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High Scratch and Etch Resistance by Optimized Cross-linking Chemistry and Density

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Summary: Target of development in the field of modern automotive clear coats is the combination of high etch and high scratch resistance.
For high etch resistance the cross-linking chemistry is the key factor. The property scratch resistance is mainly influenced by the cross-linking density and the flexibility of chains between netpoints. By combining these parameters high etch and scratch resistant clear coats can be formulated. As a representative example an optimized clear coat based on epoxy/acid cross-linking chemistry is discussed. The ways to achieve high cross-linking density are shown.

Keywords: etch resistance, scratch resistance, coatings, crosslinking, epoxy/acid

Introduction

In the recent years field damages of automotive clear coats have been observed which are caused by etchings from environmental pollution. Especially in aggressive atmosphere, clear coats based on conventional melamine cross-linking can show severe etching after short exposures. These damages have led to the development of etch resistant coatings by new cross-linking chemistries. With given polymer backbone chemistry, improved etch resistance can be achieved by delivery of cross-linking sites with better resistance against acidic attack. In figure 1 cross-linking mechanisms of clear coats are shown. These cross-linking reactions are leading to different cross-linking sites and have different potential in reachable cross-linking density. In acrylic/melamine the cross-linking sites are the weak point regarding etch resistance. On the other hand cross-linking density can be very high. Urethane structures which are generated in 2pack clear coats or by the use of blocked polyisocyanates show a much better chemical resistance. Steric hindrance of the urethane groups, increase in Tg of the coating and increase in hydrophobicity by the use of polyisocyanate hardeners based on isophorone diisocyanate increase this etch resistance even further. Cross-linking density is lower when compared to acrylic melamine systems. Other very resistant linkages are the siloxane linkage derived from silane condensation reaction and the ester

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linkage achieved by epoxy/acid addition. The ultimate in etch resistance and cross-linking density is achieved by a carbon-carbon-linkage which can be formed by radical polymerization processes like in UV-coatings.

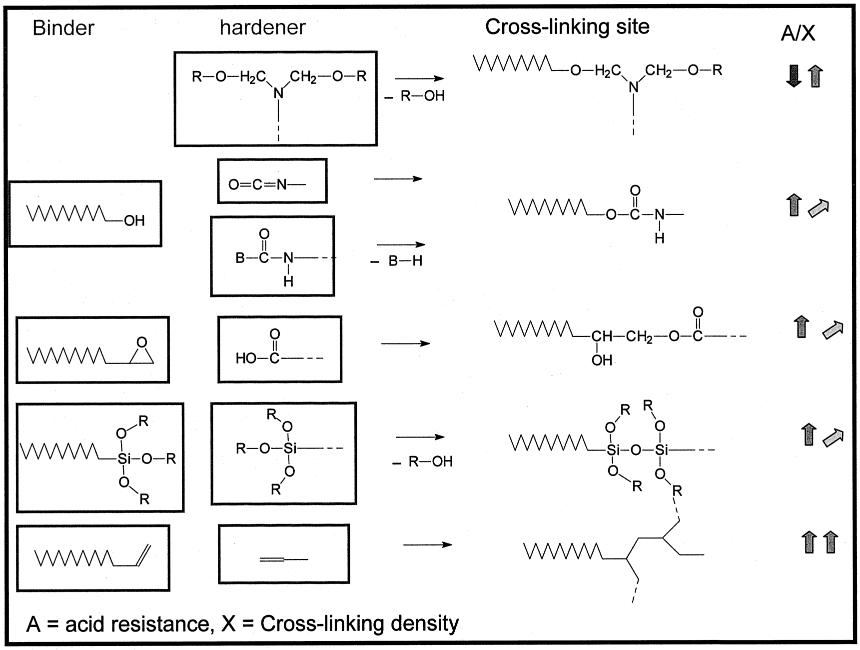

Figure 1. Different cross-linking mechanisms for automotive clear coats

Normally the increase in etch resistance is accompanied by reduced scratch resistance. Modern high performance binders combine high etch with high scratch resistance.

Testing methods

To check the etch resistance of clear coats, different artificial tests to simulate environmental influences are used. Among these artificial testing media besides sulfuric acid also a lot of different chemicals are used. Standard acrylic/melamine clear coats show severe damages after acidic attack. The clear coat is totally destroyed after a short exposure and often additionally an attack of the aluminum flakes of the base coat is observed.

