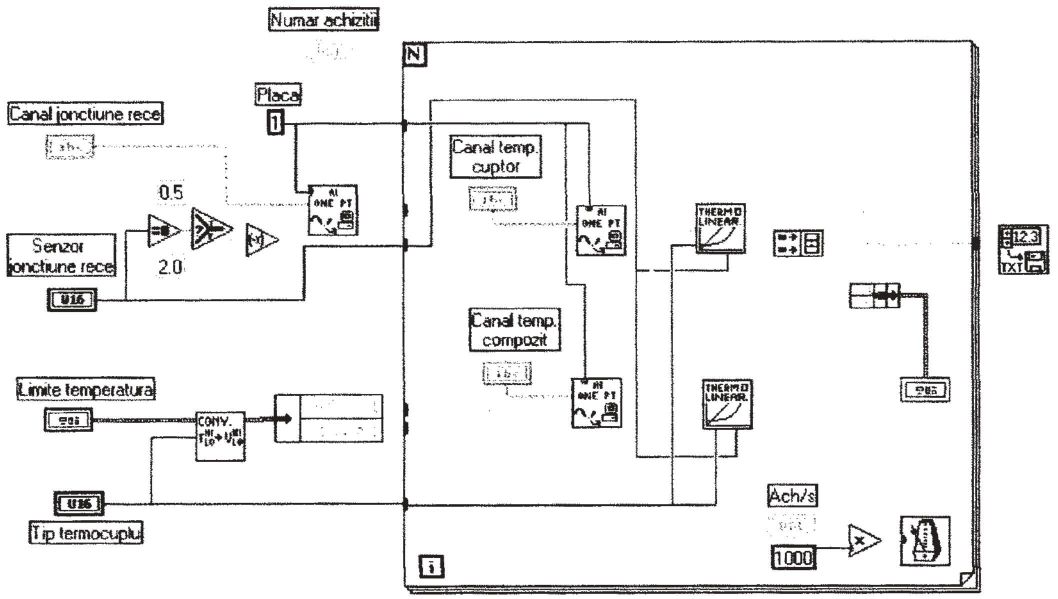

Fig. 3. Block diagram of the virtual instrument for temperature acquisition

Table 1
CHARACTERISTICS OF THE RESIN AND HARDENER USED IN THE EXPERIMENTS

Characteristics	Resin "Epilox T 19-36"	Hardener "H 10-30"
Viscosity la 25°C [mPa·s] (DIN 53 015)	1000 - 1300	180 - 280
Epoxy Equivalent Weight [g] (DIN 16 945)	190 - 210	-
Amine Equivalent Weight[g] (DIN 16 945)	-	85
Amine Value [mg KOH/g] (DIN 16 945)	-	300 - 360
Density at 20 °C [g/cm^3] (DIN ISO 4630)	cca.1,14	1,03 ± 0,02

Table 2
EWR 300 GLASS FIBER CHARACTERISTICS

No.	Properties	EWR 300
1	Specific weight (g/m^2)	315± 10%
2	Width (cm)	100± 5%
3	Thickness (mm)	0,3± 0,05%
4	Length density – weave (tex)	320
5	Cloth (roving/10 cm)	40±2
6	Ancolant content (max) %	1,0

by the use of a modified cycloaliphatic polyamine - type hardener in order to obtain high quality products made out of this mixture and to give the computed values for certain properties dictated by the beneficiary/client.

The reinforcement material used was roving weave of glass fibers E, with continuous filaments "EWR-w-300" produced by the Romanian company FIROS S.A. The characteristics of the glass fiber are presented in Table 2. The composite was realized in 20 layers of glass fibers with $[0/90]_{20}$ topology. In all experiments, both the temperature sensor and the vibrating probe were placed in the middle of the material, between layers 10 and 11 [3, 5, 6, 9].

Using the LM 335 Z sensor, one can monitor the temperature developed during the processing of a composite material at this temperatures. Furthermore, by the aid of the vibrating probe which is moving inside the composite material under the action of the electro-dynamic excitation, can be followed the influence of processing temperature over the phase transformation of the composite material, by resonance frequency modification in time as well the mechanical dynamic characteristics of the composite material. This paper presents the experimental results obtained due to processing temperature monitoring. The rest of experimental data will be presented in a future paper.

