Physicochemical analysis of self-heating of glass-epoxy composites cured by novolac

Andrzej KATUNIN – Institute of Fundamentals of Machinery Design, Faculty of Mechanical Engineering, Silesian University of Technology, Katarzyna KRUKIEWICZ – Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology

Introduction

Polymer composites found wide application in many branches of science and technology. Recent advances of materials joining and technological processes make possible application of them in the most responsible engineering constructions, i.e. turbine, helicopter and wind power stations blades, elements of turbojet engines, car bodies, etc. Such applications require discovering the properties and behaviour of polymer composites since the conception development and designing process, therefore the behaviour of these materials should be investigated properly in different loading and ambient conditions. Degradation processes of polymers and polymeric composites are very sensitive to the environmental conditions (e.g. changes of temperature, humidity, etc.), which cause irreversible structural changes and often intensify much the process of degradation.

Following the macroscopic thermomechanical definition the self-heating effect occurs, when the element made of polymer-contained material is subjected to intensive cyclic loading and, due to the viscoelastic nature of the most polymers used for machines construction, the amplitudes of applied stress and resulted deformation became out-of-phase, which results in occurrence of hysteresis. During this process the great part of mechanical energy is dissipated in the form of heat and, considering low values of thermal conductivity of investigated materials, the generated heat is stored into the structure and the self-heating temperature grows up. From operational point of view of polymeric elements there are some characteristic temperatures (e.g. critical self-heating temperature [1], glass-transition temperature), who's exceeding resulted in initiation of structural faults and necessity of their removing and replacement.

The self-heating effect occurrence in polymer-based materials could be also defined within the thermokinetic molecular interaction. Following such a definition the heating-up process is resulted by friction between single particles and polymer chains. The resistance resulted from friction could be interpreted in macro-scale as viscous damping. An increase of temperature intensifies the process in terms of Brownian motion of particles and decrease of mechanical properties is resulted by degradation of structural connections between particles and polymer chains.

The interest to the self-heating effect, occurred in polymers and polymer composites, grows in the last decade. The researchers tested different polymers under various loading and environmental conditions. The authors of [2] presented theoretical and experimental studies on testing polyacrylonitrile butadiene styrene specimens under tensile loading, when the self-heating effect occurs. Research results on the thermomechanical analysis of polymers and polymeric composites were also presented in [3]. The effect has a great impact on fatigue of polymers and polymeric composites loaded cyclically. In cases, when the self-heating temperature does not reach a steady-state in relatively small values the self-heating effect dominates fatigue process, which intensifies much structural degradation of these material. Research results presented in [4÷6] proved the crucial importance of considering the self-heating in fatigue processes.

Previous studies in the area of description of self-heating effect cover development of theoretical models and experimental research (e.g. [7, 8]) considering various loading conditions. For proving irreversibility of mechanical degradation of polymeric composites experimental studies were carried out. In order to describe experimental results properly the analysis of chemical reactions during the self-heating and thermal fatigue was presented. Such an approach of combined analysis of phenomena in micro-macro scale allows better understanding and presenting full description of above-mentioned processes.

Theoretical background

The phenomenon of self-heating of polymer-based materials could be modeled as a coupled thermoviscoelasticity problem, which is described by Boltzmann superposition principle with taking into consideration temperature and heating rate dependence of material properties and functions:

$$\sigma(t) = \varepsilon(t)E_0(\theta,\beta) - \int_0^t \varepsilon(\tau)R(t-\tau,\theta,\beta)\mathrm{d}\tau, \quad (1)$$

where: $\sigma(t)$ – time-dependent stress; $E_0(\theta,\beta)$ – temperature- and heating rate-dependent instantaneous modulus; $\varepsilon(\tau)$ – strain function depended on relaxation time; $R(t–\tau,\theta,\beta)$ – relaxation kernel depended on temperature and heating rate. The material properties could be presented as complex ones, which allow dropping the relaxation kernel in (1). Mathematically, they could be determined from the constitutive equation of thermoviscoelasticity determined by using Laplace transform to the Hooke's law. The complex modulus could be presented as sum of two parts:

$$E^*(f,\theta,\beta) = E'(f,\theta,\beta) + iE''(f,\theta,\beta), \quad i = \sqrt{-1}, \quad (2)$$

where the real part $E'(f,\theta,\beta)$ represents elastic behaviour, while the imaginary part $E''(f,\theta,\beta)$ represent viscous behaviour of the material. Both of them are frequency- and temperature-dependent.

