UDC 543.318.3+515.124

V. V. ROMANUKE

ON OPTIMIZING WLF EQUATION OVER EXPERIMENTAL VISCOSITY MEASUREMENTS BY FINITE SET OF FIXED TEMPERATURES WITH RUNNING $\mathbb{L}_w$ METRIC

Khmelnytskyy National University
Instytutska street, 11, Khmelnytskyy, Ukraine

Abstract. There has been suggested a criterion of selecting the most appropriate WLF equation within the finite set of such equations, which are obtained by the finite number of viscosity measurements. The suggested criterion is based on minimizing the space $\mathbb{L}_w[T_1; \tau]$ distance with $\tau \in (T_1; T_N]$ between a WLF equation and the $(N-1)$-linked pattern polyline, linking N viscosity measurement points. Also there has been developed and represented the MATLAB function for computing and saving all the direct and oblique parameters of the determined optimal WLF equation.

Анотація. Запропоновано критерій вибору найбільш адекватного ВЛФ-рівняння у скінченній множині таких рівнянь, які отримуються скінченною кількістю вимірювань в'язкості. Запропонований критерій заснований на мінімізації відстані у просторі $\mathbb{L}_w[T_1; \tau]$ з $\tau \in (T_1; T_N]$ між ВЛФ-рівнянням та $(N-1)$-ланковою ламаною-зразком, що з'єднує N точок вимірів в'язкості. Також розроблено і представлено MATLAB-функцію для обчислення та збереження прямих та непрямих параметрів визначеного оптимального ВЛФ-рівняння.

Аннотация. Предложено критерий выбора наиболее подходящего ВЛФ-уравнения в конечном множестве таких уравнений, которые получаются при конечном количестве измерений вязкости. Предложенный критерий основан на минимизации расстояния в пространстве $\mathbb{L}_w[T_1; \tau]$ с $\tau \in (T_1; T_N]$ между ВЛФ-уравнением и $(N-1)$-звеньевой ломаной-образцом, соединяющей N точек измерений вязкости. Также разработано и представлено MATLAB-функцию для вычисления и сохранения прямых и косвенных параметров определённого оптимального ВЛФ-уравнения.

Key words: polymer, polyethylene terephthalate, recycling, viscosity, temperature dependence, glass transition temperature, WLF equation, functional space, minimal distance, running metric, MATLAB.

INTRODUCTION TO PROBLEM OF EVALUATING THE POLYMER MATERIALS VISCOSITY TEMPERATURE DEPENDENCE

Polymer waste recycling to prevent or reduce environmental pollution is a high importance problem of now days. By recycling the molten polymer wastes it is significant to know the temperature dependence of its viscosity [1 — 4], as this fixes the regime of polymer processing and some requirements to control-measuring apparatus [5 — 8]. Moreover, the molten polymer viscosity temperature dependence essentially influences on technological and viscous-sticky properties, which are conditioned by nature characteristics and polymer composition [2, 4, 8 — 13]. The Williams — Landel — Ferry equation (WLF equation) is an unsophisticated and at the same time is exact enough formula for temperature dependence of polymer materials viscosity η [7, 14]. Actually, WLF equation is valid within the temperature segment $\left[T_g; T_g + 100\right]$ by the glass transition temperature T_g in Kelvin degrees [15], determined for the fixed polymer system [7]. Commonly, WLF equation is

$$\eta(T) = \eta_g \cdot 10^{\frac{C_1(T-T_g)}{C_2+T-T_g}} \tag{1}$$

for $T \in \left[T_g; T_g + 100\right]$ with the viscosity η_g measured by the temperature T_g, where C_1 and C_2 are constants. To speak generally, those constants are functions of T_g. Obviously, that for obtaining them it is sufficient to carry out the two viscosity measurements by the known T_g and η_g, what will give the system of two equations (1) with respect to the unknown C_1 and C_2. However, even if the glass transition temperature is fixed and learned, it is very uneasy or just impossible to measure the polymer viscosity at T_g [7, 16, 17]. Besides, this temperature may vary even for the same type of polymer waste material, depending on its vitrification speed and other operation factors. That is why generally there is need to carry out N polymer viscosity measurements

$$\left\{\eta_i\right\}_{i=1}^{N} = \left\{\eta\left(T_i\right)\right\}_{i=1}^{N} = \left\{\eta_g \cdot 10^{\frac{C_1\left(T_i - T_g\right)}{C_2 + T_i - T_g}}\right\}_{i=1}^{N},$$

$$T_i \in \left(T_g;\, T_g + 100\right) \quad \forall\, i = \overline{1,\, N}\,,\;\; T_i < T_{i+1} \quad \forall\, i = \overline{1,\, N-1}\,, \tag{2}$$

taking $N = 4$ for obtaining the constants C_1 and C_2 with also unknown T_g and η_g. But as WLF equation (1) is still just an approximately rough model of real existing and unknown temperature dependence $\eta\left(T\right)$, then for its as detailed as possible learning there is need to carry out more than four measurements. And those N measurements will give possibility to obtain $\frac{N!}{\left(N-4\right)!\cdot 4!}$ groups

$$\left\{\left\{\left\{\left\{C_1\left(T_h,\, T_j,\, T_k,\, T_l\right),\, C_2\left(T_h,\, T_j,\, T_k,\, T_l\right),\, T_g\left(T_h,\, T_j,\, T_k,\, T_l\right),\, \eta_g\left(T_h,\, T_j,\, T_k,\, T_l\right)\right\}_{h=4}^{N}\right\}_{j=3}^{h-1}\right\}_{k=2}^{j-1}\right\}_{l=1}^{k-1} \tag{3}$$

of the constants C_1 and C_2 with T_g and η_g, what will allow to have $\frac{N!}{\left(N-4\right)!\cdot 4!}$ different WLF equations

$$\left\{\left\{\left\{\left\{\eta_{hjkl}\left(T\right)\right\}_{h=4}^{N}\right\}_{j=3}^{h-1}\right\}_{k=2}^{j-1}\right\}_{l=1}^{k-1} =$$

$$= \left\{\left\{\left\{\left\{\eta_g\left(T_h,\, T_j,\, T_k,\, T_l\right)\cdot 10^{\frac{C_1\left(T_h,\, T_j,\, T_k,\, T_l\right)\left[T - T_g\left(T_h,\, T_j,\, T_k,\, T_l\right)\right]}{C_2\left(T_h,\, T_j,\, T_k,\, T_l\right) + T - T_g\left(T_h,\, T_j,\, T_k,\, T_l\right)}}\right\}_{h=4}^{N}\right\}_{j=3}^{h-1}\right\}_{k=2}^{j-1}\right\}_{l=1}^{k-1} \tag{4}$$

of the type (1). The stated problem core is how to select the most appropriate WLF equation

$$\eta_g\left(T_{h*},\, T_{j*},\, T_{k*},\, T_{l*}\right)\cdot 10^{\frac{C_1\left(T_{h*},\, T_{j*},\, T_{k*},\, T_{l*}\right)\left[T - T_g\left(T_{h*},\, T_{j*},\, T_{k*},\, T_{l*}\right)\right]}{C_2\left(T_{h*},\, T_{j*},\, T_{k*},\, T_{l*}\right) + T - T_g\left(T_{h*},\, T_{j*},\, T_{k*},\, T_{l*}\right)}} =$$

$$= \eta_g^* \cdot 10^{\frac{C_1^*\left(T - T_g^*\right)}{C_2^* + T - T_g^*}} = \eta^*\left(T\right) \in \left\{\left\{\left\{\left\{\eta_{hjkl}\left(T\right)\right\}_{h=4}^{N}\right\}_{j=3}^{h-1}\right\}_{k=2}^{j-1}\right\}_{l=1}^{k-1} \tag{5}$$

from that $\frac{N!}{(N-4)!\cdot 4!}$ WLF equations multiplicity, orienting to the $(N-1)$-linked polyline $\eta_0(T)$, that in order links the points $[T_i \quad \eta_i]$ and $[T_{i+1} \quad \eta_{i+1}]$ $\forall\ i=\overline{1,\ N-1}$ from measurements (2).

ANALYSIS OF RESEARCHES ON TEMPERATURE DEPENDENCE OF POLYMER MATERIALS VISCOSITY

Viscosity is a measure of the resistance of a polymer system, which is being deformed by either shear stress or tensional stress [1, 5, 7, 16]. Polymer viscosity describes its internal resistance to flow and may be thought of as a measure of molten polymer friction. The temperature dependence of polymer materials viscosity is the phenomenon by which polymer viscosity tends to decrease (as it usually happens) when the surrounding temperature increases [18]. Such dependence is contemporarily expressed by one of the several existing models, where WLF equation is usually used for polymer melts or other fluids that have a glass transition temperature [7, 18]. Investigation of the polymer viscosity temperature dependence $\eta(T)$ is very smart to learn the mechanism of its flow and to comprehend the macromolecular behavior by deformations. Polymer viscosity temperature dependence influences strongly on the regime of the polymer recycling process, defining the quality and certain properties of the recycled polymer ware. There are many investigators of polymer viscosity temperature dependence in WLF equation form, where, except M. L. Williams, R. F. Landel, J. D. Ferry, it ought to be underlined G. S. Fulcher, G. Tammann, W. Hesse, A. Kovacs, G. Gee, S. Ishihara, A. A. Miller, M. H. Cohen, D. Turnbull, F. Bueche, P. B. Macedo, T. A. Litovitz, R. B. Boyer, R. N. Haward, H. Breuer, G. Rehage, A. V. Tobolskiy, R. Simha, S. Krause, G. V. Vinogradov, A. Y. Malkin. The WLF equation (1) is connected with unconfined space conception [7, 14, 18] and it was grounded under that, though (1) is rather not the ideal model for polymer viscosity temperature dependence when the temperature is out of the segment $[T_g;\ T_g+100]$. Being not restricted in measuring the viscosity within the interval $(T_g;\ T_g+100)$ for only four times, there is the unsolved question of how to select the optimal WLF equation from $\frac{N!}{(N-4)!\cdot 4!}$ WLF equations (4), obtained after having measured the viscosity for N times by different temperatures $\{T_i\}_{i=1}^{N}$ for the better visualization of experimental polyline data, where $N \in \mathbb{N} \setminus \{1,\ 2,\ 3\}$.

PAPER PURPOSE AND ASSIGNMENTS

Suppose, that within the interval $(T_g;\ T_g+100)$ we have carried out the N polymer viscosity measurements (2), where $N \in \mathbb{N} \setminus \{1,\ 2,\ 3\}$. Then here is the purpose to select the most appropriate WLF equation (5) amongst $\frac{N!}{(N-4)!\cdot 4!}$ different WLF equations (4), obtained by the corresponding $\frac{N!}{(N-4)!\cdot 4!}$ groups of four parameters (3). For accomplishing this, there should be applied the minimal functional distance criterion between each element of the set (4) and $(N-1)$-linked polyline $\eta_0(T)$, that in order links the points $[T_i \quad \eta_i]$ and $[T_{i+1} \quad \eta_{i+1}]$ $\forall\ i=\overline{1,\ N-1}$. This polyline may be considered as a rough pattern of the being searched temperature dependence of the given polymer material viscosity. The greater number N the lesser roughness is in such pattern. The appropriate functional space is $\mathbb{L}_w[T_1;\ T_N]$ with its metric, ever letting get the value of distance between two functions, defined on the segment $[T_1;\ T_N]$. Eventually, procedure of optimizing the model of polymer viscosity temperature dependence in WLF equation form by the said criterion will be developed in the mathematical environment MATLAB.

