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THERMAL CHARACTERIZATION OF CURING PROCESS IN UNSATURATED POLYESTER RESIN BASED POLYMER CONCRETE

This paper presents a description of the temperature changes that take place in the curing system of polymer concrete. The research used polymer concrete composed of 30% by volume unsaturated polyester resin acting as a binder for powder fillers. Among the powder fillers, ground glass waste and sand in a volume ratio of 1:1 were used. The investigations were carried out for three volumes, 10, 100 and 1000 cm^3, respectively. The temperature in the central point of the volume (the highest temperature) was measured by the ATD method using a NiCr-NiAl thermocouple, and the temperature on the polymer concrete surface was measured using a thermal imaging camera. The temperature-time course recorded for both the measuring points allowed evaluation of the curing system parameters (gelation time, maximum curing temperature, time to maximum temperature), important for the processing of polymer concrete. Additionally, the knowledge of the temperature curves enabled a mathematical description of the heat flow between the measuring points. The conducted studies proved that the volume of the mold is important for the maximum temperature and curing time. The work is a continuation of previous research focused on polymer concrete and is an extension of information oriented to the industrial aspect. Knowledge of the temperature peaks and curing time will allow adjustments to be made to the manufacturing processes.

Keywords: curing process, polymer concrete, polyester resin, composites

INTRODUCTION

Resins are one among the most widely used groups of commercial materials, which have found their particular application as the matrix of composite materials [1, 2]. They dominate in polymer matrix composites as they contribute to obtaining good properties such as mechanical strength, electrical insulating properties, as well as resistance to environmental and chemical corrosion. Additionally, they are relatively inexpensive [3, 4].

Unsaturated polyester resins belong to the group of thermosets. A characteristic feature of these materials is that once cast into the appropriate shape and hardened by a chemical reaction between the resin and the hardener, they cannot be melted at elevated temperatures [5, 6]. The properties of resins strongly depend on the formation of a fully cross-linked structure by means of the curing (or polymerization) reaction, which results in the spatial formation of a polymer network [7, 8]. The spatial network is created by polymerization [9]. The polymerization reaction initiated with the hardener is an exothermic reaction related to the conversion of double bonds in the resin monomers [10, 11]. The course of curing depends on many factors: ambient temperature, the quality and quantity of catalysts, the presence of mechanical excitation (e.g. ultrasounds), the volume of the hardened batch or heat dissipation from the curing area [12-15].

The curing of the resin takes place in three phases. In the first phase, the resin consists only of uncured monomers, which gives the material low viscosity, low solubility, and the ability to wet and impregnate the fiber bundle. In the second phase, the monomers begin to form chains through covalent bonds, and the entire process continues until the gel point is reached. The last phase refers to the time when the resin achieves its final properties related to the insoluble and infusible structure [16].

During the curing process, changes in the Kirchhoff G shear modulus and the resin viscosity are observed [11]. The viscosity of the resin in the liquid state is mainly influenced by two phenomena – the first is the increase in the size of the particles as curing progresses, reducing their mobility, and thus increasing the viscosity. The second is the temperature, the increase in which causes a decrease in viscosity [17]. After curing initiation, the viscosity of the resin initially starts to decrease slightly and then increases significantly.

Important terms related to the resin curing process are resin life, gel time, and curing time. The pot life is defined as the time it takes for the initial viscosity to double. The measurement starts from the moment of mixing the resin and the hardener and is carried out at the temperature of 23°C [18]. Gel time is a term similar

to the life of the resin and describes the time it takes for the resin to change from sol to gel [19]. The point at which this transition takes place is gradual, which makes it difficult to define it precisely. There are numerous methods for determining the gel time: manual, semi-automatic, automatic methods, rotational viscometer, rheometer, dynamic mechanical analysis (DMA), ultrasound (US), dielectric analysis (DEA) or luminescence [20]. The curing time is the time beyond which the resin is completely cured [21].

