JOURNAL OF MATERIALS SCIENCE **34** (1999) 843 – 849

Strength changes of moulded polyamide composite caused by thermal oxidation

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Rolling-bearing cages (separators) which were made by injection moulding from polyamide 66 filled with short glass fibres were tested before and after exposures in hot air at temperatures 120, 140, 160, and 180 °C at various times ranging from a few hours to three weeks. The cages were loaded in tension and the changes of maximum force corresponding to ultimate tensile stress were studied. A very simple degradation mechanism containing the main features of the real degradation processes was proposed and its kinetic equations were derived. On the basis of the assumption that the changes of properties during ageing are proportional to the changes of chemical composition and structure a regression function was proposed. It was used for the fitting of the measured results and for the construction of predictive curves which describe the temporal and temperature dependence of strength for working temperatures and long times. © *1999 Kluwer Academic Publishers*

1. Introduction

During exposure in different media all physical and mechanical properties of polymers and polymer composites change more or less depending on temperature and time of exposure and on the type of medium. It is necessary to know the kinetics of the changes for the determination of the applicability of certain polymeric materials under certain use conditions.

As the exact theoretical description of the kinetics of the changes is rather complicated, different experimental procedures are used which allow one on the basis of short-term exposures at elevated temperatures to extrapolate the results of mechanical and physical tests to long times and working temperatures. Extrapolated values of properties are presented in the form of so-called predictive curves. Those procedures are based on the presumption that the chemical reactions in polymeric materials which play the main role in the changes of material properties are in principle the same in all the temperature ranges and the difference consists only in the reaction rates depending on temperature. The temperature dependence of the rate constants of all chemical reactions is described by Arrhenius law. However, many physical changes can be also successfully described using the same types of temporal and temperature dependences (e.g. the change of crystallinity degree, stress relaxation etc.).

The extrapolation mentioned above can be applied in a graphical or numerical way and creates the substance of many national and international standards.

2. Survey of standardized procedures

Mechanical or physical tests are carried out on specimens exposed usually at four elevated temperatures. The graphical extrapolation consists of two steps. In the first step the studied property is plotted against the time or the logarithm of the time and the time for a chosen reduction (very often 50%) of the studied property at each of test temperatures is determined. In the second step the logarithm of the time for the considered reduction of the property is plotted against the reciprocal of the absolute temperature. This step is based on modified Arrhenius equation

$$\tau = \tau_0 \exp\left(\frac{\varepsilon}{\kappa T}\right), \quad \text{i.e.} \quad \ln\tau = \frac{\varepsilon}{\kappa}\frac{1}{T} + \ln\tau_0. \quad (1)$$

where ε is the activation energy, κ is Boltzmann constant and T is absolute temperature. The quotient ε/κ can be replaced by the quotient E/R where E is the molar activation energy and R is universal gas constant. The obtained curve (so-called Arrhenius curve) is usually a straight line or a curve with relatively small curvature. The extrapolation of this curve determines the time-temperature limits for the considered reduction in the property. This procedure is used in ISO 2578-1974 [1] and DIN 53 446 [2]. The so-called *Underwriters Laboratories temperature index* [3, 4] used in English speaking countries is the temperature determined according to the procedure mentioned above for a 50% reduction in the property and an extrapolated time of 40 000 hours (i.e., approximately 4 years and 7 months). Similar but sometimes rather simplified procedures are used in national standards, e.g. [5].

For the numerical extrapolation the suitable fitting functions are needed which are sufficiently simple and on the other hand they describe well the temporal and temperature course of the studied property. For the temporal course at one test temperature some standards

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propose the function used in fatigue tests for the dependence of the fatigue stress on the number of vibrations. If the tests are carried out at more temperatures, certain rather complicated phenomenological fitting functions without direct relations to degradation processes are sometime recommended, e.g. [6]. General form of these functions is $\log \tau = f(p, T)$, where p is studied property. It means that the functions are able to describe only monotonic temporal changes of properties and, therefore, they are not applicable in our case when the studied property changes the sign of the slope of its temporal course.

