# Development of Storage-Stable 1-C Resin Formulations Using Chemically Modified Nanozeolites with Controlled-Release Functionality

## Nanocomposites for Adhesive Bonding Technology

Modern adhesives, sealants and surface coatings often contain solid, inorganic filler materials in addition to highly advanced organic polymer systems. The amount of each filler that is used depends on the specific application. For example, fillers considerably influence the rheologic behavior and the application properties of the non-cured fluid formulation, and they also affect the deformation behavior, permeability and conductivity of the cured organic-inorganic composites. The adhesion between the polymer system and the substrates and fillers plays a significant role in determining the strength and durability of the bonded resin/filler/substrate system.

When nanoscale fillers having high specific surface areas are used, then the polymer-particle interfaces – more precisely, the 3-dimensional interphases – increasingly determine the properties of the overall composite, and hence the bonded joint. This is since several years a main area of work of the Fraunhofer IFAM. In the 2004 IFAM annual report, an article by Andreas Hartwig entitled "Application of nanocomposites in adhesive bonding technology" discussed novel composites based on layer silicates and fumed silicas. Layer silicates – for example in the form of modified bentonites – are suitable as additives for fire-protection applications or as effective curing initiators in adhesive formulations.

## The NanoModule Project – Function-Integration Using Nanofillers

As part of the NanoModule project funded by the German Federal Ministry for Education and Research (BMBF), the Fraunhofer IFAM is currently undertaking further synthesis work to develop novel nanoparticles as functional additives. In addition to modified bentonites and fumed silicas, zeolites also form a central part of the IFAM development work. Zeolites – also commonly known as molecular sieves – are porous silicates whose chief feature is their cavities and channels of a few nanometers in size (Fig. 1, 2). Foreign ions and also organic molecules can become incorporated into the porous structure.

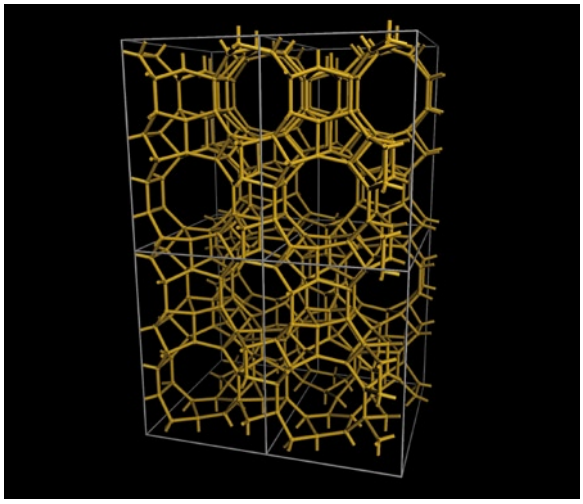

**Fig. 1:** Molecular model of a typical zeolite: In the 2.5 × 2.5 × 5.3 nanometer section of the base framework that is shown each point of intersection represents either a silicon or an aluminum atom.

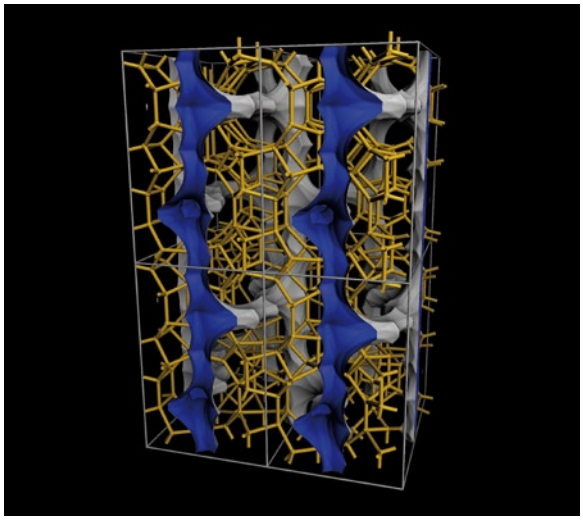

**Fig. 2:** Representation showing the internal surface of the zeolite which is accessible to solvent molecules – for example water molecules. Foreign ions and also organic molecules become immobilized in the tortuous channel structures.

