# Description of the kinetics of a model tribopolymerization process

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Received 11 December 1996; revised 13 August 1997

A three-dimensional system of ordinary differential equations of first order has been proposed to describe the kinetics of a model tribopolymerization process for which a linear coupling of the material surface dislocation density and polyreaction fields is assumed. Another important physical motivation on which the model is based stresses the predominant role of a highly rough surface under friction as a catalyst in the polyreaction process. In consequence, the fractal-like chemical reaction concept has been applied. It is demonstrated that the system proposed is suitable for describing a variety of tribopolymerization processes and possesses non-trivial time-dependent behaviour even in some limiting analytical cases studied. As a specific result, a nonlinear equation generalizing the Vogel–Fulcher temperature-dependence of the maximum time scale for the polyreaction caused by friction, characteristic of the selective transfer during friction process, has been recovered. Some comparison with an approach made earlier (G.P. Shpenkov, *Friction Surface Phenomena* (Elsevier, Amsterdam, 1995) pp. 165–172 and Ref. [239] therein) has been presented as well. Certain basic trends of modelling and experiment are in good agreement.

# 1. Introduction

In recent years friction phenomena attract permanent interest of engineers and scientists because of offering a large number of problems to solve (complexity and co-operativity, self-organization, transport processes at surfaces with chemical reaction included, fractal characteristics of rough surfaces, wear mechanism, spatio-temporal, possibly periodic, behaviour of defect-containing surface systems, etc.) as well as because of a wide range of applications in many areas of technology and engineering (lubrication in machinery systems, thin film and coating technology, oxidation for hardening of metal surfaces, production of abrasive materials, etc.) [1-3].

It is commonly accepted that when one wishes to study a friction process, both experimentally or theoretically (i.e., by formulating analytical or computer models, or by combining them), one should know at least: the type of material under friction (metal, alloy, polymer or others), its crystallographic characteristics that has to be mostly related to its surface region; the basic properties of the lubricant which may form

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an interlayer and can actively take part in friction process; and its physico-chemical characteristics (which are polymer additives, if they are applied, for example).

Specialists of tribology realize that there are many key problems which stand for the general topics listed above; e.g., to the first class may belong: crystallographic characteristics of the surface layer, information about the density of surface defects and dislocations or about roughness of the surface, or other more specific, e.g., what is its fractal dimension [3]. The second class of the above listed topics can specifically include, for instance, the chemical reaction between polymer additives and oxygen molecules, hydrogen transport through friction interlayer or permanent change of wear intensity, saturation of surface dislocations by macromolecules adsorbed, rheology of the friction interlayer, etc. [4]. The third class of problems concerns, e.g., treatment of surface layer, alteration of the dislocation density and a change in submicrorelief of the surface, periodicity of friction conditions (manifested by a periodic behaviour of such quantities like, i.e., electron work function, contact potential difference, friction coefficient or surface dislocation density, etc. [2,4]) related to the periodicity of the defect accumulation, formation of submicrocracks in separate subsurface microdomains or emergence of fatigue microcracks, "affinity" of the abrasive material to the structure of the surface under friction, growth and/or propagation of cracks, stress-strain response of the surface under friction, and many others [4-6].

Among many aspects of tribological processes (structural, dynamical, also technological, etc.) the kinetic aspect seems to be very interesting because of the possibility of predicting time behaviour of the complex and co-operative self-organized friction phenomena. In particular, we have in mind a tribopolymerization process in which one can observe a coupling of two physico-chemical factors: those which arise from the friction aspect of the phenomenon and are associated to a change of surface characteristics (like roughness or fractal dimension) under friction, and those which are related to the chemical reaction within the system.

It is then postulated that a coupling of the two main sub-processes (i.e., friction manifested by the dislocation density change and polyreaction) constitutes the whole process that we are going to study. Let us recall here some physical rationale that may justify our theoretical treatment. Namely, we are thinking of some friction pair with an interlayer consisting of a lubricant (containing surfactant or monomer) in between, where the friction process proceeds under a certain external load and some action of the load and a penetration (wetting) of the surfactant occur simultaneously. As a consequence, a plasto-elastic deformation of the surface is observed and some adsorptional reduction of its strength or energy takes place, so, the surface must be in a stress state (these are symptoms of the so-called Rehbinder's effect; cf. [4, chapter 1, pp. 31–34] for examples). Moreover, surfactant adsorption affects the interaction of dislocations with the surface by diminishing the surface energy barrier that inhibits dislocations on the surface causing some crystal softening with an insignificant decrease of interfacial energy. The absence of oxide films appears to be a beneficial effect on the movement of dislocations, and plastic deformation is enhanced just in this way. This is named the selective transfer phenomenon (ST) which is a very com-

plex phenomenon, because of being a multistage process. Following [4, section 3.11, pp. 113–120], one can observe, at least, five stages of its realization: surface dispersion due to plasto-elastic deformation and Rehbinder's effect, redox processes with hydrogen emergence, steady-state friction (where the lubricant is a disperse system saturated mostly with metal ions, colloidal metallic particles or anion-active surfactants), tribochemical transformations of the lubricant in which a monomer or surfactant is dispersed and, finally, formation of a gel-like (soft) layer (being also termed as the "servovite" layer). As a standard example here, one can mention sliding of steelcopper alloy couples in glycerin. Also, a sliding process of nickel in TSIATIM-201 with 3% wt powder fluoroplastic (ftorplast-3) greases, with a periodic behaviour of the nickel surface dislocation density in the surface volume of ca. 1  $\mu$ m thick, can serve as an example (cf. [4, chapter 4, pp. 162–165]). In such a complex phenomenon and under the above described physico-chemical circumstances, one may easily find an influence of surfactants dispersed in the lubricant on the creation and/or annihilation of surface dislocations, mostly due to the plasto-elastic deformation of the surface originated by the simultaneous action of physical adsorption (penetration or wetting) and external load together. On the contrary, it is quite natural to imagine that dislocations will act as active (catalytic) sites for the polyreaction process. This having been said, we will use this postulate in a form of some "coupling ansatzes" in our further considerations (see equations (3) and (4) in the next section). Stating it explicitly, one has to realize that the model tribopolymerization system proposed here refers to the ST-phenomenon during the friction process.