The solution of mechanical part of problem comes down to solve boundary-value problem with appropriate boundary-initial conditions for the investigated model. Achieving resulted strain function the dissipated mechanical energy Q could be determined from equation:

$$Q = 3\pi f \varepsilon_{max}^2 w^2 E''(f,\theta,\beta), \quad (3)$$

where: f – loading frequency; ε_{max} – the maximal strain; w – deflection function.

Then, the heat transfer problem should be solved in order to determine temperature distribution in the structure and its evolution. The problem with appropriate thermal boundary conditions of type III is formulated basing on heat transfer equation, where the amount of dissipated energy determined in (3) is substituted as a source function:

$$\lambda \nabla^2 \theta(X,t) = c\rho \frac{\partial \theta(X,t)}{\partial t} + Q(X), \qquad (4)$$

where: λ – coefficient of thermal conductivity; c – heat capacity; ρ – density; X – set of Cartesian coordinates. Solving equation (4) the self-heating temperature distribution and its evolution could be evaluated (for details see [7]). The only unknown parameter is the dynamic loss modulus in (3), which could be determined experimentally.

For the determination of $E''(f,\theta,\beta)$ a dynamic thermomechanical analysis could be used as the most suitable method. Using dynamic mechanical analyzer (DMA) the temperature scans of loss modulus in function of temperature could be collected for different excitation frequencies. The amount of $E''(f,\theta,\beta)$ is determined from the master curve constructed as follows. Basing on temperature scans determined from DMA experiment the glass-transition temperature θ_g is determined for various excitation frequencies (as a peak values of temperature in a given scan) in order to construct Arrhenius plot. From the modified Arrhenius law proposed in [9] the activation energy E_a is determined. Then, the shift factors $a_\theta(\beta)$ were determined:

$$\log a_\theta(\beta) = \frac{\beta_\theta E_a \log e}{R}\left(\frac{1}{\theta} - \frac{1}{\theta_r(\beta)}\right), \qquad (4)$$

where β_θ is a heating rate coefficient, R is a universal gas constant and $\theta_r(\beta)$ is a reference temperature for a given heating rate, in the investigated case $\theta_r(\beta) = \theta_g(\beta)$. Finally, the master curve is constructed by transforming temperature scans to frequency domain and considering shift factors determined from (5).

Dynamic mechanical experiments

In order to investigate mechanisms of the self-heating effect evolution and accompanying structural degradation an experimental study was carried out. The investigated composite specimens were manufactured and supplied by Izo-Erg SA The matrix of a composite was made from a mixture of epoxy resin of Epidian 6 type, phenol formaldehyde resin of a medium molecular weight as a curing agent and 2-methylimidazole as a catalyzer. A molar ratio of the epoxy groups of the epoxy resin to the phenolic hydroxyl groups of the novolac was equal to 1:1. The reinforcement of a composite was impregnated into the matrix in the form of plane weave E-glass fiber cloth with weight of 200 g/m^2 by the prepolymer acetone solution (with above-mentioned composition) and dried in a hot air, which constitutes 12-layered plate with thickness of 2.5 mm fabricated in a hydraulic press. The plates were cut to the specific dimensions of specimens: length of 80 mm and width of 10 mm.

Experiments were carried out on the own designed laboratory stand, where the specimens were clamped by two holders in both sides and operational length of specimen was 50 mm. One of the holders was made with bakelite inclusions directly contacted with specimens in order to provide thermal insulation and to limit a transfer of the generated heat. At the opposite side the specimen was subjected to cyclic bending loading by the electrodynamic shaker. During the experiment loading force was measured by a force sensor, velocity of deformation was measured by laser Doppler vibrometer in the area of self-heating effect occurrence, surface temperature evolution was measured by infrared camera and the excitation was controlled by the accelerometer mounted on the electrodynamic shaker. The scheme and detailed description of devices connection was presented in [1].

In order to investigate irreversibility of structural changes the specimens were loaded on various frequencies (20, 25 and 30 Hz) till achievement of a specific self-heating temperature, then the loading was removed and specimens were cooled in natural convection

conditions. After temperature stabilization of specimens (i.e. reaching an ambient temperature) the specimens were loaded again under the same excitation parameters. Obtained temperature curves were compared and analyzed.