The change in the process of resin curing is influenced by the appearance of a filler in it, as is the case in polymer concrete. Solid particles have their heat capacity, which takes away some of the heat from the exothermic curing reaction, thus influencing the course of the process [22]. Glass fibers are very often the reinforcement of resin matrix composites [23, 24]. Research shows that they contribute to a reduction in the temperature peak of the curing reaction, increase in the gelation time and stabilization of the curing process [25].

The article presents the results of research related to the physical and mathematical description of thermal phenomena in the curing polymer concrete system with an epoxy resin matrix. Attention is drawn to the essence of the influence of the material volume on the curing time and the temperature maximums of the curing process at room temperature. A study of the temperature course of the curing process in the center of the system was carried out using the ATD technique and surface temperature measurement by means of a thermal imaging camera. The collected data was transformed and mathematically analyzed in order to determine the heat of transformation and the actual magnitude of the temperature difference.

MATERIALS AND METHODS

For the purposes of the research, polymer concrete composed of Havelpol-1 unsaturated polyester resin (Havel Composites, Czech Republic) hardened with Butanox M50 in a weight ratio of 100:2 was used. Construction sand (KREISEL) added in 30% by volume was the coarse-grained fraction of the polymer concrete, and the fine fraction was ground glass waste. Glass grinding was carried out in a Retsch SK300 cross beater mill using separation sieves with an opening size of 0.5 mm. The powder fillers in a 1:1 volume ratio were mixed with the resin and placed in the molds. The curing process was carried out at 23°C.

Three containers were prepared, acting as molds, with volumes of 10, 100 and 1000 cm³, with dimensions where the ratio of the base diameter (*d*) to the height (*H*) was 1:1.5. The curing temperature for each container was measured at two points. The first measurement was to measure the temperature in the central part of the system using the ATD technique (temperature derivative analysis). A K-type thermocouple (NiCr-NiAl) was placed inside the polymer

concrete and the temperature course was recorded on a CRYSTALDIGRAPH 8T device. The second measuring point was located on the upper surface of the polymer concrete, and temperature changes were recorded by means of a thermal imaging camera. The scheme of the distribution of measurement points is presented in Figure 1. The recording frequency of 60 Hz was established for both measurement methods.
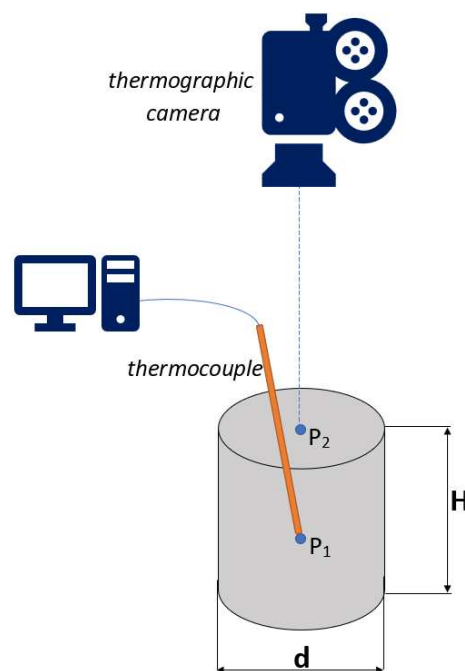

Fig. 1. Diagram of system recording curing temperature in central point of volume (P₁) and maximum temperature on sample surface (P₂)

RESULTS AND DISCUSSION

The results of the measurements carried out by the ATD method at the central point of the volume (point P1) in the form of temperature-time curves are shown in Figure 2. The recorded temperature-time curves clearly show that the volume of the curing polymer concrete system has a significant influence on the temperature maxima of the process. In the case of the smallest volume of 10 cm³, a significant decrease in the temperature peak is visible during the intense reaction. Additionally, the time shift necessary to achieve the temperature maximum is noticeable. Table 1 presents more precise time-temperature data characterizing the course of changes in the curing polymer concrete system. The maximum curing temperature of the 1000 cm³ volume of polymer concrete is 68.44°C and is achieved in 4022 s (67 min). The decrease in volume leads to a decrease in the maximum temperature inside the system, for 100 cm³ the maximum temperature is 51.31°C and is reached after 3974 s (66 min). For the smallest volume, the temperature peak was recorded at 3476 s and has a value of 37.60°C. Such large temperature differences result from the exothermic nature of curing unsaturated polyester resins, where the