The goal of this study is to propose and examine some descriptions of the kinetics of a model tribopolymerization process. Here, by a model tribopolymerization process we wish to understand a three-dimensional dynamical system (system of autonomous ordinary differential equations of the first order) in which three dependent variables are functions of time and depend upon some physico-chemical process parameters (like chemical reaction rate constant, coefficients of creation and annihilation of dislocations, order of the chemical reaction, also temperature, etc.). These three variables are: density of surface dislocations, concentration of reacting species (monomers, free radicals) present in a friction interlayer and chemical reaction rate coefficient which is time-dependent (typically, i.e., in classical chemical kinetics, it depends mostly upon temperature) [7,8]. In a previous study a two-dimensional dynamical system was successfully applied (cf. [4, section 4.6, pp. 165-172; 6]) for elucidating in a theoretical way a periodicity of some triboparameters like density of surface dislocations. In this work we generalize that approach [4,6] by assuming that the chemical reaction rate coefficient can be time-dependent which technically results in adding a third ordinary differential equation of first order to the previously proposed two-dimensional description (cf. [4] for details). Conceptually, however, it is connected with a "compression" of time scale of the process. The reason for such a generalization, however, is absolutely of physical nature: systems under friction (e.g., some pieces of alloys or amorphous materials like several polymers, ceramic-polymeric composites or even biopolymers) usually have pretty huge and well-developed surfaces (of the fractal nature; viz. selfaffine surfaces) [9,10], and therefore, the concept of classical (conventional) chemical kinetics is probably not sufficient to be applied, but rather a modern concept of fractal-like kinetics which assumes that in some highly catalytic and diffusion-reaction systems an anomalous chemical reaction may proceed (since there exist some traps, obstacles, microcavities, certain geometrical constraints like terraces or ledges (also, hills and valleys of the "surface landscape"), or, in general, some surface spots, like defects or dislocations, of slowing down or accelerating the process), being of a non-integer (fractional) order and owing time-dependent reaction rate of a power form [7,8,11]. In the dynamical system proposed here, all the dynamic (interaction) effects like coupling between the surface dislocation density and concentration of the polyreactants are clearly manifested in system behaviour. It is also possible to imagine a random walk (diffusion-reaction) [12] process in the vicinity or even directly on the catalytic surface which is now the friction surface. The fractal dimension of the surface [9,10,13] and the fractal dimension of the random walk [12] (constituting the so-called spectral or fracton dimension [12,14]) complete the system characteristics. Postulating, however, the fractal-like kinetics as the most useful tool in our description, we are also aware of, e.g., that simple second order chemical reactions are able to exhibit exotic or anomalous behaviour like periodicity, chaos (Bielousov-Zhabotinsky reaction), chemical patterns (Turring structures), negative Arrhenius activation energies, Kramers bistability in the regime of very small noise intensities, etc. But these effects are mostly some bulk kinetic effects and are not very typical for systems with constrained geometries, where many kinetic obstacles (cf. geometrical traps, chemical bonds) may exist.

The next parts of this article are organized as follows: in section 2, a brief description of the kinetics of a model tribopolymerization process is given; in section 3, an analysis of the model system and results are presented, and a discussion of them is carried out. Section 4 serves for final conclusions.

# 2. Description of the kinetics of a model tribopolymerization process. Fundamentals

It was presented before [4,6] that our tribopolymerization system consists, according to the etymology of this word, of two parts (two autonomous first order ODEs). The first equation is well-known in the tribological literature [4,6], and it looks like [15,16]

$$\dot{\rho} = b_{\rm s} + c\rho - \delta\rho^2, \quad \rho \equiv \rho(t),$$
 (1)

where  $\dot{\rho}$  stands for the first derivative of the surface dislocation density  $\rho(t)$  with respect to time t,  $b_s$  is an external source of dislocations, c is responsible for the generation of dislocations (one by one), and  $\delta$  represents a strength of pairwise annihilation of dislocations (note here that the annihilation of dislocations prevails compared with the generation of dislocations since  $\rho$  is raised to the power 2, in this case).

The origin for the processes that may lead to the formation and destruction of dislocations is inevitably related to the selective transfer (ST) phenomenon taking place under certain friction conditions (cf. [4, chapters 3–6] and references therein). One

can argue here that in such a complex phenomenon and under the physico-chemical circumstances like physical adsorption of surfactants dispersed in the lubricant on the surface under friction, simultaneous action of the surfactant penetration and external load exerted on the system, plasto-elastic deformation of the surface layer, softening of the crystal surface as well as absence of some oxide films (supported by presence of hydrogen atoms which inhibit emergence of them) or even appearance of certain hydrodynamical effects (Beilby layer) may take place. One can easily find a real influence of surfactants immersed in the lubricant medium on the formation and/or disappearance of surface dislocations. Also, it is quite natural to think that some opposite physical situation can occur, which means, that dislocations will play the role of active (say, catalytic) sites for the polyreaction process in accordance with Taylor's theory of reactive centers (cf. [4, p. 115] and Ref. [143] therein).

Thus, the second equation describing the kinetics of the process in question is equally well-known in the literature and can be of use here. This is the kinetic equation for a polyreaction (polycondensation or another type of polymerization). It is usually of the form [7,8,17]

$$\dot{\phi} = e_{\rm s} - k\phi^x,\tag{2}$$

where  $\dot{\phi}$  has the same meaning as before, but is derived for the concentration  $\phi$  of monomers (species which are able to form polymers or macromolecular ensembles) dispersed in a lubricant (or, more accurately, in a friction interlayer containing a lubricant with polymeric additives included),  $e_s$  is a production rate related to an external source of reactants [7], k stands for the chemical reaction rate coefficient, and x is the order of the reaction which may be either an integer or even a rational (non-integer!) value (also, k is not only temperature-dependent, but in our approach may directly depend upon time t, too; cf. [7,8,11] for realizing a kind of reasoning presented therein). Especially, the fractional value of x can be realized later from the behaviour presented in figure 5.

