

RESEARCH PAPER

## The Use of Optimization Algorithm for Assessing Effects of Carboxyl Functionalized MWCNTs on the Productivity of Nidltrusion Process

Iliya Aleksandrovich Kazakov\*, Aleksandr Nikolaevich Krasnovskii and Andrey Gennadievich Kuznetsov

Department of Composite Materials, Moscow State Technological University STANKIN, 127055 Moscow, Vadkovsky lane, 3a, Russia

### ARTICLE INFO

#### Article History:

Received 14 February 2017

Accepted 22 March 2017

Published 01 April 2017

#### Keywords:

Braided composite rods (BCR)

MWCNTs

Nidltrusion

Optimization

Pultrusion

### ABSTRACT

Among the several available techniques to produce the braided composite rods for construction industry, nidltrusion process is becoming the most widespread and cost-effective continuous processing technique. The work mentions the influence of carboxyl functionalized multiwalled carbon nanotubes (MWCNTs) on the maximum speed of manufacturing process. The epoxy polymer is diglycidyl ether of bisphenol F and the curing agent is an aromatic diamine. Appropriate temperature settings were determined using the optimization algorithm for two-dimensional heat transfer and curing model implemented to 8-mm diameter reinforcement with 0, 0.1, 0.2 and 0.3 wt% MWCNT. Final results allow concluding that only the use of 0.2 wt% MWCNT gives the highest nidltrusion speed. Other two batches (0.1 wt% and 0.3 wt% MWCNT) showed worse results compared to neat sample. The developed optimization algorithm can be further applied in the modeling of pultrusion process with using of different type of resin, curing agents and nanofillers.

### How to cite this article

Kazakov I.A, Krasnovskii A.N, Kuznetsov A.G. The Use of Optimization Algorithm for Assessing Effects of Carboxyl Functionalized MWCNTs on the Productivity of Nidltrusion Process. J Nanostruct, 2017; 7(2):89-96. DOI: 10.22052/jns.2017.02.001

### INTRODUCTION

The use of carbon nanotubes as an additives garnered much attention due to the possibility of significant improvements of strength and other properties of polymers. At the same time the nanotubes are added in relatively small fractions, and this make material more suitable for potential applications in various fields of national economy. Particular, in the construction industry MWCNTs can be used as an additives in production of the braided composite rods, see Fig. 1.

The braided composite rods (BCRs), presenting a high durability, resistant to repeated loading and corrosion are called to replace the steel rods commonly used nowadays for concrete

reinforcement. BCRs have high strength to weight ratio which allows to reduce the logistic costs for transportation and reinforce the concrete elements in which the weight of the reinforcing material is a constraint [1].

The BCRs are usually produced from thermoset resin (matrix) and glass or basalt fibers (filler) and possess ribbed surface providing a good adhesion to concrete. One of the most widespread and cost-effective continuous processing technique in Russia is «nidltrusion» (see Fig. 2). In this process, the roving impregnated by the thermoset resin is pulled through a helical winding device where it formed and gets the spiral protrusions on the surface, providing a good adhesion to concrete. After

\* Corresponding Author Email: kazakov\_iliya@mail.ru



Fig. 1. The BCRs produced from thermoset resin and glass fibers: a) without MWCNTs, b) modified by MWCNTs

that, BCR is cured in the heating chamber without touching its walls in contrast to conventional pultrusion process [2-5]. The heat provided by means of infrared (IR) heaters activates the exothermic cure reaction of the thermoset resin. Finally, outside the chamber, already polymerized BCR is pulled by a pulling system. Then a cut-off saw cuts the part into a desired length.

The heating chamber is divided into several (usually, 8) sections (Fig. 2). Each section is set to strictly defined power output and left in this state for the duration of the process. The process is controlled by varying the power output and speed of the nidltrusion. The last one should be maximized in order to make process more productive. At the same time, temperature for each section should be chosen so as to ensure the quality products production. The final product should be completely cured after exit from the

heating chamber and have uniform degree of cure.

The possibility to use thermoset nanocomposites for producing BCRs depends on the ability to control the interworking of the composition (resin, hardener, CNTs) and numerous interdependencies of the control variables (pulling speed, heating temperature, etc.). One of the most informative and developed methods for studying the interworking of the composition is a differential scanning calorimetry (DSC). Using the DSC technique it has been observed that addition of CNTs in the resin can act as a catalyst [6], whereas some studies revealed the retarding effect of CNTs on cure reaction [7-9].

