

## **Zero-Emission Acrylic Thermoset Technology**

**Dr. Matthias Gerst, BASF SE, Germany**

**Dr. Bernd Reck, BASF SE, Germany**

**Dr. Gero Nordmann, BASF Corporation, USA**

### **Abstract**

Acrylic thermosets - thermally cross-linkable and emission-free - open new avenues to innovative composite materials.

In today's environment, there is an ever increasing desire to 'circle the square' reaching high-performance, durability, light weight and manufacturing flexibility without increasing or even trying to lower overall system costs. This presentation will discuss a new enabling technology platform engineered towards these ends: cross-linked acrylic thermosets. These are non-flammable zero-emission systems which contain no volatile or hazardous components at any stage of their life cycle. They are easy to use in molding processes and ideally suited for today's 'greener' light-weight automotive composites. Their application potential in natural fiber as well as other fiber composites will be outlined in the presentation.

Aqueous solutions and dispersions are available which cover a broad range of product properties and hence, the acrylic binders are suitable for a great variety of different applications, especially where high binding strengths, heat and water resistance are required. The main features of the acrylic binders such as their chemical composition and curing behavior will be explained in detail, followed by two examples for selected applications: First, glass fiber bonding with an acrylic resin solution and second, natural fiber bonding with an acrylic resin dispersion.

### **Chemistry of acrylic binders**

Thermoset binders like formaldehyde-, epoxy- or polyurethane-resins are used in numerous nonwoven and composite applications where high binding strengths, heat and water resistance are required. The industry is trying its utmost to manufacture low odour and low emission products and this results in an additional demand for new phenol and formaldehyde free binder systems. Therefore, a new innovative class of thermoset acrylic resins has been introduced and protected with various patent applications by BASF under the trade name Acrodur®. The acrylic resins are available as aqueous solutions and as dispersions. The concept of the new thermoset class is based on thermally curable aqueous solutions of an acrylic-maleic acid copolymer with a hydroxyl group functional cross-linker. In the dispersions, modified thermally curable aqueous solutions are combined with classical emulsion polymers. Hence interesting new property profiles and applications can be created. Especially hydrophobic properties for water and moisture resistance and flexible/tough properties can be incorporated.

