CUSTOMIZED UV COATINGS BY FRAUNHOFER IFAM

High-quality plastic components are used in a wide range of industries including the automotive industry, rail vehicle manufacturing industry, aviation, and the consumer electronics sector. Coating of such components is often very demanding and energy-intensive. A faster and more resource-friendly coating process is highly desirable. UV technology could offer a solution here: In the automotive industry, for example, UV curing clearcoat systems could be used because they allow the generation of hard, scratch-resistant surfaces which also show good long-term resistance to chemicals, heat, and UV radiation. A requirement for this is a corresponding network structure and a high degree of crosslinking, because these two factors are directly linked to the hardness and resistance of the coating. Within the framework of the BMBF (Federal Ministry for Education and Research) funded ENSIKOM project, the experts of Paint/Lacquer Technology as well as Adhesion and Interface Research at the Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Bremen, have developed a method for evaluating the suitability of UV clearcoats for specific applications and their resulting properties in advance merely from their formulations.

Effect of the network structure on the mechanical properties

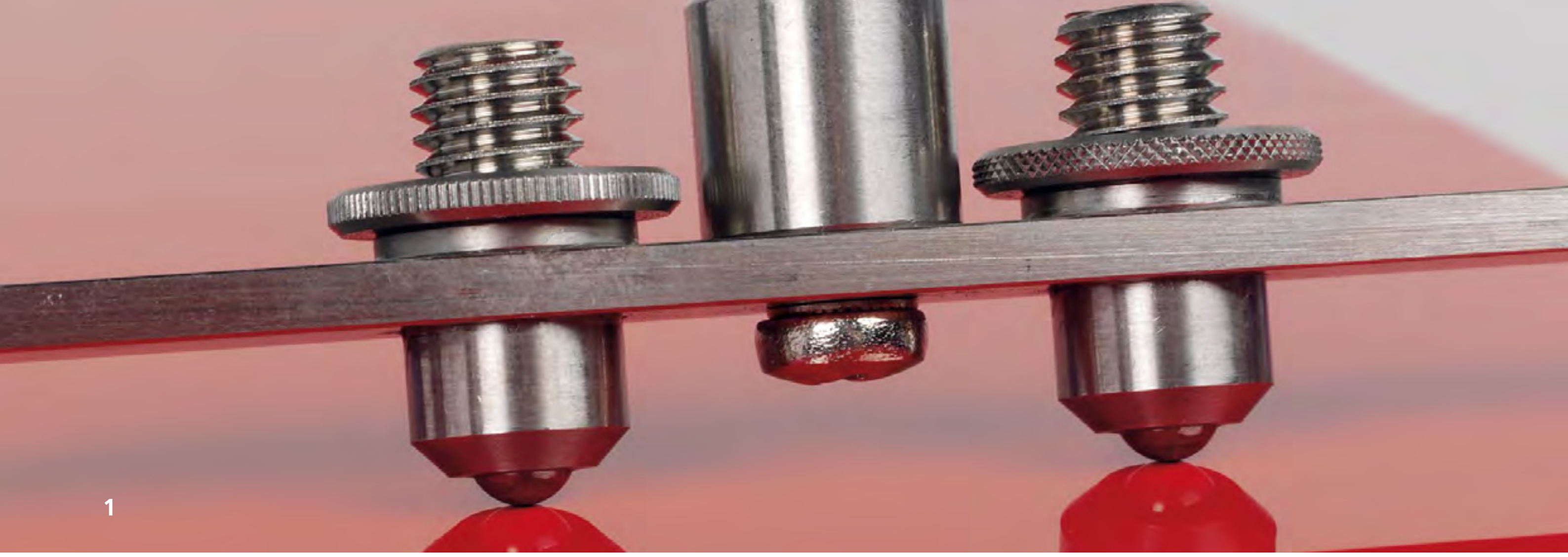
The degree of crosslinking is determined by the contributions of the different reactive groups which all add differently to the network structure. Coating systems having the same degree of crosslinking can therefore have very different properties. Analytical techniques such as dynamic mechanical analysis (DMA), infrared spectroscopy (IR), and inverse gas chromatography (iGC) only provide information about the overall degree of crosslinking.

By simulating the curing process, all the contributions to the network are taken into account and predictions can be made about the resulting properties of the coating. Carrying out such a screening procedure prior to development of a coating allows formulations for a particular application to be evaluated in advance and to shorten coating development times. The objective of the project was to develop such a simulation method.

Characterization of the UV clearcoat systems

In collaboration with BASF SE, the experts at Fraunhofer IFAM selected two UV clearcoats with different ratios of urethane acrylate to reactive diluent (system 1: 7 to 3 and system 2: 1 to 1). The crosslinking reactions and resulting properties were studied.