In order to link together the kinetic-parameter relationships and variation of the control variables and material properties the special mathematical model was developed [10]. The system of obtained equations is represented by Eq. (1-7):

$$\rho \cdot c \cdot U \cdot \frac{\partial T}{\partial x} = \rho_r \cdot (1 - v_f) \cdot H_{tot} \cdot \frac{d\alpha}{dt} + \frac{\lambda}{r} \cdot \frac{\partial}{\partial r} \left( r \cdot \frac{\partial T}{\partial r} \right), \quad (1)$$

$$d\alpha/dt = A \cdot \exp \left[ -E_a / (R_g \cdot T) \right] \cdot \alpha^m \cdot (1 - \alpha)^n, \quad (2)$$

$$T|_{x=0} = T_0, \quad -\lambda \cdot \frac{\partial T}{\partial r} \Big|_{0 \leq x \leq L, r=R} = \gamma_1 + \gamma_2, \quad -\lambda \cdot \frac{\partial T}{\partial r} \Big|_{x > L, r=R} = \gamma, \quad \frac{\partial T}{\partial r} \Big|_{r=0} = 0, \quad (3)$$

$$\gamma_1 = \varepsilon_n \cdot C_0 \cdot \left( T^4 \Big|_{r=R} - T_p^4 \right), \quad \gamma_2 = \varepsilon_n \cdot C_0 \cdot \left( T^4 \Big|_{r=R} - T_H^4 \right), \quad (4)$$

$$\rho = (1 - v_f) \cdot \rho_r + v_f \cdot \rho_f, \quad \rho_r = \alpha \cdot \rho_r^c + (1 - \alpha) \cdot \rho_r^u, \quad (5)$$

$$c = (1 - v_f) \cdot c_r + v_f \cdot c_f, \quad c_r = \alpha \cdot c_r^c + (1 - \alpha) \cdot c_r^u, \quad (6)$$

$$1/\lambda = (1 - v_f) / \lambda_r + v_f / \lambda_f, \quad (7)$$

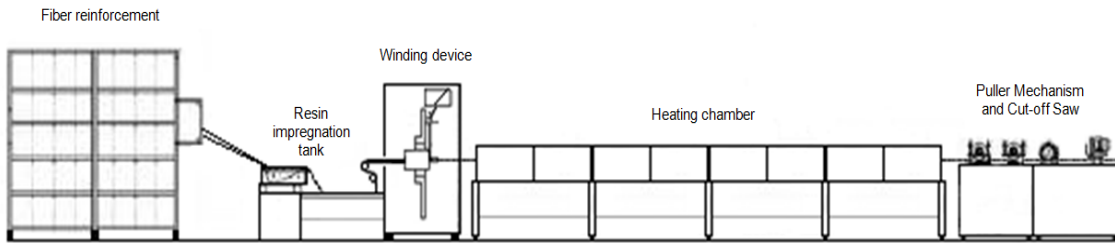


Fig. 2. Schematic view of the nidltrusion process

where  $x, r$  are the longitudinal and radial coordinates,  $\alpha$  – degree of cure,  $T$  is a temperature,  $T_0$  is initial temperature,  $T_p$  is the predetermined temperature,  $T_H$  is the temperature of the IR heater surface,  $\epsilon_n$  is the emissivity of the surface,  $C_0$  is the Stefan-Boltzmann constant,  $L$  – the length of heating chamber,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R_g$  is the gas constant,  $n, m$  are the equation superscripts,  $v_f$  – fiber volume fraction,  $H_{tot}$  – the total heat generated by the exothermic reaction of resin,  $\rho$  is the density of composite,  $\rho_r$  is the density of resin,  $\rho_f$  – the density of fiber,  $\rho_r^u, \rho_r^c$  are the densities of uncured and cured resin correspondingly,  $c_f$  is the specific heat of the fiber,  $c_r^u, c_r^c$  – are specific heat of uncured and cured resin correspondingly,  $\lambda_r, \lambda_f$  – heat-transfer coefficients for resin and fiber correspondingly.

The present work focuses on developing an optimization algorithm for nidltrusion process assuming that all sections of the heating chamber have the same heating temperature. In fact, the

heating chamber consists of several sections, each of which may have a different temperature. However, the goal of the work was also to ascertain the effects of Carboxyl Functionalized MWCNTs on the maximum speed of nidltrusion process and this assumption allows solving the problem quite enough.