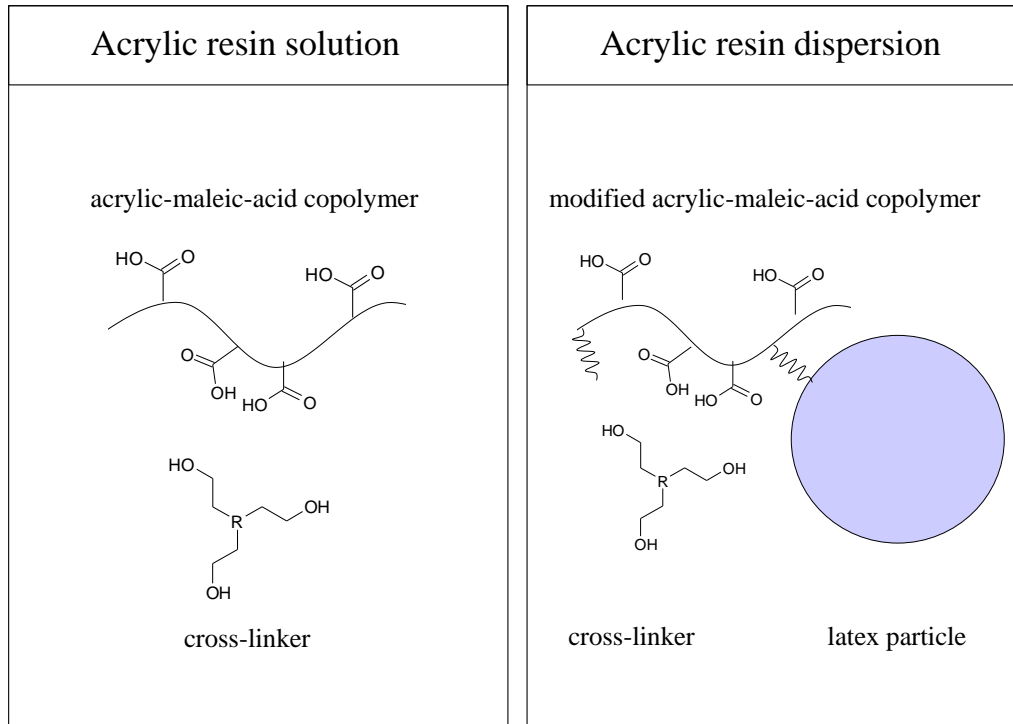


Figure 1: Concept of acrylic resin solutions and dispersions

The acid copolymers can be synthesised in water with standard free-radical-initiated chain polymerization. The copolymers under consideration are prepared from acrylic acid and maleic acid. Standard techniques can be used to adjust the degree of polymerisation, e.g. by variation of the initiator content or the polymerisation temperature. Molecular weights from  $M_w=1.000-500.000$  g/mol are achievable. Finally, a hydroxyl containing cross-linker with at least two hydroxyl groups is added. Suitable cross-linkers are e.g. glycerine, triethanol-amine or even polymeric cross-linkers.

Classical emulsion polymerisation techniques can be used for the preparation of these dispersions. <sup>[1]</sup> One possibility is the semi-continuous process, where the radical initiator and the monomers could be added continuously or in increments to the acid copolymer.

Prerequisite for this approach is the use of a specially modified acid copolymer with protective colloid properties in order to provide sufficient stability. Typically, the ratio of the acrylic acid copolymer and the latex particle is 1:1. The product properties can be varied in a broad range by simply changing the amount or type of monomers in the latex particle. Suitable monomers are acrylic acid esters, styrene, butadiene or functional monomers. Therefore new features such as stiff or flexible and hydrophobic properties can be incorporated into the acrylic binder.

### General properties

Two acrylic resin solutions and two acrylic resin dispersions are commercially available. The solids content of these aqueous one-component systems are 50%. Under normal conditions the products are stable when stored. In addition they are also miscible with water at any ratio. The pH value is around 4 due to the acid copolymer. In the case of the aqueous solutions the viscosity depends of the molecular weight of the polymers. The higher the molecular weight the higher the viscosity due to the pronounced entanglement of the polymer chains in the solution. The viscosity of the dispersions is generally lower due the latex content part. The acrylic resin solutions have different molecular weights,  $M_w=12.000$  g/mol and  $M_w=80.000$  g/mol, respectively.

The dispersions are composed of 50% modified acrylic acid copolymer and 50% latex particles. They differ in the composition of the latex particle: one has a high glass transition temperature ( $T_g$ ) of about 100°C for stiff thermoset properties, and the other a  $T_g$  of 25°C for tough-flexible thermoset properties. The particle size of the latex was intended to be relatively small with about 80 nm to ensure high binding strengths for the substrates.

Figure 2: General properties of acrylic resins

General properties of available products	Acrylic resin solutions	Acrylic resin dispersions
Storage stability	one component	one component
Miscibility with water	$\infty$	$\infty$
Solids content [%]	50	50
pH value	4	4
Viscosity [mPas]	300-1500	300-1000
$M_w$ [g/mol]	12.000 and 80.000	high
Latex particle	-	$\approx$ 50% of binder mass
	-	$T_g$ : 100°C (stiff)
	-	$T_g$ : 25°C (though/flexible)
	-	particle size $\approx$ 80 nm

### Curing behaviour

The aqueous binders are simply applied to the substrate by impregnation, spraying, rolling, dipping or using the blow line technique. After drying and before curing, the acrylic resin solutions and the dispersions still exhibit thermoplastic properties. The softening point is in the range of 50°C dependant upon the residual water content. The residual water acts as a plasticizer and supports the processing where thermoplastic properties are needed. Since the curing starts significantly at temperatures above 120°C storable semi-finished goods can be produced.

Upon curing at temperatures above 120°C ester bonds are formed due to the condensation reaction between the acrylic acid-copolymer and the hydroxyl groups. The individual polymer chains of the acid copolymer become irreversibly joined to form a three-dimensional network. The polymer properties change from a thermoplastic to a thermoset polymer, heat resistant and water insoluble material. The curing reaction is completed in less than one minute at curing temperatures of about 200 °C. Longer reaction times are usually needed at lower temperatures.