The objective of the BMBF project is to incorporate different functionalities into nanoscale fillers and so customize the nanomodules. For zeolites it is in particular the cavities and channel structures which can be utilized for this. Active materials – for example curing accelerators – can be immobilized in the zeolites in order to finally produce composites and joints having an innovative range of properties. By using the nanomodules in resin

formulations for 1-C processing, the BMBF project aims in particular to tailor the curing behavior and storage properties.

The storage stability and curing behavior have to be individually optimized because for industrial application both a low curing temperature and good storage properties must be guaranteed. The mechanical properties of the composites should be better than conventional composites, namely those with non-encapsulated curing accelerators.

## Chemically Modified Nanozeolites as Controlled-Release Additives

There are a number of reasons why zeolites are suitable substrates for the immobilization of active agents for the NanoModule project. These include the large number of known zeolite structures having different chemical compositions and the different effective pore sizes. Many zeolite structures can be synthesized and some are also commercially available. By means of an external stimulus – for example, by increasing the temperature – the active agents that are immobilized within the zeolite framework can be released, leading to rapid curing of the 1-C resin.

A filler based on a zeolite can play a particularly beneficial role when the dimensions of the primary crystals are in the nanometer range. Due to the large specific surface area, there is then immediate release of active agent from the nanomodules on reaching the release-temperature. A reduction of the crystallite size to below 0.1 µm leads to dramatic acceleration of the effective material transport. Simultaneously, a considerably more homogenous distribution of the active agents in the composite is to be expected than for release of active agents from microscale capsules. NanoScape AG has been a valuable joint partner in this project. NanoScape AG has for many years been a leader in the synthesis of nanoscale zeolites and gives this key knowledge to the project consortium.

## Computer-Aided Selection of Suitable Host-Guest Systems

Just as there is a large number of known zeolite structures having voids and channels of different dimensions, there is an equally large number of potentially active curing accelerators such as salts, complexes, Lewis acids and derivates of organic nitrogen bases. Not all possible zeolite/accelerator combinations can be tested in experiments. For this reason, simulation methods are used by the Fraunhofer IFAM in order to be able to predict the chemical interactions in the zeolite pores and hence the immobilization of organic molecules in the channels and cavities. The computer allows virtual simulation of the molecular interactions within the nanometer-sized zeolite cavities.

The objective of the simulation work is to identify promising zeolite (host) / accelerator (guest) combinations. This preselection allows the synthesis work to be focused on the most promising combinations of accelerator and zeolite. The first selection criterion to be simulated was the steric hindrance of the zeolite pores. This showed that suitable zeolite hosts are available for many potential accelerators. For geometric reasons, however, not every accelerator can be immobilized in the small pore zeolites.

The second criterion to be studied was how strongly the guest molecules are bound to the host. It was found here that the chemical interaction between the guest molecule and zeolite host was decisive. In particular, the adsorption properties and the release behavior can be decisively influenced by doping the zeolite framework with foreign ions – in the simplest case by changing the sodium and aluminum content. Immobilized alkali metal or alkaline earth metal cations not only affect the surface chemistry but also influence the effective pore diameter. This highlights the third criterion for the preselection because ultimately the host/guest nanomodule systems must be able to function as effectively as possible in applications. In the molecular simulations, the maximum degree of loading of a nanomodule can be predicted for each potential host-guest combination. If the degree of loading is too low, then use of the fillers would be disproportionately costly.