The standard of former Soviet Union GOST 9.707-81 [7] describes the changes in polymers using very simple equations of chemical kinetics regardless which property is considered. The Arrhenius law is used for temperature dependence and the temporal course is described by means of the linear combination of kinetic equations of simple homogenous chemical reactions. But as the equations are chosen above all so as to make the best fit of experimental data, the description is also in principle only phenomenological. In spite of it this procedure gives relatively good results not only for polymer properties. It was successfully used for the description of dimensional changes of rolling-bearing steels during annealing and the changes of specific electrical resistance and microhardness of CuBe alloys during age hardening.

GOST mentioned above is based on very simple calculations with the results of tests what is adequate to the time of its introduction and to the planned purpose. Nowadays it is adequate to use (nonlinear) least-square method with regression functions constructed on the basis of the GOST. The weak sides of this procedure based on phenomenological functions are very large errors of the parameters of fitting curves as well as covariant coefficients very close to ±1 declaring that the parameters are extremely interdependent. It is the direct consequence of phenomenological description with weak connection to real processes occurring in polymer materials.

The determination of extrapolation validity is solved only in some of presented standards. DIN 53 446 recommends for tests at least five samples for every temperature and time of exposure. The extrapolation is made not only for average values but also for standard deviations. GOST 9.707-81 contains rather complicated determination of the number of tested samples. Lower limits of extrapolation are determined as 2/3 of mean extrapolated values. In the case when least square regression is used, the lower limits can be determined on the basis of fitted curve and its standard deviation band.

3. Procedure considering real processes in material

Better fit of experimental data with lower parameter errors and covariances can be reached if the real degradation processes of material are considered. It is not possible (the less so for material expert without deep chemical education) to describe exactly the reactions in polymer and their influence on mechanical properties. But it seems it is enough to describe the main features of those processes even if many simplifications have to be done.

During the degradation of a polymer composite the main processes are the decomposition of long polymer chains and the weakening of the bond between polymer matrix and filler. At initial stage of decomposition it can be assumed that the initial mechanical properties change with the time proportionally to the relatively low amount of arising products of polymer decomposition and to physical changes in polymer structure. The conclusion of these considerations is the same as GOST mentioned above presents: the temporal dependence of mechanical property can be described by means of the linear combinations of kinetic equations of chemical reactions (the using of Arrhenius law for the temperature dependence of mechanical properties is out of doubt). The difference consists in the type of kinetic equations chosen – even if they must be as simple as possible, they must consider the main features of real processes in material.

4. Main processes in polymer composite during degradation

Purely degradation processes are attended with other processes which can also substantially change all the properties of polymers. The fastest changes of mechanical properties are caused by the drying of polyamide as received which contains about 2% of water. The drying causes an increase in strength and a substantial decrease in plasticity. Since it is a diffusion process, drying can be described in the time τ with the expression of $1-\exp(-k\sqrt{\tau})$. From our previous studies the value of the activation energy for drying is known $\varepsilon = 0.26\,\text{eV}$. To simplify the description this effect was avoided by preliminary drying.

The effect of the cross-linking of polyamide as well as the result of increase of crystallinity fraction are qualitatively the same as of drying (increasing strength, decreasing plasticity) but these processes are many times slower and their effect many times lower. It can be observed if the effect of drying is avoided but to distinguish the influences of these two processes on mechanical properties is very difficult. Therefore, their common effect was approximately described using the simplest rate equation

$$\Delta p_1 = a[1 - \exp(-k_1\tau)], \qquad (2)$$

where Δp_1 is the change of considered property and k_1 is rate constant. In this equation also the effect of relaxation of residual compressive stresses could be taken.

The reduction of the bond between polyamide matrix and glass fibres causes the opposite effect – decreasing strength and usually increasing plasticity. If the reduction of the bond is large and/or the volume fraction of glass fibres is high the plasticity also decreases. This phenomenon was studied only quantitatively with respect to the kind of fracture and its effect was included into the effects of the other processes.

