Eco-Friendly Acrylic Copolymers Offering Clean Manufacturing, Reduced VOC Emissions, Excellent Performance

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Abstract

A new (to North America) family of cross-linkable acrylic-copolymer binder resins is providing unique new opportunities for the production of durable, eco-friendly composites and nonwovens with comparable or improved performance vs. common thermoplastic and thermoset offerings in a variety of industries. Already used in Europe for automotive interior components, cork flooring, and various nonwoven fabrics, the technology is thermoplastic in its "B-stage," and of very-low viscosity, allowing for easy impregnation of a wide variety of fibrous and particulate reinforcements. This allows for the production of resin-impregnated fiber- or particulate reinforcements (rather than fiber-reinforced resins). These resin-impregnated reinforcements, in turn, may be used to produce either nonwoven fabrics, or thermoplastic prepregs or semi-finished goods, which subsequently are cured to form very-durable thermoset composites with excellent thermo-mechanical and physical properties. A range of formulations offers the opportunity to control ductility and stiffness of the resultant composite. Unlike most thermosets, these polymers neither contain any hydrocarbon solvents or other volatile-organic compounds (VOCs), nor produce toxic emissions during cross-linking, so no special air-handling equipment is required during processing. In fact, the only reaction by-product is water. Since they do not contain VOCs, emissions from cured components are greatly reduced, protecting air and water quality during the life of the product. Because the specific gravity of these composites even with 70% natural-fiber reinforcement is less than 1.0, they are capable of producing very-light components with excellent properties and are hence well suited for today's "greener" technologies. This paper will provide an overview of the technology, how it is typically used, and will show components from multiple industries in which the material is currently used

Pressures for Greener Materials of Construction

Interest in "green," more-sustainable products and technologies is very strong as the first decade of the twenty-first century draws to a close. In part, this is probably a reaction to the record petroleum and natural gas prices seen in 2008, but it is also likely a result of members of "Gen X and Y" coming to power in the workforce and marketplace, as well as increasing concerns in many countries over resource shortages and global climate change. Regardless of the cause of the market pressures to find more sustainable products, this can be an excellent opportunity for OEMs and their supply chain if the right materials and processes are found to produce functional components without sacrificing performance or paying a significant cost penalty.

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New trends enforcing more stringent interior air-quality standards in many industries are drawing attention to VOC emissions from plastics, which in turn is leading to scrutiny of both resin and additive systems. Additionally, growing interest in the use of bio-based resins and natural-fiber reinforcements – both of which help reduce the overall carbon footprint of components (thanks to the carbon sequestration that occurred during the life cycle of plants from which both are derived) – is also on the rise. Furthermore, in energy-intensive industries like ground transportation, which reportedly accounted for 28% of all U.S. energy consumption in 2008[2], there is great interest in reducing the mass of vehicles (and their materials of construction) in order to increase fuel economy and decrease greenhouse-gas emissions.

A new copolymer system developed in Europe[3] and now available globally for use in the production of nonwovens and polymer composites offers many benefits vs. traditional thermoplastics and thermosets with regard to meeting these pressures for "greener" materials of construction as will be described in this paper.

Combining the Best of Thermoset & Thermoplastic Matrices

Previously, there have always been tradeoffs between thermoset and thermoplastic matrices, with each chemistry providing specific benefits and challenges depending on the needs of a given application and processing method. To an extent, some of this need to compromise has been eliminated with the development of this new family of acrylic copolymers, which – owing to its unique chemistry and resultant properties – offers the convenience and lightweight versatility of thermoplastics and the durability and thermo-mechanical performance of thermosets at different stages of the production process. This makes these materials ideal for production of new "green" composites and nonwovens for use in a wide variety of industries.