### THEORETICAL MODELING AND OPTIMIZATION OF NIDLTRUSION PROCESS

Mathematical modeling of the nidltrusion allows optimizing the necessary criteria of process and calculates the design parameters of the equipment in order to improve product quality, increase productivity and reduce the manufacturing costs.

The solution to the heat transfer and curing problem is obtained using an implicit finite difference approach. This method is based on discretizing the space and time domain through transformation into a finite difference form and solving the subsequent system of algebraic equations for the temperature and cure fields. The

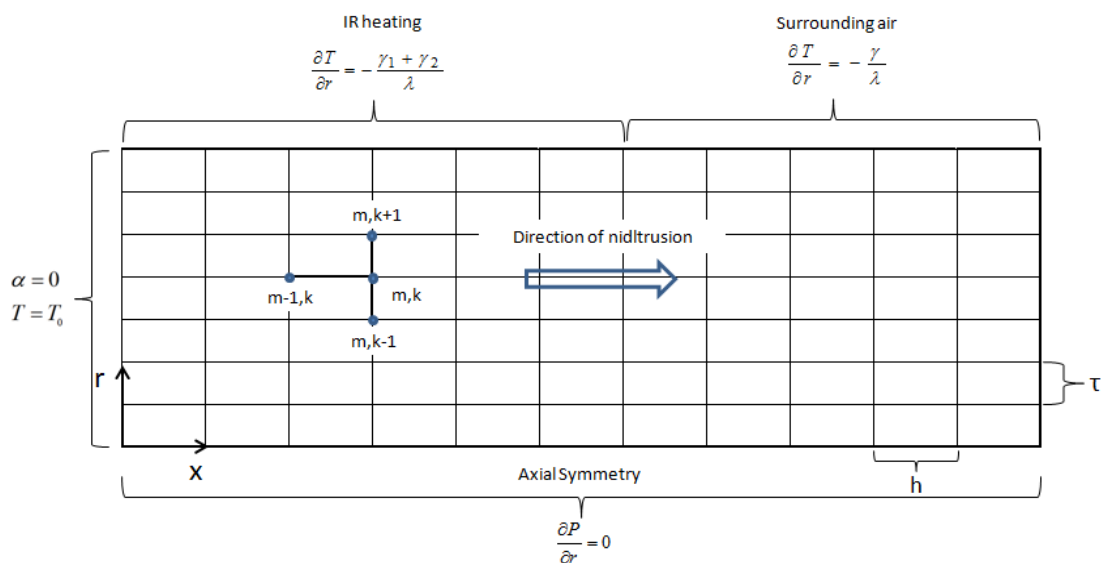


Fig. 3. Schematic of the finite-difference grid for the computational domain

finite-difference grid is presented on Fig. 3.

The computational domain is divided into two main regions, a heating chamber region where final curing of the composite is achieved and a region where the finished product cools on the ambient air.

First consider the algorithm for solving the direct problem. For each time step  $t$ , starting from the second, the unknown temperature is determined by using Eq. 1, 2 written in finite difference form:

$$\rho \cdot c \cdot U \cdot \frac{T_{k,m} - T_{k,m-1}}{h} = \rho_r \cdot (1 - \nu_f) \cdot H_{tot} \cdot A \cdot \exp\left(-\frac{E_a}{R_g \cdot T_{k,m-1}}\right) \cdot \alpha_{k,m-1}^m \cdot (1 - \alpha_{k,m-1})^n \quad (8)$$

$$+ \lambda \cdot \left( \frac{1}{(k-1) \cdot \tau} \cdot \frac{T_{k+1,m} - T_{k,m}}{\tau} + \frac{T_{k+1,m} - 2T_{k,m} + T_{k-1,m}}{\tau^2} \right),$$

where  $k, m$  are node numbers in radial and longitudinal directions, correspondingly,  $\tau, h$  are step lengths along radial and longitudinal directions.

Material properties for Eq. 8 are determined at the previous time step (9):

$$\rho_r = \alpha_{k,m-1} \cdot \rho_r^c + (1 - \alpha_{k,m-1}) \cdot \rho_r^u, \quad c_r = \alpha_{k,m-1} \cdot c_r^c + (1 - \alpha_{k,m-1}) \cdot c_r^u. \quad (9)$$

For  $N$  nodes in radial direction the system of  $N$  equations should be solved. This system is consist of  $(N-2)$  equations (8), and additional two equations are determined from the boundary conditions (10):

$$T_{1,m} = T_{2,m}, \quad -\lambda \cdot (T_{N,m} - T_{N-1,m}) / \tau = \gamma_1 + \gamma_2, \quad or \quad -\lambda \cdot (T_{N,m} - T_{N-1,m}) / \tau = \gamma. \quad (10)$$

Then, the degree of cure is determined from the Eq. (2) for the current time step (11):

$$\alpha_{k,m} = \alpha_{k,m-1} + \frac{h}{U} \cdot A \cdot \exp\left(-\frac{E_a}{R_g \cdot T_{k,m}}\right) \cdot \alpha_{k,m-1}^m \cdot (1 - \alpha_{k,m-1})^n \quad (11)$$

Thus, the solution is determined on all the nodes of finite-difference grid.