The outdoor performance of clear coats normally is checked via outdoor exposure in aggressive atmosphere like e.g. in Jacksonville/Florida. Only three months of exposure are necessary to see severe damages in case of clear coats with poor etch resistance.

For the determination of scratch resistance also a lot of different test methods have been developed and established. The most common test in Europe is the bench top car wash simulation test with Amtec/Kistler device. Besides this simulation of real car washing stresses, a more scientific method has been developed with the nano scratch determination. In this test a single scratch is generated with a diamond indenter and increasing force. The plastic resistance (plastic deformation of the coating at a given force) and the fracture resistance (force at which an irrepairable fracture occurs) of the coating is measured in this experiment.

Binder chemistry

To achieve a high etch and scratch resistance three main parameters have to be fulfilled.

1. it is essential to generate cross-linking sites with good stability against chemical attack
2. a high cross-linking density has to be achieved
3. flexible chains between two net points have to be present.

If these parameters are adjusted in the right way, nearly every coating can be optimized according to superior etch/scratch performance.

As a representative example a 1pack etch resistant clear coat based on epoxy/acid cross-linking will be discussed in detail.

Figure 2 shows the basic cross-linking reaction. An epoxy functional resin is cross-linked via a carboxylic groups bearing hardener. During the addition reaction a hydroxyl group is generated which offers the opportunity of further cross-linking with auxiliary binders, like blocked polyisocyanates, melamine resins or transesterification hardeners.

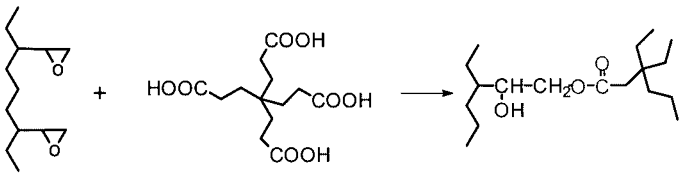

Figure 2. Basic cross-linking mechanism

To guarantee a good weatherability for clear coat applications aromatic epoxy resins based on bisphenol-A-diglycidylether can not be used. The binder class of choice are copolymers of glycidyl methacrylate with other appropriate co-monomers (Figure 3). The choice of the other co-monomers is mainly influenced by important features like hardness, hydrophobicity, flexibility, compatibility and flow behavior of the resulting main binder/ clear coat.

As a cross-linking agent a carboxy functional binder is used. Compared to acrylic resins acidic polyester resins show a higher reactivity and are the preferred binder class. The schematic structure of the acidic polyester hardener is shown in Figure 4. It is based on a highly branched polyester resin. The structure of this polyester resin is strongly influencing the mechanical properties of the cross-linked film. By using highly elastic hardeners with a high functionality, films with an excellent hardness/scratch resistance balance are obtained. An important structural feature is the partly addition of ε-caprolactone to the acidic groups. By this reaction the mobility of the acidic groups is increased and the reactivity is enhanced. On the other hand these flexibilising groups contribute also to the good scratch performance of the cross-linked film.

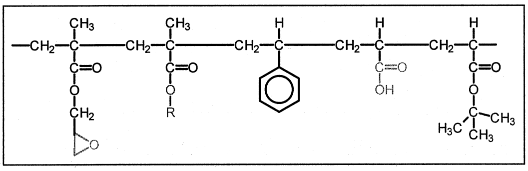

Figure 3.Schematic structure of epoxy acrylate

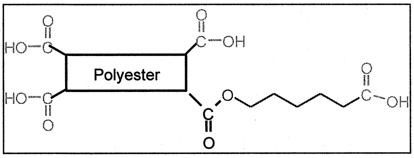

Figure 4. Schematic structure of acidic polyester

Cross-linking density

The reaction between epoxy and carboxy groups is an exothermic addition reaction. In Figure 5 the reaction of an epoxy functional and an acidic binder is observed via DSC. The highly exothermic reaction starts at approximately 110°C. In comparison the reaction of a butanonoxime blocked polyisocyanate (based on isophorone diisocyanate) with a hydroxyfunctional resin is in the first step an endothermic reaction starting at app. 130°C.

This high reactivity leads to increased cross-linking density. With this high reactivity it is possible to use binders with lower Tg and higher flexibility. Hardness of the final film is not mainly derived from the Tg of the binder but also from the Tg increase by cross-linking.