USING $\mathbb{L}_w[T_1;\ T_N]$ METRIC FOR DETERMINING THE OPTIMAL TEMPERATURE DEPENDENCE AMONGST THE FUNCTIONS (4)

In $\mathbb{L}_w\left[T_1; T_N\right]$ the distance $\rho_{\mathbb{L}_w[T_1;T_N]}\left(\eta_{hjkl}(T), \eta_0(T)\right)$ between the polymer viscosity temperature dependence $\eta_{hjkl}(T)$ and pattern polyline $\eta_0(T)$ is the norm of their difference $\eta_{hjkl}(T)-\eta_0(T)$, that is

$$\rho_{\mathbb{L}_w[T_1;T_N]}\left(\eta_{hjkl}(T), \eta_0(T)\right)=\left(\int_{T_1}^{T_N}\left|\eta_{hjkl}(T)-\eta_0(T)\right|^w dT\right)^{\frac{1}{w}},$$

$$h=\overline{4,\, N},\ j=\overline{3,\, h-1},\ k=\overline{2,\, j-1},\ l=\overline{1,\, k-1}. \tag{6}$$

The temperature function $\eta_{hjkl}(T)$ in (6) is substituted with the corresponding element from the set (4). The pattern polyline $\eta_0(T)$ in (6) is

$$\eta_0(T)=\alpha_{i+1,i}+\beta_{i+1,i}T \text{ by } T\in\left[T_i; T_{i+1}\right]\ \forall\, i=\overline{1,\, N-1}, \tag{7}$$

where

$$\alpha_{i+1,i}=\eta_i-T_i\frac{\eta_i-\eta_{i+1}}{T_i-T_{i+1}}\ \forall\, i=\overline{1,\, N-1} \tag{8}$$

and

$$\beta_{i+1,i}=\frac{\eta_i-\eta_{i+1}}{T_i-T_{i+1}}\ \forall\, i=\overline{1,\, N-1}. \tag{9}$$

Hence, taking (4) and (7) — (9) explicitly, the distance (6) between $\{h,\, j,\, k,\, l\}$-dependence $\eta_{hjkl}(T)$ and pattern polyline $\eta_0(T)$ is

$$\rho_{\mathbb{L}_w[T_1;T_N]}\left(\eta_{hjkl}(T), \eta_0(T)\right)=\left(\sum_{i=1}^{N-1}\int_{T_i}^{T_{i+1}}\left|\eta_{hjkl}(T)-\eta_0(T)\right|^w dT\right)^{\frac{1}{w}}=$$

$$=\left(\sum_{i=1}^{N-1}\int_{T_i}^{T_{i+1}}\left|\eta_g\left(T_h, T_j, T_k, T_l\right)\cdot 10^{\frac{C_1(T_h, T_j, T_k, T_l)\left[T-T_g(T_h, T_j, T_k, T_l)\right]}{C_2(T_h, T_j, T_k, T_l)+T-T_g(T_h, T_j, T_k, T_l)}}-\eta_i+T_i\frac{\eta_i-\eta_{i+1}}{T_i-T_{i+1}}-\frac{\eta_i-\eta_{i+1}}{T_i-T_{i+1}}T\right|^w dT\right)^{\frac{1}{w}}=$$

$$=\left(\sum_{i=1}^{N-1}\int_{T_i}^{T_{i+1}}\left|\eta_g\left(T_h, T_j, T_k, T_l\right)\cdot 10^{\frac{C_1(T_h, T_j, T_k, T_l)\left[T-T_g(T_h, T_j, T_k, T_l)\right]}{C_2(T_h, T_j, T_k, T_l)+T-T_g(T_h, T_j, T_k, T_l)}}+\frac{\eta_i-\eta_{i+1}}{T_i-T_{i+1}}\left(T_i-T\right)-\eta_i\right|^w dT\right)^{\frac{1}{w}},$$

$$h=\overline{4,\, N},\ j=\overline{3,\, h-1},\ k=\overline{2,\, j-1},\ l=\overline{1,\, k-1},\ w\geqslant 1. \tag{10}$$

Surely, that for determining the optimal temperature dependence amongst the functions (4) now it is sufficient to find that dependence from (4), for which the distance (10) is minimal. However, the consumer of such optimal WLF model not necessarily intends to apply it over the whole range $\left[T_g; T_g+100\right]$ or even $\left[T_1; T_N\right]$. This means that there is some part $\left[T_{\min}; T_{\max}\right]$ of the segment $\left[T_1; T_N\right]\supset\left[T_{\min}; T_{\max}\right]$ which is going to be used anyway, and the rest part $\left[T_1;\, T_N\right] \backslash \left[T_{\min};\, T_{\max}\right]$ of this segment is not needed or just ignored.

SWITCHING TO $\mathbb{L}_w\left[T_1;\, T_N\right]$ RUNNING METRIC FOR CONTINUAL DETERMINATION OF THE OPTIMAL TEMPERATURE DEPENDENCE AMONGST THE FUNCTIONS (4)

If the temperature range of applying the being searched optimal WLF model of polymer viscosity temperature dependence $\eta^*\left(T\right)$ is narrower than $\left[T_{\min};\, T_{\max}\right]$, say, may it be from $T = T_1$ up to $T = T_{N-1}$, then we will be interested only in minimal functional distance between the shortened pattern polyline

$$\eta_0\left(T\right) = \alpha_{i+1,i} + \beta_{i+1,i}T = \eta_i - T_i \frac{\eta_i - \eta_{i+1}}{T_i - T_{i+1}} + \frac{\eta_i - \eta_{i+1}}{T_i - T_{i+1}} T \quad \text{by} \quad T \in \left[T_i;\, T_{i+1}\right] \quad \forall\, i = \overline{1,\, N-2}\,, \tag{11}$$

and the elements of the set (4), defined on the subsegment $\left[T_1;\, T_{N-1}\right] \subset \left[T_1;\, T_N\right]$. Therefore instead of the distance (10) in the space $\mathbb{L}_w\left[T_1;\, T_N\right]$ it is essential to define the running distance

$$\rho_{\mathbb{L}_w\left[T_1;\, \tau\right]}\left(\eta_{hjkl}\left(T\right),\, \eta_0\left(T\right)\right) = \left(\int\limits_{T_1}^{\tau} \left|\eta_{hjkl}\left(T\right) - \eta_0\left(T\right)\right|^w dT\right)^{\frac{1}{w}} =$$

$$= \left(\sum_{m=1}^{M-1} \int\limits_{T_m}^{T_{m+1}} \left|\eta_{hjkl}\left(T\right) - \eta_0\left(T\right)\right|^w dT + \int\limits_{T_M}^{\tau} \left|\eta_{hjkl}\left(T\right) - \eta_0\left(T\right)\right|^w dT\right)^{\frac{1}{w}} =$$

$$= \left(\sum_{m=1}^{M-1} \int\limits_{T_m}^{T_{m+1}} \left|\eta_g\left(T_h,\, T_j,\, T_k,\, T_l\right) \cdot 10^{\frac{C_1\left(T_h,\, T_j,\, T_k,\, T_l\right)\left[T - T_g\left(T_h,\, T_j,\, T_k,\, T_l\right)\right]}{C_2\left(T_h,\, T_j,\, T_k,\, T_l\right) + T - T_g\left(T_h,\, T_j,\, T_k,\, T_l\right)}} + \frac{\eta_m - \eta_{m+1}}{T_m - T_{m+1}}\left(T_m - T\right) - \eta_m\right|^w dT + \right.$$

$$\left. + \int\limits_{T_M}^{\tau} \left|\eta_g\left(T_h,\, T_j,\, T_k,\, T_l\right) \cdot 10^{\frac{C_1\left(T_h,\, T_j,\, T_k,\, T_l\right)\left[T - T_g\left(T_h,\, T_j,\, T_k,\, T_l\right)\right]}{C_2\left(T_h,\, T_j,\, T_k,\, T_l\right) + T - T_g\left(T_h,\, T_j,\, T_k,\, T_l\right)}} + \frac{\eta_M - \eta_{M+1}}{T_M - T_{M+1}}\left(T_M - T\right) - \eta_M\right|^w dT\right)^{\frac{1}{w}}$$

$$\text{by } \tau \in \left[T_M;\, T_{M+1}\right],\; M \in \left\{\upsilon\right\}_{\upsilon=1}^{N-1},\; h = \overline{4,\, N},\; j = \overline{3,\, h-1},\; k = \overline{2,\, j-1},\; l = \overline{1,\, k-1},\; w \geqslant 1\,. \tag{12}$$

Properly speaking, the distance (12) corresponds to the space $\mathbb{L}_w\left[T_1;\, \tau\right]$ that is the subspace of $\mathbb{L}_w\left[T_1;\, T_N\right]$. From this it follows that in the point $T = \tau$ by $\tau \in \left[T_M;\, T_{M+1}\right]$ with $M \in \left\{\upsilon\right\}_{\upsilon=1}^{N-1}$ the optimal WLF equation amongst the $\dfrac{N!}{\left(N-4\right)! \cdot 4!}$ different WLF equations (4) is determined as

$$\eta^{*}(\tau) \in \arg \min_{\substack{\eta_{hjkl}(\tau) \\ h=\overline{4,\, N} \\ j=\overline{3,\, h-1} \\ k=\overline{2,\, j-1} \\ l=\overline{1,\, k-1}}} \rho_{\mathbb{L}_w[T_1;\, \tau]}\left(\eta_{hjkl}(T),\, \eta_0(T)\right) =$$

$$= \min_{\substack{\eta_{hjkl}(\tau) \\ h=\overline{4,\, N} \\ j=\overline{3,\, h-1} \\ k=\overline{2,\, j-1} \\ l=\overline{1,\, k-1}}} \left\{ \left(\sum_{m=1}^{M-1} \int_{T_m}^{T_{m+1}} \left| \eta_g\left(T_h,\, T_j,\, T_k,\, T_l\right) \cdot 10^{\frac{C_1(T_h,\, T_j,\, T_k,\, T_l)\left[T - T_g(T_h,\, T_j,\, T_k,\, T_l)\right]}{C_2(T_h,\, T_j,\, T_k,\, T_l) + T - T_g(T_h,\, T_j,\, T_k,\, T_l)}} + \frac{\eta_m - \eta_{m+1}}{T_m - T_{m+1}}\left(T_m - T\right) - \eta_m \right|^{w} dT + \right.\right.$$

$$+ \int_{T_M}^{\tau} \left| \eta_g\left(T_h,\, T_j,\, T_k,\, T_l\right) \cdot 10^{\frac{C_1(T_h,\, T_j,\, T_k,\, T_l)\left[T - T_g(T_h,\, T_j,\, T_k,\, T_l)\right]}{C_2(T_h,\, T_j,\, T_k,\, T_l) + T - T_g(T_h,\, T_j,\, T_k,\, T_l)}} + \right.$$

$$\left.\left. + \frac{\eta_M - \eta_{M+1}}{T_M - T_{M+1}}\left(T_M - T\right) - \eta_M \right|^{w} dT \right)^{\frac{1}{w}} \right\} \quad \forall\ \tau \in \left(T_1;\, T_N\right]. \tag{13}$$

Certainly, that in the point $\tau = T_N$ the distance (12) coincides with (10).