The optimization task includes the determination

of the maximum nidltrusion speed. At the same time at this speed the product must be fully cured ( $\alpha \geq 0.95$ ) and have no evidence of decomposition ( $T < T_{max}$ ). For this purpose, a mathematical algorithm to optimize the nidltrusion process was developed (see Fig. 4).

At the beginning of the calculation, the maximum desired speed of pultrusion  $U_{max}$  should be set. The speed of nidltrusion process  $U$  is recalculated for each optimization step depending on the result of calculation (the maximum temperature of composite should not be greater than  $T_{max}$ , and  $\alpha$  at the outlet of heating chamber should be greater than 0.95). The optimal solution is found, if the difference in the speed for the current and previous optimization step is not greater than 0.001. This algorithm runs for each temperature of the heating chamber. Thus, each temperature of the heating chamber corresponds to the optimum speed of nidltrusion for chosen resin system.

## MATERIALS AND METHODS

The primary material used in this study is the various percentages MWCNT modified composite which consist of epoxy resin (base matrix, 40% volume fraction) and a glass fiber (macro filler, 60% volume fraction).

The epoxy was Epon 862 – diglycidyl ether of bisphenol F and the the curing agent was aromatic diamine EpiCure W. COOH–functionalized multi-walled carbon nanotubes were synthesized by catalytic chemical vapor deposition (CCVD) method and procured from Nanocyl Inc (average diameter of 9.5 nm and average length of less than 1.5  $\mu$ m).

Cure behavior of various percentages MWCNT modified epoxy resin (net resin, resin with 0.1, 0.2 and 0.3 wt% MWCNT) was observed through total heat of reaction and activation energy using curve-fitting method on the basis of numerical data presented in [12]. The dynamic DSC thermograms for pure epoxy and MWCNT modified epoxy nanocomposites at four different heating rates from 2°C/min - 15°C/min has been shown in Fig. 5.

The value of the integral thermal effect of the reaction  $H_{tot}$  was determined from the DSC curves as the area of the region bounded by the exotherm and the baseline. Other constants for Eq. 2 (pre-exponential factor  $A$ , equation superscripts  $m, n$  and activation energy  $E_a$ ) were determined using curve-fitting method [13]. All these data have been summarized in Table 1. Another parameters utilized for mathematical model are displayed in Table 2.