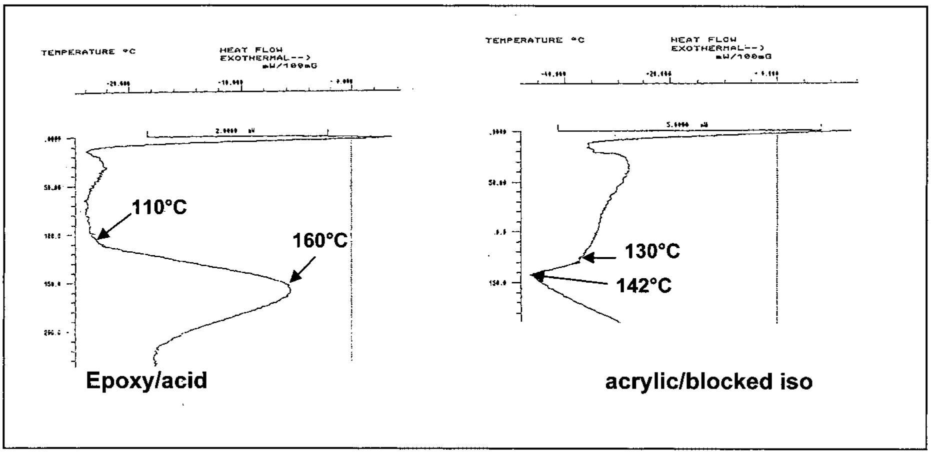

Figure 5. DSC measurements

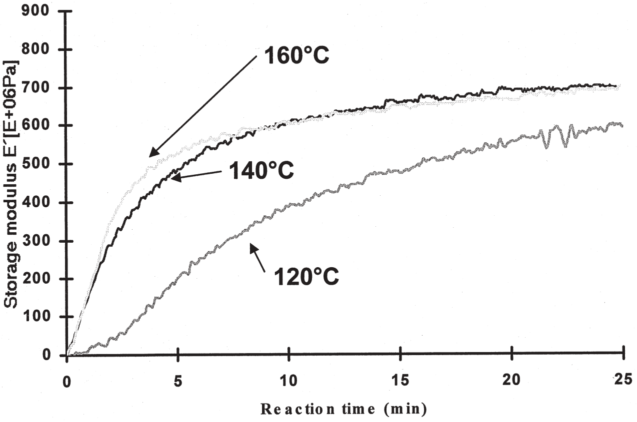

Figure 6. Determination of cross-linking density via DMA

The increase of cross-linking density in dependence of the baking temperatures and time can be measured by dynamic mechanical analysis. To perform the experiment the lacquer was applied on natural silk as a carrier. Figure 6 shows the results of this experiment. The cross-linking was monitored at 120°C, 140°C and 160°C over a period of 25 minutes, by determination of the storage modulus. The resulting curves show the increase of storage modulus which is a function of the cross-linking density during baking time. The higher the storage modulus the higher is the cross-linking density. The measured curves show, that the reaction at 120°C is slower than at 140° and 160°C, but after 25 minutes a similar level of cross-linking is reached. The reaction at 140°C and 160°C shows the same speed. After 10-15 minutes the final cross-linking density is reached. The baking at 160°C has no further advantages compared with the lower baking temperature [1].

The described experiments demonstrate the high reactivity of the epoxy/acid system. Despite the high reactivity of this system a good storage stability is realized.

Increase of cross-linking density under low bake conditions

For increased network density not only the high degree of branching of the acidic polyester hardener but also the structure of the main epoxy functional acrylic binder plays an important role. A further enhancement of the cross-linking density under low bake conditions can be achieved by different routes.

By incorporation of acrylic acid in the monomer mixture an internal addition reaction takes place. (Figure 7). During polymerization the acrylic acid reacts with the epoxy groups which leads to branched polymer chains, more net points in the final network and therefore increased cross-linking density.

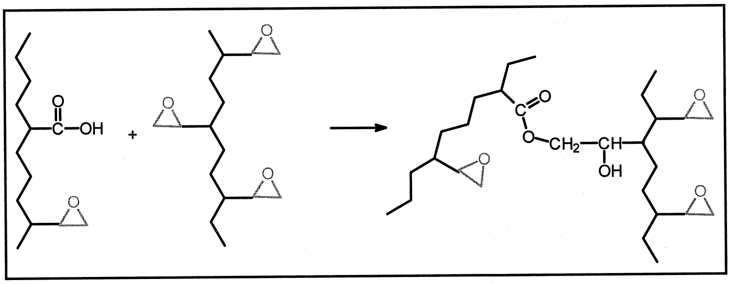

Figure 7. Internal branching during co-polymerization

The amount of branching is mainly depending on the amount of acid used in the polymerization. Figure 8 shows the differences in molecular weight in dependence of the amount of incorporated acrylic acid. The left column shows the result without acid, the middle column with an acid number of 3 (= 0,4% on monomer mixture) and the right one with an acid number of 5 (= 0.6% on monomer mixture). It is obvious, that by increasing the amount of acid the weight average of molecular weight increases. The number average of molecular weight stays on the same level. The dominant part of molecules shows no branching and therefore the viscosity of the resins at comparable solids contents is not much differing.