Generally, thermoset matrices – owing to their ability to cross-link under specific conditions – offer greater resistance to thermal, mechanical, and chemical stresses than do thermoplastics, producing durable products with long service life. And since many thermosets are available in the form of very-low viscosity liquids prior to cross-linking, they are able to offer extremely long flow lengths and good wetout of reinforcements at low pressures to produce low-stress moldings, depending on the chemistry and processing method used. Some thermosets are highly viscous solids in their "B-Stage" prior to cross-linking, so allow the production of semi-finished goods prior to forming and cross-linking, although generally these must be refrigerated and have a limited shelf life in this form.

Thermoplastics, on the other hand, having already being prepolymerized by the resin supplier or compounder, possess a nearly unlimited storage life as long as temperatures do not approach their softening point. Since they must be pre-melted prior to processing, and many must be pre-dried prior to melting / softening, the viscous liquids they become require elevated temperatures and pressures to form into finished goods. On the other hand, they can be softened, formed, and solidified multiple times in high-speed, mostly automated production processes and provide excellent surface aesthetics right out of the tool, reducing or eliminating many of the secondary operations required for thermoset resins.

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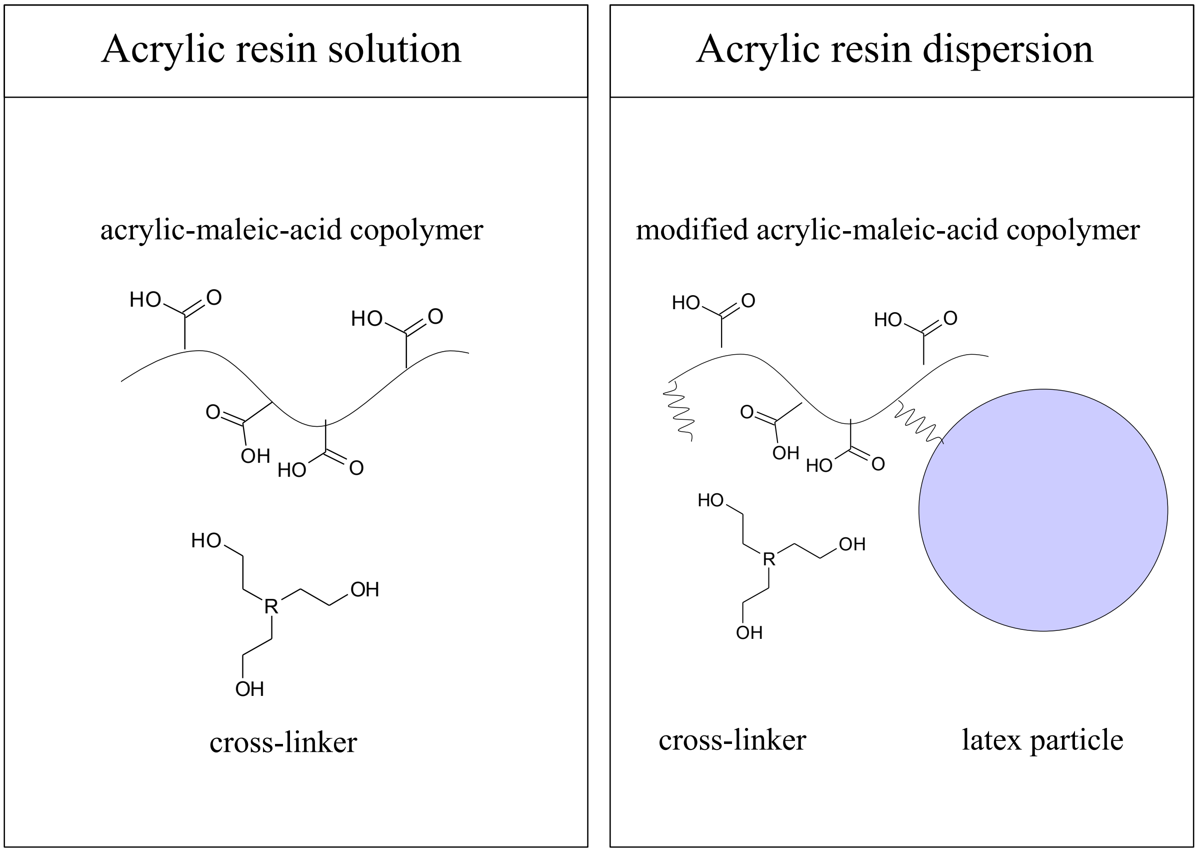
[2] http://kec.kansas.gov/energy_plan/09Plan-Ch10-Overview.pdf , *which reports that of this roughly one-third of all U.S. energy consumption is used by the transportation sector (with 61% of that amount being consumed by personal vehicles and another 19% being consumed by commercial trucks). Over the past decade, energy consumption within the transportation sector has outpaced all other sectors other than the commercial sector, with which it was tied.*