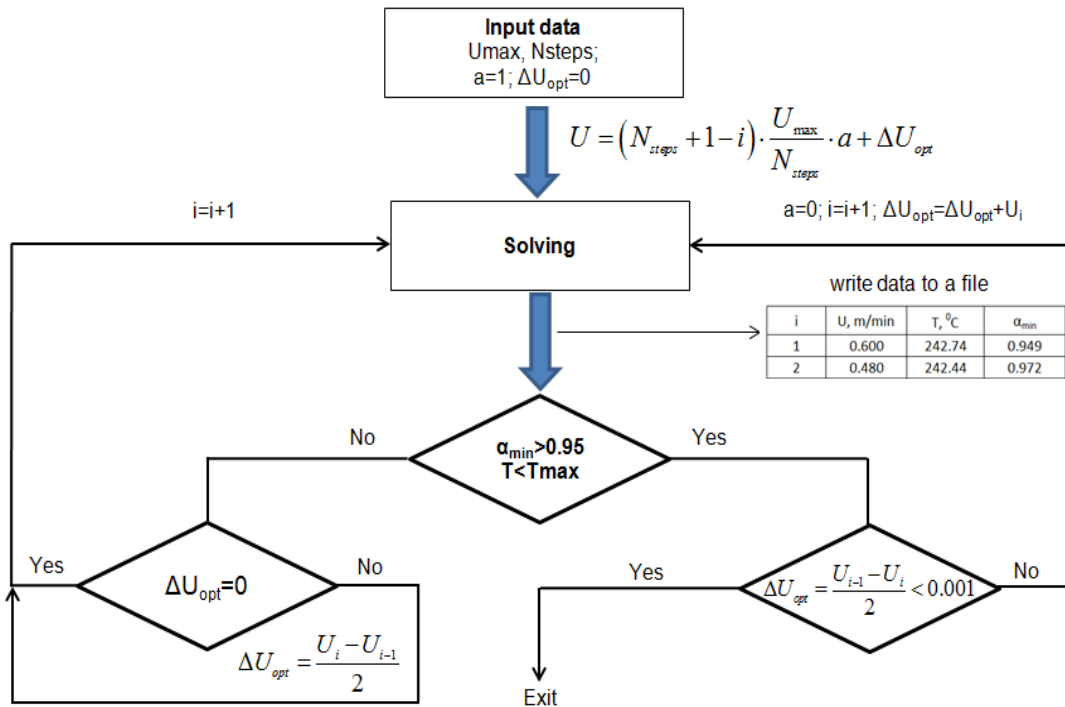


Fig. 4. Optimization algorithm for nidltrusion process.

The special Software based on mathematical model (8)-(11) was utilized for the simulation of curing of fiberglass/epoxy BCR during nidltrusion process. As example, the computed temperature and the degree of cure distributions for the longitudinal section of 8-mm BCR are shown on Fig. 6. As was mentioned above, at the maximum nidltrusion

speed U the product must be fully cured ( $\alpha \geq 0.95$ ) and have no evidence of decomposition ( $T < T_{max}$ ).

### RESULTS AND DISCUSSION

With the using of developed optimization algorithm the maximum speed of nidltrusion of 8-mm diameter BCR was determined. Fig. 7 shows

Table 1. Constants for kinetic equation (2)

Resin/coeff.	$\Delta H_{tot}$ , [J/g]	A, [s <sup>-1</sup> ]	m	n	E <sub>a</sub> , [J/mol]
Net resin	315.95	93021	0.45	1.77	62022
0.1% MWCNT	294.81	41681	0.29	1.72	60487
0.2% MWCNT	315.38	15528	0.33	1.52	56573
0.3% MWCNT	332.93	24345	0.28	1.73	58753

Table 2. Parameters for mathematical model

Property	Value
Fiber density, [g/cm <sup>3</sup> ]	2.56
Specific heat capacity of the fibers, [J/(g·K)]	0.84
Heat-transfer coefficient of the fibers, [W/(m·K)]	1.1
Uncured resin density, [g/cm <sup>3</sup> ]	1.06
Cured resin density, [g/cm <sup>3</sup> ]	1.27
Specific heat capacity of uncured resin, [J/(g·K)]	1.69
Specific heat capacity of cured resin, [J/(g·K)]	1.36
Heat-transfer coefficient of resin, [W/(m·K)]	0.2
Inlet temperature, [°C]	24
The emissivity of the surface	0.7
Decomposition temperature, T <sub>max</sub> , °C	250

a convergence of solution to the exact nidltrusion speed value for the resin system with 0.2% MWCNT. The temperature set of heating chamber is 190 °C. The result shows that the developed optimization algorithm allows getting the convergence on step #8.

The plots of predicted optimal nidltrusion speed versus the temperature set of heating chamber for different resin systems are shown in Fig. 8. As can be seen, the use of net resin and the resin with 0.2 wt% MWCNT gives the highest nidltrusion speed.

