

# Relating Mechanical Properties of UV-Cured Coatings to the Molecular Network:

## A New Approach to Predict Crosslinking of Coatings

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A new approach to simulate the crosslinking reaction of UV-cured coatings and to generate realistic atomistic model structures as a function of the formulation and the ambient conditions has been developed. With these models, the mechanical properties of UV-cured coatings can be related to the molecular network.

At first, an extensive experimental characterization of the relevant coatings was performed to establish parameters and validate the simulation approach. Additionally, atomistic model structures of coating components were prepared and optimized via molecular mechanical methods. Using these as a basis, model structures of the uncured coatings were generated according to the formulation.

Afterward, the relevant reaction steps were identified and a corresponding reaction scheme was established. With this, the energetics of the relevant reactions were calculated via density-functional theory (DFT) delivering the reaction probabilities and velocities of the polymerization. For the simulation of the polymerization of the UV-cured coatings, a crosslinking algorithm

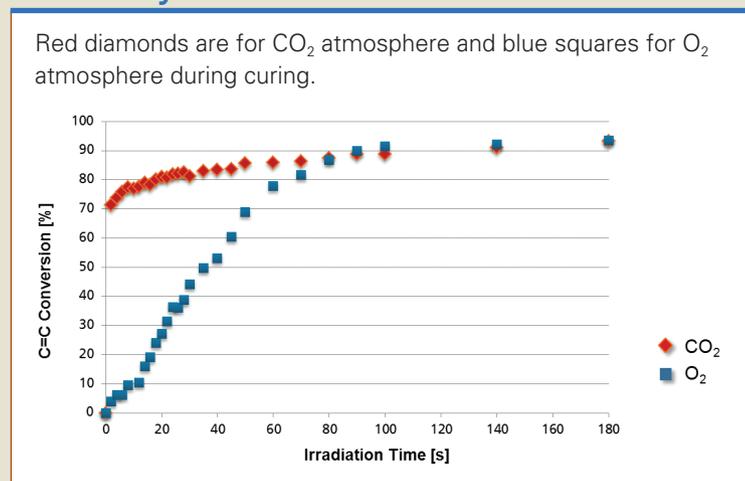
corresponding to the derived reaction scheme was implemented into a molecular dynamics code. Finally, model structures of the cured coatings were generated and could be related to the mechanical properties of the coatings.

### Introduction

The number of applications for high-quality plastic parts in various industries is still increasing, including automotive, medical technology, railway transport, aeronautics, household appliances and consumer electronics. Correspondingly, there is a broad variety of requirements for the relevant coatings. In the automotive industry (in which basecoat and clearcoat paint systems are extensively used due to its superior appearance and high stability of gloss)<sup>1</sup>, coatings have to possess long-term resistance to chemical agents; high and low temperatures; UV radiation; and scratching—all without any reduction in performance.<sup>2</sup> The requirements for scratch resistance of automotive clearcoats have especially soared in recent years. Here, scratching of surfaces and the associated decrease of gloss are considered critical. In particular, scratches on dark surfaces are a serious problem.

## FIGURE 1

### C=C conversion-time plot from ATR-IR spectroscopy of Model System 2



For these basecoat/clearcoat coatings, different ways to accomplish scratch-resistant surfaces are available—one of them is UV curing.<sup>3</sup> Here, it is highly desired to obtain a maximum degree of crosslinking in a short reaction time, since this is directly related to the hardness and durability of the coating. On the other hand, formulators also want to obtain some elasticity and flexibility of the coating so the product won't be too brittle. Thus, the degree of crosslinking or crosslinking density is considered a vital parameter for the coating formulations.