[3] *This patented technology was developed and is produced by BASF SE under the tradename Acrodur®.*

A new class of resins based on acrylic copolymers offers the convenience of thermoplastics and the durability of thermosets in a very-clean manufacturing process that answers many of the emerging needs for cleaner, greener materials of construction in a wide variety of industries.

Chemistry Makes the Difference

This new class of thermally curable thermosets was originally developed as binder resins for the nonwovens industry. The base products are comprised of acrylic-acid copolymers plus latex (in particulate form) in a 1:1 ratio. However, the ratio of latex and the ratio and/or types of monomers (e.g. acrylic-acid esters, styrene, butadiene, or other functional monomers) can be varied to create products with a broad range of properties. Additionally, standard techniques can be used to adjust the degree of polymerization and produce molecular weights between M_w=1,000–500,000 g/mol. Hence, from this versatile chemistry come products in two form factors – aqueous solutions and aqueous dispersions – that offer a wide range of properties. Simplified diagrams of the basic structure of both form factors are provided in Figures 1a & 1b.



Acrylic resin solution

Acrylic resin dispersion

Figures 1a & b: Simplified structure of acrylic resin solutions and dispersions

Because of the presence of the acrylic acid, the pH of both dispersions and solutions is approximately 3.5-4.0 depending on formulation. Viscosity of the aqueous solutions is dependent on the molecular weight of the polymers involved; as would be expected, the higher the molecular weight, the higher the viscosity is due to extensive chain entanglement. Dispersions, on the other hand, have lower viscosity due to their 50% latex content. Size of the latex particle is relatively small (≈ 80 nm) to ensure high binding strengths with substrates / reinforcements. In fact, once cured, the copolymer and latex form an interpenetrating polymer network. Two compositions with different latex particles are available for the dispersions: one with a higher T_g of about 100C (which yields cured thermosets with good stiffness) and the other with a T_g of 25C (which yields thermosets with good toughness properties).

In each case, the copolymers are a one-part and thermally cross-linkable system, so no mixing or addition of catalyst is required prior to cure. Unlike many common thermosets with which they compete, these products are completely free of hydrocarbon solvents, formaldehyde, phenol, and isocyanate, and other VOC sources, so they do not require special air-handling systems during processing, nor do they contribute to VOC outgasing once cross-linked. In fact, the only by-product of cure is water. This makes them safer for workers to handle, and better for the environment and for consumers who will use products containing the cured polymers. In fact, recent 03150 small-chamber emissions testing per California Air Resource Board (CARB) requirements for indoor air quality on the parent grade of this resin family verified that there were zero (0) emissions from the neat, uncured acrylic copolymer film. Since the resins are infinitely miscible in water prior to cross-linking, cleanup is also fast and easy, further eliminating the need for solvents.

Thermoplastic (Pre-Cured) Films

One of the unique properties of this chemistry is that the acrylic binder resins are thermoplastic in their “B-stage” prior to curing, and therefore offer the opportunity to produce thermoplastic resin-impregnated reinforcements at room temperature. This is possible at such a low temperature because these are solution / dispersion polymers and water acts as a plasticizer. Of course, once dried and subsequently thermally cross-linked, the copolymers behave like classic thermoset resins, with good mechanical properties and high thermal and chemical resistance.