Evaluation of experimental results

Two programs were realized: double-loading and triple-loading of specimens. The values of a self-heating temperature at which the excitation was stopped were elevated from 30°C till 80°C with a step of 5°C. The infrared images were collected for each loading period. Exemplary curves of evolution of maximal values of a self-heating temperature were presented in Figure 1.
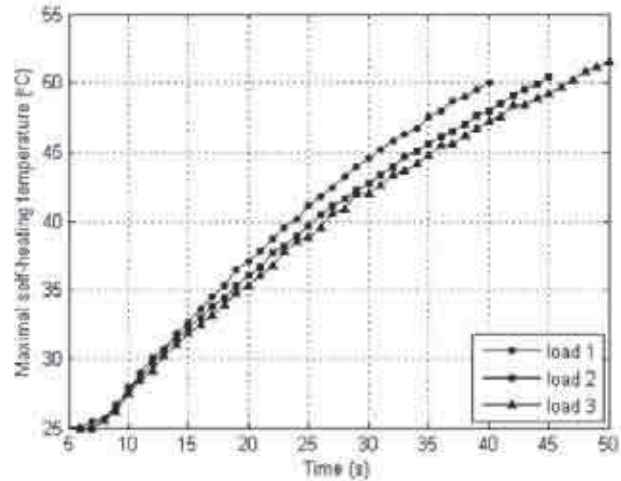

Fig. 1. **Self-heating temperature evolution during triple-loading of a specimen**

Presented results clearly show, that the evolution of a self-heating temperature differs from loading to loading. Such changes may be a result of residual cross-linking processes in the area of the self-heating effect occurrence. As it was described in Legrand and Bellenger, during the polymerization process epoxy prepolymers form a 3-dimensional network [10]; the scheme of epoxy resin formation was presented in Figure 2. This exothermic reaction can induce an increase in temperature that may lead to local thermal degradation of a resin. Therefore, it is possible that formed epoxy resin is not fully cross-linked. The process of cross-linking is closely related to the mechanical properties of a composite, particularly with evolution of parts of a complex dynamic modulus (2). The intensity of residual cross-linking is in dependence of loading frequency, the temperature achieved by the composite during self-heating and the velocity of its growth. Thus, dynamic mechanical properties of a composite during the process of residual cross-linking could be described by generalized Arrhenius principle (5).
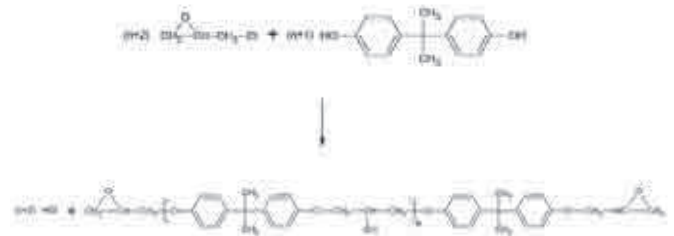

Fig. 2. **The scheme of epoxy resin formation**

The most often applied curing agents for epoxy resins are amines and amine derivatives. However, the application of polyphenols curatives results in tougher and low moisture absorbing void-free resins [11]. The structure of phenol-formaldehyde resin, applied as a curing agent for epoxy resins, was presented in Figure 3. Curing of epoxy resin with novolac type phenol formaldehyde resin makes use of

the reaction between hydroxyl groups and epoxides; the mechanism of epoxy curing with phenol formaldehyde resin was presented in Figure 4. The phenol-epoxy reaction is usually performed in the presence of catalysts, since the phenol-epoxy reaction is less facile than amine-epoxy reaction. The curing occurs at the temperature range between 120°C and 150°C.
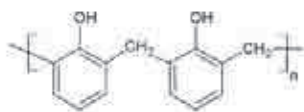

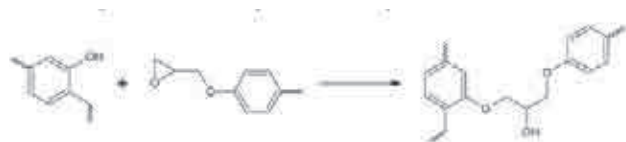**Fig. 3. The structure of phenol-formaldehyde resin**

Fig. 4. The mechanism of epoxy curing with phenol formaldehyde resin

If the epoxy resin has not been fully cross-linked, i.e. the temperature of moulding is not sufficiently high, the residual cross-linking may take place during the material operation. When the element made of polymer-contained material is subjected to intensive cyclic loading, the self-heating temperature grows up. Creation of additional connections during cross-linking in higher temperatures may be a reason for the increase of stiffness and mechanical dynamic moduli, which was effected as longer time of reaching the temperature of 50°C during each subsequent loading. The residual cross-linking resulting from self-heating effect is expected to proceed *via* the reaction between hydroxyl groups and epoxides, according to Figure 4.