The main degradation process of polyamide composite is the decomposition of macromolecular chains.

The result of this process is decreasing both strength and plasticity. Let us try to describe this process by the kinetic equation as simple as possible. When the original chain A_0 dissociates into two chains A_1, their lengths are long enough to have nearly the same chemical properties as the original chain A_0. It means that the dissociation of A_0 into A_1 and A_1 into A_2 etc. can be described with the same rate constant k_2. In general the whole decomposition can be described with diagram of manifold consecutive reaction

$$A_0 \xrightarrow{k_2} A_1 \xrightarrow{k_2} A_2 \xrightarrow{k_2} \cdots \xrightarrow{k_2} A_{n+1} \tag{3}$$

with rate equation

$$x_2 = 1 - e^{-k_2\tau}\left[1 + \sum_{i=1}^{n} \frac{(k_2\tau)^n}{n!}\right] \tag{4}$$

where x_2 is conversion variable.

5. Regression function considering real processes in material

On the basis of the assumption that the changes of properties are proportional to chemical and physical changes of material the value of any property change Δp can be written in the form of linear combination of Equations 2 and 4,

$$\Delta p = \Delta p_1 + b x_2. \tag{5}$$

Especially for maximum force F at which the cages break, the regression equation can be written

$$F(\tau, T) = c - a e^{-k_1\tau} + b e^{-k_2\tau}\left[1 + \sum_{i=1}^{n} \frac{(k_2\tau)^n}{n!}\right], \tag{6}$$

where a, b, and c are positive constants. Their meaning with respect to the shape of time dependence is clear from next equations:

$$F(\tau = 0) = c - a + b, \tag{7}$$

$$F(\tau) \approx c + b \quad \text{for } \frac{1}{k_1} \ll \tau \ll \frac{1}{k_2}, \tag{8}$$

$$F(\tau \to \infty) = c. \tag{9}$$

Formal difference between Equations 5 and 6 consists in the fact that c means in Equation 6 not initial but final value of mentioned property.

The temperature dependence of $F(\tau, T)$ consists in temperature dependence of rate constants k_1, k_2 described by Arrhenius equation

$$k_i(T) = k_{i\infty} \exp\left(-\frac{\varepsilon_i}{\kappa T}\right). \tag{10}$$

The pre-exponential constants $k_{i\infty}$ are rate constants extrapolated for infinite temperature. The errors of their values determined by regression are usually larger than the values alone and least-square computation needs many iterations to find the minimum. From practical point of view it is better to choose relative temperature T_0 from the range of testing temperatures or from near neighbourhood of this range and to rewrite the Equation 10 in the form

$$k_j(T) = k_j(T_0) \exp\left[-\frac{\varepsilon_j}{\kappa}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \tag{11}$$

in which the rate constants $k_i(T_0)$ for temperature T_0 have small errors and the number of iterations is substantionally reduced.

The regression function (6) was written for maximum force but the function for any other property has the same form and the same parameters k_1, k_2 (with the same temperature dependence i.e. with the same parameters ε_1, ε_2), only the values and signs of parameters a, b, and c are individual for each property. It was presented in previous work [8] where maximum force and total elongation at rupture were commonly studied.

6. Tested samples and test conditions

For mechanical tests the cages 7201 BETNG of angular-contact ball bearings were used which were injection moulded from stabilized polyamide 66 Technyl A 218 V25 (producer Rhône-Poulenc, France) filled with 25 vol % of short glass fibres of 10 μm diameter and about 0.5 mm mean length. Injection moulding was made using machine Battenfeld 300 CD at following conditions: temperatures of polymer in machine zones were 275, 290 and 295 to 300 °C (injection temperature was the same as the temperature of last zone), single cavity mould with radially sliding punches was tempered at 80 °C, injection – pressure 85 MPa and time 2 s, moulding – pressure 72 MPa and time 6 s, time of cooling in mould 12 s, moulding cycle 22 s. These cages of ring shape (outside diameter 23.9 mm, inside diameter 18.7 mm, width 6.4 mm, 11 holes – pockets for balls – with diameter 4.9 mm in radial directions) were loaded in tension in such a way that two half-cylinders were inserted into cage and moved radially outward with velocity 0.36 mm/s (see Fig. 1). Maximum force