FINDING PARAMETERS (3) WITH MATLAB SOLVER OF SYSTEMS OF NONLINEAR EQUATIONS OF SEVERAL VARIABLES

For finding the optimal WLF dependence $\eta^{*}(T)$ that may consist of different WLF equations, it is preferable to use the technical computing environment MATLAB. Firstly there should be solved each of the $\frac{N!}{(N-4)!\cdot 4!}$ systems of the four nonlinear equations

$$\eta_\lambda - \eta_g \cdot 10^{\frac{C_1(T_\lambda - T_g)}{C_2 + T_\lambda - T_g}} = 0,\ \lambda \in \{h,\, j,\, k,\, l\},\ h = \overline{4,\, N},\ j = \overline{3,\, h-1},\ k = \overline{2,\, j-1},\ l = \overline{1,\, k-1}, \tag{14}$$

with respect to the four unknown parameters

$$C_1\left(T_h,\, T_j,\, T_k,\, T_l\right),\ C_2\left(T_h,\, T_j,\, T_k,\, T_l\right),\ T_g\left(T_h,\, T_j,\, T_k,\, T_l\right) \text{ and } \eta_g\left(T_h,\, T_j,\, T_k,\, T_l\right),$$

where the s-th system is solved by the fixed $h \in \left\{\overline{4,\, N}\right\}$, $j \in \left\{\overline{3,\, h-1}\right\}$, $k \in \left\{\overline{2,\, j-1}\right\}$ and $l \in \left\{\overline{1,\, k-1}\right\}$, $s = \overline{1,\, \frac{N!}{(N-4)!\cdot 4!}}$. The system (14) may be numerically solved, using the remarkable MATLAB solver of systems of nonlinear equations of several variables, whose help screenshot is on figures 1 — 8.

Hereinafter there will be an example with $N = 5$ viscosity measurements, so on figure 9 the corresponding MATLAB solver of the system (14) for finding the five groups of parameters (3) is screenshot. Note, that this solver routine may be run by one of the three ways: from the MATLAB Command Window line, typing “wlf_eval”; from within any script or MATLAB function, launching them; just pressing F5 key when the “wlf_eval” code window is active. This code uses beforehand saved mat-file “viscosity01”, containing the measurements (2). Also there is used the subfunction “four_wlf_eq”, which role is clear from the screenshot on figure 6.

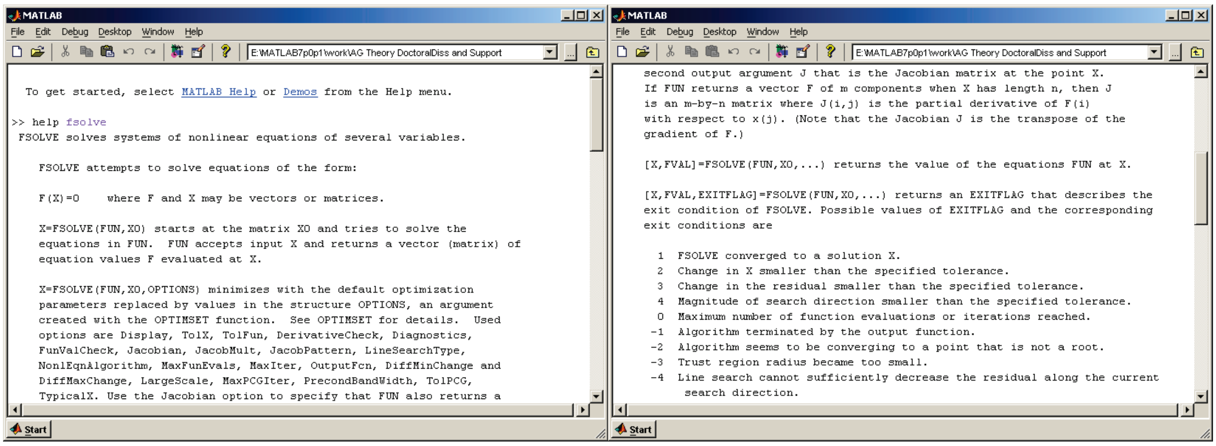


Fig. 1. Help on MATLAB solver of systems of nonlinear equations of several variables (taken from MATLAB Command Window)

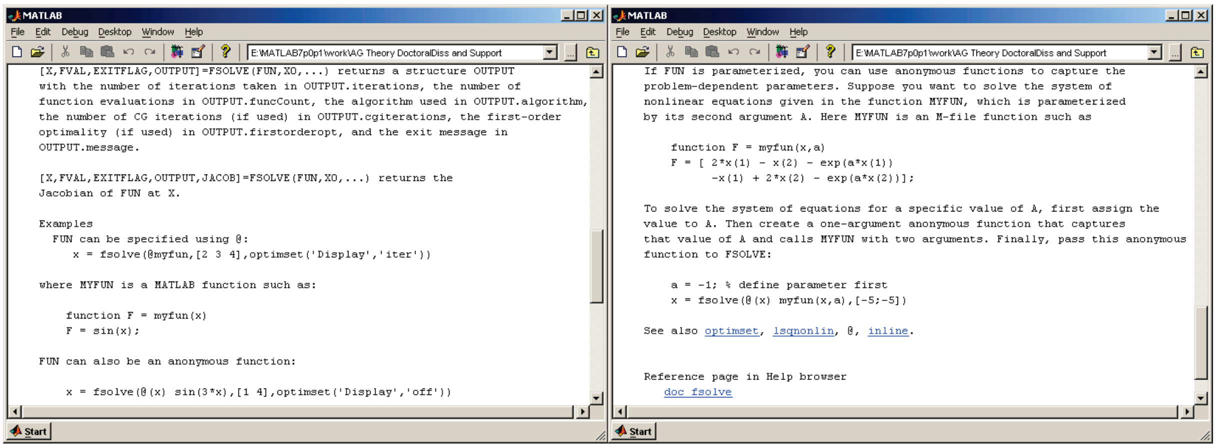


Fig. 2. End of help on MATLAB solver of systems of nonlinear equations of several variables (taken from MATLAB Command Window)

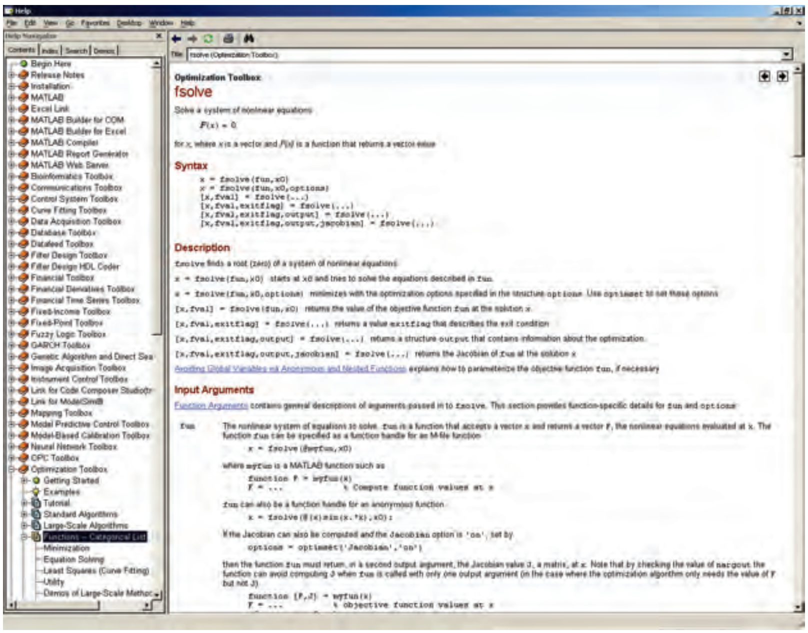


Fig. 3. First part of help on MATLAB solver of systems of nonlinear equations of several variables (taken from MATLAB Help Window)

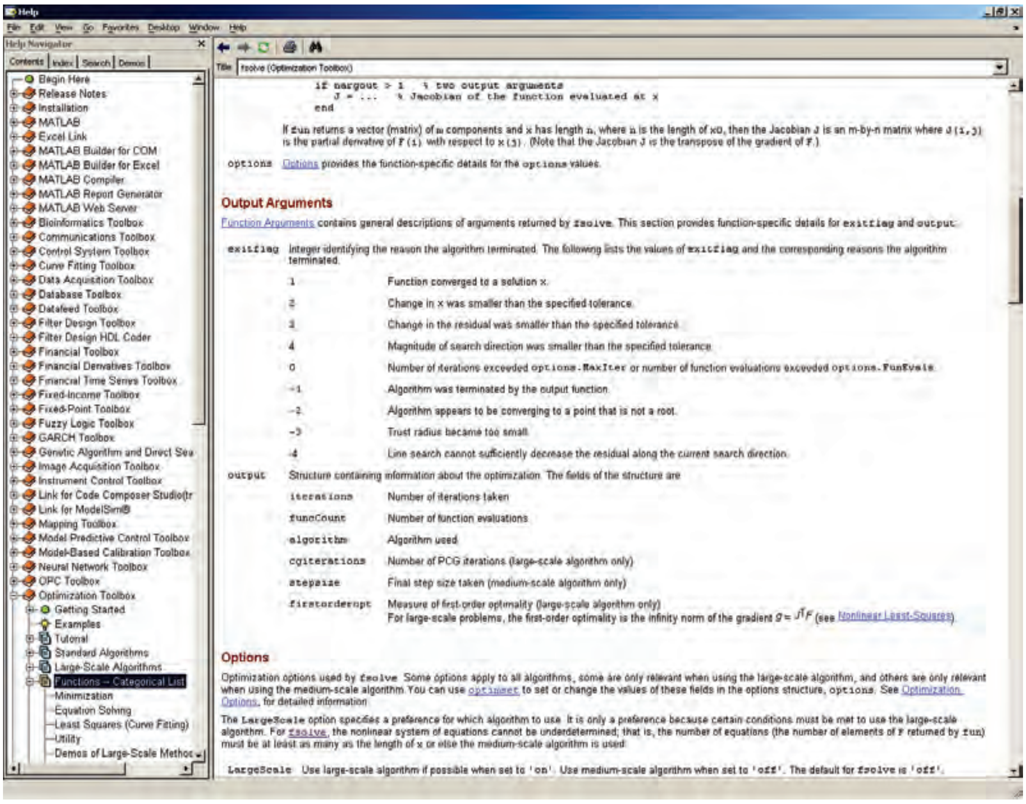


Fig. 4. Second part of help on MATLAB solver of systems of nonlinear equations of several variables (taken from MATLAB Help Window)

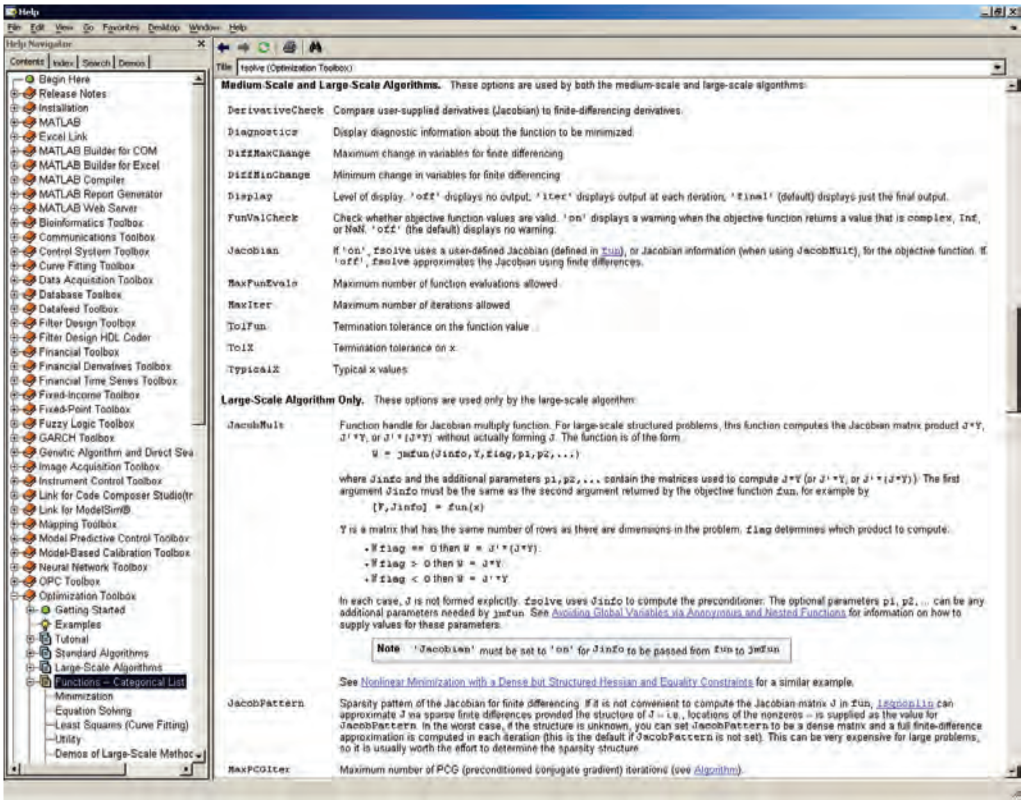


Fig. 5. Third part of help on MATLAB solver of systems of nonlinear equations of several variables (taken from MATLAB Help Window)