The experiments were performed at various curing temperatures of the composites materials: 25, 40 and 50°C. Because the resin-hardener system is a mixture aimed at both cold and warm processing (through modification of the quantity of hardener) several tests were performed at processing temperatures of 60 and 70°C.

Before using the LM335Z sensor, one needs to calibrate it. LM335Z is a temperature sensor with digital circuitry. It has a high precision and operates like a Zenner terminal (avalanche). When it is calibrated at 25°C, the LM335Z sensor has a typical error smaller than 1°C over a scale of 100°C. The output signal of the sensor V_{OUTT} is computed with the relation:

$$V_{OUT_T} = V_{OUT_{T_0}} \frac{T}{T_0} \qquad (6)$$

where :

T is the unknown temperatuire ;

T_o – reference temperature (in K).

A calibration variant for ease of reading is depicted in Figure 4a and b. Allowing to control the output voltage at a nominal value equivalent to the reference temeprature (25°C), by modifying the value of resistor 1. The output signal is calibrated at 10 mV/K. As a result of calibration, the output signal that is read correctly for a certain temperature is also correct for other temperatures. The

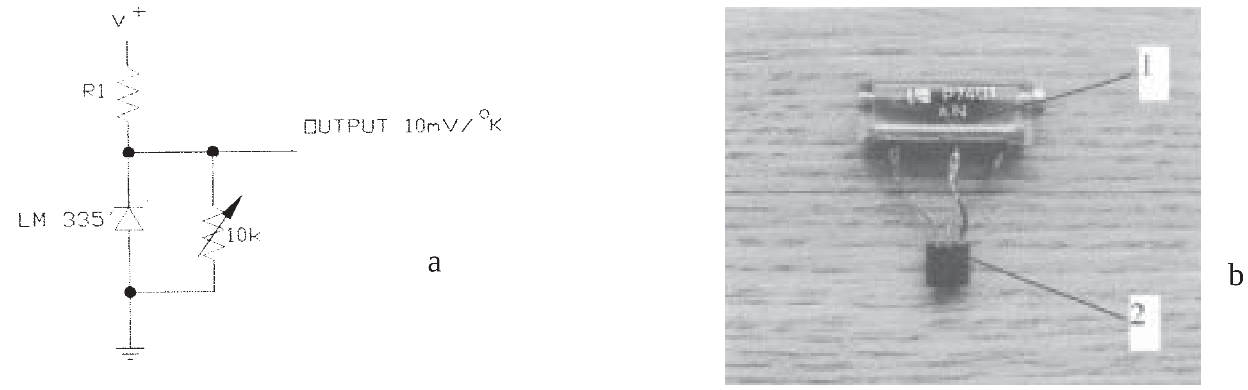

Fig. 4. LM 335Z sensor: a - Electrical scheme of the LM335Z sensor calibration; b - LM 335Z sensor calibration : 1 – variable resistor of 10 KΩ; 2 –LM 335Z sensor

Table 3

VOLTAGE VALUES AS A FUNCTION OF TEMPERATURE FOR THE CALIBRATION PROCESS OF LM 335Z SENSOR

No.	Temperature [K]	Voltage [V]	No.	Temperature [K]	Voltage [V]	No.	Temperature [K]	Voltage [V]
1	293.15	2.932	9	333.15	3.332	17	373.15	3.732
2	298.15	2.982	10	338.15	3.382	18	378.15	3.782
3	303.15	3.032	11	343.15	3.432	19	383.15	3.832
4	308.15	3.082	12	348.15	3.482	20	388.15	3.882
5	313.15	3.132	13	353.15	3.532	21	393.15	3.932
6	318.15	3.182	14	358.15	3.582	22	398.15	3.982
7	323.15	3.232	15	363.15	3.632	23	403.15	4.032
8	328.15	3.282	16	368.15	3.682	24	408.15	4.082