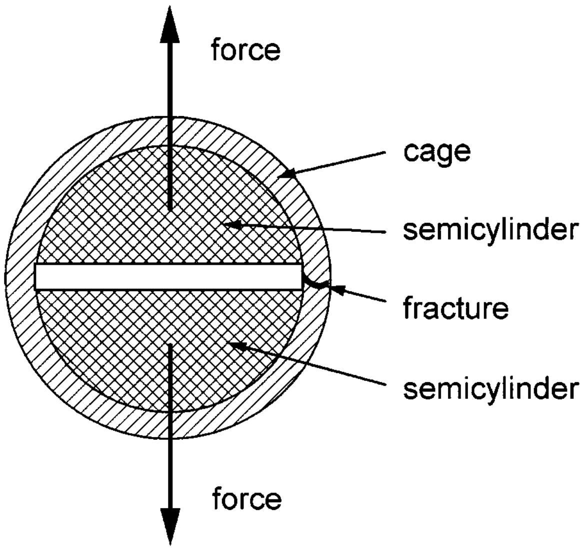

Figure 1 Experimental setup of mechanical tests of cages.

at which the cages broke (i.e. fracture force) was determined. This force is one of the most important property of cages. It is the product of ultimate tensile stress and the least total cross section of cage 9.61 mm^2 (it means the double of the least single cross section).

To avoid the effects connected with drying the cages were pre-dried 24 hours at 80 °C. The cages were loaded to fracture directly after pre-drying (6 pieces) and also after the exposures at various times ranging from a few hours to three weeks in hot air at temperatures of 120, 140, 160, and 180 °C (4 pieces for each of couple time – temperature). The temperature was controlled and measured with accuracy better than 1 °C. The cages were enclosed in a small glass vessel and also the oven was sealed to limit the ventilation and to reduce the smell. The oven was arranged and made safe for long-term operation.

The testing of rolling-bearing details was preferred to the testing of standardized samples to find the influence of injection moulding in the case of relatively complicated form of the cages (other reason for testing of finished cages was the aim of the producer to produce high-quality bearings). To avoid the different influence of weld lines the injection moulded cages had defined orientation between the gates and the direction of loading.

7. Experimental results, their fitting and discussion

The results of tests are presented in Figs 2 and 3. Both figures contain the dependence of maximum force at which the cages were broken on exposure time for all four temperatures mentioned above. Fig. 2 has linear time axes which are suitable for presenting the results for times higher than 100 hours (approx. 4 days). In this figure also the axis of approximate fracture stress (ultimate tensile stress) is added. For lower exposure times the logarithmic time axis is more suitable what can be seen in Fig. 3. The disadvantage of logarithmic axis is the impossibility to present directly the initial values for zero time which are added before the break of time axis.

Both figures contain experimental points and fitted curves. In temporal course of maximum force two different regions can be distinguished – the former with relatively fast increase of maximum force can be imputed to cross-linking and increase of crystallinity fraction, the latter with slower decreasing of the force is the result of decomposition of macromolecular chains (the increase of maximum force as the result of drying was suppressed by preliminary drying). Therefore the function (6) was used for regression. The best fit was obtained for the value of $n = 1$ in this function. In previous paper [8] dealing with partially stabilized polyamide the optimum value $n = 3$ was obtained. The lower value n for professionally stabilized polyamide what means lower number of chain dissociations is in agreement with expectation. The obtained values of regression parameters and their errors are presented in Table I (rate constants are calculated for a relative temperature $T_0 = 150$ °C).