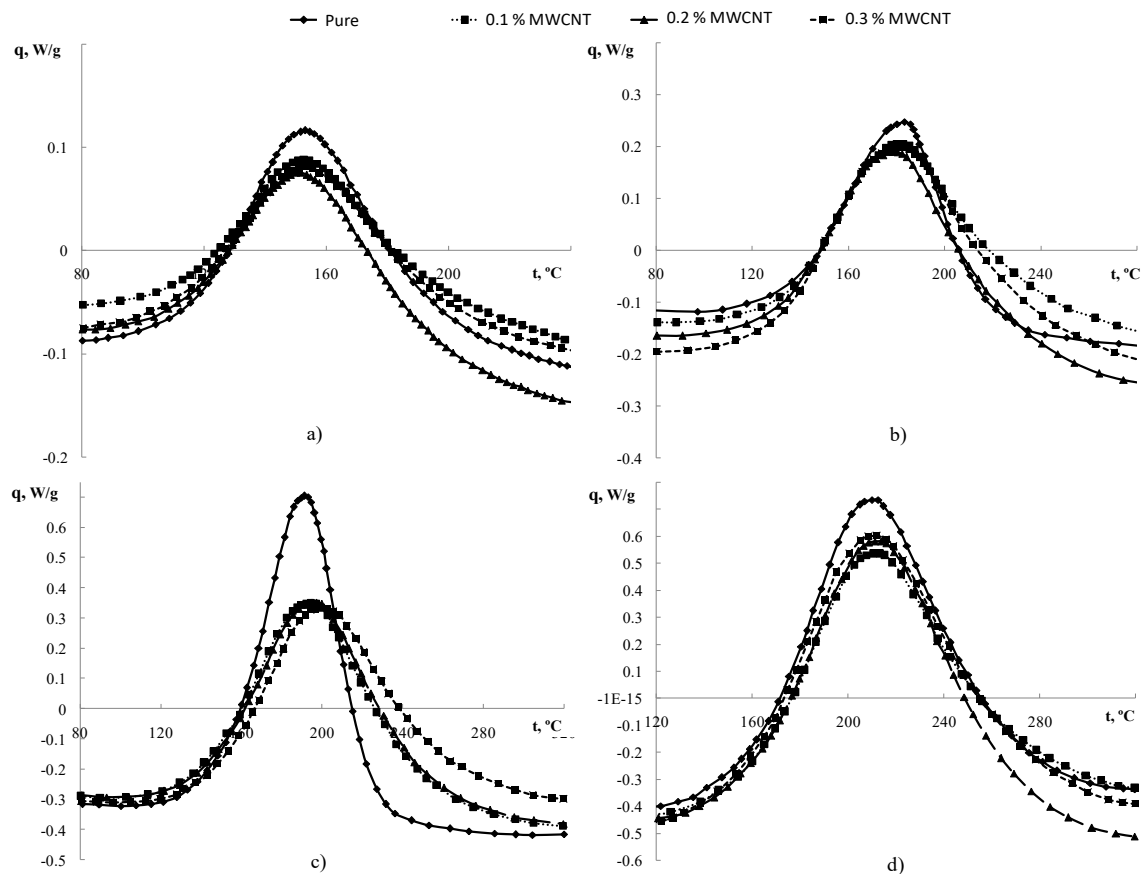


Fig. 5. Dynamic DSC thermograms of different system at various heating rate (a) 2; (b) 5; (c) 10; and (d) 15 deg/min [12]

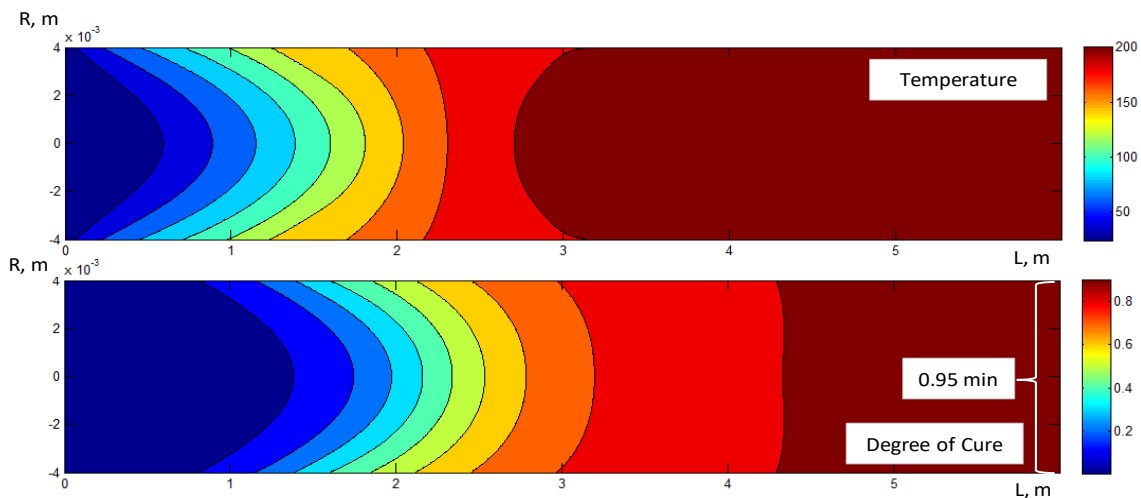


Fig. 6. Temperature and degree of cure distributions within the BCR [10]

The probable cause of the observed phenomena is that the presence of up to 0.2% MWCNTs in epoxy lowers the exothermic peak height than that of neat epoxy which indicates increased degree of interaction of MWCNTs with epoxy resin as well as physical hindrance by nanotubes to the polymer chain mobility. Whereas relative higher percentage of MWCNTs have significant retarding effect on curing characteristics of epoxy since it

requires longer post curing time.