Typical experimental techniques for measuring the degree of crosslinking are dynamic mechanical analysis (DMA); swelling experiments; vapor sorption techniques; vapor pressure osmometry; nuclear magnetic resonance (NMR); infrared spectroscopy (IR); and inverse gas chromatography (IGC).<sup>4-10</sup> Unfortunately, all of these techniques have something in common—they can only provide the overall value of crosslinking. For the mechanical

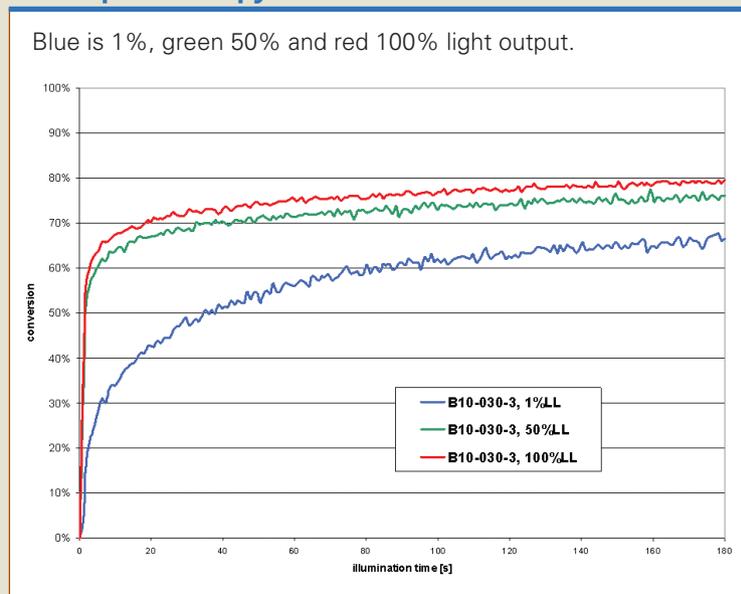
and physical properties of a coating, this summed-up value of all kinds of crosslinks formed during curing is relevant, but so is the kind and

amount of the different reactive groups (from different binders and reactive diluents) contributing to the network formation—especially the ones that do not react and, thus, do not contribute to the network. With this additional information, formulators would be able to much more efficiently tailor the mechanical properties of UV-cured coatings with regard to their formulation.

Hence, we propose a new approach to simulate the crosslinking reaction of UV-cured coatings and to generate realistic model structures as a function of the formulation and the curing conditions. With these models, the mechanical properties of UV-cured coatings can be directly related to the molecular network and deeper insight regarding the correlation of scratch-resistance and the long-term resistance to chemical, mechanical and physical damage versus elasticity of the coating can be obtained.

## FIGURE 2

### C=C conversion time plot for inert conditions of a model system similar to System 1 for three different light outputs of an Hg medium-pressure lamp from RT-IR spectroscopy



## Experimental Characterization for Parameterization and Evaluation of the Curing Simulation

### Model Systems

Two different clearcoat model systems were chosen for the investigation of their curing reaction and the resulting coating properties. Both consist of two main components—one being an aliphatic urethane acrylate as binder and the other an acrylic acid ester as reactive diluent. Additionally, two different photoinitiators were chosen. The main difference between the two coatings is the mixing ratio of binder and reactive diluent, being 7:3 in the case of Model System 1 and 1:1 for Model System 2. The clearcoats were crosslinked in a UV-Inert Cube in oxygen and CO<sub>2</sub> atmosphere, respectively. The investigated curing time was two seconds to 180 seconds.