The most important parameters are activation energies which are important characteristics of degradation

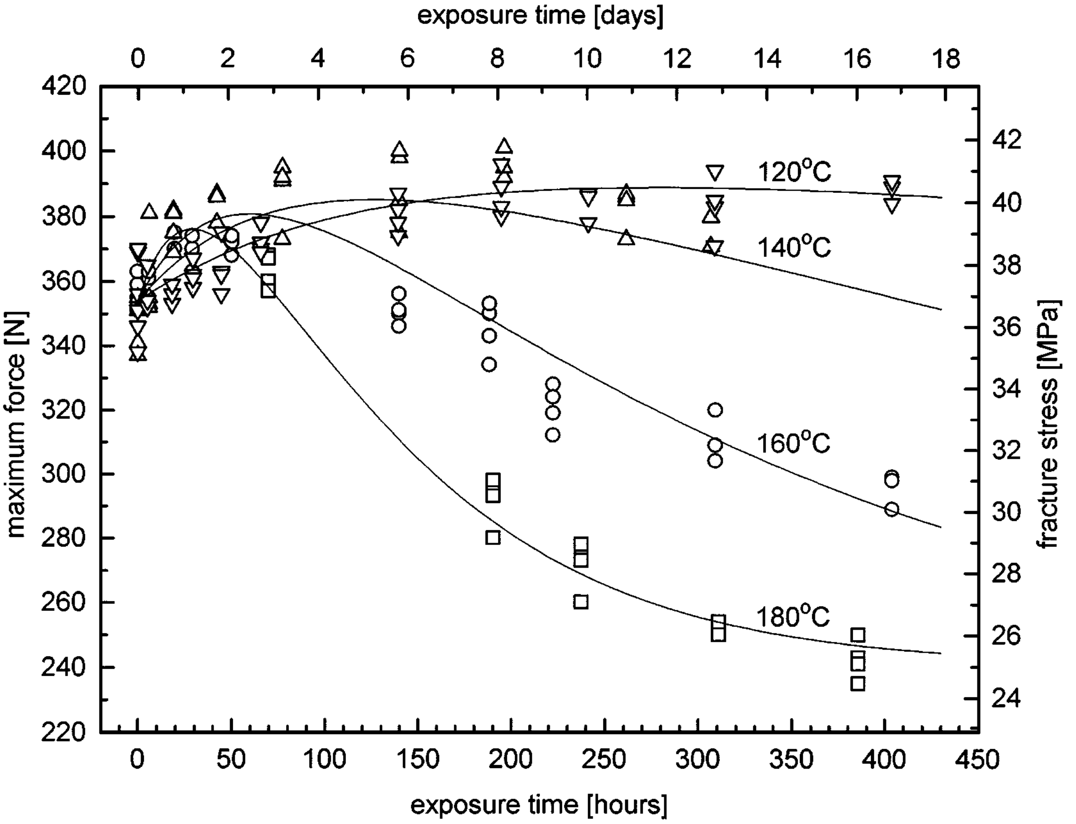

Figure 2 Temporal dependences of maximum force for different temperatures (linear time axes in hours and days). On right axis the approximate fracture stress is presented.