The curing of the clearcoats was carried out under a CO_2 atmosphere and the conversion of the double bonds at different curing times was monitored using IR spectroscopy. In addition,



1 *Pendulum damping test according to König at Fraunhofer IFAM.*

the scientists measured the pendulum damping according to König (Fig. 1) and the scratch resistance using a Crockmeter.

At the end of the curing time, about 93 percent of the double bonds had reacted in system 2 whilst only a conversion of about 80 percent was measured for system 1 with the higher acrylate functionality. The pendulum damping tests showed that curing under an inert atmosphere produced sufficiently hard films. System 2 showed the higher hardness. The same results were found for the Crockmeter measurements. Consequently system 2 proved to be the better coating.

Simulation of the curing reaction

Two things are required to simulate the curing: A reaction scheme covering the reactions that take place during curing plus their relevant probabilities and a starting structure model which describes the coating system and its components immediately after mixing – namely before the curing.

First of all the individual steps of the curing reaction were identified and a suitable reaction scheme under inert conditions was established. The starting point for this was the formulation of the clearcoat systems (binder, reactive diluent, and two photo initiators).

For the reactions, molecular modeling was used to calculate the relevant educts and products. By comparing the energy differences between the highest occupied molecular orbital of the radical and the lowest unoccupied orbital of the relevant monomer for the respective reaction, in combination with activation energy data, the relevant reaction probabilities can be calculated. This resulted in two competing reactions each (Fig. 2).

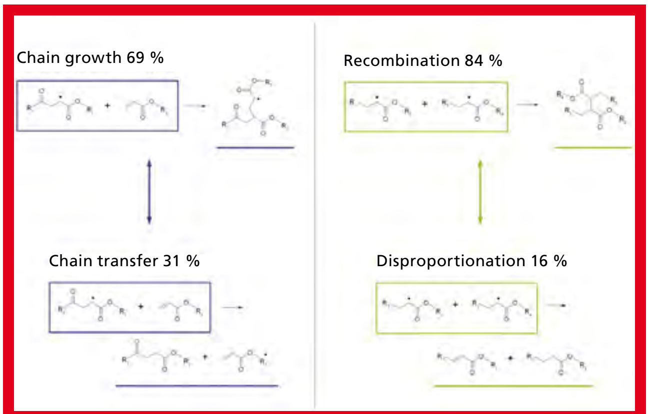


Fig. 2: Probabilities of the four curing reactions.

The formulations of the coating systems also allowed the individual components and their number respectively ratio to be determined – a prerequisite for preparing structure models for the non-cured coatings. By applying the reaction scheme, structure models for the cured coating systems could be generated via molecular dynamics simulation of the crosslinking process (simulation of the movement of the atoms at a given pressure and temperature). The calculated conversion of C=C double bonds agreed well with the time-dependent conversion of C=C double bonds measured by IR (Fig. 3).

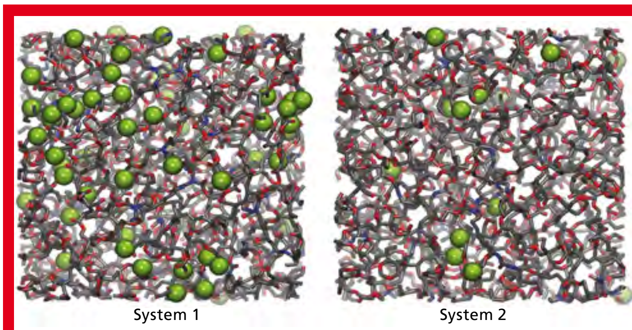


Fig. 3: Structure models of the two clearcoats. The remaining non-crosslinked double bonds are indicated as green spheres.

Evaluation of the formulations

The characteristic structural properties were now evaluated using these structure models. It was shown that system 2 had a greater crosslinking density – more crosslinks per volume – and a lower "defect density", i. e., considerably fewer non-crosslinked double bonds per volume (Fig. 4).

There was also a more efficient and more homogeneous crosslinking observed for system 2 since it showed a higher average number of crosslinks per reactive group and considerably smaller standard deviations (Fig. 5). System 2 also had a more efficient topology: Due to the greater fraction and more efficient incorporation of the reactive diluent it possesses a higher hardness for the same elasticity. Hence system 2 – as in the experiments – was classified as the better coating.

Conclusion

The simulation method developed by Fraunhofer IFAM allows the properties of new UV coatings to be predicted based solely on the formulation and allows different formulations to be compared in advance of actual development work. This leads to significantly lower development cycles for new coatings.

