11IL-01
THERMAL ANALYSIS IN BUILDING MATERIALS STUDIES FROM POINT OF VIEW OF ENVIRONMENT PROTECTION

ANDRZEJ MALECKI

AGH Universty of Science and Technology, Faculty of Materials Science and Ceramics, Al. Mickiewicza 30, 30-059 Krakow malecki@agh.edu.pl

Buildings and constructions using concrete or other building materials have to be considered as intrinsic part of environment, especially if we remember that consumption of building materials reaches many millions ton each year. Production of building materials, their application and finally their degradation ("stages of life" of building materials) have significant influence on environment. Discussion about this influence can be divided into three parts. First part devoted to changes in environment during extracting raw materials and production of building materials. The second part is related to existence of buildings and other constructions in human environment. This concerns for example changes in landscape, changes in microclimate etc. The third part connected with degradation of building materials includes problems related to slow natural wear out as well as rapid processes of degradation for example in result of fire.

On the field of the above pointed "stages of life" of building materials, thermal analysis methods play an important role, as methods of estimation of real and potential risks of introducing some dangerous substances into environment.

In the first stage of life of building materials (production) the thermal analysis (TA) methods can be used for characterization of raw materials including their behavior under thermal conditions corresponding to production process in which these raw materials are used. TG/DTA/DSC and GC (gas chromatography) techniques coupled with evolved gas analysis (EGA) by infrared absorption or mass spectrometry permit on determination of sort and quantity of gaseous substances potentially liberated to environment during technological process.

Applications of thermal analysis (TA) methods related to influence on environment of building and finishing materials (paneling, flooring, carpets, paints, varnishes, plastics, furniture etc.) in their second "stage of life" is limited to identification of VOCs (Volataile Organic Compounds) evolved from the mentioned materials as well as to determination of the kinetic parameters corresponding to VOC liberation rate. The most important and unsolved problems concerning application of TA on that field are relationships between results of a rapid TA tests and real kinetics of VOC liberation inside buildings. In this case isothermal tests performed in different temperatures are carried out very often.

Third "stage of life" of building and finishing materials corresponds to their either slow or rapid degradation (waste utilization, recycling, house fire) which is usually connected with production of many different substances potentially dangerous for environment. At this stage TA methods belong to the most important techniques which permit on determination of risk for environment related to utilization of discussed materials.

REFERENCES

1. Smykatz-Kloss W., Heil A. , Kaeding L., Roller E. in book: *Thermal Analysis in the Geosciences, chap. Thermal analysis in environmental studies*, Springer Berlin/ Heidelberg 1991.
2. Van Grieken R., Delalieux F., Gysels K.: Pure Appl. Chem. *12*, 232 (1998).
3. Brown S. K.: *Indoor Air Pollution – Lowering Emissions of Chemicals Released From Manufactured Products*, *Hazmat2003 Conference,* Stamford Grand, N. Ryde, NSW, Australia, 29.–30.4.2003.
4. Fariborz Haghighat, De Bellis L.: Building and Environment *33*, 261 (1998).
5. Wolkoff P.: Sci. Total Environ. *227*, 197 (1999).
6. InspectAPedia: http://www.inspectapedia.com/ BestPractices/VOC_Guide.htm
7. Hewitt J.: *Sick Building Syndrome*, ed. Lulu.com (2007).
8. Vangipuram Seshachar Ramachandran: *Handbook of thermal Analysis of construction materials*, ed. Noyes publications/William Andrew Publishing Norwich NY.

11IL-02
NOVÁ METODA VYUŽITELNÁ PŘI STUDIU KINETIKY KRYSTALIZACE SKLOVITÝCH MATERIÁLŮ

JIŘÍ MÁLEK*, ZUZANA ZMRHALOVÁ, JAROSLAV BARTÁK a PAVLA HONCOVÁ

Katedra fyzikální chemie, Fakulta chemicko-technologická, Univerzita Pardubice, Studentská 573, 532 10 Pardubice jiri.malek@upce.cz

Studium kinetiky krystalizace sklovitých materiálů se těší poměrně velké oblibě a každoročně je v této oblasti publikováno více jak 1000 prací v impaktovaných časopisech. Převážná většina těchto prací je založena na aplikaci běžných termoanalytických metod jako například Diferenciální termická analýza (DTA) nebo Diferenciální skenovací kalorimetrie (DSC). Tyto metody jsou velmi efektivní v případech, když je možné spolehlivě měřit tepelné efekty související s krystalizací. V případě velmi rychlých krystalizačních procesů však může dojít k nepříznivému ovlivnění kvality kinetických dat v důsledku tepelné setrvačnosti přístroje. Podobně limitováno je použití klasických metod jako DTA nebo DSC v případě velmi pomalých dějů, kdy naopak tepelný efekt je blízko detekčního limitu přístroje.

Z tohoto pohledu je velmi zajímave diskutovat alternativní metody pro studium kinetiky krystalizace sklovitých materiálů, které jsou vhodné i v případech, kdy není možno použít běžných termonalytických postupů. Slibnou metodou v tomto směru je například mikroskopické pozorování růstu (případně i nukleace) krystalů ve sklovité matrici. Řada těchto metod má však také jistá omezení. Například přímé pozorování růstu krystalů optickou mikroskopií je limitováno na opticky transparentní materiály[1] nebo na materiály s výrazně odlišnou reflektivitou sklovité matrice a krystalické fáze[2].