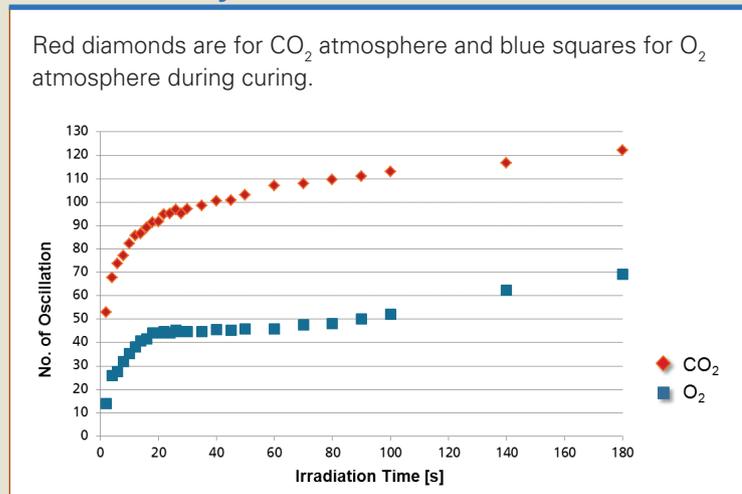
### Experimental Characterization

The following experimental characterization of the clearcoats was needed for the parameterization and evaluation of the simulation approach. Property profiles of the two model coatings were obtained by measurement of (a) the double bond conversion via ATR-IR spectroscopy; (b) the surface hardness via the pendulum test (König); and (c) the scratch resistance via the Crockmeter test. All these measurements were carried out at different curing times in oxygen and CO<sub>2</sub> atmosphere in a test series with a UV intensity of 366 mW/cm<sup>2</sup>.

It could be shown that the curing of Model System 2 in CO<sub>2</sub> atmosphere was much faster than in oxygen atmosphere as expected (see Figure 1). After 180 seconds of irradiation time, the conversion was finally the same for both conditions reaching approximately 93% of crosslinking. Model System 1 with higher acrylate

FIGURE 3

### Measurement of surface hardness via pendulum test of Model System 2



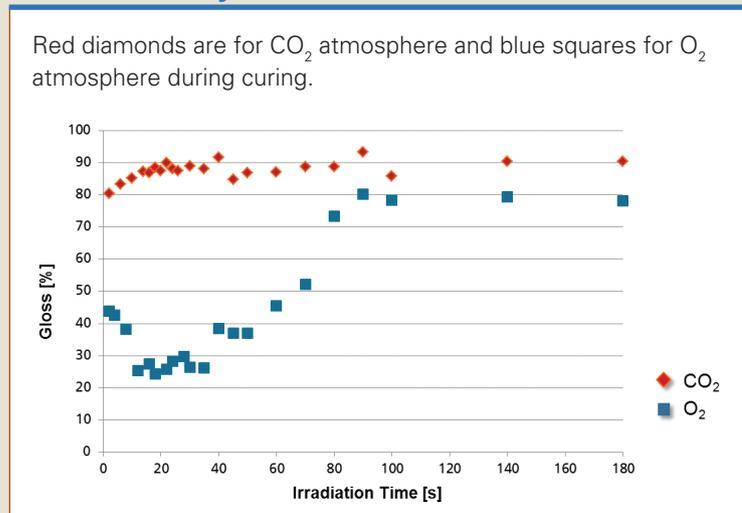
functionality showed the same behavior, but the final conversion after 180 seconds was only around 85%. This data will be used later on for the assignment of the generated atomistic models to the real systems.

In addition, the C=C conversion of a model system similar to System 1 for

three different light outputs of an Hg medium-pressure lamp was measured via RT-IR spectroscopy (see Figure 2). A 1% light output corresponds to an intensity of 100 mW/cm<sup>2</sup>, 50% to 4,400 mW/cm<sup>2</sup>, and 100% to 8,800 mW/cm<sup>2</sup> (measured with a dosimeter). The dependence of the conversion on

FIGURE 4

### Measurement of stability of gloss via Crockmeter test of Model System 2



the irradiated light output and UV intensity, respectively, could be clearly shown. The system reached a conversion of more than 73% after one minute and more than 75% after 100 seconds at 50% and 100%. With 1%, 67% conversion was reached after approximately 180 seconds.

The same difference between the two atmospheres could be seen in the determination of the surface hardness of Model System 2 (see Figure 3). Here, the coating cured in O<sub>2</sub> atmosphere was very soft and finally reached only half of the value as the one cured in CO<sub>2</sub> atmosphere. Again, Model System 1 showed almost the same behavior, but reached a lower number of oscillations indicating a softer coating.