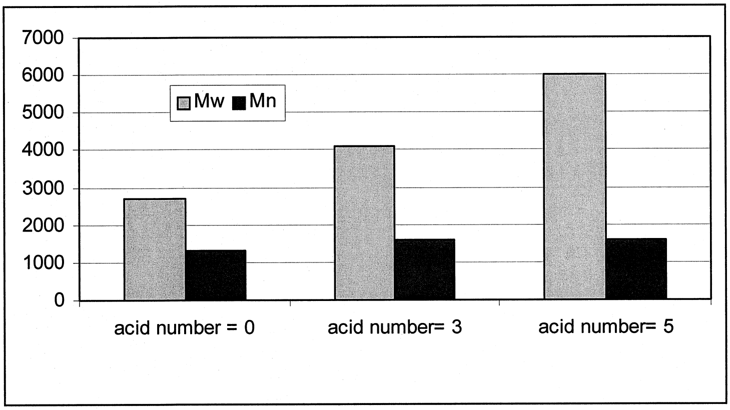

Figure 8. Dependence of molecular weight on acid number

Nevertheless this slight branching of the resins leads to a significant increase of cross-linking density in underbake conditions. The cross-linking density can be checked by determination of the xylene resistance of the film. During this test the baked film is penetrated for 10 minutes with xylene. 15 minutes after penetration the surface hardness of the film is measured by pendulum experiment (König). After 2h the measurement is repeated to control the regeneration of the film. The lower the cross-inking density is, the higher is the degree of decrease of hardness after xylene penetration.

Whereas the non-branched resin shows a strong decrease of hardness after xylene penetration, the branched resins show a very good xylene resistance.

Investigations on branched epoxy acrylates

For a better understanding of the process of branching several investigations were made. Besides the amount of acid in the monomer mixture also the speed of the different reactions, co-polymerization and addition is of importance. During synthesis of the binder different reactions will occur:

a) Copolymerisation of GMA

b) Copolymerisation of AA

c) Formation of a GMA/AA-adduct

d) Copolymerisation of the GMA/AA-adduct

e) Addition of an epoxyfunctional chain to a carboxyfunctional chain

To check which reaction dominates a comparative experiment was performed. If the reaction of GMA with AA is much faster than the co-polymerization, similar products would be achievable by substitution of AA against butanediol diacrylate (BDDA).

As can be seen in Figure 9, by using butanediol diacrylate both the weight and number average molecular are reduced dramatically. This observation leads to the conclusion that the co-polymerization is the faster reaction and the carboxy/epoxy addition takes place preferably only between already growing chains. Usually more than two chains are connected which leads to a broad molecular weight distribution.

The ratio of the reaction speed is depending on the reaction temperature.

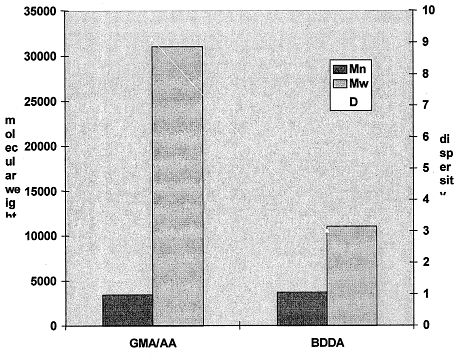

Figure 9. Use of BDDA versus GMA/AA

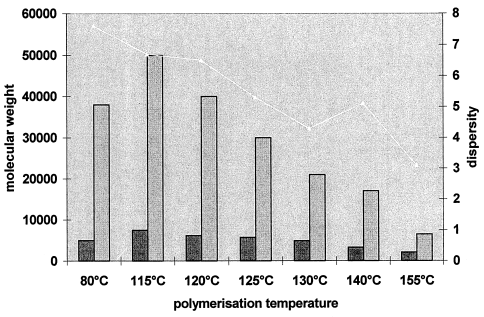

Figure 10. Influence of temperature

By elevating the reaction temperature from 80 to 155°C the molecular weight distribution is getting narrower (Figure 10). At higher temperatures the differences in reaction speed are smaller, so the weight average of molecular weight is reduced.