The ability to produce thermoplastic films as an intermediate product enables the production of glass-, carbon-, or natural-fiber reinforced thermoplastic prepregs, and semi-finished goods like films, blanks, rollstock, and even sandwich panels. No refrigeration of the prepregs is required, as with thermosets like sheet-molding compound (SMC) or bulk-molding compound (BMC), and the shelf life of these semi-finished goods is in principle unlimited as long as they are kept in their original packaging, which allows a specific moisture content to be maintained. (Not only does the water in the film act as a plasticizer, but some of it also functions as an initiator to start cross-linking.) By eliminating typical storage and shelf-life issues, the acrylic binder resins reduce energy usage and waste.

Polymer film produced from the aqueous solutions of this polymer family can be fully cross-linked with no residual thermoplastic regions left unconverted. Hence, these cured films yield thermoset products with high tensile strength and thermal resistance plus high durometer.

In contrast, the aqueous dispersions with latex yield cured products with different properties because the latex remains thermoplastic after the acrylic copolymer cross-links. This is further modified depending on which type of latex particle is used in the emulsion. The higher T_g latex produces a cured plastic with high stiffness; the lower T_g latex produces a cured plastic that has good impact strength (toughness) and ductility. Additionally, both forms of dispersions offer greater hydrolytic stability than the films produced from the solution.

A simplified summery comparing the relative properties of the cross-linked polymers that result from the solutions and dispersions (with low and high T_g latex emulsions) are given below in Table I.

Table I: Relative Properties of Cured Polymers from Solutions & Dispersions

Form Factor	Aqueous Solutions	Aqueous Dispersions (High-T_g Latex (100C))	Aqueous Dispersions (Low-T_g Latex (25C))
Temperature for Film Formation	Room Temperature	Room Temperature	Room Temperature
Stiffness (Cured at 180C for 30 s)	**++**	**+**	**0**
Flexibility (Cured at 180C for 30 s)	**0**	**+**	**++**
Hydrolytic Stability			
(Cured at 120C for 30 s)	**–**	**+**	**+**
(Cured at 180C for 30 s)	**++**	**++**	**++**

The morphology of the acrylic-acid film produced from the latex dispersions is also interesting. Figures 2a & b below show transmission-electron micrograph (TEM) images of a dispersion film (formulated with the higher temperature latex particle) prior to cure (left) and after cross-linking (right). To enhance contrast between the acrylic copolymer and latex phases, the pre-cured polymer was stained with OsO_4.[5]. In the images, the acrylic copolymers are "darker" and the latex particles are "lighter" in shade. In the pre-cure image on the left, the small, spherical latex particles (less than 100 nm in diameter) are embedded in a continuous matrix of the acrylic resin solution. In the post-cure image on the right, the polymer film has been heated above the T_g of the latex particles, causing what previously had been two distinct phases to begin to merge, forming a second, continuous phase, which persists in the cured polymer.