volume is of key importance. In the investigated polymer concrete system, the high content of fillers is important as they effectively absorb the heat of reaction, thus extending the curing process. According to the data of the procedure, the gelling time of the system at room temperature and a volume of 100 cm^3 is approximately 20 minutes. When referring to the manufacturer's data for unfilled polyester resin and the results obtained for polymer concrete, a three-fold extension of the gel time in the same volume can be observed.
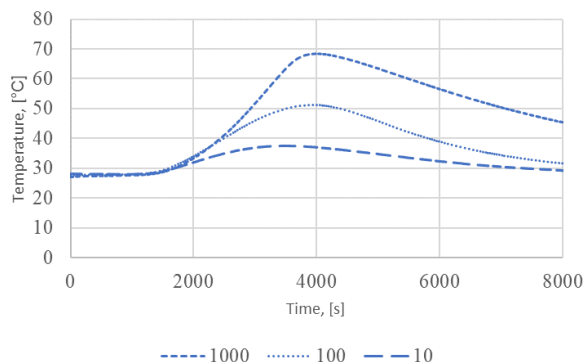

Fig. 2. Temperature-time relationship for polymer concrete curing process in central point inside system for volumes of 1000, 100 and 10 cm^3

TABLE.1. **Maximum temperature of polymer concrete curing process and time to achieve it, measured in central point of volume (point P_1)**

Volume [cm^3]	Maximum temperature [°C]	Time of reaching maximum temperature [s]
1000	68.44	4022
100	51.31	3974
10	37.60	3476

During the study, changes on the surface of the curing polymer concrete were recorded. Figure 3a presents the temperature changes recorded on the surface of the material with the volume of 1000 cm^3, and Figure 3b

shows the temperature changes in the polymer concrete with the volume of 100 cm^3. For the smallest volume (10 cm^3), no significant changes in temperature were recorded on the surface of the curing polymer concrete. It is noticeable that the highest temperature on the surface is in the middle of the measurement field.

The comparison of the temperature changes inside the system and on the surface is shown in Figures 4 and 5, where series with volumes of 1000 and 100 cm^3 were successively registered. Additionally, in Table 2 the temperature-time data are collected, which describe the time to reach the maximum temperature and the maximum curing temperature measured by two different methods. The maximum temperature recorded in the center of the volume (point P1) of a sample with the volume of 1000 cm^3 is 68.44°C and the maximum temperature on the surface (point P_2) is 63°C; the time needed to reach the maximum temperature is approx. 4000 s. For polymer concrete with the volume of 100 cm^3 the maximum temperature at point P_1 is 51.31°C and at point P_2 41.20. The temperature difference between the measuring points is greater the smaller the volume of the investigated material. The time to reach the maximum temperature varies little and is around 3900 seconds.

TABLE. 2. **Peak (maximum) temperature of curing process and time to reach it – measurement at center point P_1 and on surface P_2 for volumes of 1000 cm^3 and 100 cm^3**

	Point P_1 in volume 1000 cm^3	Point P_2 in volume 1000 cm^3	Point P_1 in volume 100 cm^3	Point P_2 in volume 100 cm^3
Maximum temperature [°C]	68.44	63.00	51.31	41.20
Time of reaching maximum temperature [s]	4022	3960	3974	3840