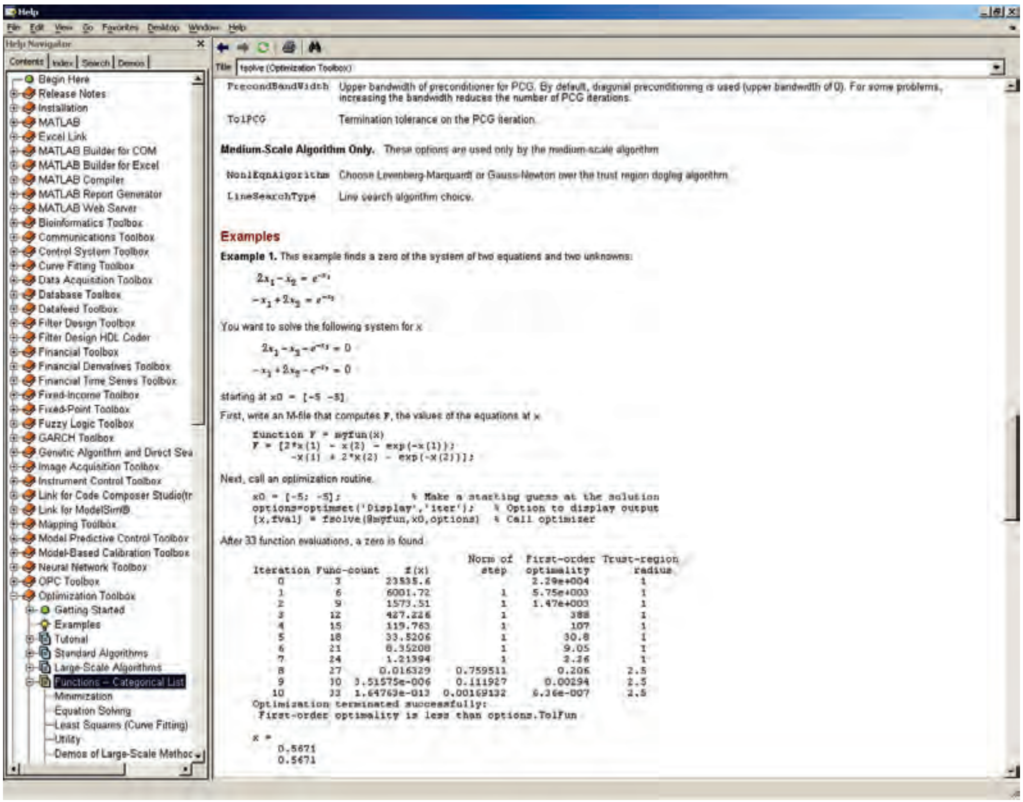


Fig. 6. Fourth part of help on MATLAB solver of systems of nonlinear equations of several variables (taken from MATLAB Help Window)

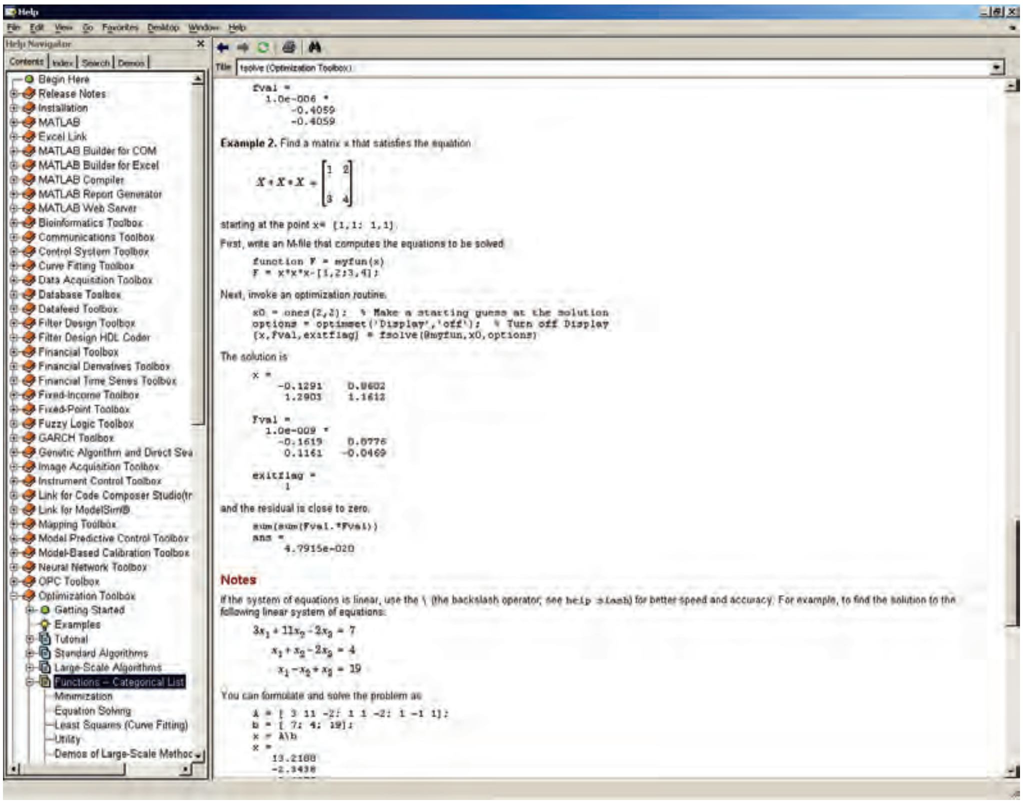


Fig. 7. Fifth part of help on MATLAB solver of systems of nonlinear equations of several variables (taken from MATLAB Help Window)

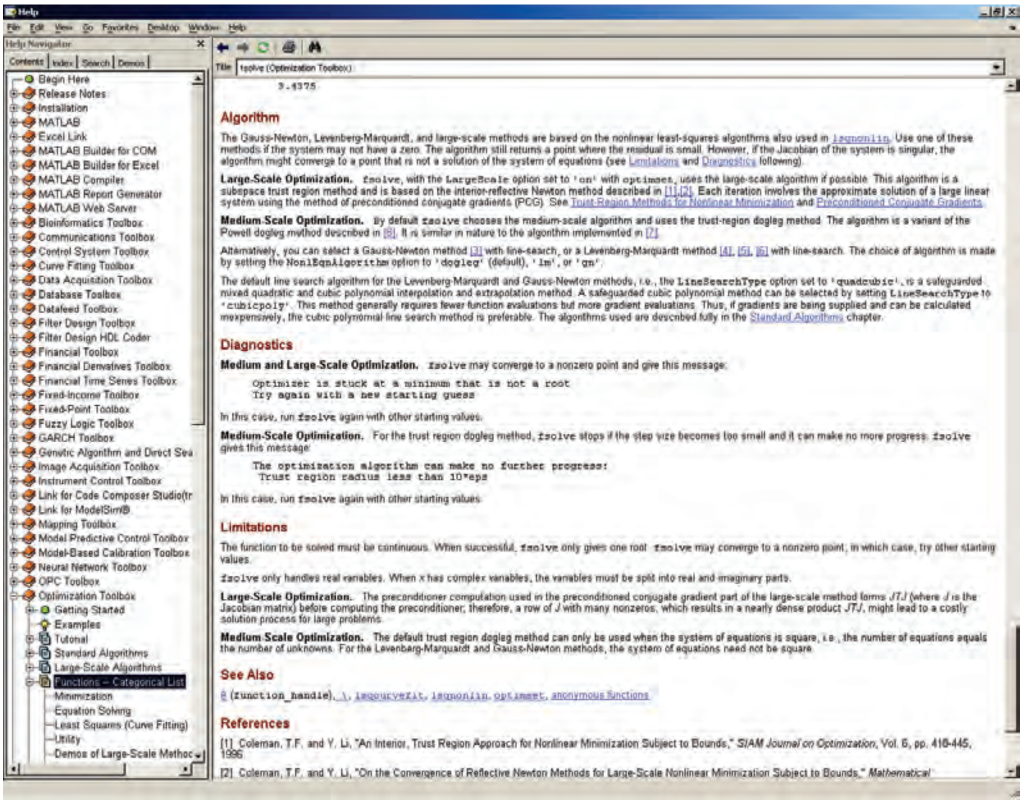


Fig. 8. Sixth part of help on MATLAB solver of systems of nonlinear equations of several variables (taken from MATLAB Help Window)

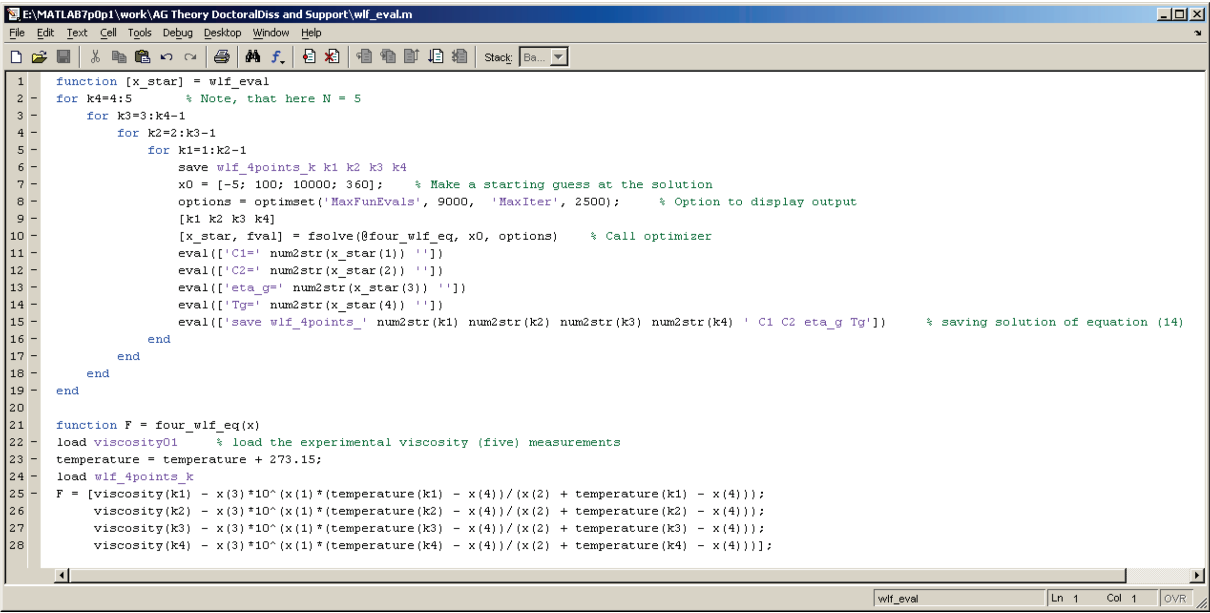


Fig. 9. The system (14) solver code for $N = 5$

Also may it be noted, that a starting guess at the solution, typed in the line 7 of “wlf_eval”, has been based on the generalized notion of that $C_1 < 0$ and $C_2 > 0$, and the glass transition temperature of the polymer material to be submitted is about 60 — 90 Celsius degrees [7, 19, 20]. And when the $\dfrac{N!}{(N-4)!\cdot 4!}$ systems (14) are solved, parameters

$$C_1^* = C_1\left(T_{h*}, T_{j*}, T_{k*}, T_{l*}\right),\ C_2^* = C_2\left(T_{h*}, T_{j*}, T_{k*}, T_{l*}\right),\ T_g^* = T_g\left(T_{h*}, T_{j*}, T_{k*}, T_{l*}\right)$$