The transition from the thermoplastic to the cross-linked state can be readily followed using a dynamic-mechanical thermo analysis. Upon heating a sand bar (quartz sand F34) with 5% uncured acrylic resin from room temperature up to 200°C (2°C/minute) one could observe firstly a decrease of the modulus at approximately 50° followed by an increase of the modulus at about 110°C due to the cross-linking reaction (Fig. 3a). The increase of the modulus indicates clearly the behaviour a classical themroset materials, e.g. phenol formaldehyde resins. <sup>[2]</sup> Once cured, the acrylic resins show permanently the thermoset characteristics, which means, that no softening point or loss in modulus is observed by reheating the resin again. In the case of the acrylic resin dispersions only the  $T_g$  of the latex particle can be detected (Fig. 3b).

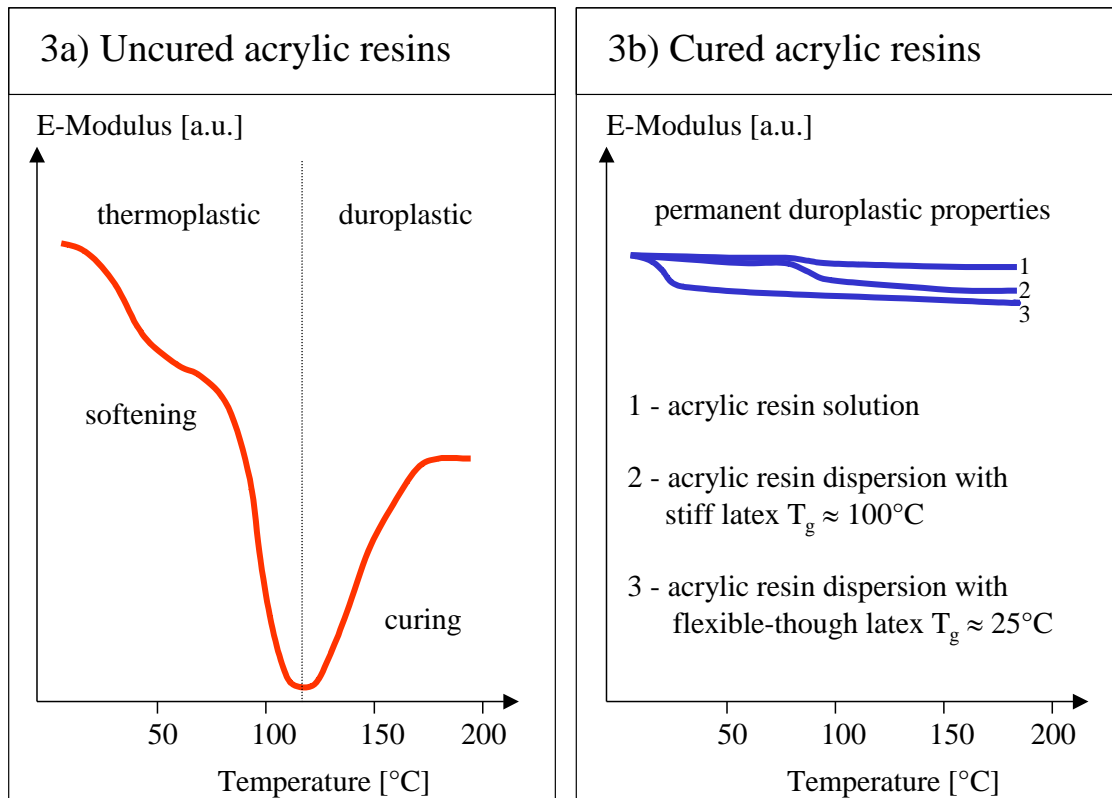


Figure 3: DMA analysis of uncured and cured acrylic resins. <sup>[3]</sup>

Figure 3a) DMA response while heating a specimen composed of quartz sand (F34) bound with 5 wt.-% of uncured acrylic resin from room temperature to 200°C. Heating rate 2°C/minute. The behaviour of acrylic solutions and of acrylic dispersions is comparable. Hence only one representative curve is depicted.

Figure 3b) DMA response of cured quartz sand specimen (1h, 150°C).