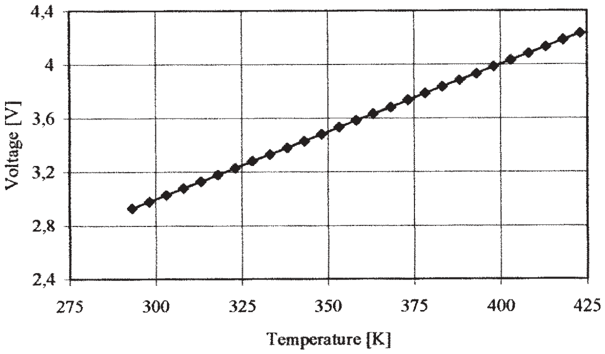

Fig. 5. Calibration curve of the LM 335Z sensor

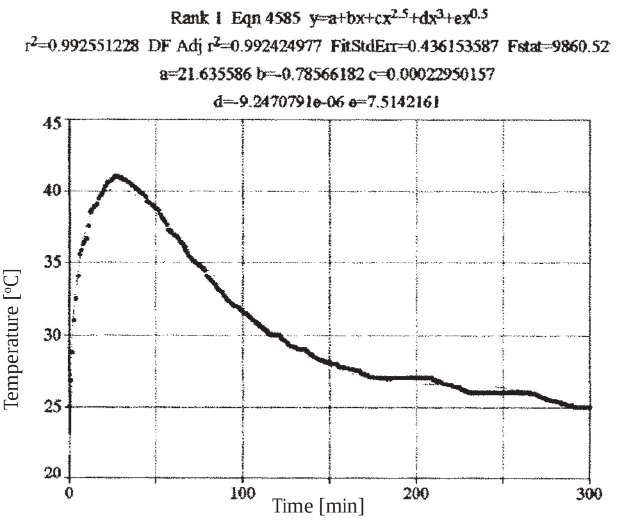

Fig. 6. Temperature variation curve approximation with an polynomial function of the composite curing at 25⁰C

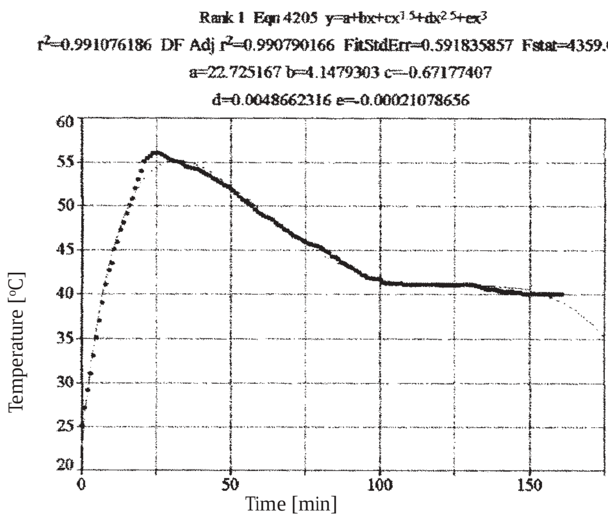

Fig. 7. Temperature variation curve approximation with an polynomial function of the composite curing at 40⁰C

calibration curve is presented in figure 5. Table 3 presents tha values of the voltage as a function of temperature.

The temperature developed inside the composite material during processing was acquired with the aid of “VI Thermometer” created with the LabVIEW software. The LM 335Z sensor was linked at the I/O box, the electric signal generated (voltage) being amplified in order to be accepted by the acquisition card. The computer, through the virtual instrument had the role of storing, processing and displaying in real time the temperature evolution inside the composite material. The temperature values are written with subVI “Write to Spreadsheet File” in a text file for future analysis. This analysis was realized based on statistical indicators.

Experimental data were processed with the aid of the spreadsheet software TC2D. Figure 6 - 9 are presenting the resulted time variation curves of curing temperatures. In order to process the acquisitioned data, the values were imported into the TC2D program. For the elaboration of the mathematical model, the data acquisitioned with the aid of the “VI Thermometer” was used. For the ease of choosing the most adequate function shape, the software uses parallel visualization of the graphic representation of the string of data, the proposed function and the level of trust. It is also possible to choose the estimating precision.