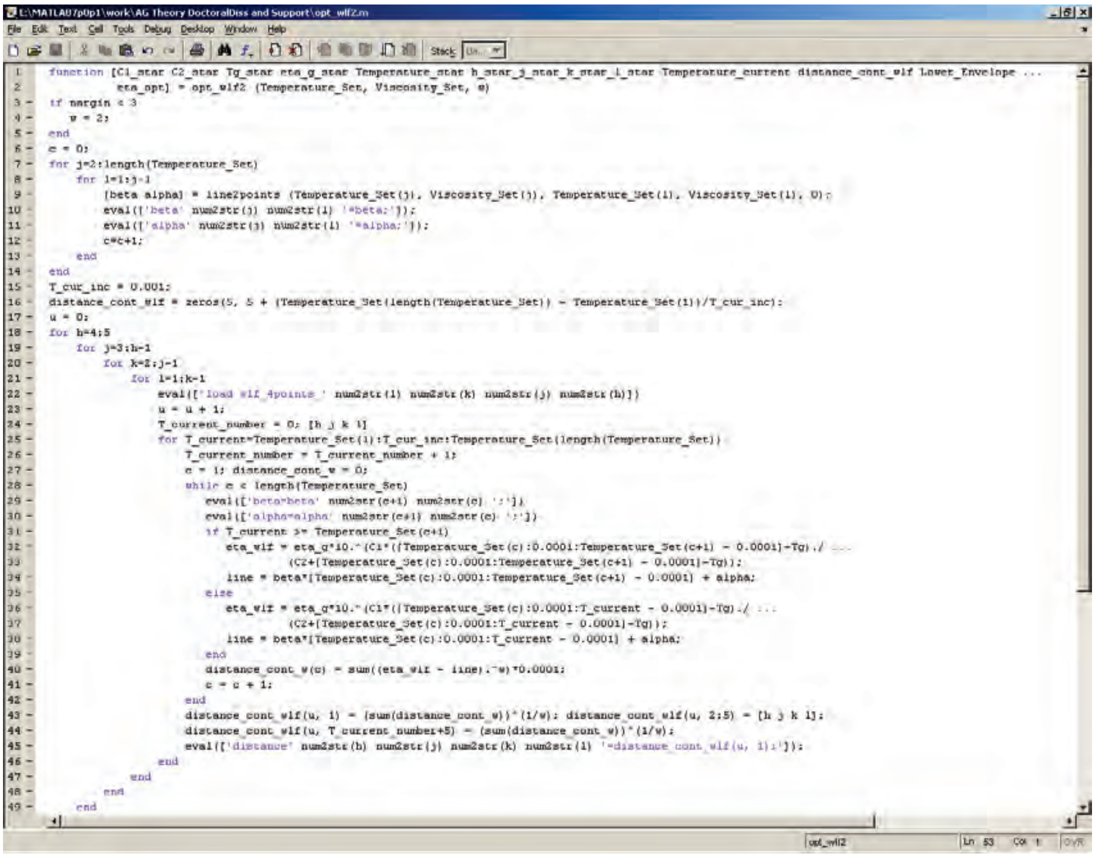
and

$$\eta_g^* = \eta_g\left(T_{h*}, T_{j*}, T_{k*}, T_{l*}\right)$$

of the function $\eta^*(T)$ in (5) should be considered as the most appropriate for the given polymer material viscosity measurements; besides, the temperatures T_{h*}, T_{j*}, T_{k*} and T_{l*} should be regarded as the basic points for measuring the given polymer class viscosity within the segment $[T_1; T_N]$. After having run and accomplished the code of “wlf_eval”, there are saved $\dfrac{N!}{(N-4)!\cdot 4!}$ mat-files with the found numerically unknown parameters in (3).

DETERMINING THE OPTIMAL WLF EQUATION BY (13) IN MATLAB

For computing (13), where integrals will be taken numerically also, there is the developed MATLAB function “opt_wlf2”, been screenshot into figures 10 and 11. This function accepts those mat-files, saved in the line 15 of the system (14) solver code, and processes each of them.



```
function [C1_star C2_star Tg_star eta_g_star Temperature_star h_star j_star k_star l_star Temperature_current distance_cont_wlf Lower_Envelope ...
        eta_opt] = opt_wlf2 (Temperature_Set, Viscosity_Set, w)
if nargin < 3
    w = 2;
end
c = 0;
for j=2:length(Temperature_Set)
    for l=1:j-1
        [beta alpha] = line2points (Temperature_Set(j), Viscosity_Set(j), Temperature_Set(l), Viscosity_Set(l), 0);
        eval(['beta' num2str(j) num2str(l) '=beta;']);
        eval(['alpha' num2str(j) num2str(l) '=alpha;']);
        c=c+1;
    end
end
T_cur_inc = 0.001;
distance_cont_wlf = zeros(5, 5 + (Temperature_Set(length(Temperature_Set)) - Temperature_Set(1))/T_cur_inc);
u = 0;
for h=4:5
    for j=3:h-1
        for k=2:j-1
            for l=1:k-1
                eval(['load wlf_4points_' num2str(l) num2str(k) num2str(j) num2str(h)])
                u = u + 1;
                T_current_number = 0; [h j k l]
                for T_current=Temperature_Set(1):T_cur_inc:Temperature_Set(length(Temperature_Set))
                    T_current_number = T_current_number + 1;
                    c = 1; distance_cont_w = 0;
                    while c < length(Temperature_Set)
                        eval(['beta=beta' num2str(c+1) num2str(c) ';'])
                        eval(['alpha=alpha' num2str(c+1) num2str(c) ';'])
                        if T_current >= Temperature_Set(c+1)
                            eta_wlf = eta_g*10.^(C1*([Temperature_Set(c):0.0001:Temperature_Set(c+1) - 0.0001]-Tg)./ ...
                                    (C2+[Temperature_Set(c):0.0001:Temperature_Set(c+1) - 0.0001]-Tg));
                            line = beta*[Temperature_Set(c):0.0001:Temperature_Set(c+1) - 0.0001] + alpha;
                        else
                            eta_wlf = eta_g*10.^(C1*([Temperature_Set(c):0.0001:T_current - 0.0001]-Tg)./ ...
                                    (C2+[Temperature_Set(c):0.0001:T_current - 0.0001]-Tg));
                            line = beta*[Temperature_Set(c):0.0001:T_current - 0.0001] + alpha;
                        end
                        distance_cont_w(c) = sum((eta_wlf - line).^w)*0.0001;
                        c = c + 1;
                    end
                    distance_cont_wlf(u, 1) = (sum(distance_cont_w))^(1/w); distance_cont_wlf(u, 2:5) = [h j k l];
                    distance_cont_wlf(u, T_current_number+5) = (sum(distance_cont_w))^(1/w);
                    eval(['distance' num2str(h) num2str(j) num2str(k) num2str(l) '=distance_cont_wlf(u, 1);']);
                end
            end
        end
    end
```

Fig. 10. MATLAB function “opt_wlf2” code (first part) for completing the optimal WLF equation determination by (13)

```
E:\MATLAB7p0p1\work\AG Theory DoctoralDiss and Support\opt_wlf2.m
            for l=1:k-1
                eval(['load wlf_4points_' num2str(l) num2str(k) num2str(j) num2str(h)])
                u = u + 1;
                T_current_number = 0; [h j k l]
                for T_current=Temperature_Set(1):T_cur_inc:Temperature_Set(length(Temperature_Set))
                    T_current_number = T_current_number + 1;
                    c = 1; distance_cont_w = 0;
                    while c < length(Temperature_Set)
                       eval(['beta=beta' num2str(c+1) num2str(c) ';'])
                       eval(['alpha=alpha' num2str(c+1) num2str(c) ';'])
                       if T_current >= Temperature_Set(c+1)
                          eta_wlf = eta_g*10.^(C1*([Temperature_Set(c):0.0001:Temperature_Set(c+1) - 0.0001]-Tg)./ ...
                                    (C2+[Temperature_Set(c):0.0001:Temperature_Set(c+1) - 0.0001]-Tg));
                          line = beta*[Temperature_Set(c):0.0001:Temperature_Set(c+1) - 0.0001] + alpha;
                       else
                          eta_wlf = eta_g*10.^(C1*([Temperature_Set(c):0.0001:T_current - 0.0001]-Tg)./ ...
                                    (C2+[Temperature_Set(c):0.0001:T_current - 0.0001]-Tg));
                          line = beta*[Temperature_Set(c):0.0001:T_current - 0.0001] + alpha;
                       end
                       distance_cont_w(c) = sum((eta_wlf - line).^w)*0.0001;
                       c = c + 1;
                    end
                    distance_cont_wlf(u, 1) = (sum(distance_cont_w))^(1/w); distance_cont_wlf(u, 2:5) = [h j k l];
                    distance_cont_wlf(u, T_current_number+5) = (sum(distance_cont_w))^(1/w);
                    eval(['distance' num2str(h) num2str(j) num2str(k) num2str(l) '=distance_cont_wlf(u, 1);']);
                end
            end
        end
    end
end
Lower_Envelope = zeros(1, length(distance_cont_wlf) - 6);
eta_opt = zeros(1, length(distance_cont_wlf) - 6);
for T_current_number=1:length(distance_cont_wlf) - 6
    h_star_j_star_k_star_l_star(T_current_number, :) = ...
    distance_cont_wlf(find(distance_cont_wlf(:, T_current_number + 6) == min(distance_cont_wlf(:, T_current_number + 6))), 2:5);
    Temperature_current(T_current_number) = Temperature_Set(1) + (T_current_number)*T_cur_inc;
    eval(['load wlf_4points_' num2str(h_star_j_star_k_star_l_star(T_current_number, 4)) num2str(h_star_j_star_k_star_l_star(T_current_number, 3))...
                              num2str(h_star_j_star_k_star_l_star(T_current_number, 2)) num2str(h_star_j_star_k_star_l_star(T_current_number, 1))])
    C1_star(T_current_number)=C1; C2_star(T_current_number)=C2; Tg_star(T_current_number)=Tg; eta_g_star(T_current_number)=eta_g;
    Temperature_star(T_current_number, 1:4) = [Temperature_Set(h_star_j_star_k_star_l_star(T_current_number, 4)) ...
                                               Temperature_Set(h_star_j_star_k_star_l_star(T_current_number, 3)) ...
                                               Temperature_Set(h_star_j_star_k_star_l_star(T_current_number, 2)) ...
                                               Temperature_Set(h_star_j_star_k_star_l_star(T_current_number, 1))];
    Lower_Envelope(T_current_number) = min(distance_cont_wlf(:, T_current_number + 6));
    eta_opt(T_current_number) = eta_g_star(T_current_number)*10.^(C1_star(T_current_number)*...
                           (Temperature_current(T_current_number)-Tg_star(T_current_number))./ ...
                           (C2_star(T_current_number)+Temperature_current(T_current_number)-Tg_star(T_current_number)));
end
save wlf_5points_distance_cont_wlf C1_star C2_star Tg_star eta_g_star Temperature_star h_star_j_star_k_star_l_star Temperature_current distance_cont_wl
```

Fig. 11. MATLAB function “opt_wlf2” code (second part)
for completing the optimal WLF equation determination by (13)