Now, we shall state two basic assumptions which we wish to call for obvious reasons [4,6] the coupling ansatzes. The coupling ansatzes read

$$b_{\rm s} = a + b\phi, \quad b_{\rm s} \equiv b_{\rm s}(\phi),$$
 (3)

$$e_{\rm s} = e + f\rho, \quad e_{\rm s} \equiv e_{\rm s}(\rho),$$
(4)

where a and b as well as e and f are some constants, and such expressions follow mathematically from the McLaurin expansion of  $b_s$  and  $e_s$  around 0 with respect to  $\phi$  and  $\rho$ , respectively, up to the first order (this means that the ansatzes proposed are linear in  $\phi$  and  $\rho$ , respectively; the further generalization of this procedure will take up higher orders of the McLaurin series, i.e.,  $b_s$  and  $e_s$  may be nonlinear in  $\phi$  and  $\rho$ , respectively, and also some "mixed" terms, like const  $\cdot \phi \rho$ , may appear in other types of generalizations of formulae (3) and (4) assuming, however, that either  $b_s$  or  $e_s$ , or both, are functions of  $\phi$  and  $\rho$ ; this, however, will not be the subject of study in this work). Expressions (3) and (4) reflect the experimental fact [2,4,17] that there is a coupling (or a kind of mutual influence) between the production of polymer or its destruction (or degradation), and annihilation or creation (generation) of dislocations; moreover, such a process may proceed in a periodic (in time) way which was shown, e.g., in [4] (cf. section 4.6 for details) or [6].

Thus, a physical situation in which some polyreaction effects, like presence of surfactants, partially reacted intermediates, colloidal metallic particles and ions, may cause a change in the dislocation density is probably more difficult to understand. Such a possibility offers, however, the ST-regime in which one may discover that the triboelectrochemical reaction in the system is accompanied by the hydrogen production and adsorption on the fresh metal film inhibiting with large effectiveness the oxidation process. Lack of oxide films has a visible effect on the movement of surface dislocations, that means, it facilitates a plastic deformation, e.g., of copper in sliding; also, a huge mobility of dislocations may be achieved by the action of tribosurfactants (cf. [4, p. 120]). Obviously, it would be hard to imagine that the only mechanism causing a change in the dislocation density will be that related to monomer adsorption onto the surface itself. At least, the plasto-elastic deformation of the surface layer caused by simultaneous action of the physical monomer and/or surfactants adsorption and external load has to be present; as a prototype example one can recall wetting of aluminum by mercury mixed up with zinc 4% wt which directly leads to the adsorptional softening of the metallic surface under the regime of tensile stress of the material (Rehbinder's effect [4, section 1, pp. 31-34]).

The next assumption that we shall make is novel when comparing with that stated previously [4]. It takes into account some anomalies like the chemical reaction order (denoted above by x), being a rational number, and also a time-dependent chemical reaction rate coefficient. This assumption may be valid for some catalytic, diffusion-reaction systems like the one modelled here, and it looks more realistic from the physical viewpoint than that presented in the approach proposed earlier (cf. [4,6]). It seems to be strongly recommended [3] for such systems with "fancy", quite irregular "moving" (i.e., changed in course of time during the friction process) interfaces like that studied here (e.g., think of a piece of material of quite well-developed surface being lubricated and polished by means of another possibly abrasive material; or the friction process due to interaction of, e.g., two bones, via the (bio)liquid between them, inside our fingers or legs, i.e., a self-adaptive process). We wish to choose, for the same reasons as those presented in [7,8,11], the mathematical form of the chemical reaction rate coefficient to be

$$k(t) = k_0 (1 + (t/\tau))^{-n},$$
(5)

where  $k_0 = k(0) > 0$  is the initial value of k,  $\tau$  represents the length of a "long time" period after which a stationary state is possible to reach (it is assumed that  $\tau \gg 0$ , because typically the stationary state can be approached after a sufficiently large time interval), and h is designed to be a physico-chemical parameter of the tribopolymerization process which is related to its spectral or fracton dimension (denoted by  $d_s$ ) by [7,8,12]

$$h = 1 - (d_s/2).$$
 (6)

Thus, the quantity x introduced above is of the following form [7]:

$$x = 1 + (1 - h)^{-1}, \text{ if } d_{s} < 2$$
 (7)

(note that if  $d_s = 2$  than x = 2; in general, x > 1). It is also worth mentioning that  $h \in [0, 1]$ .

The spectral dimension, in turn, can generally be inferred from the probability of the system's return to its initial state (origin) (denoted by  $P_{\text{ret}}$ ) which obeys an asymptotic (scaling) relation

$$P_{\rm ret} \simeq t^{-d_{\rm s}/2}.\tag{8}$$

One can also get  $d_s$  utilizing the Alexander–Orbach conjecture [7,18] which is, however, not proved for all cases [12], but it may be useful for some practical purposes. Upon accepting that, we can write as follows [7,12]:

$$d_{\rm s} = 2d_{\rm f}/d_{\rm w},\tag{9}$$

where  $d_f$  is the fractal dimension [9] of the surface of a material under friction and  $d_w$  has the meaning of the random walk fractal dimension (this random walk must be equivalent to a diffusion-reaction process which takes place during friction; for details see [2] and references therein). The first quantity, i.e.,  $d_f$ , can be measured, e.g., by the box-counting method [9] (or in a more rigorous way [13]), namely,

$$N \simeq \ell^{d_{\rm f}},\tag{10}$$

where N is the number of boxes of size  $\ell$  covering the surface. The second quantity  $d_w$  obeys an asymptotic equation [12] (see also [19] and references therein) of the form

$$\left\langle X^2(t)\right\rangle \simeq t^{2/d_{\rm w}},\tag{11}$$

where  $\langle X^2(t) \rangle$  is the mean square displacement of the random walk [12]. It was shown [20], however, that an effective dimension of the friction surface which is, in fact, a reactive surface (or a catalyst) during the whole tribopolymerization process, is not  $d_f$  but a slightly smaller quantity  $d'_f = (d_f + 1)/2$ . Hence, the Alexander–Orbach conjecture [7,14] provides

$$d_{\rm s} = 2d_{\rm f}'/d_{\rm w} = (d_{\rm f} + 1)/d_{\rm w}.$$
(12)

Thus, on the basis of equations (1)–(5), we are able to write down the whole threedimensional system of ordinary differential equations of first order in an autonomous form (cf. [21] and references therein), i.e., when the right-hand sides of the equations of system (13) do not depend explicitly on time t. This can be written as

$$\dot{\rho} = a + b\phi + c\rho - \delta\rho^2,$$
  

$$\dot{\phi} = e + f\rho - k\phi^x,$$
  

$$\dot{k} = -vk^y,$$
(13)

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where

$$v = h\tau^{-1}k_0^{-1/h},\tag{14}$$

$$y = 1 + h^{-1} \tag{15}$$

(note here that also x = (2-h)/(1-h);  $\dot{k}$ , as previously, means differentiation of k(t) with respect to time; in general, y > 1).