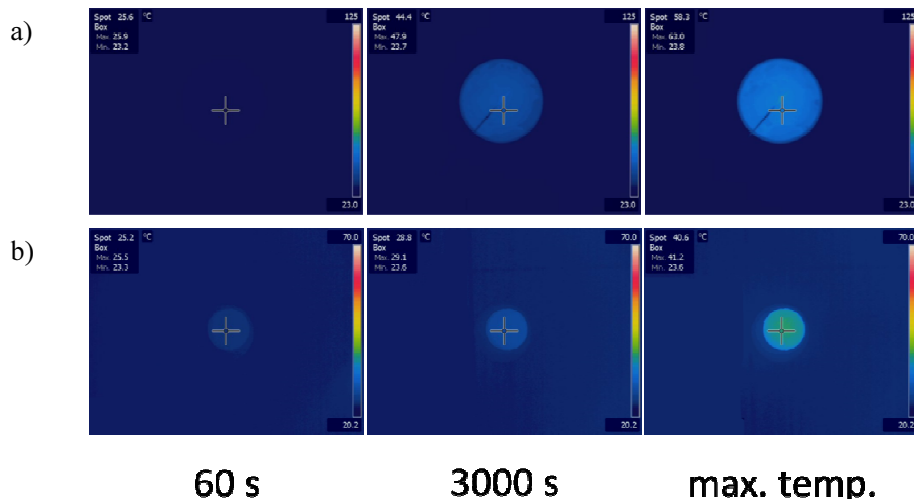60 s   3000 s   max. temp.

Fig. 3. Temperature changes in polymer concrete on surface during curing, for sample with volume of: a) 1000 cm^3, b) 100 cm^3
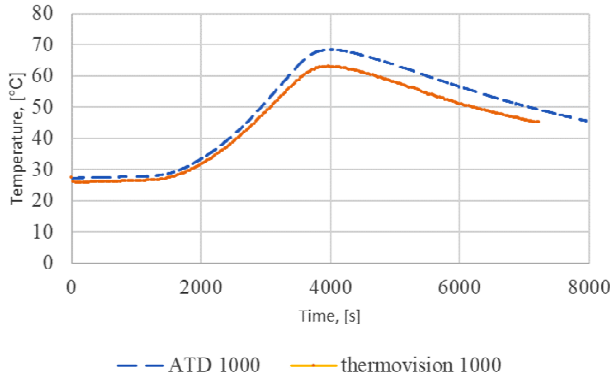
Fig. 4. Temperature-time relationship for curing process of polymer concrete with volume of 1000 cm³, measured in central point and on surface
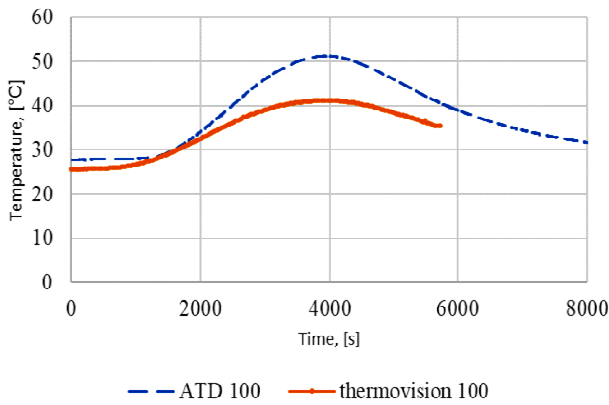

Fig. 5. Temperature-time relationship for curing process of polymer concrete with volume of 100 cm³, measured in central point and on surface

Mathematical description

The functionality of the monomers determines the level of curing polymerization at which gelation occurs. If f_E is a reactive epoxy group and f_A is reactive hydrogen, they would react with a diamine to form a network. Then α_{gel} is the degree of curing polymerization at gelation [26]. The prediction of gel point conversion is essential when developing thermosetting materials because thermosets cannot be treated or molded after this point. The amount of reaction at the gel point, assuming a stoichiometric amount, is given as

$$\alpha_{gel} = \left(\frac{1}{(f_A - 1)(f_E - 1)} \right)^{1/2} \qquad (1)$$

Another important physical process that might occur during curing polymerization is vitrification. This is the transition of the system into a solid, glassy state. This phenomenon is well described in [26, 27]

$$T_g = T_{g,0} + \frac{\lambda \alpha (T_{g,\infty} - T_{g,0})}{1 - (1 - \lambda)\alpha} \qquad (2)$$

where λ is the thermal conductivity of the reference sample, T_g is the glass transition temperature at the extent of polymerization α, and $T_{g,0}$ and $T_{g,\infty}$ are respectively the glass transition temperatures of the epoxy monomer and completely cured polymer.