The Model System 2 in inert atmosphere showed a good performance according to scratch resistance compared to the one in oxygen atmosphere (see Figure 4). However, it reached only 90% gloss while Model System 1 showed 98%. From these results it could be shown that the scratch resistance of the coating is directly related to the double-bond conversion.

## Simulation of the Curing Reaction as a Function of Formulation and UV Intensity

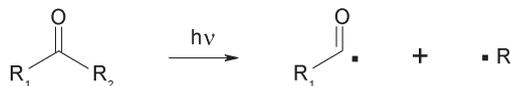
### Key Reactions

At first, the relevant reaction steps of the polymerization reaction were identified and a corresponding reaction scheme was established. Here, it was assumed that the reactions take place at inert conditions since in the relevant curing process there is less than 0.2% of oxygen. The starting point was the molecular structures of the binder components and the reactive diluent, having four different functionalities altogether, and the two photoinitiators with again two different functionalities.

Hence, after the chain start reaction, there are theoretically eight

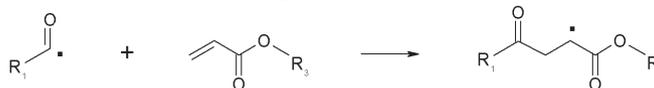
## KEY REACTIONS

### Initiator decay (one key reaction)



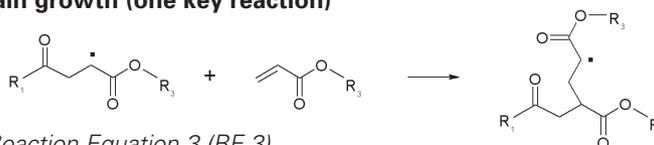
Reaction Equation 1 (RE 1)

### Chain start reaction (one key reaction)



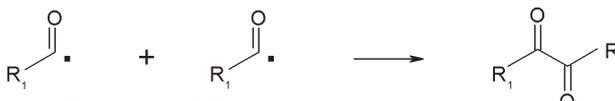
Reaction Equation 2 (RE 2)

### Chain growth (one key reaction)

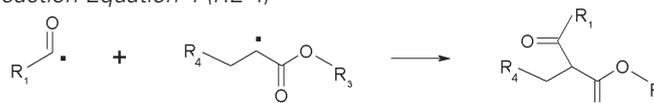


Reaction Equation 3 (RE 3)

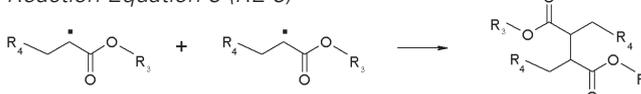
### Competing Reactions: (a) Chain termination via recombination (three key reactions)



Reaction Equation 4 (RE 4)

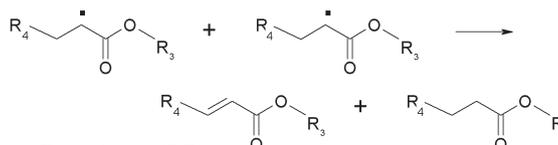


Reaction Equation 5 (RE 5)



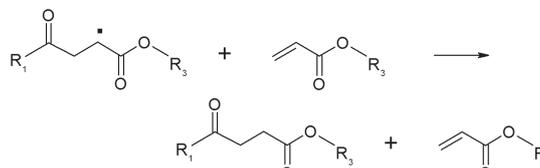
Reaction Equation 6 (RE 6)

### Competing Reactions: (b) Chain termination via disproportionation (one key reaction)



Reaction Equation 7 (RE 7)

### Competing Reactions: (c) Chain transfer (one key reaction)



Reaction Equation 8 (RE 8)

possible reaction products. For the first chain growth step, there are already 32 different possible reaction products; for the second one 128; for the third again a factor of four and so on. Such a large amount of reactions is barely manageable and not reasonable for an efficient simulation of the curing mechanism. Therefore, the reactions were reduced to eight characteristic key reactions and, thus, their amount was significantly cut down. (See “Key Reactions” sidebar on page 21.)