IR spectroscopic investigations indicate that the ester bonds are formed through cyclic anhydride structures as reactive intermediates. Figure 4 shows the carbonyl bands of three IR spectra of an acrylic resin solution. The IR spectra were detected at room temperature with samples cured at different temperatures (100°C, 175°C, 200°C). Clearly, the absorption of carboxylic acid, ester and anhydride groups can be identified. With increasing temperature, which means advanced cross-linking, the signal of the free carboxylic acid disappears in favour of an ester signal. Furthermore, especially at higher curing temperatures, signals of anhydride structures can be observed. It is known from the literature that such cyclic anhydride structures are reactive intermediates. Compared to the free carboxylic groups, these anhydride groups can react more quickly with the hydroxyl group to give an ester. <sup>[4]</sup>

Accordingly to these observations one can conclude the following reaction mechanism: At higher temperatures, the anhydride ring is formed followed by a nucleophilic attack of the hydroxyl group. This reaction is acid catalyzed, since the reaction velocity sharply decreases at pH values above 5. In general, no other additional catalysts are needed. Interestingly, IR spectroscopic studies on homopolymers of acrylic acid revealed that the maleic anhydride ring is formed much faster and at lower temperatures. This explains why the reactivity of maleic acid containing copolymers is higher compared to the homopolymer of acrylic acid itself.

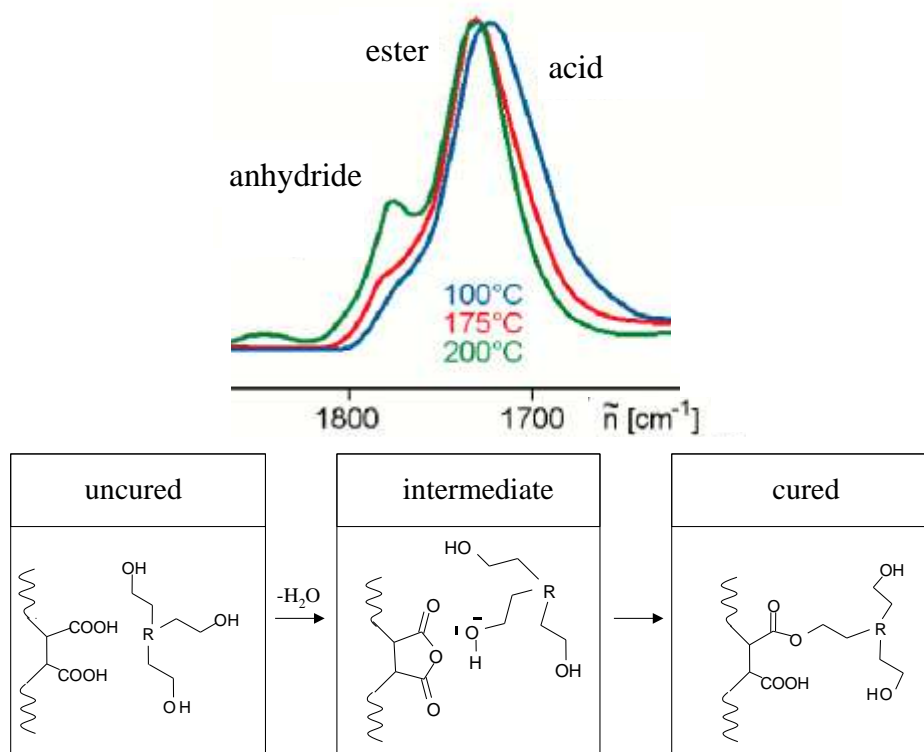


Figure 4: Model for curing mechanism

## Polymer films

The acrylic resins form thermoplastic clear polymer films already at room temperature, even though the glass transition temperature of the acrylic maleic acid copolymers is above room temperature. This observation can be explained with the plastification of the copolymers with water.

Once cured - after drying - the acrylic resins show classic thermoset properties such as heat or solvent resistance. The polymer films of the acrylic resin solutions can be fully cross-linked without any thermoplastic parts left. They give hard polymer films with high tensile strength and heat resistance. On the other hand, the acrylic resin dispersions show different properties due to the remaining thermoplastic latex particle in the cured polymer film. A high  $T_g$  of the latex of 100 °C yield stiff duroplastic polymer films, a lower  $T_g$  of 25 °C yield tough-flexible duroplastic polymer films. Compared to the acrylic resin solutions, a high performance level concerning the water uptake and climate or moisture resistance can be achieved even at low curing temperatures of about 120°C. An overview about the fine tuned product portfolio with its film properties is given in figure 5.