Furthermore, it is possible to derive statements about the resistance to chemicals, volume shrinkage, and elasticity of the coatings. The method can be easily applied to other formulations and systems, for example, adhesives cured via thermally initiated polymerization.

Project funding

Federal Ministry for Education and Research (BMBF)
Project ENSIKOM – "Development, simulation and effective implementation of more environmentally friendly and more

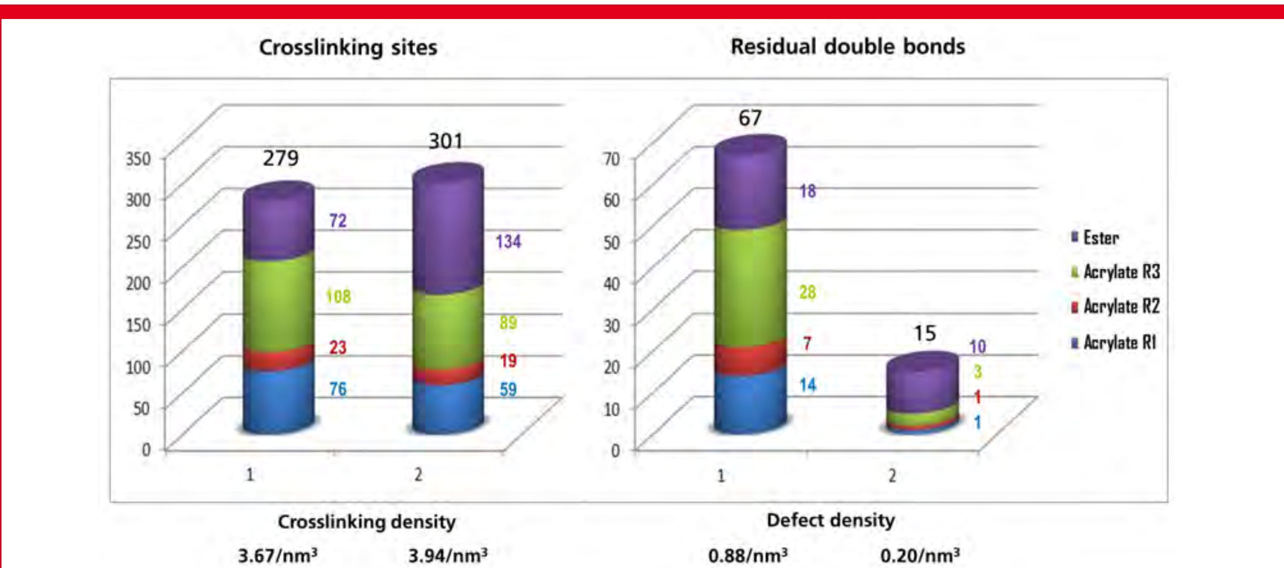


Fig. 4: Comparison of the crosslinking density and "defect density" of the two clearcoats.

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Project partners

- JKL Kunststoff Lackierung GmbH
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6 *High performance computer cluster of the Applied Computational Chemistry department at Fraunhofer IFAM for the calculation of structural properties of UV clearcoats.*

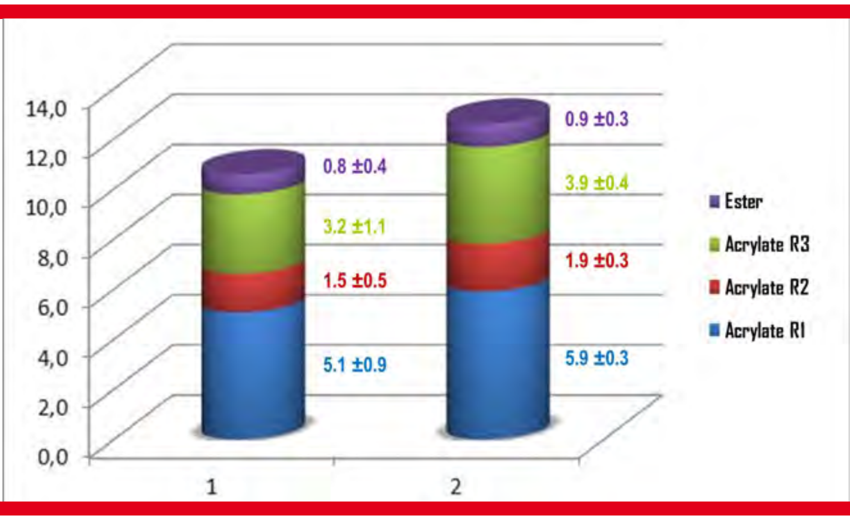

Fig. 5: Average number of crosslinks per reactive group and standard deviation of the two clearcoats in comparison.