System (13) is a three-dimensional dynamical system with the initial conditions of  $\rho(0) = \rho_0$ ,  $\phi(0) = \phi_0$  and  $k(0) = k_0$  as we stated above (the quantities  $\rho_0$ ,  $\phi_0$  and  $k_0$ are positive constants). Its solutions can be derived either in an explicit form, e.g.,  $\rho(t)$ , or, as a three-dimensional curve, in the phase space ( $\rho, \phi, k$ ) (a phase portrait can be presented [22,23]). Generally, they can only be obtained numerically. Some limiting (or reduced) cases can be found in an analytical way. Let us formally mention that for  $c = \delta = k = 0$ , and if one of pairs *a* and *b* or *e* and *f* (cf. equations (3) and (4)) is of the opposite sign, then system (13) reduces to a linear oscillator system [22]. Taking into account nonlinear ansatzes instead of those given by equations (3) and (4), especially with some "mixed" terms like const  $\cdot \phi \rho$ , one can be able to gain some other known dynamical systems like prey-predator or competition systems (it may give rise to some interesting effects like presence of bifurcations of stationary solutions or even existence of deterministic chaos, i.e., "strange attractors", in the system; cf. [4,6,22,23] and references therein). Notice also that the parameters of the system can be partitioned into four groups:

- (i) free constant reference source (or shift) parameters: a and e;
- (ii) coupling parameters: b and f;
- (iii) surface dislocation generation and annihilation parameters: c and  $\delta$ ;
- (iv) chemical reaction parameters:  $k_0$ ,  $\tau$  and h.

An interplay among them will influence the overall behaviour of the system under study.

#### 3. Analysis of the model and results

In this paper, we wish to present a rather qualitative analysis of the model formulated above. Although, some analytical results will be given as well. The analysis will be carried out for three different cases concerning the h-value, namely,

(i) h = 0, or equivalently,  $d_s = 2$  (i.e., in the case when the fracton dimension reaches its maximum value; in our "dimensional language" it means that the fractal dimension of the surface under friction is equal to the fractal dimension of the random walk which is true for a pure random walk or Markovian process with no constraints like geometrical obstacles or traps, cf. equation (9) and also [8,12]); it formally reduces to the case presented before, and the phase portrait for this

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Figure 1. The phase portrait of system (13) and its cross-section for x = 2 and a = 0, b = c = 0.5,  $\delta = 0.005$ , e = 250.1, f = -250.0, y = 200, v = 0, that is comparable with a case studied in [4,6] and stands for a manifestation of the periodicity of the system in question. The initial conditions are:  $\rho(0) = 1$ ,  $\phi(0) = k(0) = 0.1$ ; the time interval was assumed to be  $t \in [0, 20]$ , but at  $t \cong 13.08$  an "escape to infinity" of the phase trajectory was observed. The picture is obtained by using *Mathematica*, version 2.2.3.

case looks fairly unstable (a relatively quick escape to infinity is observed), but manifests the periodicity of the system studied (cf. [4,6] for details; here its  $\rho\phi$ -projection is plotted in figure 1);

- (ii)  $h \in (0, 1)$ , or equivalently,  $d_s < 2$  (clearly,  $d_s > 0$ ), where the full dynamical system (13) represents the kinetic behaviour (the numerical results [24] show, however, that there are no qualitative changes when comparing with the two-dimensional system [4,6]);
- (iii) h = 1, or equivalently,  $d_s = 0$  (i.e., if either the fractal dimension of the surface approaches zero and  $d_w \neq 0$  or  $d_w$  goes to infinity; cf. equation (9)); the former case can only be thought of as a rather realistic case, where some very rarely distributed "cusps" or peaks of a rough surface under friction exclusively account for the whole tribopolymerization process, like in mountains, where mostly the highest peaks are those which eventually may come "into action", i.e., may stand for the "reactive sites", where the concentration of monomeric species in a friction interlayer vanishes very fast to zero or even disappears (e.g., it can flow out), and mostly the effects of generation and annihilation of dislocations in the material surface play a relevant role (here, some analytical results will be presented).

Also, a certain consideration of the stationary states of the system in question, i.e., when

$$\dot{\rho} = \dot{\phi} = \dot{k} = 0, \tag{16}$$

will complete the investigation.

Let us look at the point (i). Because of h = 0 one gets  $k(t) = k_0 = \text{const}$ (cf. equation (5) for details). In this case, the system (13) reduces to a two-dimensional dynamical system studied before [4,6], with x = 2, which can be called a model tribopolycondensation process in which the role of catalyst is played by the whole friction surface (in the standard polymer kinetics literature, e.g., in [17], the polycondensation process with a catalyst is a second order chemical polyreaction; here presence of the catalytic friction surface may cause the formation of a polycondensate during the friction process). Since such a system (i.e., for h = 0 and additionally for e = 0) was analyzed in [4,6] numerically, we only recall the main results. Namely, that the system possesses the periodic solutions  $\rho(t)$  and  $\phi(t)$ . It is possible to control the amplitudes of those periodic functions by changing  $k_0$ . One is also able to regulate the frequency of that periodic behaviour by varying the coupling parameters b and f (cf. equations (3) and (4)). Moreover, the case of x = 2 seems quite unstable, that means, the periodicity of the system is easy to be lost in a sufficiently long time period, most probably, because of a polycondensate formation (an increase of the product concentration  $\phi(t)$ ) in course of time is observed; see [4,6] and figures presented therein). Observations of reaching by the system a limit cycle and of how to get a steady state have also been done [4,6]. Some control of the trajectories escaping to infinity (a "blow-up" effect) in a phase space by either  $\rho(t)$  or  $\phi(t)$  has been demonstrated as well. It is also possible to consider here analytically a "reduced" case, i.e., when  $\rho(t) \equiv \rho_0 = \text{const}$  (it could be "an equilibrium friction state" in which the production of surface dislocations is compensated by their annihilation), with a weak coupling of those two sub-processes only (we set b = 0, but still  $f \neq 0$ ; see equations (3) and (4)); as always in this case  $k(t) \equiv k_0 > 0$ . Assuming that, the system (13) can be replaced by one equation of the form