Vyhledem k tomu, že k růstu nové krystalické fáze ve sklovité matrici obvykle dochází nad teplotou skelné transformace, v prostředí slilně podchlazené a vysoce viskózní sklo-

tvorné kapaliny lze očekávat, že postupně rostoucí krzstalyická fáze bude zpomalovat viskozní tok až postupně dojde k jeho zastavení. Tento proces může být sledován s využitím Termomechanického analyzátoru (TMA)[3]. V přednášce je popsán vývoj nové metody využitelné ke studiu krystalizace sklovitých materiálů založené na principu TMA. Použití metody je ilustrováno na několika chalkogenidových sklech systému $(GeS_2)_x(Sb_2S_3)_{1-x}$, jejichž krystalizaci v některých případech nelze sledovat standardními experimentálními postupy.

Tato práce vznikla za podpory grantu GA ČR 104/08/1021.

LITERATURA

1. Shánělová J., Málek J., Alcalá M. D., Criado J. M.: J. Non-Cryst. Solids *351*, 527 (2005).
2. Málek J., Švadlák D., Mitsuhashi T., Haneda H.: J. Non-Cryst. Solids *352*, 2243 (2006).
3. Málek J., Zmrhalová Z., Barták J., Honcová P.: Thermochim. Acta, odesláno.

11IL-03
ISOCONVERSIONAL METHODS IN THERMO-ANALYTICAL KINETICS BASED ON NON-ARRHENIAN TEMPERATURE FUNCTIONS

PETER ŠIMON

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava
peter.simon@stuba.sk

Mechanisms of the processes in condensed phase are very often unknown or too complicated to be characterised by a simple kinetic model. They tend to occur in multiple steps that have different rates. To describe their kinetics, methods based on the single-step approximation are frequently used[1–3].

It is recognized that the rate of the processes in condensed state is generally a function of temperature and conversion. The single-step approximation employs the assumption that the reactin rate can be expressed as a product of two separable functions independent of each other, the first one, $k(T)$, depending solely on the temperature T and the other one, $f(\alpha)$, depending solely on the conversion of the process, α. The rate of the complex multi-step condensed-state process thus can be formally described as[1–3]

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

This equation is mostly called the general rate equation. Indeed, it resembles a single-step kinetics equation, even though it is a representation of the kinetics of a complex condensed-phase process. In general, kinetics of a complex process should be described by a set of rate equations. The single-step approximation thus resides in substituting the set of kinetic equations by the sole single-step kinetics equation[1–3]. The temperature function is mostly expressed by the Arrhenius equation. In papers[2,4] it has been justified that, due to complexity of the processes, the temperature function can hardly be considered the rate constant so that there is no reason to be confined to the Arrhenius temperature function. It has been verified that the results most conforming with reality can be obtained for the following temperature function[5]:

$$k(T) = A_k e^{DT}$$

where A_k, and D are parameters.

Isoconversional methods represent probably the most widely employed category of methods applied in thermal analysis. Their basic idea is that the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion. Under these conditions, the value of conversion function $f(\alpha)$ is constant and the reaction rate is a function of temperature only.

Combining both equations, after a sequence of manipulations[2–4] one can get the relationship for the dependence of isoconversional temperature, T_α, on the heating rate, β:

$$T_\alpha = \frac{1}{D}\ln(AD\beta + 1)$$

where A and D are adjustable parameters obtained in the procedure of minimizing the sum of squares between the experimental and calculated values of T_α. Knowing the parameters A and D, the isothermal induction period, i.e. the oxidation induction time for a chosen temperature can be assessed as:

$$t_\alpha = Ae^{-DT}$$

A reverse approach is also possible. In the degradation tests we very often observed that the dependence $T_\alpha = f(\beta)$ can be plausibly described by the function

$$T_\alpha = T_\infty\left(1 - \exp\left[-\beta^a\right]\right)$$

where T_∞ is the isoconversional temperature at an infinite heating rate and a is an exponent. It can be derived that the isoconversional time in his case can be assessed as

$$t_\alpha(T) = (T_\infty - T)a\left(\ln\frac{T_\infty}{T_\infty - T}\right)^{\frac{a-1}{a}}$$

The kinetic parameters T_∞ and a are adjustable and they are obtained from the treatment of experimental dependence[6] $T_\alpha = f(\beta)$.

The isoconversional methods are widely applied in the predictions of material lifetimes[4]. In the presentation, the following case studies will be presented: stability of edible oils; stability of dried milk; stabilization of biodiesels; efficiency of antioxidants in the thermooxidative degradation of rubber; synergism of antioxidants and equivalence between desert and Xenotest stability tests in polyurethane coatings.

The financial support from the Slovak Scientific Grant Agency, grant No. VEGA 1/0660/09, and from the Slovak Research and Development Agency, grant No. APVV-0446-07 is gratefully acknowledged.

REFERENCES
1. Šimon P.: J. Therm. Anal. Calorim. *88*, 709 (2007).
2. Šimon P.: J. Therm. Anal. Calorim. *79*, 703 (2005).
3. Šimon P.: J. Therm. Anal. Calorim. *82*, 651 (2005).
4. Šimon P.: J. Therm. Anal. Calorim. *84*, 263 (2006).
5. Šimon P., Hynek D., Malíková M., Cibulková Z.: J. Therm. Anal. Calorim. *93*, 817 (2008).
6. Šimon P.: J. Therm. Anal. Calorim. *97*, 391 (2009).