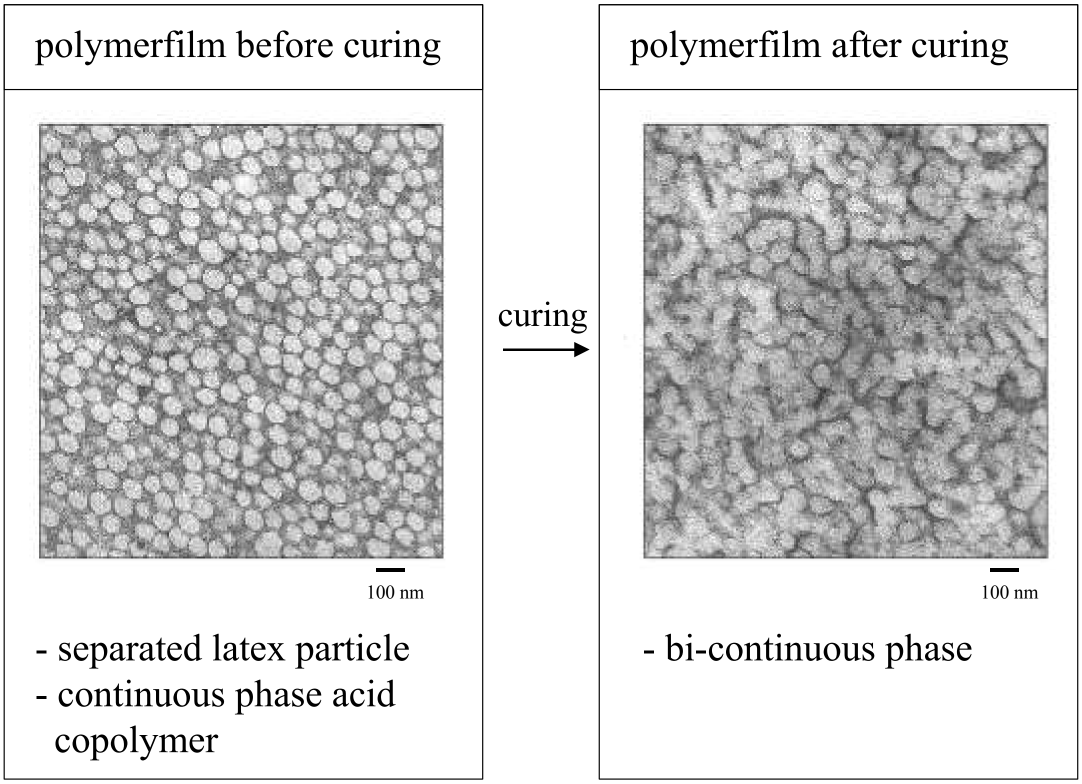


Figure 2: TEM images of polymer films produced with acrylic resin dispersions before and after curing (using latex particle with higher T_g*)*

Wetout / Encapsulation of Reinforcements

Another useful property of the acrylic copolymers is that while they are still dispersions / solutions, their low viscosity and unique chemistry lead to high wetout of fibrous or particulate reinforcements. In fact, they form chemical (covalent) as well as mechanical (van der Waals) bonds with their reinforcements, creating a true interpenetrating network between matrix and reinforcement. Therefore, at a nano level, the result is a unique new material that is different from the resin and reinforcement that were the initial inputs. The resultant high bond strengths allow for the production of thermoplastic films with quite high reinforcement / resin ratios, and this ratio shifts even higher once the polymer is cross-linked and residual moisture is released. In turn, this helps produce composites and nonwovens with high reinforcement levels – what is essentially a resin-reinforced fiber mat rather than fibrous-mat reinforced resin. With this system, it is possible to produced molded parts that either have a resin-rich surface (at lower reinforcement loading levels) or a fiber-rich surface (with higher fiber loading levels), the latter which is somewhat permeable to air. This has proven advantageous for applications in the automotive industry, for example, where the molded part is subject to secondary operations that vacuum-form a vinyl skin / foam laminate over the substrate. Because of the porous nature of the parts, no laser drilling of holes is required prior to vacuum lamination, which saves process steps, time, and money. In the cork flooring industry, the ability to have a particle-rich surface contributes to production of cork tiles that have a warm, natural look and feel, yet have the enhanced durability and cohesiveness that the resin brings. A further benefit this high-reinforcement / matrix ratio brings in applications reinforced with carbon-sequestering natural fibers is that it helps reduce the amount of non-renewable content (petroleum-based polymer) and therefore the overall carbon footprint of the final part without sacrificing performance (and in some cases aesthetics). Cost may also be reduced in such cases.