There is MATLAB subfunction “line2points” inside “opt_wlf2”, which is applied for obtaining the line (7) constants (8) and (9). This subfunction code is in figure 12.

```
E:\MATLAB7p0p1\work\line2points.m
function [beta alpha] = line2points (x1, y1, x2, y2, equation_display)
%   It returns the coefficients of the line, passing through the two points [x1 y1] and [x2 y2].
% Also it returns the equation of the line if needed and been checked in the input.
if nargin == 4
   equation_display = 0;
end
if x1 == x2
   beta = []; alpha = [];
   if equation_display ~= 0
      disp(['     The equation of the line, passing through the two points [' num2str(x1) ' ' num2str(y1) '] and [' num2str(x2) ' ' num2str(y2) '], is'
      disp ([' x = ' num2str(x1)])
   end
   return
end
beta = (y1 - y2)/(x1 - x2);
alpha = y1 - x1*(y1 - y2)/(x1 - x2);
if equation_display ~= 0
   disp(['     The equation of the line, passing through the two points [' num2str(x1) ' ' num2str(y1) '] and [' num2str(x2) ' ' num2str(y2) '], is'])
   if beta == 0
      disp ([' y = ' num2str(alpha)])
   else
      if alpha < 0
         disp ([' y = ' num2str(beta) ' x - ' num2str(abs(alpha))])
      else
         if alpha == 0
            disp ([' y = ' num2str(beta) ' x'])
         else
            disp ([' y = ' num2str(beta) ' x + ' num2str(alpha)])
         end
      end
   end
end
```

Fig. 12. MATLAB subfunction “line2points” code for obtaining the constants (8) and (9) of the line (7)

The return from “opt_wlf2” into MATLAB Workspace is parameters C_1^*, C_2^*, T_g^*, η_g^*, temperatures

T_{h*}, T_{j*}, T_{k*}, T_{l*}, numbers $h*$, $j*$, $k*$, $l*$, the digitized temperature halfinterval $(T_1; T_N]$, the family of functions

$$\left\{\left\{\left\{\left\{\rho_{\mathbb{L}_w[T_1;\,\tau]}\left(\eta_{hjkl}(T),\, \eta_0(T)\right)\right\}_{h=4}^{N}\right\}_{j=3}^{h-1}\right\}_{k=2}^{j-1}\right\}_{l=1}^{k-1} \quad \forall\ \tau \in (T_1; T_N] \tag{15}$$

and their lower envelope, determining $\eta^*(\tau)$ by (13); ultimately, the optimal WLF dependence $\eta^*(T)$ is returned in digitized form, though it may be reconstructed continuously with already known parameters C_1^*, C_2^*, T_g^* and η_g^*. Totally, those returns are saved into a mat-file (line 69 on figure 11).

CONSIDERING AN EXAMPLE WITH MEASUREMENTS ON THE POLYETHYLENE TEREPHTHALATE RECYCLABILITY SAMPLE

There were carried out the five viscosity measurements

$$\{\eta_i\}_{i=1}^{5} = \{133.8,\ 69.9,\ 37.5,\ 21.3,\ 12.9\} \tag{16}$$

of the polyethylene terephthalate (Dacron) [19, 20] by the temperatures

$$\{T_i\}_{i=1}^{5} = \{403.05,\ 412.15,\ 422.15,\ 432.05,\ 442.05\} \tag{17}$$

with the Brookfield viscometer CAP2000+ (figure 13). As it is known, the polyethylene terephthalate is a product of polycondensation of terephthalic acid

$$(\mathrm{OH})-(\mathrm{CO})-\mathrm{C_6H_4}-(\mathrm{CO})-(\mathrm{OH})$$

and monoethyleneglycol [20]

$$(\mathrm{OH})-\mathrm{C_2H_4}-(\mathrm{OH})$$

giving the linear macromolecule

$$\cdots\left[-\mathrm{O}-(\mathrm{CH_2})_2-\mathrm{O}-(\mathrm{CO})-\mathrm{C_6H_4}-(\mathrm{CO})-\right]\cdots$$

of polyethylene terephthalate. Its glass transition temperature lies between 67 and 81 Celsius degrees, where accordingly the amorphous polyethylene terephthalate has $T_g \approx 340.15$ K, and crystalline polyethylene terephthalate has $T_g \approx 354.15$ K. Then, theoretically, temperatures $\{T_i\}_{i=1}^{4}$ from (17) belong to the segment $[T_g; T_g + 100]$ by $T_g \in [340.15; 354.15]$. Moreover, if, before processing to recycle, the being recycled polymer has been crumbled up as it actually comes, the glass transition temperature of such deformed polymer becomes lower [15]. Nevertheless, the stated above polyethylene terephthalate glass transition temperatures are just averaged evaluations, which may vary broadly, depending on the being recycled polymer stage of deformation [20, 21]. Hence the temperature set (17) here may be considered as the practical example for demonstrating the developed MATLAB software in building the optimal WLF dependence $\eta^*(T)$ by (13).

There on figure 14 are shown the evaluated in the line 10 (MATLAB function "wlf_eval" on figure 9) five groups (3), which were saved on the line 15 (the same figure 9). As it is seen from the figure 14 screenshots, by the five viscosity measurements (16) here has been obtained even greater polyethylene terephthalate glass transition temperature, than expected before running the systems (14) solver.

Fig. 13. The applied Brookfield viscometer CAP2000+ and some its characteristics [22]

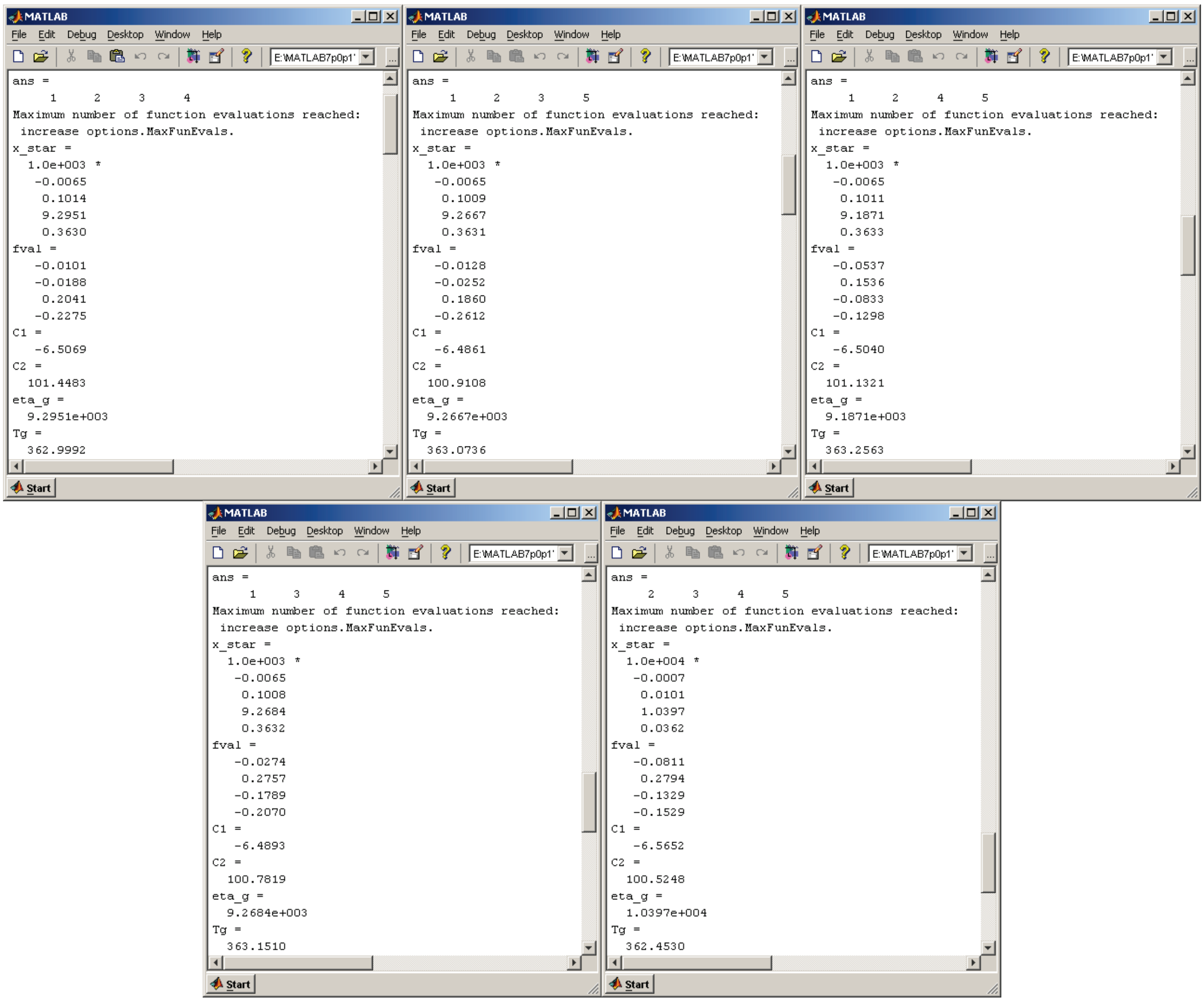


Fig. 14. Result of having applied the MATLAB function “wlf_eval”:
five groups (3) of the evaluated parameters C_1 and C_2 with T_g and η_g in WLF equation (1);
also on screenshots there are ordinal numbers of the four used temperatures from (17)
and residual between left and right members of (1)

Now it is proper phase to run MATLAB function "opt_wlf2" for determining the optimal WLF equation by (13). The screenshot of how to run correctly the MATLAB function "opt_wlf2" is represented in figure 15.

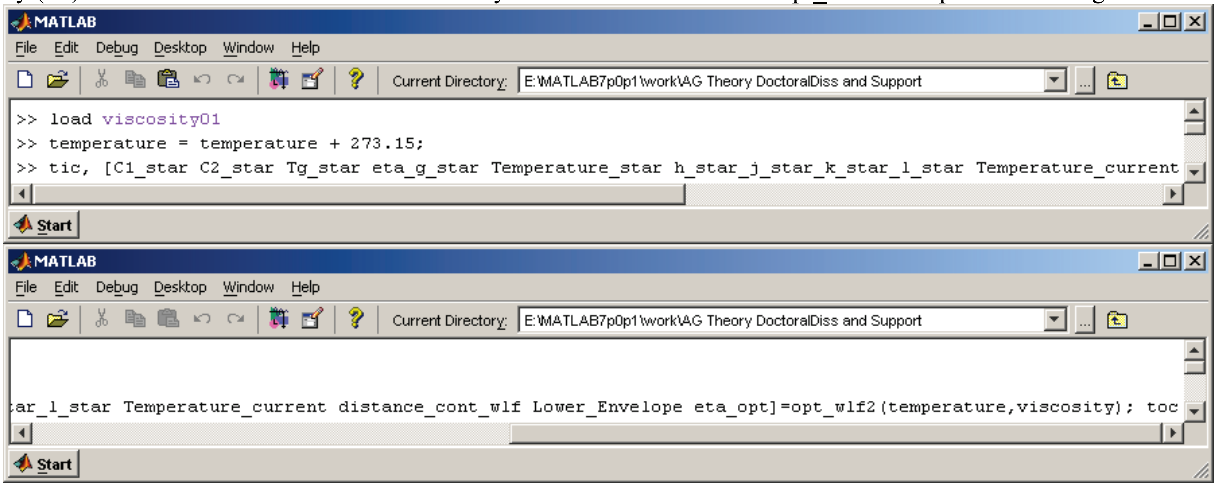


Fig. 15. Launching "opt_wlf2"