Following the data processing, the composite material temperature variation equations during processing were determined. The results are the approximation curves of the 3 curing temperatures presented in figure 6, 7, 8 and 9.

Among the functions proposed for the approximation of the composite material temperature variation when processed at 25°C, the polynomial function was chosen because: the level of trust was 99%, the standard overlapping error computed and displayed is 0.436 well inside the exclusion level; the value of the correlation coefficient r^2, that needs to be between 0 and 1 has values over 0.9925, very close to the ideal level of acceptance; the estimation is efficient – the lowest spread among all estimations. Thus, the curve can be approximated through a polynomial function type equation (7). Its graphical representation is depicted in figure 6.

$$y = a + bx + cx^{2.5} + dx^3 + ex^{0.5} \qquad (7)$$

In a similar way the composite material was processed at 40°C. For the composite material curing at 40°C, the curve can be approximated through a polynomial function type equation:

$$y = a = bx + cx^{1,5} + dx^{2,5} + ex^3 \qquad (8)$$

Its graphical representation is depicted in figure 7. The proposed level of trust is of over 90%, the standard error of overlapping is computed and displayed at 0.59 (inside the level of exclusion); the value of the correlation coefficient r^2 has values of over 0.99 (close to the ideal level of acceptance).

For the composite material curing at 50°C, the curve can be approximated through a polynomial function type equation of shape:

$$y = a = bx + cx^2 + dx^{2,5} + ex^3 \qquad (9)$$

The above shape was chosen because it presents the maximum level of trust $r^2 = 0.982$, very close to the proposed one of over 99%. Its graphical representation is depicted in figure 8, where one can notice an almost total overlapping of the theoretical curve with the experimental results.

For the composite material processed at 60°C, the curve can be approximated as the other curves through an polynomial equation :

$$y = a = bx + cx^2 + dx^{2,5} + ex^3 \qquad (10)$$

The graphical representation of this is depicted in figure 9, where can be seen again an almost total overlapping of the theoretical curve with the experimental results.

The viability of the LM 335 Z sensor and its performance in the monitoring process of composite materials temperature during processing is proven by the fact that all temperature variation graphics were approximated through the same polynomial and exponential functions with an approximation error below 0.1-0.3%.

Figure 10 depicts the temperature variation of the composite material during processing. One can notice from figure 10 that the resulted temperature inside the

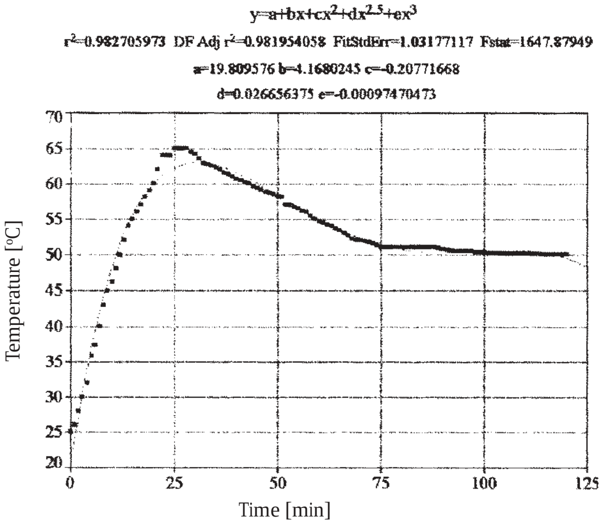

Fig. 8. Temperature variation curve approximation with an polynomial function of the composite curing at 50°C