Literature

1. Katunin A.: *Critical self-heating temperature during fatigue of polymeric composites under cyclic loading*. Composites Theory Pract. 2012, **12**, 72-76.
2. Luo W., Yang T., Li Z., Yuan L.: *Experimental studies of the temperature fluctuations in deformed thermoplastics with defects*. Int. J. Solids Struct. 2000, **37**, 887-897.
3. Liu Z.Y., Beniwal S., Jenkins C.H.M. and Winter R.M.: *The coupled thermal and mechanical influence on a glassy thermoplastic polyamide: Nylon 6,6 under vibro-creep*. Mech. Time-Depend. Mat. 2004, **8**, 235-253.
4. Bellenger V., Tcharkhtchi A., Castaing P.: *Thermal and mechanical fatigue of a PA66/glass fibers composite material*. Int. J. Fatigue 2006, **28**, 1348-1352.
5. Goel A., Chawla K.K., Vaidya U.K., Chawla N., Koopman M.: *Characterization of fatigue behavior of long fiber reinforced thermoplastic (LFT) composites*. Mater. Charact. 2009, **60**, 537-544.
6. Ramkumar A., Kannan K., Gnanamoorthy R.: *Experimental and theoretical investigation of a polymer subjected to cyclic loading conditions*. Int. J. Eng. Sci. 2010, **48**, 101-110.
7. Katunin A.: *Analytical model of the self-heating effect in polymeric laminated rectangular plates during bending harmonic loading*. Ekspl. Niezawodn. 2010, **48**, 91-101.
8. Katunin A., Fidali M.: *Self-heating of polymeric laminated composite plates under the resonant vibrations: theoretical and experimental study*. Polym. Compos. 2012, **33**, 138-146.
9. Katunin A., Gnatowski A.: *Influence of heating rate on evolution of dynamic properties of polymeric laminates*. Plast. Rubber Compos. 2012, **31**, 233-239.
10. Legrand M., Bellenger V.: *Estimation of the cross-linking ratio and glass transition temperature during curing of amine-cross-linked epoxes*. Compos. Sci. Technol. 2011, **61**, 1485-1489.
11. Reghunadhan Nair C.P.: *Advances in addition-cure phenolic resins*. Prog. Polym. Sci. 2004, **29**, 401–498.

Translation into English by the Author

Andrzej KATUNIN – Ph.D., graduated from the Faculty of Mechanical Engineering, Silesian University of Technology, Gliwice (2008) and defended his Ph.D. dissertation in the same Faculty, Gliwice (2012) in the area of mechanics of composites. He is a member of the Polish Society of Composite Materials (since 2012) and the European Society for Composite Materials (since 2010). He is a member of the editorial board of the International Journal of Composite Materials (Scientific & Academic Publishing).

Scientific interests: degradation of polymer composites, structural health monitoring of composite structures, mathematical modeling of physical phenomena, wavelet theory and applications, fractal geometry.

e-mail: andrzej.katunin@polsl.pl

Katarzyna KRUKIEWICZ – M.Sc., graduated from the Faculty of Chemistry, Silesian University of Technology, Gliwice (2011); currently being Ph.D. student at the same University. She was invited to join the editorial board of CHEMIK and CHEMIK*light*. Scientific interests: electrochemical polymerization, biomedical applications of conducting polymers, surface physicochemistry.

e-mail: katarzyna.krukiewicz@polsl.pl

European Winter School on Physical Organic Chemistry (E-WiSPOC)
27 January – 1 February
Bressanone, Italy, Europe

The European-Winter School on Physical Organic Chemistry (E-WiSPOC), at its seventh edition, constitutes an unique opportunity to gain expertise in the field of Organic Chemistry. If you are interested in WHY and not only HOW chemical reactions proceed you MUST attend this School. If you consider Physical Organic Chemistry an obsolete discipline you are wrong: it is more alive than ever!

Physical Organic Chemistry is now being applied in studying catalysis, biochemistry, photochemistry, reactivity in the vapour phase, surface science, materials sciences, and other areas.

The School is part of the cultural initiatives of the Organic Division of the Italian Chemical Society and it has the endorsement of the Organic Division of EUCHEMS. The topic of the 2013 edition is Supramolecular Chemistry.

The 2013 edition of the European-Winter School on Physical Organic Chemistry (E-WISPOC 2013) will take place in Bressanone (South Tyrol, Italy) January 27- February 1, 2013. The School will be held at the "Greuner Baum" where lecturers and students will be also accommodated in a friendly environment.

Web site: http://www.chimica.unipd.it/wispoc/pubblica

science