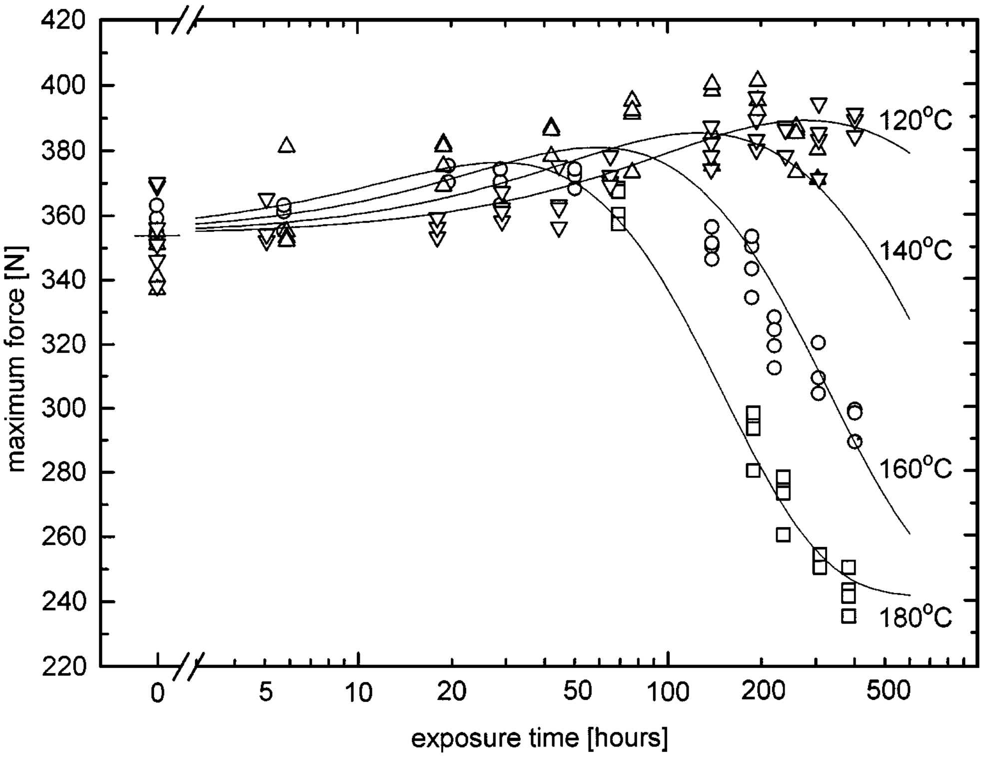

Figure 3 Temporal dependences of maximum force for different temperatures (logarithmic time axis with initial values).

TABLE I Regression parameters in function (6) with $n = 1$ and their errors (mean square deviations)

Symbol	Unit	Value	Error
a	N	43.1	4.5
b	N	155.9	6.2
c	N	241.0	4.9
k_1	10^{-3}/h	21.3	5.1
k_2	10^{-3}/h	3.91	0.30
ε_1	eV	0.405	0.082
ε_2	eV	0.673	0.043

processes. First of them $\varepsilon_1 = (0.41 \pm 0.08)$ eV $= (39 \pm 8)$ kJ/mol is higher than activation energy of drying 0.26 eV determined in previous works. It demonstrates that the process with the increase of destructive force appearing in short exposure times is really no drying or drying creates only negligible portion of that process. Activation energy of the process with the decrease of destructive force (degradation process in a strict sense) in professionally stabilized polyamide $\varepsilon_2 = (0.67 \pm 0.04)$ eV $= (65 \pm 4)$ kJ/mol is higher than the activation energy (0.46 ± 0.05) eV determined for that process in partially stabilized polyamide [8] what is also one of the evidences of better stabilization.

Approximate fracture stress presented in Fig. 2 was calculated as the quotient of maximum force and double cross section of the cage in the fracture point (9.61 mm^2). The fracture usually occurred in the pocket for a ball where the cross section is minimal and the pocket divides the cage in two cage-ends. Rather complicated shape of the cage which causes uneven distribution of stress between two cage-ends and within each of them as well as complicated flow of polyamide melt in the mould is the reason of relatively low fracture stress (about 40 MPa) in comparison with ultimate tensile stress which is warranted by producer for standardized tensile samples made from dried composite (about 160 MPa). In spite of that it can be said with respect to cage shape and test conditions that the cages were made in high quality.

In previous paper [8] also the values of deformation at fracture was determined. Exposures and mechanical tests described in this paper were made in different laboratories and the time between them had strong influence on the results of mechanical tests. Already the difference of several hours of that pause caused higher dispersion of results of maximum force and fully depreciated the results of deformation at fracture. Therefore the deformation results could not be used. The reason of it had to be the fast change of water content in cages even if the cages were transported in closed polyethylene pouches. It seems that the times between the exposure at elevated temperatures and mechanical tests have to be comparable and as short as possible.