Figure 5: Polymer film properties

Furthermore, the comparison of the film properties of the acrylic resin dispersions before and

	solutions	dispersion $T_g \text{ latex} \approx 100^\circ\text{C}$	dispersion $T_g \text{ latex} \approx 25^\circ\text{C}$
film formation	RT	RT	RT
stiffness ( $180^\circ\text{C}/30'$ )	++	+	<b>0</b>
flexibility ( $180^\circ\text{C}/30'$ )	<b>0</b>	+	++
water resistance ( $120^\circ\text{C}/30'$ )	-	+	+
	( $180^\circ\text{C}/30'$ ) ++	++	++

after curing gives interesting insights. The polymer films were investigated with transmission electronic microscopy (TEM) after staining the polymer with  $\text{OsO}_4$ .<sup>[5]</sup> With this technique the acrylic copolymers are more “coloured”, which means more contrast for the picture. The latex particles are less “coloured”. On the left side of figure 6 one can see the polymer film of the acrylic resin dispersion (example with the  $T_g$  of the latex particle of about  $100^\circ\text{C}$ ) only dried at room temperature. The small spherical latex particles with less than 100 nm in diameter are embedded in a continuous matrix of the acrylic resin solution. Upon heating the polymer film above the glass transition temperature of the latex particles they start to flow under the formation of a second continuous phase. Especially such bi-continuous phases, which remain in the cured polymer film, are known to exhibit synergistic and outstanding properties.

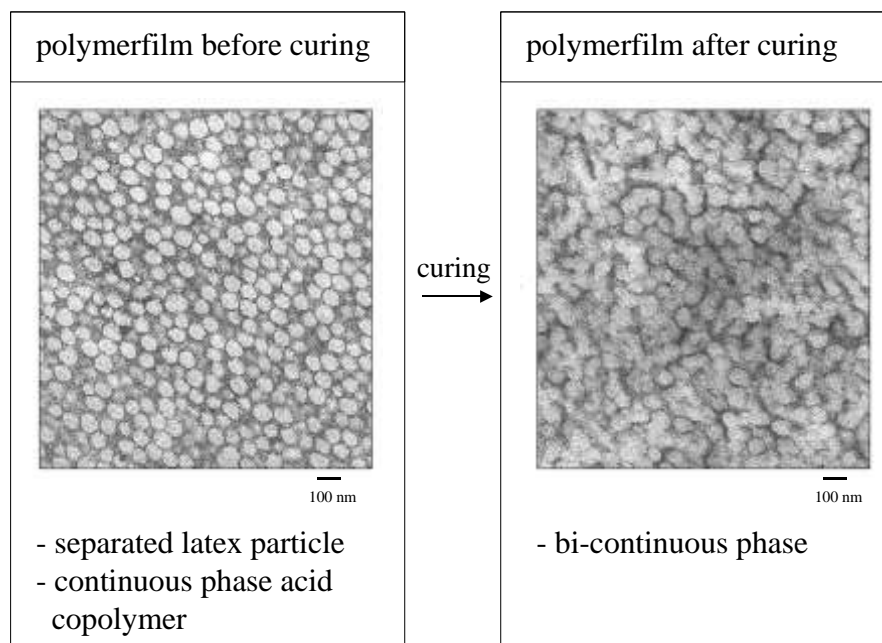


Figure 6: TEM-pictures of polymer films with acrylic resin dispersions before and after curing ( $T_g \text{ latex particle} \approx 100^\circ\text{C}$ ).

## Applications

From the numerous possible applications, two selected examples will be presented. Firstly, the use of acrylic resin solutions as binders for glass or mineral fibers will be discussed. The most common applications here are “heat insulation materials” and “glass fiber mats” for wet laid glass mats, e.g. for PVC flooring.

For the production of heat insulation mats the binder can be applied by spraying the diluted acrylic resin solution onto the glass fibers during the fiber spinning process. After collecting the fibers on a conveyor belt to a mat, the acrylic resin can be cured within one minute at 200°C. The wet laid glass mats can be bath impregnated or sprayed with binder and cured afterwards in a hot air oven. For both applications the acrylic resin solutions can be used in existing production processes.