For all considered resin systems optimal speed of nidltrusion process begins to decline sharply after the heating chamber temperature of 190 °C. This is due to the fact that one of the optimization conditions ( $\alpha \geq 0.95$ ) becomes impossible at the highest speed, but it is possible to find lower optimal speed. At high temperature and low speed composite material polymerizes rapidly in the

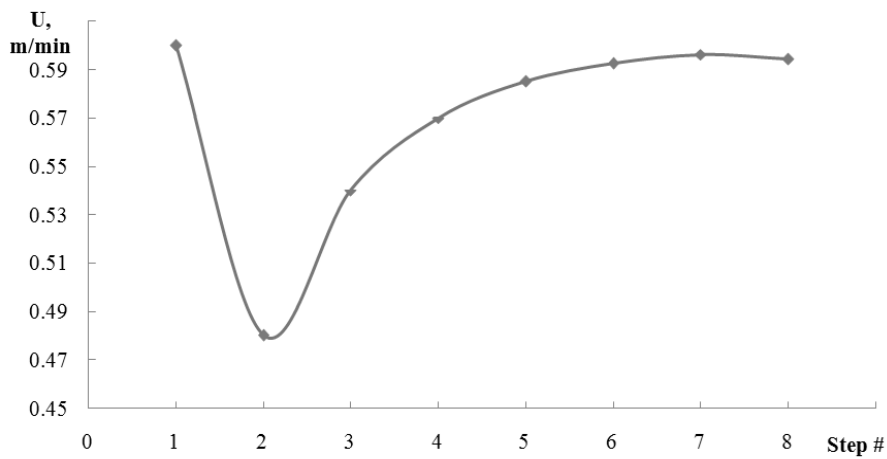


Fig. 7. The convergence of solution to the exact nidltrusion speed value

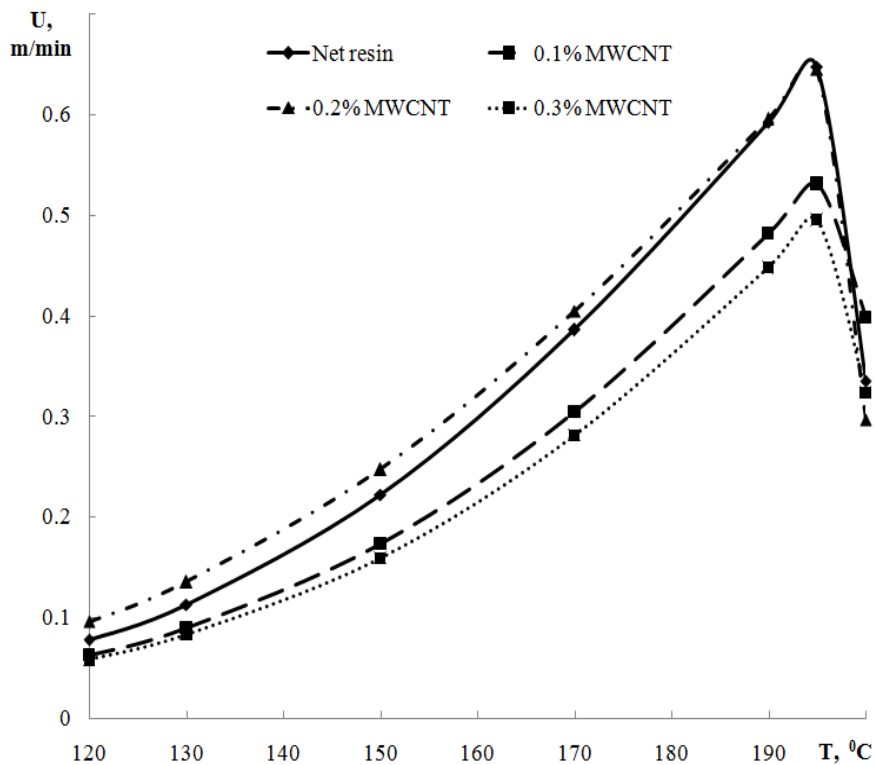


Fig. 8. Temperature-dependent optimal nidltrusion speed for different resin systems

heating chamber making it possible to perform two optimization conditions.