The temperature distribution in the differential thermal analysis specimen holders obeys the overall heat flow equation

$$\frac{\partial T}{\partial t} - \frac{\lambda}{\rho C} \nabla^2 T = \frac{1}{\rho C} \frac{dq}{dt} \qquad (3)$$

where T is the temperature [K], t is the time [s], λ is the thermal conductivity [W/(m·K)], ρ is the density [kg/m³], C is the specific heat [J/K·kg] and dq/dt the rate of heat generation [W] according to the chemical reaction per unit volume of the sample.

The ATD curves are responsible for the similar condition of the same heating curve; T_r (t) usually in a linear form as $T_r = T_0 + \phi t$, where ϕ is the heating rate, T_0 is the initial temperature, T_r the temperature at the center of the reference sample.

From the balance of heat fluxes for the sample and reference sample, the measured temperature difference between the sample and the reference is proportional to both the speed of transformation of the sample $\left(\frac{d\alpha}{dt} \right)$ and the speed of change in a temperature difference $\left(\frac{d\theta}{dt} \right)$ [28]. The temperature disparity $(\Delta T = \theta)$ is the temperature variation between the centers of two samples.

According to the equation originally derived by Vold [29] and re-evaluated by work [30]

$$-\left(\frac{d\theta}{dt} \right) = -\left(\frac{K}{C_s} \right)\theta + \left(1 - \frac{C_r}{C_s} \right)\beta + \left(\frac{dq}{dt} \right)\frac{1}{C_s} + \frac{\Delta K(T)}{C_s} \qquad (4)$$

where K is an instrumental constant [W/K], C_s are heat capacities of the sample (s) and reference (r), and ΔK [T] reflects the difference between the heat transfer conditions of the sample and reference. By differentiating with respect to time and rearrangements, we can obtain

$$\frac{d\theta}{dt} - \left(\frac{C_s}{K} \right)\frac{d^2\theta}{dt^2} = \left(\frac{d^2q}{dt^2} \right)\frac{1}{K} \qquad (5)$$

Substituting

$$\left(\frac{dq}{dt} \right) = -H \left(\frac{d\alpha}{dt} \right) \qquad (6)$$

where H is the reaction enthalpy change ($H < 0$ at the exothermic process when heat is generated inside the sample), $\frac{d\alpha}{dt}$ is the reaction rate, and neglecting the second and the fourth right-side terms in Equation (4), ($C_r \approx C_s$) and $\Delta K \approx 0$, we can write Equation (5) in the form

$$-\left(\frac{d\theta}{dt} \right) = -\left(\frac{K}{C_s} \right)\theta - \left(\frac{H}{C_s} \right)\left(\frac{d\alpha}{dt} \right) \qquad (7)$$

It follows from Equation (7) that at maximum deviation of the temperature difference $|\theta_p| = $ max at temperature of apex T_p, we have $\frac{d\theta_p}{dt} = 0$, so that

$$\frac{d\alpha_p}{dt} = -\left(\frac{K}{H}\right)\theta_p \qquad (8)$$

Rearranging Equation (7)

$$\frac{d\alpha}{dt} = \left(\frac{C_s}{H}\right)\left(\frac{d\theta}{dt}\right) - \left(\frac{K}{H}\right)\theta \qquad (9)$$

Let us define θ_1 and θ_2 differential temperatures at t_1 and t_2 respectively. The integral of the second term on the right-hand side of Equation (9) is the area under the peak, whereas that of the first term is $(\theta_2 - \theta_1)$, where θ_1 and θ_2 are the values of θ at the start and end of the time period. This equation helps us to calculate the heat of transformation and the actual magnitude of differential temperature.

