Application of thermal analysis for the design of novel inorganic-organic hybrid materials

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Thermal analysis techniques are widely applied in materials science for characterisation and design on novel materials with advantageous thermal and mechanical properties, as well as with lowered flammability. Valuable information on the decomposition routes can be gained from thermoanalytical data obtained by using hyphenated thermal analysis – spectroscopic methods, such as TG-FTIR. They enable identifying of the volatile products which emission can be directly assigned to mass loss steps. Among various materials studied nowadays, inorganic-organic hybrid materials synthesized through covalent bonding of nanosized fillers with macrochains are considered an interesting and promising class of materials. Versatile nanobuilding blocks that can be used to create a wide variety of hybrid materials, where precise control of nanostructures and properties is required, include polyhedral oligomeric silsesquioxanes (POSS) which are a class of discrete, 3-dimensional polycyclic compounds. Condensed silsesquioxanes have the general formula $(RSiO_{1.5})_{2n}$, where n is an integer and R can be a large number of substituents including hydrogen, alkyl, alkenyl, phenyl, halogen and siloxy groups. Common structures of silsesquioxanes include random, ladder and cube or cage type structures. Octameric cage structures (cages with eight silicon atoms) have the general formula $(R_8Si_8O_{12})$ and are *ca.* 1.2 nm in diameter. These pseudo-cubic POSS cages are one of the most commonly encountered and studied examples of silsesquioxanes [1].

[1] K. Pielichowski, J. Njuguna, B. Janowski, J. Pielichowski, *Adv. Polym. Sci.,* **201** (2006) 225.
Reactive oligosilsesquioxanes can be incorporated into polymeric chains *via* copolymerization, grafting and blending processes. Three primary POSS-polymer architectures (bead, pendant, or cross-linked) are available for use in thermoset systems or in copolymers, including polyurethanes (PUs), consisting of the soft (SS) and hard (HS) segments and displaying complex microphase separated morphology [2,3].

[2] K. Raftopoulos, B. Janowski, L. Apekis, P. Pissis, K. Pielichowski, *Polymer*, **54** (2013) 2745.
[3] K. Raftopoulos, M. Jancia, D. Aravopoulou, E. Hebda, K. Pielichowski, P. Pissis, *Macromolecules*, **46**(18) (2013) 7378.

In this lecture synthesis and thermal characterization of novel inorganic-organic hybrid materials on the example of polyurethane/POSS systems will be presented.

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