### Reaction Probabilities

For all of these key reactions, atomistic model structures of the educts and products were prepared and a structure optimization using a density-functional theory (DFT)<sup>11-12</sup> approach with the exchange-correlation functional of Becke and Perdew (BP86) with the new def2-TZVP basis set, giving accurate results within the Turbomole software,<sup>13</sup> was performed. The total energies of all educts and products and the corresponding reaction enthalpies were derived from that. With the energetics of the relevant reactions, the reaction probabilities of the polymerization were calculated later on.

In addition to the chain start key reaction (RE 2), all eight possible “real” reactions (two different radicals with four different functional groups of the monomers) for the chain start were also calculated via DFT to obtain a comparison with the energetics obtained from the key reactions and to evaluate the model of the simplified key reactions. It could be shown that the reaction enthalpy of the key reaction of 84.2 kJ/mol represented the reaction enthalpies of the eight “real” reactions being in a range of 72.0 to 86.7 kJ/mol quite well (see Figure 5). Therefore, it could be shown that the model of the key reactions is meaningful and delivers feasible results.

The reaction enthalpy of the chain growth (RE 3) was 63.7 kJ/mol and the ones of the three-chain termination via recombination reactions (RE 4 to RE 6) were 271.0 kJ/mol, 260.2 kJ/mol and 239.9 kJ/mol, respectively. For the chain termination via disproportionation (RE 7), one obtained 207.7 kJ/mol. By comparison of the energetics of the single reactions, especially of the distance of the highest occupied molecular orbital (HOMO) of the radical and the lowest unoccupied molecular orbital (LUMO)

of the monomer of the corresponding reaction, the related reaction probabilities were calculated.

Before that was done, some further assumptions were made to simplify the model. It was assumed that the number of generated radicals is correlated to the irradiated UV intensity. Thus, a number of radicals are already given in the corresponding atomistic model from the beginning and stay fixed. The correlation of the model to the irradiated intensity and UV intensity, respectively, will be done via comparison with the conversion from ATR-IR and RT-IR. These radicals being in the atomistic model from the beginning were labeled as “effective radicals.” It was assumed that every “effective radical” always induces a chain start reaction and that the corresponding recombinations in RE 4 and RE 5 will not take place. Hence, only four “effective reactions” remained being the chain growth (RE 3), the last recombination (RE 6), the disproportionation (RE 7), and the chain transfer reaction (RE 8). A direct implication of this is that the chain growth and the chain transfer reaction are in direct competition against each other as are the recombination and the disproportionation reaction. With these

## FIGURE 5

Reaction enthalpies in kJ/mol of the key reaction of the chain start (left) and corresponding ‘real’ reactions (right)

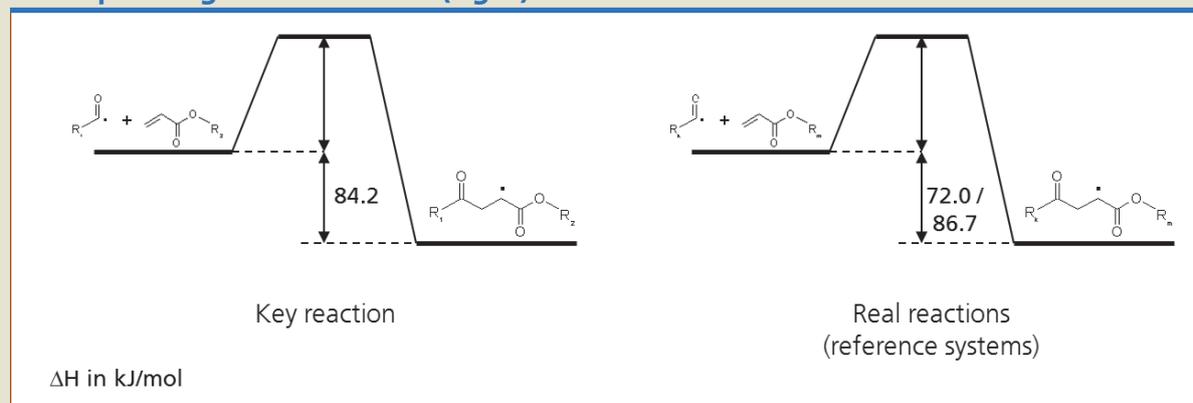


FIGURE 6

Reaction probabilities of the final four competing key reactions. Chain growth and chain transfer reaction are competing directly and so do the recombination and disproportionation reaction.