A graphical or numerical integration of Equation (9) over the time the transformation occurs, yields a value for the heat of the transformation. The values probably have little significance at low heating rates as they are determined primarily by the rate at which heat is made available to the sample. From the differential cooling curves or high heating rate, the values of $\frac{d\alpha}{dt}$ are an attractive property of the system under study (Fig. 2). When $\frac{d\alpha}{dt} = 0$ before the transformation has begun, $\frac{d\theta}{dt} = 0$ and $\theta = \theta_s$, where θ_s is a steady state value of the differential temperature obtained at a sufficiently long time after the initial condition. When $\frac{d\alpha}{dt} = 0$ after the transformation, $\frac{d\theta}{dt}$ is equal in value and opposite in sign to $\left(\frac{K}{H}\right)(\theta - \theta_s)$. Its main advantage is in determining the transition temperatures rather than calculating the heat effects.

CONCLUSIONS

Based on the obtained research results, it can be concluded that:
- the most accurate results regarding the curing time and temperature of the system can be obtained using a thermocouple placed at the center of the volume,
- the study of temperature changes on the surface of the curing material is sensible for large volumes (above 1000 cm^3), while for smaller volumes there is a large scatter of results or the temperature changes during curing process cannot be registered at all,
- knowledge of the temperature changes in the volume center and on the surface of the curing system enables a mathematical description of the temperature changes, and this in turn helps to calculate the heat of transition and the actual magnitude of the temperature difference,

- knowledge of the curing time of the resin system allows an accurate description of the working time of the polymer concrete, which is important in production processes. Measurement of the temperature on the surface of curing polymer concrete by means of thermal imaging cameras allows accurate estimation of the working time and control of the maximum temperature.

REFERENCES

[1] Mulligan S., Hatton P.V., Martin N., Resin-based composite materials: elution and pollution, British Dental Journal 2022, 232(9), 644-652.

[2] Azlin M.N.M., Sapuan S.M., Zainudin E.S., Zuhri M.Y.M., Natural fibre reinforced polyester composites: a review, 7th Postgraduate Seminar on Natural Fibre Reinforced Polymer Composites 2020.

[3] Pielichowski J., Czub P., Penczek P., Bończa-Tomaszewski Z., Chemia i technologia żywic epoksydowych, Warszawa 2016.

[4] Bello S.A., Agunsoye J.O., Hassan S.B., Kana M.G.Z., Raheem I.A., Epoxy resin based composites, mechanical and tribological properties: a review, Tribology in Industry 2015, 37(4), 500-524.

[5] Brydson J.A., Plastic Materials, 7th ed., Oxford 1996.

[6] Bradly S., Epoxy/Clay Nanocomposites: Effect of Clay and Resin Chemistry on Cure and Properties, M.SC. Thesis, School of Science and Applied Chemistry, Queensland University of Technology 2004, l.

[7] Jouyandeh M., Rahmati N., Movahedifar E., Hadavand B.S., Karami Z., Ghaffari M., Taheri P., Bakhshandeh E., Vahabi H., Ganjali M.R., Properties of nano-Fe$_3$O$_4$ incorporated epoxy coatings from Cure Index perspective, Prog. Org. Coat. 2019, 133, 220-228, DOI: 10.1016/j.porgcoat.2019.04.034.

[8] Saleh N.J., Razak A.A.A., Tooma M.A., Aziz M.E., A study mechanical properties of epoxy resin cured at constant curing time and temperature with different hardeners, Eng. & Tech. Journal 2011, 29(9), 1804-1818.

[9] Muc A., Romanowicz P., Chwał M., Description of the resin curing process-formulation and optimization, Polymers 2019, 11(1), 127, DOI: 10.3390/polym11010127.

[10] Lloyd C.H., Joshi A., McGlynn E., Temperature rise produced by light sources and composites during curing, Dental Materials 1986, 2(4), 170-174.

[11] McHugh J., Stark W., Doering J., Evaluation of the cure behavior of epoxy resin using rheometric and ultrasonic techniques, Non Destructive Characterization of Materials 2003, XI, 6, 651-657.

[12] Mistewicz K., Jesionek M., Kim H.J., Hajra S., Kozioł M., Chrobok Ł., Wang X., Nanogenerator for determination of acoustic power in ultrasonic reactors, Ultrasonic Sonochemistry 2021, 78, 105718, DOI: 10.1016/j.ultsonch.2021.105718.