$$\dot{\phi} = A - k_0 \phi^x,\tag{17}$$

where  $A = e + f \rho_0$ ; one can solve analytically [25] this equation for x = 2 (or h = 0). The solution reads (cf. figure 2 which visualizes the quasi-equilibrium friction state with a weak coupling of surface dislocation density and polyreaction fields)

$$\phi(t) = \frac{\phi_0}{1 + \phi_0 k_0 t},\tag{18}$$

where, as we see,  $\phi_0 = \phi(0)$ . This result is valid for any  $\Delta = 0$ , where  $\Delta = 4k_0A$  which is equivalent to  $\rho_0 = -e/f$ . This means that *e* and *f* must be of the opposite sign because  $\rho_0$  is always positive. For the case  $\Delta > 0$ , it turns out that

$$\frac{\phi(t) - \lambda}{\phi(t) + \lambda} = \frac{\phi_0 - \lambda}{\phi_0 + \lambda} e^{-2k_0\lambda t},$$
(19)

where  $\lambda = ((e + f\rho_0)/k_0)^{1/2}$ . For getting a visualization of the solutions that also characterize well another quasi-equilibrium state

$$t(\phi) = (k_0/2\lambda) \ln\left(\frac{\phi + \lambda}{\phi - \lambda} \frac{\phi_0 - \lambda}{\phi_0 + \lambda}\right)$$
(20)



Figure 2. A quasi-equilibrium friction state with a weak coupling of the surface dislocation density and polyreaction fields, i.e., the solution to the problem (17) (see text) for  $\rho_0 = -e/f$ , where  $\rho_0$  is the initial density of the surface dislocations, and e and f are some coupling parameters used in equation (4), being of the opposite sign ( $\phi_0 = 1$  and  $k_0 = 0.5$ , 1, 1.5 from top to bottom, respectively).



Figure 3. Monomer concentration  $\phi$  versus time *t*-dependence for  $\rho_0 > -e/f$  and for two regimes A and B distinguished: in regime A (here  $\lambda = 0.95$ ),  $\phi$  decreases with time *t* starting from the initial value  $\phi_0 = 1$ , but in regime B ( $\lambda = 1.05$ ) quite opposite situation is observed, though the process proceeds in time with different "intensities" (both curves are depicted for the same number of points).

is used (see figure 3). Some interesting approximate solutions of equation (17), for x > 2, are also possible to obtain and will be presented below.

As to the point (ii), i.e., when  $h \in (0, 1)$ , we wish to divide our analysis into three sub-cases:

(a) h = 0.5 (or x = 3) which could describe or represent a tribopolycondensation process with no catalyst [17], i.e., the friction surface does not play any significant role (for example, it is not well-developed or too smooth, or it is somehow



Figure 4. A model tribopolymerization process with no catalyst. The  $\rho\phi$ -projection of the phase portrait of system (13) for x = 3 and v = 0.5; all the remaining parameters and initial conditions of system (13) take the same values as in figure 1 (also  $t \in [0, 20]$ ), but the phase portrait possesses somewhat chaotic character and the trajectory tends to a region of shrinking volume in the phase space. The picture is obtained by using *Mathematica*, version 2.2.3.

"neutralised" by free radicals dispersed in the friction interlayer); here, a numerical demonstration of the phase portrait (a  $\rho\phi$ -projection) is given in figure 4; in this way a periodicity of the system as well as its chaotic character is manifested (i.e.,  $\phi$  and  $\rho$  are periodic in time) and the trajectory tends to a region of shrinking volume in the phase space (contrary to the case of x = 2 mentioned above);

- (b)  $h \in (0, 0.5)$  (or  $x \in (2, 3)$ ) which would be responsible for certain intermediate states: the smaller is the *h*-value the more the role of the friction surface as a catalyst is pronounced, and conversely, the bigger is this value the less significant the influence of the friction surface on the polycondensation reaction can be;
- (c)  $h \in (0.5, 1)$  (or x > 3) which may stand for some chemical polyreaction kinetics of higher order and will be postponed because of troubles in finding a clear physico-chemical picture assigned to it (we only know that both  $\phi(t)$  and k(t)decrease quite rapidly in time; perhaps, it is the process regime in which the friction mechanism is dominating, and the machinery of creation and annihilation of surface dislocations takes a favour, what will be clearly shown below in a limiting case  $h \rightarrow 1$ , where the process is completely friction controlled, i.e., an interplay between some parameters c,  $\delta$  and  $\rho_0$  is crucial).

For the sake of brevity we do not wish to present some numerical solutions to the problem (13). It was done in [24], and no qualitative difference was found between them and those presented in [4] or [6] on that level of the studies (cf. discussion of the point (i)) except of the formal one, that means, those offered in [24] are frequently

depicted in a three-dimensional phase space  $(\rho, \phi, k)$  (cf. equation (13)). Unfortunately, no analytical results were found for a full system like that given by equation (13). However, all the effects described in [4,6] and also briefly listed above (e.g., periodicity, regulation of amplitude and/or control of frequency of  $\rho(t)$  and  $\phi(t)$  or an unstable state for x = 2, etc.) are confirmed. The only quantitative difference is that the form of k(t) (see equation (5)) "impinges" on the system another faster "time dynamics" (in fact, the function k(t) is an inverse (power) function of time; notice also that its form is invariant under time rescaling like  $t \to \alpha t$ , where  $\alpha > 0$ ). An interesting analytical estimate is easy to recover in the case of 0 < h < 1 (or x > 2) as well. Assuming that  $\phi_0 \to \infty$  (the initial concentration of monomers is very large) and  $\phi(\tau) = 0$  (after a quite long time there are no monomers, i.e., a polymer is formed during the friction process or all the monomers are somehow washed out, e.g., by mechanical removing from the system during the processing), from equations (2), (5) and (17), one can find [25] that

$$\int_0^\infty \left( A - k(\tau)\phi^x \right)^{-1} \mathrm{d}\phi = -\frac{\pi}{k(\tau)x\sin(\pi/x)} = -\int_0^\tau \,\mathrm{d}t = -\tau, \tag{21}$$

