BIOBASED MONEMERS AND THIOL-ENE CHEMISTRY - A VERSATILE COMBINATION FOR PHOTOPOLYMERIZATION

Mats Johansson

KTH Royal Institute of Technology, Department of Fibre & Polymer Technology, SE-100 44 Stockholm, Sweden

Unsaturated monomers from renewable resources are abundant and available from a large number of sources such as terpenes, vegetable oils, lignin, etc [1]. Most of these unsaturations are however di- or tri-substituted alkenes with lower reactivity compared to monomers normally used in photopolymerization systems. New routes must thus be employed to enhance the rather low reactivity of these monomers and here can thiol-ene chemistry play an important role. The thiol-ene reaction already described in 1905 [2] is a free radical reaction between a thiol and an alkene that proceeds as a stepwise reaction with addition of a thiyl radical to an alkene and then subsequent hydrogen abstraction of a thiol hydrogen to form a thio ether linkage between the monomers. Thiol-ene chemistry has in general obtained a significantly increased attention during the last decades due to its versatility. [3, 4, 5] The reaction is very rapid and efficient and can allow for normally less reactive monomers to be employed. The reaction rate strongly depends on the exact structure of the alkene monomers (electron density and degree of substitution) as well as possible side reactions (homopolymerization of the alkenes).

The presentation will address how free radical thiol-ene reactions can be employed to enable the use bio-based monomers in photocurable systems. The effect of the alkene structure, combination of different alkenes, reaction kinetics, and details on the reaction pathways will be given. Monomers included, will range from fatty acids, terpenes (e.g. limonene), to lignin derivatives.

[1] Monomers, Polymers and Composites from Renewable Resources, ed. M. Belgacem and A. Gandini, Elsevier, 1st edn, 2008.

[2] Posner T. Ber Dtsch Chem Ges 1905; 38: 646–57

[3] Hoyle, C. E.; Lee, T. Y.; Roper, T. Thiol-Enes: Chemistry of the Past with Promise for the Future. J. Polym. Sci., Part A: Polym. Chem. 2004, 42 (21), 5301− 5338.

[4] C. E. Hoyle and C. N. Bowman, Angew. Chem., Int. Ed., 2010, 49, 1540–1573.

[5] Kade, M. J.; Burke, D. J.; Hawker, C. J. The Power of Thiol-ene Chemistry. J. Polym. Sci., Part A: Polym. Chem. 2010, 48 (4), 743− 750.