Incorporation of latent acidic groups

Another route to increased cross-linking density is the incorporation of latent acidic groups into the epoxy functional binder. The latent acidic groups are easily incorporated by co-polymerization of tertiary butylacrylate. This monomer has the attribute to decompose at elevated temperature especially in the presence of acid into isobutene and acrylic acid. During co-polymerization the acid content is too low to initiate the fragmentation. During baking in the presence of the highly acidic polyester the fragmentation takes place and additional carboxylic groups are generated, capable for additional cross-linking (Figure 11).

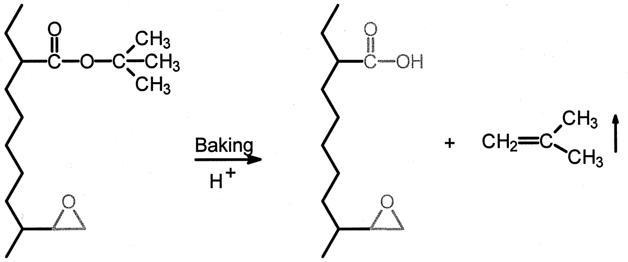

Figure 11. Latent acidic groups

The fragmentation of the tertiary butylester group can be easily observed via infrared spectroscopy. As can be seen in Figure 12 the absorption bands of the epoxy and the tertiary butylester groups decrease significantly during baking at 140°C.

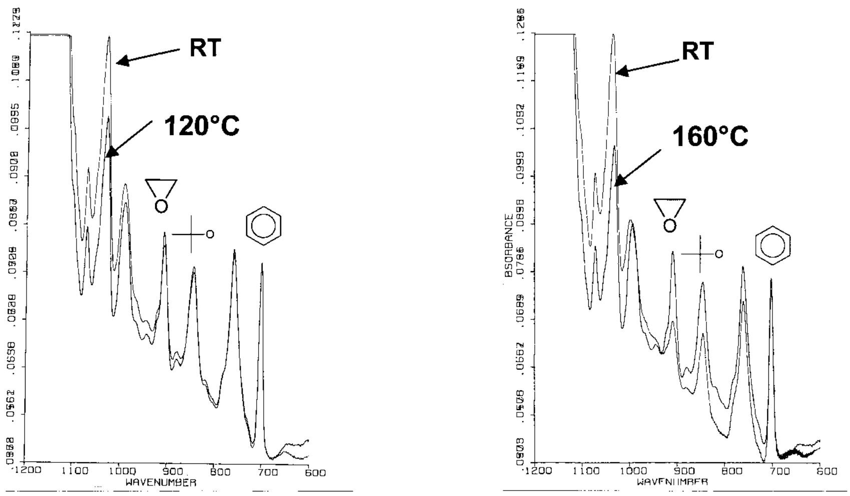

Figure 12. Fragmentation of tert.butylester group (Infrared Spectroscopy)

Etch and Scratch Performance

The superior performance of this optimized clear coat system has not only been proven by artificial etch tests but has also been demonstrated in outdoor exposure experiments in aggressive atmosphere. Whereas conventional 1K-TSA clears show significant etching in Jacksonville, the epoxy/acid clear coat hardly shows any damage. This clear coat shows the best performance in Jacksonville testing and can be compared with 2K clear coats.

Scratch resistance can be increased to up to 70% residual gloss after Amtec testing by implying the described techniques. Overall an excellent etch/scratch performance is achievable.

The concepts of this clear coat can be transferred to other cross-linking mechanisms. The sratch/etch performance of 2pack and 1pack clear coats can be increased significantly leading to new high performance systems with superior properties.

Conclusion

Mechanical properties like scratch resistance of a clear coat can be influenced by the cross-linking density and the flexibility of the coating. A combination of high cross-linking density with high flexibility of binder and/or hardener leads to increased scratch resistance. If these attributes are combined with a cross-linking reaction leading to cross-linking sites with high resistance against chemical attack the result is a high etch and scratch resistant coating.

References

[1] W. Schlesing, M.Osterhold, H.Hustert, C.Flosbach, farbe+lack, 101 (1995) S.277-280