where  $k(\tau) = 2k_0$  (see equation (5)), and we have utilized the following features of the Euler Gamma-function  $\Gamma(z) = \int_0^\infty e^{-t} t^{z-1} dt$  (Re z > 0) [25]:

$$\Gamma(y+1) = y\Gamma(y);$$
  $\Gamma(y)\Gamma(1-y) = \pi/\sin(\pi y)$  and  $\Gamma(1) = 1$  (22)

for a real value y; moreover, we have applied the identity  $\int_0^{\infty} \ldots = -\int_{\infty}^0 \ldots$ . Let us recall here that  $\rho(t) \equiv \rho_0 > 0$  also in this case. Thus, from (21) and (22) it follows that

$$(x/\pi)\sin(\pi/x) - p \stackrel{\text{def}}{=} F(x;p) = 0,$$
 (23)

where  $p = (2k_0\tau)^{-1}$ , which is a relationship among three physical quantities characterizing the chemical polyreaction, namely, x,  $k_0$  and  $\tau$  (note here that F is a nonlinear function of x, being exclusively of negative value when x becomes fractional, and it does not depend upon  $A = e + f\rho_0$  (see equation (17)); this will be plotted against the parameter p in figure 5). For  $x \gg 1$  (i.e., for chemical reactions of higher order, rather, or for h-values approaching one or  $d_s$  tending to zero; cf. equation (17)) one can write

$$\sin(\pi/x) \cong \pi/x \tag{24}$$

and, applying equations (23) and (24), one gets immediately a very simple result

$$\tau \cong 1/(2k_0),\tag{25}$$

which means that in such an asymptotic regime (see above) the only dominating thing is chemical polyreaction after the friction process being completed (or finished). The result (25) looks quite natural and it expresses the fact that the more slowly the rate of the chemical reaction may be pronounced, the larger are times  $\tau$  after which a



Figure 5. The generalization of the Vogel–Fulcher-type formula corresponding to the selective transfer during the friction process, i.e., the solution to problem (13) given by equation (27) which is the nonlinear (periodic in x) function F(x; p), defined in equation (23) (see text), plotted against some values of the parameter  $p = (2k_0\tau)^{-1}$  (p = 0.5, 1.0 and 1.5, from top to bottom, respectively), where  $k_0$  is the initial value of the chemical reaction rate coefficient, and  $\tau$  is a time after which a stationary state can be reached and for which  $k(\tau) = 2k_0$  (see equation (5) for details).

"stationary state" is reached. Notice also that  $k_0$  could often be taken by the Arrhenius formula, i.e.,

$$k_0 = k_{00} \exp(-E_{\rm a}/R(T-T_{\rm c})),$$

from which one learns that the bigger  $E_{a}$ -values or the smaller T-values are the smaller is also the chemical reaction rate constant  $k_0$  (here  $E_a$  denotes the activation energy of the reaction process enhanced by friction, T is its absolute temperature, and  $k_{00}$ , T<sub>c</sub> and R are positive constants). Following this kind of reasoning, one may go a step further and conclude that time  $\tau$ , that exhibits the maximum time scale for the polyreaction caused by friction, is of the experimentally observed Vogel-Fulcher form [26], i.e.,  $\tau = C_1 \exp(C_2/(T - T_c))$ , where one gets  $C_1 = 1/(2k_{00})$  and  $C_2 = E_a/R$  (look just at equation (25) and apply the Arrhenius formula to  $k_0$ ). Such a type of temperature dependence is quite frequently met in glassy materials under, e.g., intense grinding (under shock or irradiation) [27], also, in some amorphous (disordered; also partially ordered) polymers or ceramics, or even biomaterials under certain physico-chemical treatment (it is worth noticing here that, in general, some non-Arrhenius behaviour may take place, e.g., for fragile liquids or non-Newtonian fluids like lubricants with polymeric additives) [27,28]. Such a relationship can also be found as being characteristic of Rehbinder's effect (cf. [4, chapter 1, p. 33, equation (1.28)]) and, as expected, of ST-phenomenon (look at [4, chapter 3, p. 115, equation (3.2)] once again). It may also provoke to expect the friction coefficient of the system f to be of the same form, namely,  $f = f_0 \exp(E_a/R(T - T_c))$ . The "structure" of the activation energy of the process,  $E_{\rm a}$ , appears to be the most interesting fact here since it can be represented by  $E_{\rm a} \propto U - \gamma \sigma$ , where U is the excessive energy as compared to the average molecular energy at a given temperature that molecules should possess in order to react chemically (i.e., it depends upon the energy of active centres),  $\gamma$  is a parameter which depends, e.g., upon the dislocation density, structural changes, etc., and  $\sigma$  stands for the stress of the material under friction. Equation (23), in turn, can be understood in terms of generalization of the Vogel-Fulcher dependence valid for any chemical polyreaction degree x (one can get strict Vogel–Fulcher temperature behaviour for  $x \gg 1$  in equation (23) and by applying to  $k_0$  the Arrhenius formula). Moreover, since we are now in regime of 0.5 < h < 1, we may probably expect that the process studied follows the Kohlrausch-Williams-Watts "relaxation" dynamics [28,29], but in the full case only, i.e., when equation (5) is applied (note, that above we have only studied a limiting case  $k(t) = k(\tau) = 2k_0 = \text{const}$ .

The problem associated with point (iii), i.e., when  $h \to 1$ , is fully solvable analytically. Since, in this case  $x \to \infty$ , and  $\phi(t)$  vanishes very rapidly to zero (practically, within an initial time  $t = t_0$  which, as previously, we set for simplicity  $t_0 = 0$ ). Now, the solution to problem (13) looks like

$$k(t) = k_0 / (1 + (t/\tau))$$
(26)



Figure 6. A variety of the  $\rho$  versus t behaviour, i.e., the solution to problem (13) given by equation (27) (see text) for  $\Delta = c^2 + 4\delta a = 0$ , where c and  $\delta$  are some coupling parameters (cf. equation (1) for details;  $\delta$  is set to be equal to one here, also,  $\rho_0 = 1$ ) and quantity a stands for a parameter assigned to the external source of surface dislocations of a material under friction; it is presented in some qualitatively different regimes: the horisontal line  $-\rho$  is constant for r = 1; the decreasing middle line  $-\rho$  decreases with time t for r = 0.5; the two remaining cases  $-r = 1.5 - \rho$  decreases with time t along a vertical asymptote t = 2 for some "long" and "short" times, respectively; negative values of  $\rho$  should be discarded from the physical point of view.