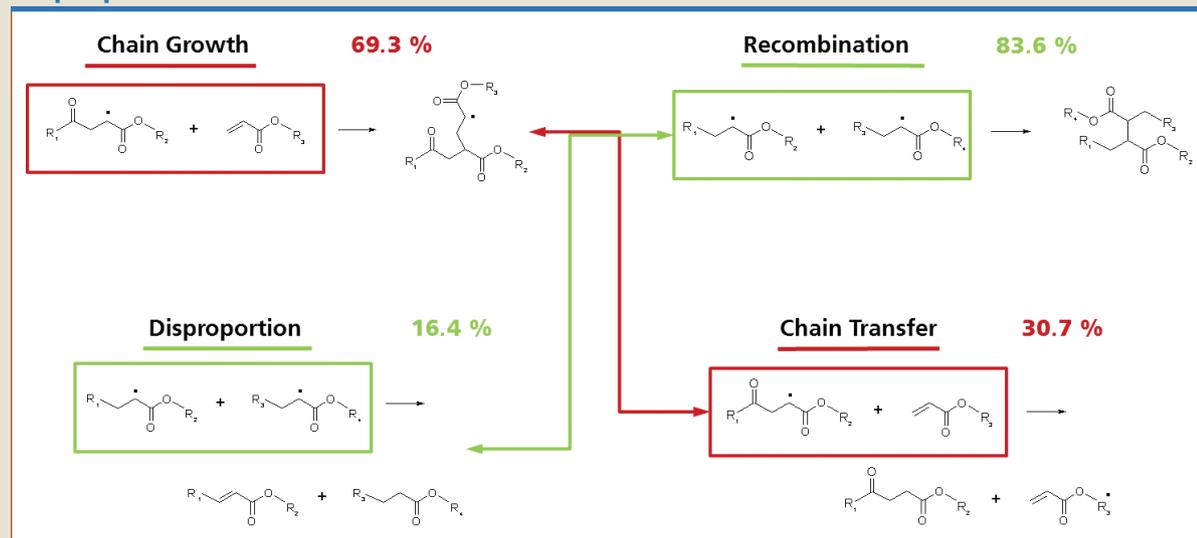
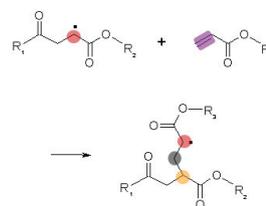
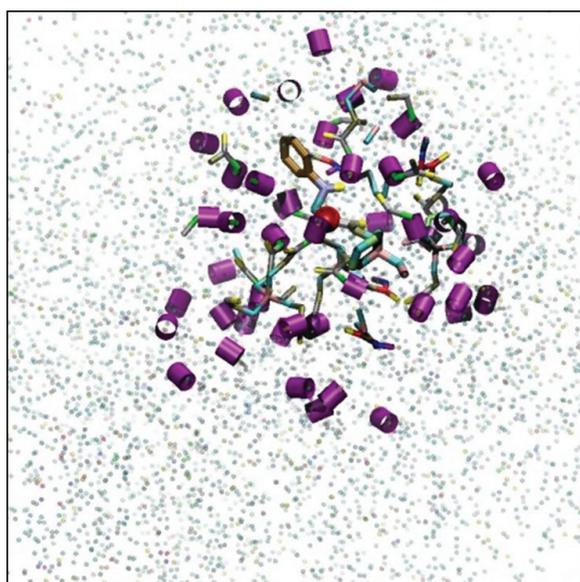


FIGURE 7

Atomistic model of a coating corresponding to Model System 1 with one 'effective' radical at the beginning of the crosslinking simulation

The active radical is shown as red sphere (in the middle of the violet cylinders). The violet cylinders display the carbon double bonds in the close vicinity of the radical (sphere with radius of 6 Å) being at disposal for the chain growth reaction.