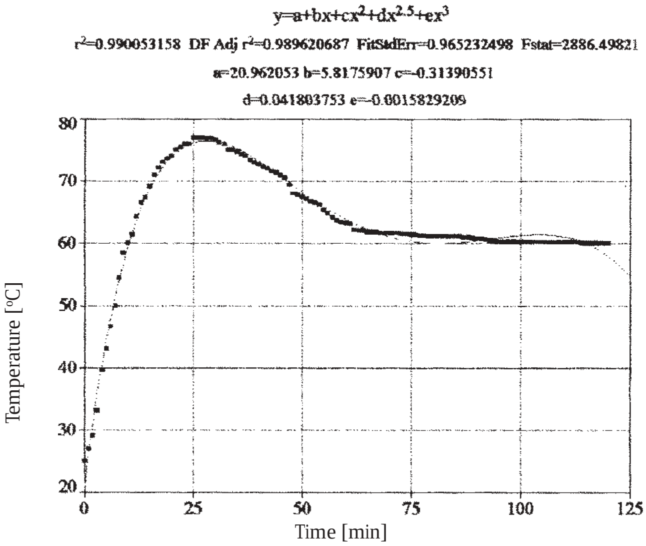

Fig. 9. Temperature variation curve approximation with an polynomial function of the composite curing at 60°C

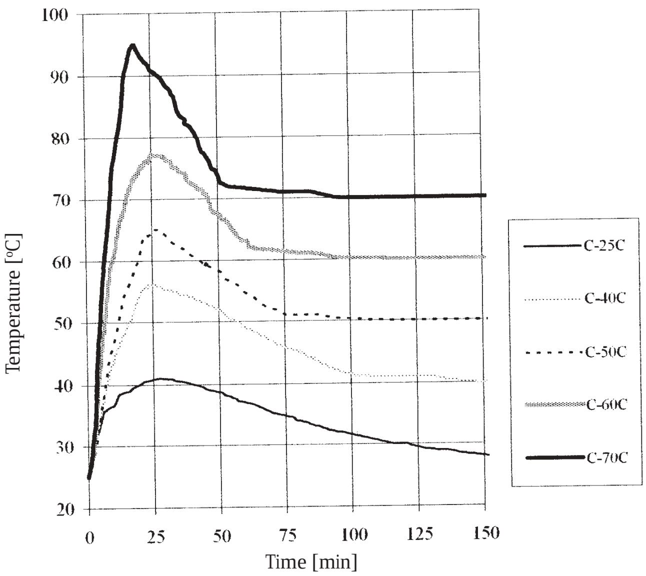

Fig. 10. Temperature variation of the composite material during processing monitored with the LM 335Z sensor

composite material increases along with the processing temperature. Furthermore, it can be observed the fact that the exothermic maximum is produced as early as the processing temperature is higher, decreasing the duration of the reticulation cycle [1,3]. Sadly, the processing temperature cannot be raised too much. It is influenced by the glass transition of the resin-hardener system: 60-62^{0}C in the case of cold processing and approximately 90^{0}C for the warm processing [1, 3, 9].

From the figure 10 it can be notice that in the case of processing at 60 and at 70^{0}C, the maximum resulted temperature during processing is very close to the glass transition, even exceeding it (95^{0}C) in the case of 70^{0}C processing. The exothermic maximum in this case is produced rapidly, at approximately 19 min from the material manufacturing. This phenomenon produces a more than normal acceleration of the polymerization reaction with unfortunate consequences over the molecular links and implicitly over the final properties of the composite material. This phenomenon was noticed during the monitoring of the dynamic mechanical properties of the composite material processed at 60 and 70^{0}C temperatures. It can also be noticed that in all cases, after the reaching of maximum exotherm temeprature, there is a drop in the reaction temperature. The temperature can reach the level of the processing temperature and maintains constantly onwards irrespective of the duration of keeping it in the oven.

Conclusions

The implemented experimental stand that includes a PC with an acquisition card and a corresponding software system (LabVIEW), allows the real time monitoring of composite material temperature during processing with the aid of the LM 335Z temperature sensor. This new generation digital sensor has proven to be more efficient than the classical thermo-couplings that are affected by the electromagnetic radiations (such as those provoked by the outputs of the heating elements located within the ovens). In all variants of curing of composite materials, its temperature variation graphics monitored with this sensor were approximated with the same polynomial functions determined with a TC2D program (the approximation error being below 0.1 – 0.3 %). This fact shows the viability of the chosen sensor in composite materials temperature monitoring during processing.

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