The main requirements for the binder after the curing are a high binding strength and a high heat resistance. As shown in figure 7 (example of an impregnated glass mat with 20% binder, dried and cured at 200°C for 2 minutes) the acrylic resin solution equals the performance compared to a phenol formaldehyde resin. The binding strength at room temperature, at high temperatures (heat resistance at 180°C) and after under “wet” conditions (3h in water at 80°C) is at least comparable to PF resins. This indicates clearly the thermoset behaviour of the acrylic resins.

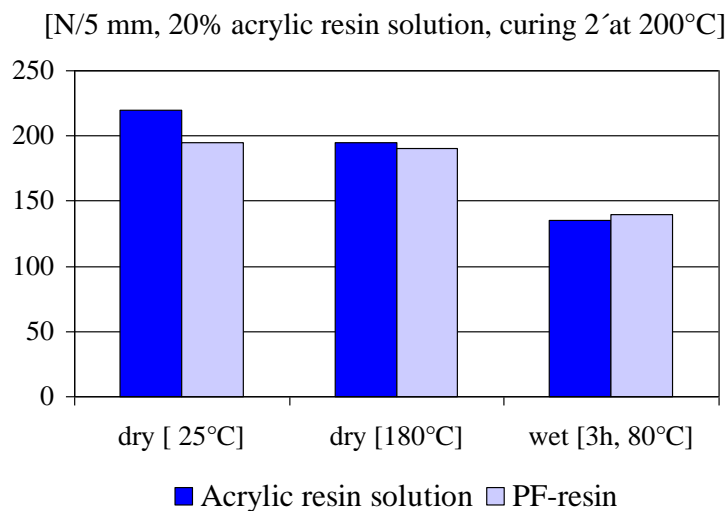


Figure 7: Example for an acrylic resin solution: bonding of glass fibers

An example of a suitable application for acrylic resin dispersions is the binding natural fibers such as wood, flax, hemp or sisal. <sup>[6]</sup> A typical example of such an application is the production of shaped panels for automobile interiors. For this purpose, both acrylic dispersions are suitable, e.g. the “stiff thermoset” version for high tensile strength and the “flexible-tough thermoset” version for high impact resistance.

Each raw material can be resinated in different ways. Wood fibers are impregnated with the resin using the “blow line” technique and can be further processed to fiber mats. Sufficient binding strength is achieved with 10-15% binder. With other natural fibers like flax, hemp or sisal, preformed mats are impregnated with the acrylic resin dispersion. The optimum binder content for these fibers is about wet 30-35%.

Both methods give pre-bond fiber mats with good storage stability and thermoplastic deformability. During the final hot press step, the desired shapes are formed and the resin is cross-linked. Typical curing conditions are 180-200°C for approximately one minute.

They show high stiffness and strength and meet the ecological requirements of the automotive industry. Finally the composite parts can be laminated with decorative foils to yield automotive interior parts, e.g. door trims, dash boards or seat backings.



Figure 8: Application example for acrylic resin dispersions: bonding of natural fibers

Besides the two examples, bonding of glass fibers with acrylic resin solutions and the bonding of natural fibers with acrylic resin dispersions, a great variety of other natural and man-made fibres of the nonwoven industry or even granulated materials can be bonded with the new binder system (e.g. PET-fibers, cork, sand). Furthermore, a wide range of tailor made binder properties can be obtained by formulation, e.g. by blending with polymer dispersions, reactive additives like epoxides or silanes, wetting agents, defoamers or water repellents.

## Summary

Acrylic thermosets - thermally cross-linkable and free of formaldehyde and other emissions - offer new routes to innovative composite materials.

Different aqueous products are available: resin solutions and resin dispersions. The aqueous binders are simply applied to the substrate by impregnation or spraying. After drying and before curing, the acrylic binders still exhibit thermoplastic properties. Upon curing at temperatures above 120°C, ester bonds are formed. The polymer properties change from a thermoplastic polymer to a thermoset, heat resistant and water insoluble material. Depending on the products, stiff thermoset to flexible/though thermoset polymer films are available. The acrylic binders cover a broad range of product properties and hence a whole series of different applications for the composite industry is obtainable. The two examples presented, mineral fiber bonding with an acrylic resin solution and natural fiber bonding with an acrylic dispersion highlight this.

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