Additionally, the excellent wetout / encapsulation of reinforcements provides opportunities either to increase mechanical performance at comparable wall thickness (vs. common thermoplastics or thermosets that are being replaced), or to reduce costs and weight by going to thinner walls. With a specific gravity of less than 1.0 even with 70% natural-fiber reinforcement, there is an excellent opportunity to reduce component mass with the resins. The excellent performance of these parts also increases their use life and may enable them to perform in more challenging environments. Finally, owing to the excellent wetout of these resins on fibrous or particulate reinforcements, there is an opportunity to reduce or eliminate coupling agents and their resultant VOC emissions, odor, and fogging.

Production & Curing of Thermoplastic Films

Generally, the aqueous binder resins will be applied to a reinforcement or substrate via impregnation (bath), spraying, rolling, dipping, or by the blow-line technique common with wood-fiber-based composites. Once the reinforcements are coated or impregnated, the resultant thermoplastic film may be allowed to dry prior to rolling / cutting and wrapping in an airtight package to maintain the residual moisture content, or it may be cured right away. Depending on the final moisture content of the thermoplastic film, its softening point will be ≈50C, allowing it to be handled and shaped if subsequent processing requires thermoplastic properties (deformability) prior to achieving cross-linking at temperatures above 120C (to a maximum of 200C) as would be the case with a molded composite rather than a nonwoven fabric.

Once cure temperatures are reached, a condensation reaction occurs and, as noted previously, a highly 3D, interpenetrating network between matrix (now with thermosetting properties) and reinforcement is formed. This yields parts with high thermal and chemical resistance and – depending on the formulation – either high stiffness or excellent toughness. Higher temperatures produce faster cure times. At 200C, the reaction is complete in <1 min. Figure 3 shows dynamic mechanical analysis (DMA) curves of the uncured (thermoplastic) and cured (thermoset) behavior of the acrylic binder resins.

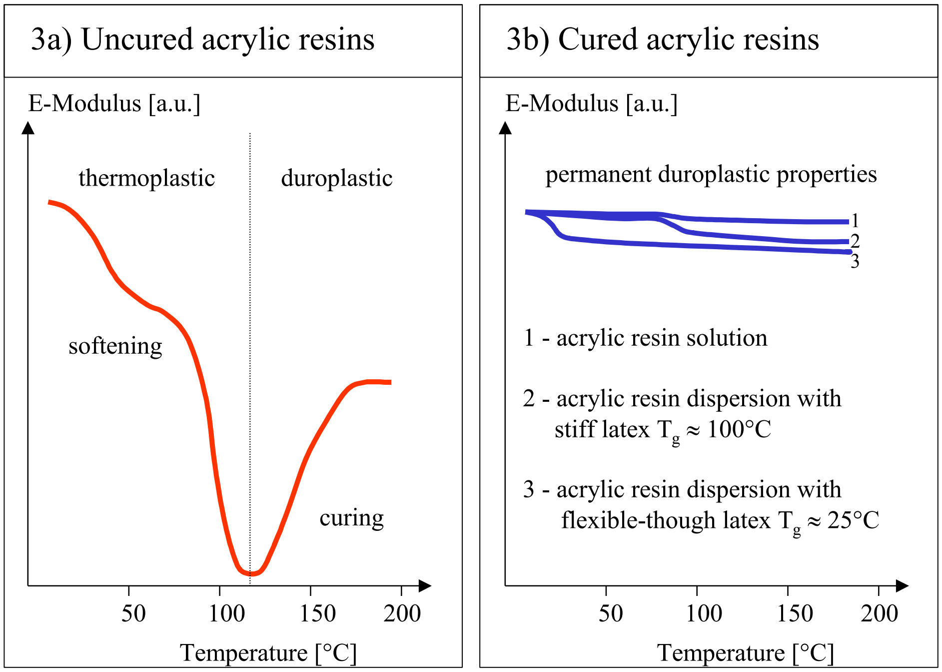


Figure 3: DMA analysis of uncured (left) and cured (right) acrylic resins. [3]