The screenshot of the function "opt_wlf2" run result is on figure 16, whence instantly the optimized WLF equation (1) by the criterion (13) is

$$\eta^{*}(T)=\frac{1-\operatorname{sign}(T-403.06)}{2}\times$$

$$\times\left(\frac{1-\operatorname{sign}(T-403.06)}{2}-\frac{1+\operatorname{sign}(T-403.059)}{4}\cdot\operatorname{sign}|T-403.059|\right)\cdot\eta_{4321}(T)+$$

$$+\frac{1+\operatorname{sign}(T-403.059)}{2}\left(\frac{1+\operatorname{sign}(T-403.059)}{2}-\frac{1-\operatorname{sign}(T-403.06)}{4}\cdot\operatorname{sign}|T-403.06|\right)\times$$

$$\times\frac{1-\operatorname{sign}(T-403.065)}{2}\times$$

$$\times\left(\frac{1-\operatorname{sign}(T-403.065)}{2}-\frac{1+\operatorname{sign}(T-403.064)}{4}\cdot\operatorname{sign}|T-403.064|\right)\cdot\eta_{5321}(T)+$$

$$+\frac{1+\operatorname{sign}(T-403.064)}{2}\left(\frac{1+\operatorname{sign}(T-403.064)}{2}-\frac{1-\operatorname{sign}(T-403.065)}{4}\cdot\operatorname{sign}|T-403.065|\right)\times$$

$$\times\frac{1-\operatorname{sign}(T-403.077)}{2}\times$$

$$\times\left(\frac{1-\operatorname{sign}(T-403.077)}{2}-\frac{1+\operatorname{sign}(T-403.076)}{4}\cdot\operatorname{sign}|T-403.076|\right)\cdot\eta_{5431}(T)+$$

$$+\frac{1+\operatorname{sign}(T-403.076)}{2}\left(\frac{1+\operatorname{sign}(T-403.076)}{2}-\frac{1-\operatorname{sign}(T-403.077)}{4}\cdot\operatorname{sign}|T-403.077|\right)\times$$

$$\times \frac{1-\operatorname{sign}(T-403.244)}{2} \times$$

$$\times \left(\frac{1-\operatorname{sign}(T-403.244)}{2} - \frac{1+\operatorname{sign}(T-403.243)}{4} \cdot \operatorname{sign}\left|T-403.243\right| \right) \cdot \eta_{5421}(T) +$$

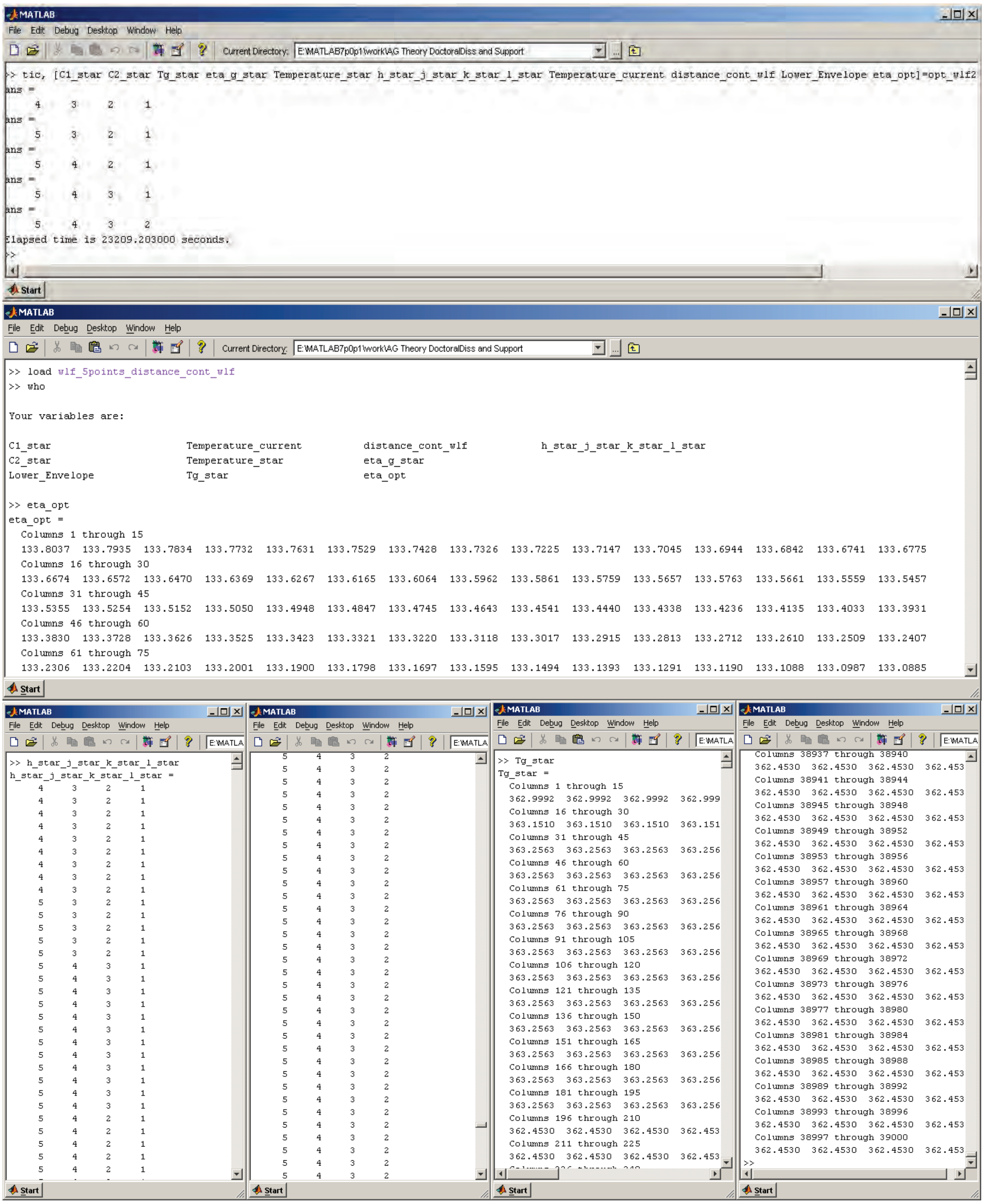


Fig. 16. The optimized WLF equation (1) and its parameters by the criterion (13); it took the elapsed time that is more than 6.44 hours to have processed the data (16) and (17)

$$+\frac{1+\operatorname{sign}(T-403.243)}{2}\times$$

$$\times\left(\frac{1+\operatorname{sign}(T-403.243)}{2}-\frac{1-\operatorname{sign}(T-403.244)}{4}\cdot\operatorname{sign}|T-403.244|\right)\cdot\eta_{5432}(T)=$$

$$=\frac{1-\operatorname{sign}(T-403.06)}{2}\left(\frac{1-\operatorname{sign}(T-403.06)}{2}-\frac{1+\operatorname{sign}(T-403.059)}{4}\cdot\operatorname{sign}|T-403.059|\right)\times$$

$$\times 9295.1238\cdot 10^{\frac{-6.5069(T-362.9992)}{101.4483+T-362.9992}}+$$

$$+\frac{1+\operatorname{sign}(T-403.059)}{2}\left(\frac{1+\operatorname{sign}(T-403.059)}{2}-\frac{1-\operatorname{sign}(T-403.06)}{4}\cdot\operatorname{sign}|T-403.06|\right)\times$$

$$\times\frac{1-\operatorname{sign}(T-403.065)}{2}\left(\frac{1-\operatorname{sign}(T-403.065)}{2}-\frac{1+\operatorname{sign}(T-403.064)}{4}\cdot\operatorname{sign}|T-403.064|\right)\times$$

$$\times 9266.6738\cdot 10^{\frac{-6.4861(T-363.0736)}{100.9108+T-363.0736}}+$$

$$+\frac{1+\operatorname{sign}(T-403.064)}{2}\left(\frac{1+\operatorname{sign}(T-403.064)}{2}-\frac{1-\operatorname{sign}(T-403.065)}{4}\cdot\operatorname{sign}|T-403.065|\right)\times$$

$$\times\frac{1-\operatorname{sign}(T-403.077)}{2}\left(\frac{1-\operatorname{sign}(T-403.077)}{2}-\frac{1+\operatorname{sign}(T-403.076)}{4}\cdot\operatorname{sign}|T-403.076|\right)\times$$

$$\times 9268.4485\cdot 10^{\frac{-6.4893(T-363.151)}{100.7819+T-363.151}}+$$

$$+\frac{1+\operatorname{sign}(T-403.076)}{2}\left(\frac{1+\operatorname{sign}(T-403.076)}{2}-\frac{1-\operatorname{sign}(T-403.077)}{4}\cdot\operatorname{sign}|T-403.077|\right)\times$$

$$\times\frac{1-\operatorname{sign}(T-403.244)}{2}\left(\frac{1-\operatorname{sign}(T-403.244)}{2}-\frac{1+\operatorname{sign}(T-403.243)}{4}\cdot\operatorname{sign}|T-403.243|\right)\times$$

$$\times 9187.1344\cdot 10^{\frac{-6.504(T-363.2563)}{101.1321+T-363.2563}}+$$

$$+\frac{1+\operatorname{sign}(T-403.243)}{2}\left(\frac{1+\operatorname{sign}(T-403.243)}{2}-\frac{1-\operatorname{sign}(T-403.244)}{4}\cdot\operatorname{sign}|T-403.244|\right)\times$$

$$\times 10396.6651\cdot 10^{\frac{-6.5652(T-362.453)}{100.5248+T-362.453}} \qquad (18)$$

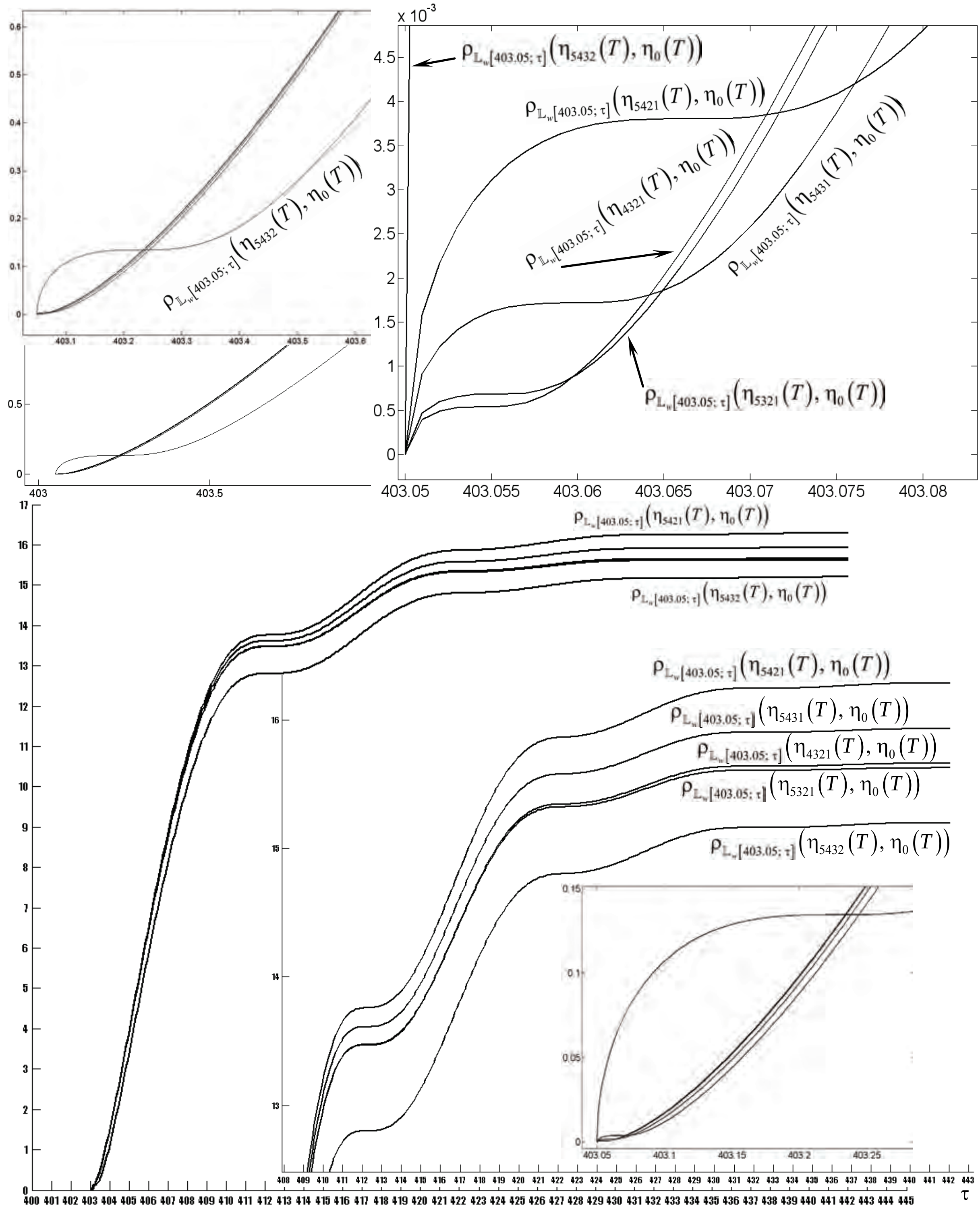


Fig. 17. Five plots of distances (19) by the data (16) and (17) for the investigated polyethylene terephthalate sample viscosity