8. Predictive curves

Calculated regression parameters allow to construct the predictive curves for working conditions, i.e. lower temperatures and longer times in comparison with test temperatures and times. The predictive curves were constructed in Fig. 4 for temperatures of 120, 100 and 80 °C and working times in months and in Fig. 5 for temperatures of 80, 60 and 40 °C and working times in years (full lines). Also the lower one-side tolerance limits were constructed (dash lines). It can be said with 90% certainty that 90% of cages will have higher maximum destructive force than those limits.

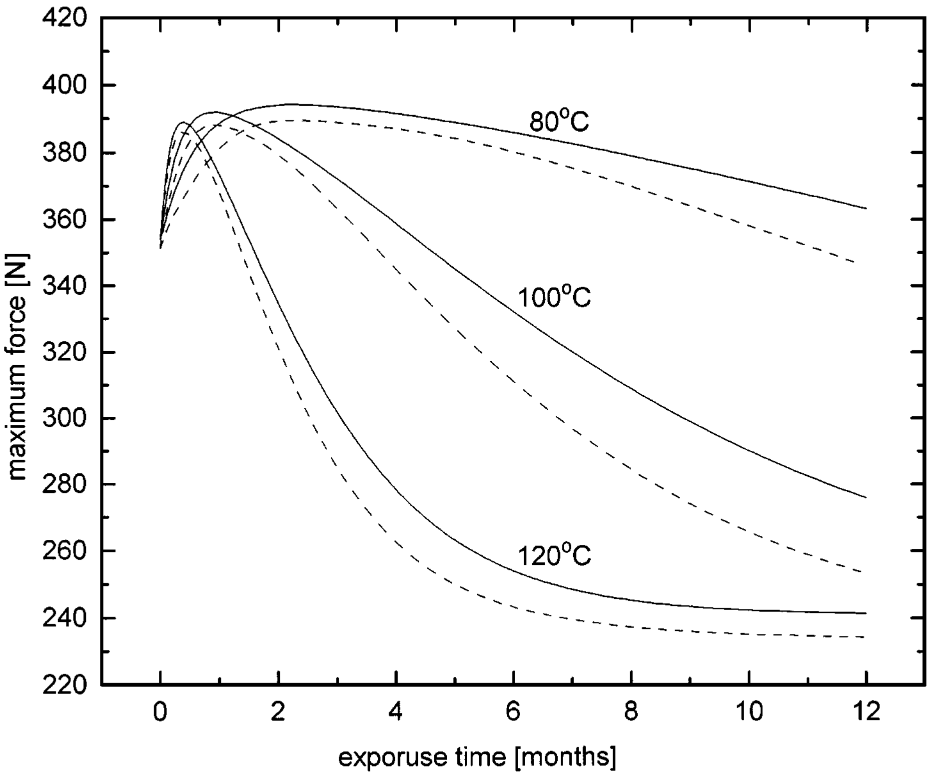

Figure 4 Predictive curves of maximum force and their lower tolerance limits for higher temperatures (exposure time in months).