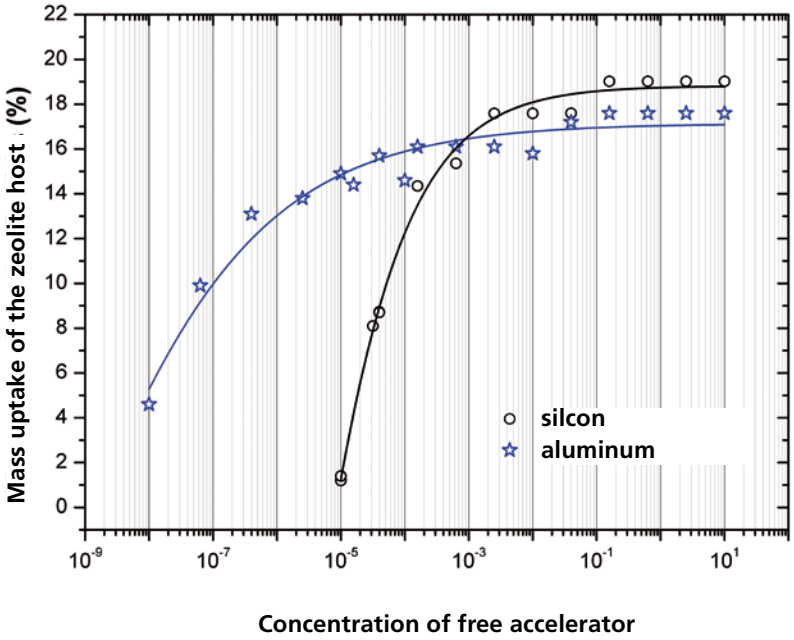


Fig. 3: Simulation of the loading of a zeolite framework as a function of the concentration of free active agent in a mobile phase. A higher aluminum content ($Al_2O_3$ / $SiO_2$ ratio) results in a significant increase in the mass uptake of the nanomodule at low accelerator concentrations.

The simulations show how sensitively the degree of loading and the energetics of the interaction depend on the foreign ion content of the zeolite framework. By way of example Figure 3 shows how the adsorption properties of the nanoporous material are influenced by the aluminum content of the aluminosilicate framework. Both the bonding of the initiator and the total adsorption capacity can be customized by purposefully varying the foreign ion content. The same applies for utilizing the release-properties of the nanomodules. By varying the way the host materials are synthesized, the release-properties can be optimized.

## Customized Synthesis and Chemical Modification of the Nanozeolites

Following the predictions obtained via computer simulation, NanoScape AG manufactured customized chemically-specified zeolites as host materials for the nanomodules. For example, Figure 4 shows the scanning electron micrograph of a zeolite powder whose chemical composition was optimized for the load of active material.

For synthesizing the nanomodules the second step was to condition the powders at the Fraunhofer IFAM in order to make the pore surface optimally accessible, so favoring interaction with guest molecules. After the conditioning, specific surface areas of several hundred square meters per gram were measured using low temperature nitrogen adsorption. The methods for synthesizing nanomodules that have been developed at the Fraunhofer IFAM within this project allow in particular controlled loading and also give

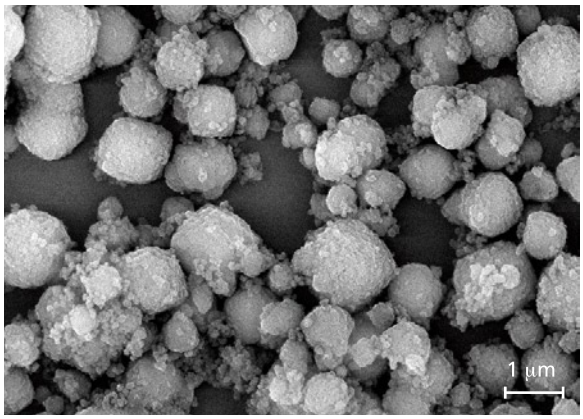


Fig. 4: Scanning electron micrograph of a nanomodule development product based on zeolites which contain active curing accelerator.

a specific radial distribution of the adsorbates in the zeolite grains. In addition, technical processes for modifying the hosts and the load of active agent were developed in the laboratory, then on a small pilot-plant scale and will finally be scaled up to industrial production conditions.