- Radical
- Reacted Radical
- Reacted CH<sub>2</sub>
- C=C Site

assumptions, the reaction probabilities of the single key reactions shown in Figure 6 were derived from the energetics of the DFT calculations. These are the reaction probabilities in case of a close approach of two possible reaction partners during the molecular dynamics. The diffusion and, thus, the probability of an approach of two possible reaction partners itself is governed by the concentration of the corresponding monomers and their interaction with each other during molecular dynamics.

### Crosslinking Algorithm and Atomistic Model Structures

Next, the atomistic model structures of the single coating components were optimized via molecular mechanics methods using the PCFF force field<sup>14-16</sup> as input for the generation of the cured polymer models. With these, first model structures of the uncured coatings (periodic unit cells) were generated according to the formulations using the Amorphous Cell module with the PCFF force field of the Materials Studio software package by Accelrys Software Inc.<sup>17</sup> The generated cubic periodic cells had an edge length of around 4 nm and contained more than 7,000 atoms each.

The calculated reaction probabilities built the basis for the generation of realistic molecular models of the cured clearcoat. For the simulation of the curing reaction, a corresponding crosslinking algorithm adjusted to the model assumptions, key reactions and reaction probabilities introduced above was needed. This was implemented in the molecular dynamics code LAMMPS from Sandia National Labs.<sup>18-19</sup> The algorithm works like this—during the molecular dynamics simulation of the system, within a sphere of a given radius (e.g., 6 Å), all possible reaction partners around a radical are identified. The

closest one is going to react with the radical with the given probability for that specific kind of reaction. In the case of the chain growth reaction (e.g., the double bond is broken), the new bond with the CH<sub>2</sub> is formed, and the radical site is moved to the CH of the former double bond (see Figure 7).

For the other key reactions, this works analogously. Afterward, the newly formed bonds were energetically optimized and equilibrated. This procedure is repeated until no new reaction partners are found within the given radius of the radical. If this is the case for all radicals for some given time, the final conversion is reached. Using this crosslinking algorithm together with the concept of the “effective radicals” and the “effective reactions,” first structures of the Model System 1 were generated to test the algorithm (see RE 7 and RE 8 on page 21).

### Correlation with Mechanical Properties

Several atomistic model structures with a different number of “effective radicals” were generated via the described algorithm for the two clearcoat model systems. From these, the final conversion as a function of the number of “effective radicals” was calculated and also the amount of the different reactive groups (from binder and reactive diluent) contributing to the network formation was evaluated. These results were compared to the conversions obtained by the ATR and RT-IR measurements (see Figures 1 and 2) and the corresponding atomistic models could be assigned to the real clearcoat systems. Hence, realistic atomistic model structures could be established for the two clearcoat systems as a function of the UV intensity used for curing. With this, the number of “effective radicals” could also be correlated with the light output of the Hg lamp and the UV intensity,

respectively, giving information about the efficiency of the irradiation.

With these models, the mechanical properties of the UV-cured coatings could be related to the molecular network by correlating the structural information of the models—such as the degree of crosslinking and amount of the different reactive groups contributing to the network—with the measurements of surface hardness via pendulum test (Figure 3) and stability of gloss via Crockmeter test (Figure 4). This provided a deeper insight regarding the correlation of scratch resistance and long-term resistance to chemical, mechanical and physical damage with the elasticity of the clearcoats. It could be shown that the surface hardness and the stability of the coating gloss increase with the amount and intensity of UV irradiation and strongly depend on the formulation (i.e., the components and the mixture of the clearcoat) and especially on the different reactive groups contributing to the network. In addition, the type and radical yield of the initiator strongly affect the crosslinking process as does the mobility of the monomers and their atomistic interaction with each other.