## CONCLUSIONS

In this study, the optimization algorithm for two-dimensional heat transfer and curing model was presented. It allows predict the maximum speed of nidltrusion process for various resin systems at the different chamber temperatures. The developed algorithm allows to determine the solution sequentially at each time step without constituting a big system of equations for the entire computation domain. This significantly reduces the computation time and makes the task more „physical“. The numerical results are stable due to an implicit finite difference method was used.

The impact of carboxyl functionalized multiwalled carbon nanotubes on the maximum speed of nidltrusion process was shown by the example. It was shown that the low loading of MWCNTs (0.1 wt%) and the higher loading of MWCNTs (0.3 wt% ) have retarding effects on the speed of nidltrusion. It is important to note the following: the addition of CNTs to the epoxy resin affects the productivity of the nidltrusion process, and requires a change in the temperature-speed regime in order to obtain a high-quality product.

The developed optimization algorithm can be further applied in the modeling of pultrusion process, in particular, for the production of anisotropic rods [13].

## ACKNOWLEDGMENT

The authors would like to thank Moscow State Technological University STANKIN for financial support of this work.

## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

## REFERENCES

1. Benmokrane, B., Masmoudi, R., FRP C-Bar as Reinforcing Rod for Concrete Structures. *Adv Compos Mater, Proc Int Conf* , 2<sup>nd</sup>, The Canadian Society for Civil Engineering. 1996.
2. Grigoriev, S. N., Kazakov, I. A., Krasnovskii, A. N., The stress-strain state determination of a large diameter composite rod during pultrusion process, *Adv Mater Res, Proc Int Conf ICCASCE 2015*, CRC Press, 2016, 329-333.
3. Meyer, R. M. *Handbook of pultrusion technology*, Chapman and Hall, New York, 1985.
4. Grigoriev, S. N., Kazakov, I. A., Krasnovskii, A. N., The Impact of Pre-heating on Pressure Behavior in Tapered Cylindrical Die in Pultrusion of Large-sized Composite Rods, *Adv Mat Res*, 2015, 1064, 120-127.
5. Grigoriev, S. N., Kazakov, I. A., Krasnovskii, A. N., et al., An analytic definition of the border polymerization line for axisymmetric composite rods, *Appl Compos Mater*, 2013, 20 (6), 1055-1064.
6. Qiu, S. L., Wang, C. S., Wang, Y. T., et al., Effects of Graphene Oxides on the Cure Behaviors of a Tetrafunctional Epoxy Resin. *Express Polym Lett*, 2011, 5 (9), 809-818.
7. Tao, K., Yang, S., Grunlan, J. C., et al., Effects of Carbon Nanotube Fillers on the Curing Processes of Epoxy Resin-Based Composites. *J Appl Polym Sci*, 2006, 102 (6), 5248-5254.
8. Abdalla, M., Dean, P., Robinson, D. and Nyairo, E., Cure Behavior of Epoxy/MWCNT Nanocomposites: The Effect of Nanotube Surface Modification, *Polymer*, 2008, 49 (15), 3310-3317.
9. Zhou, T., Wang, X., Liu, X. and Xiong, D., Influence of Multi-Walled Carbon Nanotubes on the Cure Behavior of Epoxy/Imidazole System, *Carbon*, 2009, 47 (4), 1112-1118.
10. Grigoriev, S. N., Kazakov, I. A., Krasnovskii, A. N., Nidltrusion as the method for composite reinforcement production. Part I: Mathematical model of heat transfer and cure, *Adv Mater Mech Struct Eng, Proc Int Conf, 2<sup>nd</sup>*, AMMSE 2015, CRC Press, 2016, 207-210.
11. Kamal, M. R., Thermoset Characterization for Moldability Analysis, *Polym Eng Sci*, 1974, 14, 231-239.
12. Jahan, N., Narteh, A., Hosur, M., et al., Effect of Carboxyl Functionalized MWCNTs on the Cure Behavior of Epoxy Resin, *Open J Compos Mater*, 2013, 3(2A), 40-47.
13. Kazakov, I. A., Krasnovskii, A. N., Effect of functionalized multiwalled carbon nanotubes on the feasibility of fabrication of composite glass fiber reinforced plastic rebars, *Russ J Appl Chem+* , 2016, 89(8),1309-1316.
14. Kutin, A. A., Krasnovskii, A. N., Kazakov, I. A., The fiber orientation angle determination for a composite anisotropic solid rod in pultrusion, *Adv Mater Res*, 2014, 941(944), 2273-2278.