The release of the accelerator from the nanomodules was characterized at the Fraunhofer IFAM, e. g. using thermoanalytical methods (Fig. 5). This showed for a given host that the maximum loading of 20 weight percent which was predicted from the simulation work and is reached on saturation of the adsorption sites, agrees very well with the experimental findings. Comparison of the experimental data with the simulation results gave valuable information for customizing the adsorption processes as well as for further optimization of the synthesis. The observed maximum value of 20 weight percent is sensible from a technological point of view.

The thermoanalytical tests showed there were temperature regions within which there was very marked weight loss (Fig. 5). A more strongly bound guest molecule must be more strongly thermally activated in order to leave the zeolite cavities. It consequently desorbs at a higher temperature than a more weakly adsorbed molecule. The desorption temperatures are therefore on the one hand characteristic of the strength of interaction of different surface groups for the accelerator molecules. On the other hand, they allow estimation of the release-temperature of accelerator molecules into a heated resin formulation. Reliable prediction of these desorption temperatures based on simulation-calculations is extremely helpful for the customized development of materials.

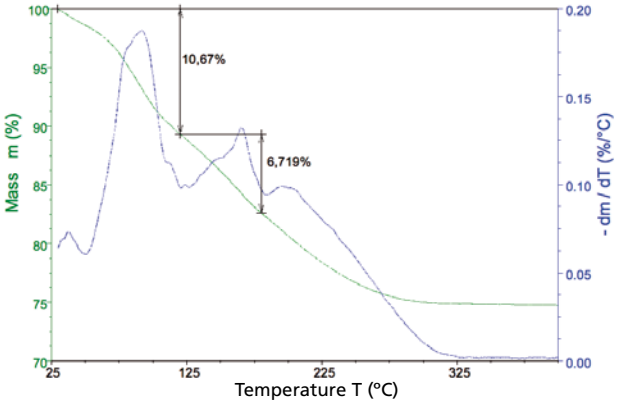


Fig. 5: Thermogravimetric analysis (TGA) of a nanomodule based on a zeolite loaded with active agent. The mass loss is mainly due to the release of the guest molecules. Noteworthy is the fact that the active agent for accelerating the curing reaction already starts being released at about 95 °C – a relevant release temperature for technical implementation.

## Future Work to be Carried out as Part of the BMBF Funded NanoModule Project

The results presented here regarding the synthesis of the nanozeolites and in particular the described thermal release of the immobilized active agents are very promising. It is possible to synthesize nanomodules based on zeolites. For optimizing the synthesis, computer simulations can be used to predict the material properties. The customized development of multifunctional materials can be very effectively inspired and accompanied by the simulation work.

Future project work must demonstrate the practical effectiveness of the release properties of the chemically modified nanomodules in adhesive formulations. The next step is to tailor the controlled-release functionality of the fillers to technologically advanced adhesive formulations and cast resin formulations. To achieve this, nanomodules will be incorporated into different 1-C resin formulations and then adhesively bonded joints will be prepared in order to demonstrate the effectiveness of the innovative materials. Of special importance here is the manufacturing and dispersing process for the nanoscale accelerator systems which must be optimized for specific applications. The same applies for the production costs and production safety.

Finally, the project work will investigate how the mechanical and thermal properties of the nano-

composites can be controlled by the curing conditions. The technologically required application properties are prescribed by an experienced consortium. Achieving the project objective will be aided by the extensive analytical expertise available in the consortium and will be tested under technologically relevant conditions.

This approach allows effective, knowledge-driven optimization of the polymer systems. The formulation of systems for specific applications will focus on control of the network structure and dynamics as well as on the application, cohesion, adhesion, wetting and ageing properties.

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**Project partners**

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Information about the current progress of the project can be found on the project website at www.nanomodule.de