Figure 7. Three solutions of equation (29) showing that  $\rho$  is an increasing function of time t are presented for  $\Delta > 0$  and a > 0, and for different three values of  $\delta = 9/19$ , 10/19 and 11/19 from bottom to top, respectively (here we set  $\rho_0 = 1$ , r = 0.95,  $\Delta = 1$ ); a small increase in value of parameter  $\delta$  may produce here a blow-up phenomenon.

(which automatically follows from equation (5)), and (cf. figure 6 for a picturesque outlook)

$$\rho(t) = r + \frac{\rho_0 - r}{1 + \delta(\rho_0 - r)t}, \quad r = c/(2\delta),$$
(27)

for  $\Delta = c^2 + 4\delta a = 0$  (pay attention to the notation used in section 2). For  $\Delta > 0$  and



Figure 8. Solutions of equation (30) are depicted for a = 0, i.e., with no external yield of surface dislocations of the material under friction and for different values of parameter r, namely, r = 0.49, 0.5, 0.51, 0.55 and 0.6 going from the thickest to the thinest curve, respectively. Values for other parameters:  $\rho_0 = 1$  and c = 1.

a > 0 one obtains

$$\frac{\rho(t) - r - (\sqrt{\Delta}/(2\delta))}{\rho(t) - r + (\sqrt{\Delta}/(2\delta))} = \frac{\rho_0 - r - (\sqrt{\Delta}/(2\delta))}{\rho_0 - r + (\sqrt{\Delta}/(2\delta))} e^{-\sqrt{\Delta}t}$$
(28)

(where  $r = c/(2\delta)$ , once again, and  $\Delta$  is defined above) [25]. The time behaviour of  $\rho(t)$  will be demonstrated in figure 7 using a more convenient (inverse) form, namely,

$$t(\rho) = \Delta^{-1} \ln \left[ \frac{\rho - r + (\sqrt{\Delta}/(2\delta))}{\rho - r - (\sqrt{\Delta}/(2\delta))} \frac{\rho_0 - r - (\sqrt{\Delta}/(2\delta))}{\rho_0 - r + (\sqrt{\Delta}/(2\delta))} \right].$$
 (29)

In the case of a = 0 (no external yield of surface dislocations) one has (figure 8)

$$\rho(t) = \frac{2r}{1 - (1 - (2r/\rho_0))\exp(-ct)},\tag{30}$$

for which  $\rho(t)$  is either an increasing function of time (for  $2r < \rho_0$ ) or a decreasing function of time (for  $2r > \rho_0$ ), or it is constant (for value  $\rho_0 = 2r$ ).

A general remark is appropriate here. Namely, some of the solutions presented above in this section are quite interestingly related to some experimental situations measured; e.g., figures 1 and 4 reflect reasonably the time periodic character (note that the model neglects spatial effects) of the dislocation density as well as of the monomer (surfactant) concentration, improved much in many experimental situations (cf. [4] and references therein, once again, mostly chapters 3–6). The other cases presented reveal some well-oriented trends towards the experimental studies, but because of being "the limiting analytical cases" they do not conform strictly to some experimental curves. Figure 5, in turn, being even a generalization of the Vogel–Fulcher behaviour shows at least some very promising tendencies and a knowledge on the behaviour

of F with respect to x could serve as a criterion whether kinetics of the process are of integer order or non-integer (fractional) order, rather (note that the most reduced case here represents the exponential dependence for the relaxation time,  $\tau$ , being characteristic of Rehbinder's effect and ST-process; cf. equations (23)–(25) and the discussion thereafter; also, an interesting almost-self-similar behaviour of the F(x; p)dependence with respect to different chemical reaction order "scales" or values has to be underlined).

Last but not least, we have to utilize equation (16) to get the stationary states of the system. A strict calculus gives

$$\rho_{\rm st} = -e/f, \qquad \phi_{\rm st} = \frac{\delta\rho_{\rm st}^2 - c\rho_{\rm st} - a}{b}, \qquad k_{\rm st} = 0 \tag{31}$$

(where b and f must evidently be non-zero parameters) and reflects an interesting fact that in the stationary regime chemical polyreaction and friction processes are coupled with each other, but the chemical reaction rate coefficient in the stationary state goes to zero (cf. equation (5) once again).

## 4. Final remarks

In this paper, we have proposed a three-dimensional system of ordinary differential equations of first order which has been used to describe in a more qualitative than quantitative way the kinetics of the tribopolymerization process, in which both friction and polyreaction fields are coupled with each other. The description is based on more realistic physico-chemical foundations than those utilized in [4,6] for a twodimensional case. It is so, because we have taken into account a predominant role of the geometry of the friction surface (we have introduced some measures of it in section 2) as a catalyst as well as some relevance of the chemical reaction taking place in the vicinity of it. The idea comes straightforwardly from experimental grounds [2,4,6] which undoubtedly show that there is a coupling between friction and chemical reaction of polymerizing species [27] dispersed in a lubricant (in fact, some interesting theoretical ideas for a confined polymeric system have also been contained in [30]). The generalization means also that the fractal-like chemical reaction kinetics is applied because the system in question possesses frequently very much irregular rough surface which catalyzes the chemical polyreaction as well.

As it was demonstrated in [4,6] for k being time-independent the system has non-trivial periodic behaviour. Also, some numerical work was done to show that for k given by equation (5) the time behaviour is essentially "of the same quality" when comparing with the two-dimensional one [4,6,24].

In this article, we have shown a robustness of our approach by solving analytically some limiting analytical cases (cf. equations (17)–(20) and (26)–(30)) in which, however, a linear coupling of two main fields (surface dislocations' density and polyreactants' concentration) has been expressed by means of the parameters (see above) characterizing the phenomenon under study. Some qualitative behaviour, however, of a full dynamical system (13) has been described in sections 2 and 3.

The stationary states have been calculated as well. It demonstrates a kind of coupling (or mutual influence) between friction and polyreaction characteristics which is expressed by presence in equation (31) of parameters a, b, e, f, c and  $\delta$ .