[13] Czub P., Bończa-Tomaszewski Z., Penczek P., Pielichowski J., Chemia i technologia żywic epoksydowych, WNT, Warszawa 2002.

[14] Penczek P., Kłosowska-Wołkowicz Z., Królikowski W., Nienasycone żywice poliestrowe, WNT, Warszawa 2010.

[15] Kozioł M., Nasycanie ciśnieniowo-próżniowe zszywanych oraz tkanych trójwymiarowo preform z włókna szklanego, monografia, Wydawnictwo Politechniki Śląskiej, Gliwice 2016.

[16] Dykeman D., Minimizing Uncertainty in Cure Modeling for Composites Manufacturing, Ph.D. Dissertation, Department of Materials Engineering, University of British Columbia, Vancouver, BC Canada, 2008.

[17] Hubert P., Cure Kinetics and Viscosity Models for Hexcel 8552 Epoxy Resin, Proceedings of the 46th International SAMPE Symposium. Long Beach, CA, USA 2001, 2341-2354.

[18] Epoxy Technology Inc., Pot Life, Working Life and Gel Time of Epoxies, online at: https://www.epotek.com/docs/ en/Related/Tech%20Tip%2026%20Pot%20Life,%20Worki ng%20Life%20and%20Gel%20Time%20of%20Epoxies. pdf (accesed: 06.06.2022).

[19] Smoleń J., Olesik P., Gradoń P., Chudy M., Mendala B., Kozioł M., The use of the ATD technique to measure the gelation time of epoxy resins, Materials 2021, 14, 6022, DOI: 10.3390/ma14206022.

[20] Shimkin A.A., Methods for the determination of the gel time of polymer resins and prepregs, Russian Journal of General Chemistry 2016, 86(6), 1488-1493.

[21] Ramis X., Salla J.M., Time-temperature transformation (TTT) cure diagram of an unsaturated polyester resin, J. Polym. Sci. Part B: Polym. Phys. 1997, 35, 371-388.

[22] Kozioł M., Mocek P., Jankowski P., Wpływ objętości próbki chemoutwardzalnej żywicy poliestrowej na przebieg jej utwardzania, Polimery 2016, 61(2), 133-141.

[23] Kupke M., Wentzel H.-P., Schulte K., Electrically conductive glass fibre reinforced epoxy resin, Mat. Res. Innovat. 1998, 2, 164-169.

[24] Baron M.R., Caulk D.A., The effect of deformation and thermoset cure on heat conduction in a chopped-fiber reinforced polyester during compression molding, International Journal of Heat and Mass Transfer 1979, 22(7), 1021-1032.

[25] Kozioł M., Gradoń P., Effect of glass fibre presence on curing process of unsaturated polyester resin, Composites Theory and Practice 2018, 18(4), 191-195.

[26] Cho S., Douglas E.P., Lee J.Y., Transition diagrams for a liquid crystalline thermoset containing a rigid-rod epoxy, Polym. Eng. Sci. 2006, 46, 5, 623-629, DOI: 10.1002/ pen.20496.

[27] Pascault J.P., Williams R.J.J., Glass transition temperature versus conversion relationships for thermosetting polymers, J. Polym. Sci. Part B Polym. Phys. 1990, 28, 1, 85-95, DOI: 10.1002/polb.1990.090280107.

[28] Šesták J., Holba P., Heat inertia and temperature gradient in the treatment of DTA peaks: Existing on every occasion of real measurements but until now omitted, J. Therm. Anal. Calorim. 2013, 113, 3, 1633-1643, DOI: 10.1007/s10973- 013-3025-3.

[29] Vold M.J., Differential Thermal Analysis 1949, 2, 6, 6.

[30] Šesták J., Holba P., Imperfections of Kissinger Evaluation Method and the Explanation of Crystallization Kinetics of Glasses and Melts, [in:] Thermal Physics and Thermal Analysis, 11, eds. J. Šesták, P. Hubík, J.J. Mareš, Cham, Springer International Publishing 2017, 213-236, DOI: 10.1007/978-3-319-45899-1_10.