Dynamic generation of inorganic and organic polymer structures in hybrid polymers

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*Org*anically *mo*dified *cer*amics – Ormocer®s – belong to the Sol-Gel derived hybrid materials and combine typical properties of organic polymers like flexibility or processability with the hardness of the ceramics. They cover a wide range of applications, from coatings and dental filling materials to optical waveguides [1]. They are synthesized in a two-step process. In a polycondensation reaction silanols and alkoxysilanes act as precursors to form the so-called resin. The alkoxysilanes are bound covalently to the polymerizable organic moieties. In the following, these moieties can undergo a polymerization reaction, which is initiated thermally or photochemically, to form the hybrid polymer [2]. Force field methods are used to get a better understanding of the atomistic structures of the resin and of the hybrid polymer.

In classical force field methods, no reactions can be described. To reflect the formation of the structures in the synthesis of these materials, pseudo-reactive algorithms are used to obtain realistic structure models. For this purpose, we developed two different methods to generate models for the products of the condensation and polymerization respectively.

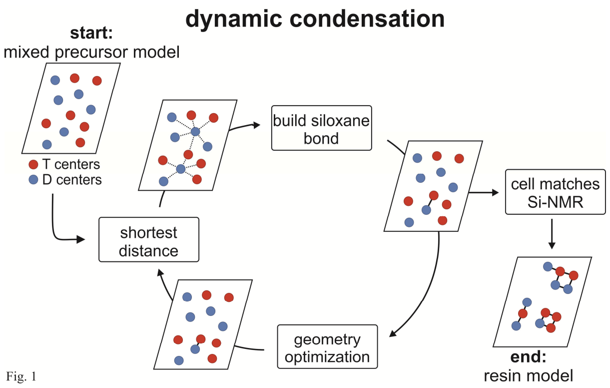

Fig. 1

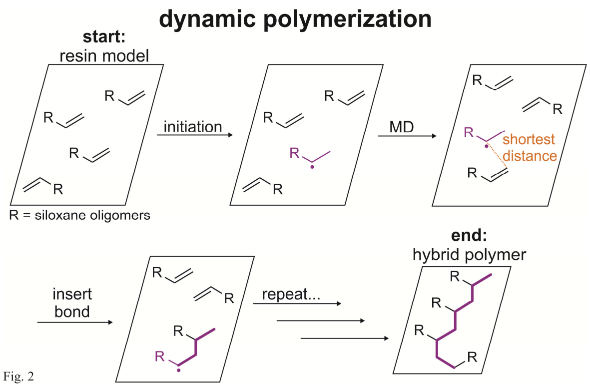

Fig. 2

The dynamic condensation process, shown in Fig. 1, is useful to form resin structures for systems with more than two different precursors. From cells containing the precursors in the experimental ratio, the algorithm creates resin cells which reflect the experimental determined ^{29}Si-NMR results of the resin. In this process parameters are added to avoid certain structures like three membered rings and ringspearing structures or promote favourable arrangements like four membered rings [3]. Additionally, certain parameters are added to be able to adjust the algorithm to represent either acidic or basic conditions, leading to long siloxane chains or more branched clusters.

The dynamic polymerization method shown in Fig. 2 is used to create polymer structures of the previously created resins. The polymerization is modeled to represent a radical chain-growth polymerization by searching for the closest distance between a radical and an unreacted polymerizable group during molecular dynamics, and creating a bond between them. Two different variants of this method are presented, differing in the search time modes. Fixed and a flexible search times can be used, varying in the required calculation time and the quality of the obtained models. The suitability and the quality of the modeling approach is presented for both simulation steps, the resin and the polymer, for two different Ormocer® systems.

[1] C. Sanchez et al., *Chem. Soc. Rev.*, **2011**, *40*, 696–753.
[2] R. Buestrich et al., J. *Sol-Gel Sci. Technol*., **2001**, *20*, 181–186.
[3] S. Fessel et al., *J. Sol-Gel. Sci. Technol.*, **2012**, *63*, 356–365.