Also, we would like to state clearly that there is no direct dependence between fractal characteristics of the process manifested by h or x and the tribopolymerization phenomenon itself, but it is implicitly assumed that, e.g., the fractal dimension of the surface will remain unchanged during the whole process under investigation. It seems to be worth mentioning that some other, more powerful theoretical systems, like that presented in [31], can surely be applied to describe the kinetics of the phenomenon or subtleness of its time behaviour in a possibly natural way. In such a case of the so-called anequilibrium dynamics, however, all the first order time derivatives have to be replaced by some non-integer (rational) order time derivatives (cf. [31] for details).

The relationship between the system analyzed in this paper and the concept of tribological interfaces is hypothesized in terms of the anomalous random walk process, where the physical as well as geometrical characteristics of the active interface can be done using a common "dynamic" exponent, i.e., the fracton dimension  $d_s$ , being, according the Alexander–Orbach conjecture, easily determined by the fractal dimension of the surface as well as by the fractal dimension of the random walk process proceeding on it or at the vicinity of it (see discussion in section 2). Such a treatment of tribological interfaces, but mostly due to the fractal dimension of the surface under friction and its changes during the friction process is well known in the tribological literature [3] (see also the whole proceedings volume cited in [6]).

As to the removal of the polymer during the process in question and for having technologists satisfied (say, to some extent), we are of the opinion that it does not appear to be a central problem of this study, at least, for two reasons. First, because our system is a model system, and it is only presumed that a sufficient amount of the monomer or surfactant is present in it, and if needed, the resulting polymer structures either depolymerize during the whole process or a certain destruction of the polymer chains or some presence of the intermediate reaction products is preserved. Second, because the system described is an open thermodynamical dissipative system, which means, that it may, in fact, constantly exchange the matter and energy with its surroundings, and a change of the useful (friction) work into the dissipated heat is expected to take place during the whole process. For revealing this general property of the system, one has to benefit from the modern theory of dynamical systems [32]. The idea is whether a bounded volume element of the phase space ( $\rho$ ,  $\phi$ , k), designated by V(t), diminishes in the course of time evolution. From the divergence theorem, it follows that (cf. [32, chapter 5])

$$\dot{V} = \int_{V} d^{3}\mathbf{x} \sum_{i=1}^{3} F_{x_{i}}^{i},$$
(32)

where  $\dot{V}$  is the time derivative of V with respect to t and  $F_{x_i}^i$  are the partial derivatives of  $F^i$  with respect to  $x_i$  representing the right-hand sides of the equations constituting system (13) for i = 1, 2, 3, respectively, from top to bottom (here  $x_1 \rightarrow \rho$ ,  $x_2 \rightarrow \phi$ and  $x_3 \rightarrow k$  and the integration runs over k,  $\phi$  and  $\rho$ , respectively), and if the system dissipates energy then

$$\dot{V} < 0 \tag{33}$$

(otherwise, it is a non-dissipative or conservative system). Evaluating the integral in (32) one arrives at

$$\dot{V} = -VW(t),\tag{34}$$

where

$$W(t) = W_0(t) - c (35)$$

and

$$W_0(t) = \delta(\rho(t) + \rho_0) + \frac{1}{2}(k(t) + k_0)W_1(t) + W_2(t),$$
(36)

$$W_1(t) = \frac{\phi^x(t) - \phi_0^x}{\phi(t) - \phi_0},\tag{37}$$

$$W_2(t) = \frac{k^y(t) - k_0^y}{k(t) - k_0} \tag{38}$$

(one can find all the symbols included in equations (35)-(38) in section 2; see equations (1)–(15) for details.) If W(t) > 0 then the whole system is dissipative. Here, we are of the opinion that it is the case (since  $W_0(t)$  is positive to a large extent, that means, in a respective time domain and for some quite broad interval of the parameter action chosen). The only contradictory cases would be when c, i.e., the parameter responsible for the generation of dislocations, will reach enormously large values, or when the process takes place at its early stages. The former is rather very unphysical or much unprobable (also, it does not appear to be the assumption of our modelling). The latter could happen in some specific initial condition regimes (if at all). Also, if we are looking at the numerical solution in the phase space, presented in figure 4, we can say that it is, at least, in a qualitative agreement with the aforepresented reasoning. It is so, indeed, because the trajectory starting from an initial point has rather chaotic character and is attracted by a certain point (or a region) of the phase space (also, the volume of the attraction basin shrinks to zero). It may imply that the Kolmogorov entropy (cf. [33] and references therein), denoted by K, i.e., a measure of the chaotic versus non-chaotic behaviour of the system is positive, and the mean time, say  $T_m$ , in which chaotic behaviour is observed appears to be the bigger the more carefully we are able to look at the situation under study or to measure it (let us denote the accuracy of these measurements by  $\xi$ ). In such a case one takes on always the relationship  $T_m \propto K^{-1} \ln(\xi^{-1})$  which is a useful theoretical formula to be applied by experimentalists as well. Technologically speaking, a constant removal of an excessive polymer or surfactant dispersed in the lubricant is realized, as in the sliding experiment for steel and copper alloy couples with TSIATIM and fluoroplast greases [2,4] or others [34].

Finally, let us notice an interesting (in our opinion) correspondence between the original systems of equations (equations (1)–(5)) and basic diffusion–reaction systems (mostly, the Fisher's equation), where, however, the diffusion term must be replaced by our coupling linear ansatz (equation (3) is inserted into equation (1)). Thus, our problem is a problem of selection of dislocations taken from dislocation field  $\rho(t)$  with the selection intensity equal to one. The selection field in our case is obviously not the diffusion field with a constant intensity, as it was invented for the original Fisher's problem, but chemical concentration field  $\phi$  taken from equations (2) and (4) (cf. [35] for details). Moreover, some analogy to problems for oscillator with quadratic friction (quadratic damping term can be related to the annihilation term from equation (1)) and/or avalanches in granular matter in the mean-field approximation can be accepted at least from a qualitative as well as mathematical points of view [36].

### Acknowledgements

It is a pleasure to thank very much the technical, organizational and financial support of my colleagues from the Institute of Mathematics and Physics and from the Department of Physics II of the University of Technology and Agriculture in Byd-goszcz, without whom it would not have been possible to prepare and write this paper in such an ordered way. The permanent interest of Felicja and Ewa Gadomski in my professional activity is acknowledged. I am also thankful to Dr. Ryszard Skulski of the Silesian University in Katowice for useful discussions and some literature information.

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