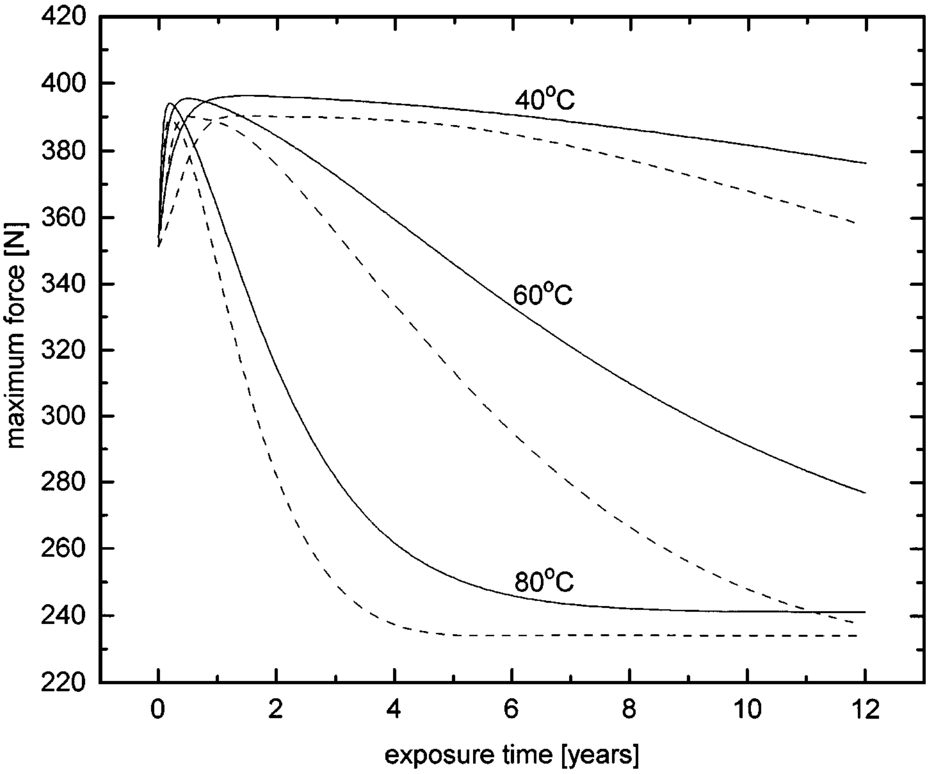

Figure 5 Predictive curves of maximum force and their lower tolerance limits for lower temperatures (exposure time in years).

9. Conclusion

The temporal and temperature courses of mechanical properties of polymers and polymer composites during exposure in hot air can be approximated with linear combinations of kinetic equations of chemical reactions. The approximation is good if the simplified kinetic equations consider the main features of the chemical reactions and physical changes. In the case of the destructive force of cages made from polyamide composite the equation of manifold consecutive reaction was successfully used for a description of chemical changes. The regression function using that equation together with exponential function describing all other changes allowed not only to fit the experimental results but also to construct the predictive curves and their tolerance limits.

The same access (generally with other kinetic equations) is applicable also for other materials, not only for polymers. Temporal and temperature dependences of different properties of the same material can be described by the same type of equations in which the rate constants and activation energies have the same values, only the remaining parameters (having the same units as studied property) have different values.

Acknowledgements

The author is indebted

— to Ministry of Defence for partial supporting of the work by grant MO 50170896306,

— to the firm S.L.B. Ltd. Brno (especially to Dipl.-Ing. F. Stárek) for the cages given gratis for tests and stimulating discussions,

— to Bc. P. Pospíšil for much experimental work.

References

1. ISO 2578-1974 Plastics, Determination of time–temperature limits after exposure to prolonged action of heat.
2. DIN 53 446 Testing plastics, Determination of time-temperature limits (in German).
3. M. I. COHAN (ed.), “Nylon Plastics” (John Wiley & Sons, New York, 1973) p. 375.
4. H. REYMERS, *Mod. Plast.* **47** (1970) 78.
5. ČSN 64 0768 Testing Plastics, Determination of time-temperature limits (in Czech).
6. ČSN 64 0007 Plastics, Statistical methods for evaluation of long-time test results of mechanical properties (in Czech).
7. GOST 9.707-81 Unified system of corrosion and ageing protection, Polymeric materials. Methods of accelerated climatic ageing tests (in Russian).
8. J. KOHOUT, in Proceedings of International Conference on Advanced materials and Technologies, Plzeň, June 1995, editor not mentioned (ŠKODA–Research Plzeň & Technical University of Brno, Plzeň and Brno, 1996) Vol. 2, p. 24. Czech translation in *Jemná mechanika a optika* **41** (1996) 255.

Received 19 May 1997
and accepted 8 October 1998