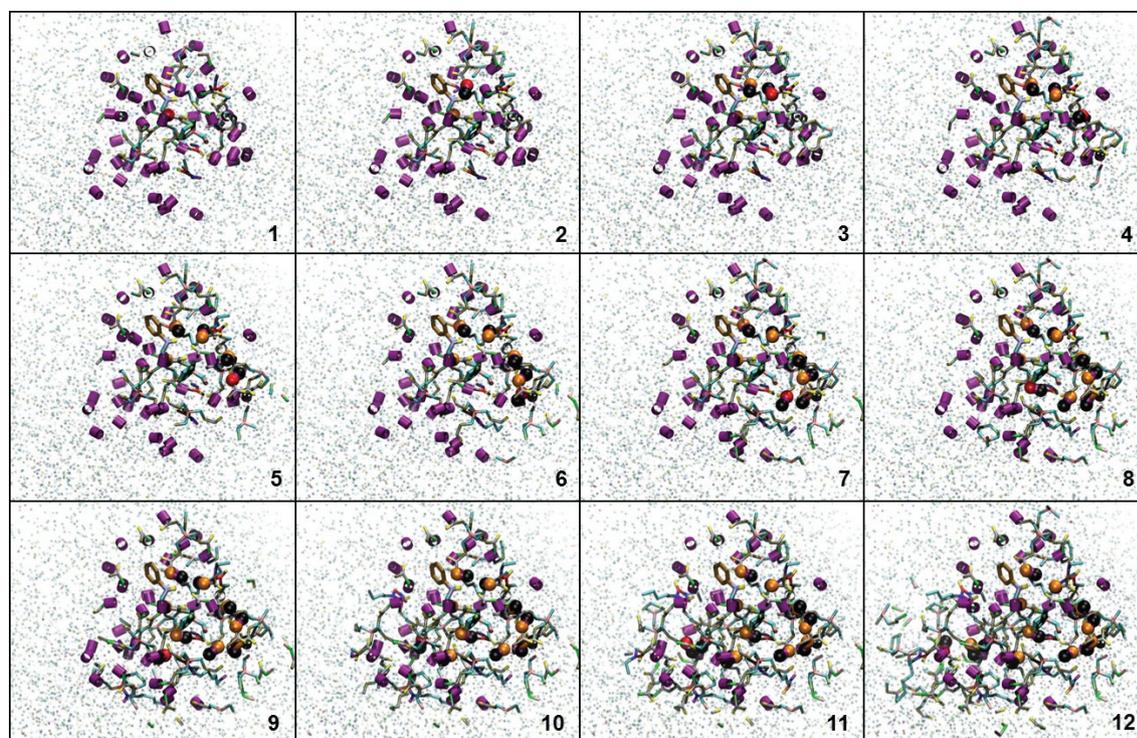
### Conclusion

A new approach to simulate the crosslinking reaction of UV-cured coatings and to generate realistic atomistic model structures as a function of the formulation and the UV irradiation has been developed. With this, the mechanical properties of UV-cured coatings (such as stability of gloss and surface hardness) can be related to the molecular network. It could be shown that the properties of the coating increase with the amount and intensity of UV irradiation and strongly depend on the formulation—i.e., the components, mixture and different reactive groups contributing to

## FIGURE 8

### Atomistic model structures corresponding to Model System 1 with one 'effective' radical of a chain growth reaction during the crosslinking simulation

The active radical is shown as red sphere, the orange ones represent reacted radicals and the black ones reacted  $\text{CH}_2$  groups. Progress is from left to right and from top to bottom. The violet cylinders display the carbon double bonds in the close vicinity of the radical being at disposal for the chain growth reaction.



the network formation of the clearcoat. On the other hand, the type of the initiator and its radical yield strongly affect the crosslinking process, as does the mobility of the binder and reactive diluent and their atomistic interaction with each other. The established method can also be applied to other kinds of curing or crosslinking processes—such as thermal curing—and, thus, can provide important information for the formulation and evaluation of different kinds of coatings.

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