within the segment $\left[T_g^*; T_g^*+100\right] = \left[363.2563; 463.2563\right]$, involving the set (17). The optimal WLF equation (18) has been obtained by the criterion (13) in the space $\mathbb{L}_2\left[403.05; 442.05\right]$ and consists of all the five WLF equations $\eta_{4321}(T)$, $\eta_{5321}(T)$, $\eta_{5431}(T)$, $\eta_{5421}(T)$ and $\eta_{5432}(T)$, defined on the segment $\left[403.05; 442.05\right]$ on the plane $\mathbb{R}^2$. Figure 17 contains plots (five graphs) of the function family

$$\left\{\rho_{\mathbb{L}_w[403.05;\,\tau]}\left(\eta_{4321}(T),\,\eta_0(T)\right),\,\rho_{\mathbb{L}_w[403.05;\,\tau]}\left(\eta_{5321}(T),\,\eta_0(T)\right),\,\rho_{\mathbb{L}_w[403.05;\,\tau]}\left(\eta_{5421}(T),\,\eta_0(T)\right),\right.$$
$$\left.\rho_{\mathbb{L}_w[403.05;\,\tau]}\left(\eta_{5431}(T),\,\eta_0(T)\right),\,\rho_{\mathbb{L}_w[403.05;\,\tau]}\left(\eta_{5432}(T),\,\eta_0(T)\right)\right\}, \quad (19)$$

and their lower envelope by $w=2$, containing each element of the set (19), though predominantly this envelope has coincided with $\rho_{\mathbb{L}_w[403.05;\,\tau]}\left(\eta_{5432}(T),\,\eta_0(T)\right)$. Finally, figure 18 is the visualized optimal WLF equation (1) as the appropriate temperature dependence of the investigated polyethylene terephthalate sample viscosity by the data (16) and (17), where the four-linked polyline $\eta_0(T)$ is on background for comparison.

After all, the obtained optimal WLF equation (18), being not perfect for the given polymer material, becomes more fitting as the temperature runs up to the right end of the segment $[403.05;\,442.05]$ (it may be seen as from figure 17, as well as from figure 18, though figure 17 gives more analytical conclusion on it because of becoming stabilized distances).

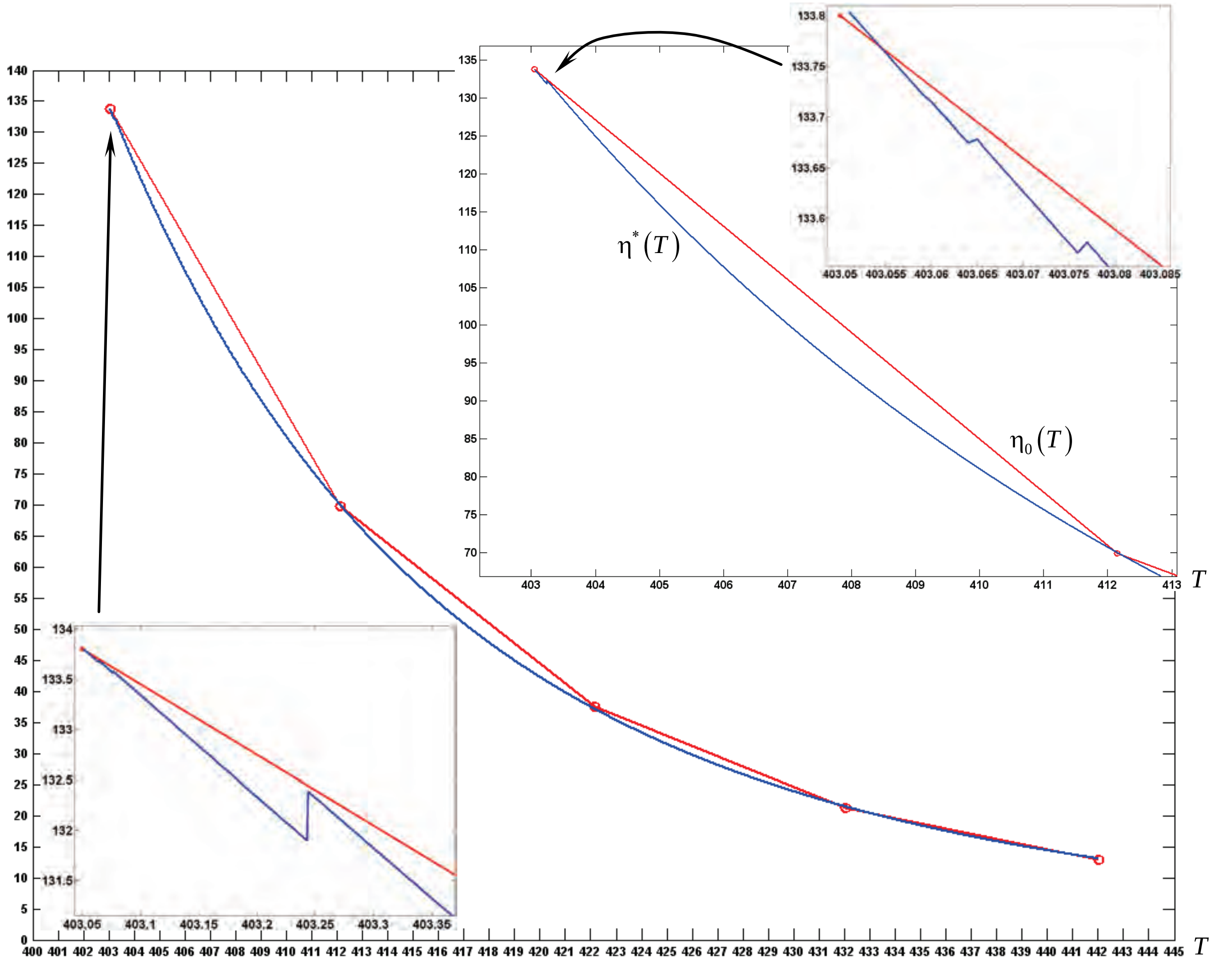


Fig. 18. The optimal WLF equation (18) with four-linked polyline $\eta_0(T)$
for the five viscosity measurements (16) by the set of fixed temperatures (17)

CONCLUSIONS AND PERSPECTIVE FOR FURTHER WLF INVESTIGATION

The stated optimizing model of WLF equation (1), using the space $\mathbb{L}_w[T_1;\,T_N]$ running metric (12) for continual determination of the optimal temperature dependence amongst the functions (4), allows to get the optimal WLF equation by the criterion (13), piecing this equation continuously point after point. Theoretically, the optimal WLF equation by the criterion (13) may be constituted from two and more elements of the set (4), and by that the number of transitions from one WLF equation to another may be infinite. Nevertheless, the exampled polyethylene terephthalate material has the single WLF equation $\eta_{5432}(T)$ in constituting $\eta^*(T)$. Then it is presumable, that for other similar polymer materials the composite WLF equation $\eta^*(T)$ will be formed with the finite number of transitions from one WLF equation to another. Trustworthy knowing of polymer material viscosity temperature dependence is utterly needful by recycling polymeric wastes, where there is always the problem to melt them, heating up to some temperature, for to fix the liquid melt viscosity.

The developed and represented MATLAB functions work on the stated criterion, computing the distances (15) and their lower envelope to determine $\eta^*(T)$. Those 10 returns, appearing within MATLAB Workspace, are saved into a mat-file (line 69 on figure 11), and may be used in further investigations with the given polymer material.

However, there are some problems, still facing on. Firstly, if number of measurements N is too small, then the temperature segment to survey has to be shortened, though how it should be done is unclear. Secondly, for the given temperature segment to survey there is vagueness in the question on how many viscosity measurements an investigator should do for a polymer within the given temperature range. These items are the subject for further investigation of the temperature dependence of polymer materials viscosity in the WLF equation (1) form.

REFERENCES

1. Viscosity [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Viscosity
2. Polymer [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Polymer
3. Biopolymers [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Biopolymers
4. Polyethylene [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Polyethylene
5. Smart material [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Smart_materials
6. Viscoelasticity [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Viscoelasticity
7. Виноградов Г. В. Реология полимеров / Г. В. Виноградов, А. Я. Малкин. — М. : Химия, 1977. — 440 с.
8. Polymer chemistry [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Polymer_chemistry
9. Polymer physics [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Polymer_ physics
10. Polymer science [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Polymer_ science
11. Polymerization [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Polymerization
12. Step-growth polymerization [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/ Step-growth_polymerization
13. Chain growth polymerisation [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/ Addition_polymerization
14. Williams M. L. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids / M. L. Williams, R. F. Landel, J. D. Ferry // J. Am. Chem. Soc. — 1955. — V. 77, N. 14. — P. 3701 — 3707.
15. Glass transition [Electronic resource]. — Access mode : http://en.wikipedia.org/wiki/Glass_ transition_temperature
16. Малкин А. Я. Диффузия и вязкость полимеров. Методы измерения / А. Я. Малкин, А. Е. Чалых. — М. : Химия, 1979. — 304 с.
17. Фогельсон Р. Л. Температурная зависимость вязкости / Р. Л. Фогельсон, Е. Р. Лихачев // Журнал технической физики. — 2001. — Т. 71, вып. 8. — С. 128 — 131.
18. Temperature dependence of liquid viscosity [Electronic resource]. — Access mode : http://en. wikipedia.org/wiki/Temperature_dependence_of_liquid_viscosity
19. Цены на вторсырье [Электронный ресурс]. — Режим доступа : http://www.recyclers. ru/modules/soapbox/
20. ПЭТ — полиэтилентерефталат [Электронный ресурс]. — Режим доступа : http://www. ekoresurs.ru/pet__polietilentereftal
21. Отходы термопластов — Направления использования вторичного сырья — Статьи [Электронный ресурс]. — Режим доступа : http://www.recyclers.ru/modules/section/category.php? categoryid=17
22. Brookfield Viscometers, Rheometers and Texture Analyzers for viscosity measurement and control and texture analysis [Electronic resource]. — Access mode : http://www.brookfieldengineering.com

Надійшла до редакції 02.09.2010р.

Romanuke V. V. – candidate of technical science, associate professor of the Applied Mathematics and Social Informatics Department, Khmelnytskyy National University, Khmelnytskyy, Ukraine.