How the Aqueous Solutions & Dispersions are Typically Used

One important note about the solutions and dispersions: any substrate (reinforcement) may be used with any grade of these aqueous solutions or dispersions depending on the final properties that are desired. With this polymer system, it is not the process or substrate that determines the resin grade selected, but rather the final cured properties. In the case of a nonwoven such as production of a thermal-insulation material, the aqueous acrylic resin solution will typically be diluted sufficient to be sprayed, then applied to glass or mineral fibers during the fiber spinning process. The coated fibers will then be collected on a conveyor to form a mat, which is then heated at 200C for 1 min. to cure the resin. Similarly, in the case of wet-laid fiber mat, which is used as backing for vinyl flooring, mats can be either bath impregnated or sprayed with the acrylic resin solution and cured in a hot-air oven. In these applications, the acrylic resins provide high binding strength and thermal resistance and typically replace phenol-formaldehyde resins at comparable performance while eliminating VOC emissions during processing and during the use life of the product

In contrast, the production of a natural-fiber-reinforced composite for an automotive interior component would use the acrylic resin dispersions. If the application required high stiffness, the dispersion with the higher T_g latex particles would be selected; if the application needed high impact strength and a measure of flexibility / ductility, then the dispersion with the lower T_g latex particles would be more suitable. Nearly any type of natural fiber (e.g. wood, flax, hemp, sisal, etc.) or particle (e.g. wood flour) can be used. Low-aspect ratio wood fiber would typically be impregnated via the blow-line technique and then further processed into fiber mats. For such an application, 10-15% (dry weight) binder will provide sufficient bond strength. For longer (higher aspect ratio) natural-fiber reinforcements (e.g. flax, hemp, or sisal), pre-formed mats are typically bath or dip impregnated using the acrylic resin dispersion. In such applications, 30-35% (dry weight) binder content is sufficient. Each method produces pre-bonded fiber mats with good storage stability and thermoplastic deformability. These thermoplastic prepregs will typically be shaped via compression molding in a heated tool. Unlike glass-mat thermoplastic (GMT) composite sheet products, there is no need to preheat the blanks (via infrared or convection ovens) prior to molding, saving process time and space as well as energy use. As previously mentioned, the only by-product of cross-linking is water, which must be vented from the tool during the molding cycle. Typical cycle times are on the order of 45-60 s for a door panel inner, for example, which is comparable with that for GMT and much faster than is typical for urethane, SMC, or BMC. Faster molding cycles help reduce energy usage and the cost of finished parts. Since they contain no VOCs, no emissions must be managed from the resin during prepreg production, part molding, or part use life.

There are a great number of other synthetic or natural fibers and particles that can be bonded with the acrylic resin solutions or dispersions, including PET fibers, cork, sand, etc., to produce products as diverse as filtration media and flooring products. Additionally, properties can be further tailored by manipulating the formulation (e.g. by blending with polymer dispersions, reactive additives like epoxides or silanes, wetting agents, defoamers, or water repellents). With such versatile and clean chemistry, numerous applications could benefit from use of these resins.

Limitations

Although this exciting new resin family provides unique opportunities to produce “greener” products (owing to elimination of VOCs and reduction of time and energy during processing), it is not be appropriate for all applications and processing methods. For example, because the products are currently available only as aqueous solutions or dispersions, they cannot be processed via pultrusion or extrusion. Their pre-cure viscosity is so low that they would not be practical for injection molding, particularly since the solutions / dispersions contain significant water that would need to be flashed off during the molding cycle, possibly creating voids in the finished product. While the cured polymers are not melt-reprocessable at end of part life, it is easy to energy-cycle them to recoup stored energy, particularly when natural-fiber reinforcement is used.

Summary

A new family of acrylic-acid copolymers has been developed in the form of aqueous solutions and dispersions that can be used to produce a wide variety of nonwovens as well as molded composite parts. These polymers are infinitely miscible in water prior to cure. They contain no solvents or other VOCs, and do not contribute odors or cause fogging once cured. They are providing the opportunity to replace numerous thermoplastic and thermoset resin matrices and produce cleaner, greener products at comparable or higher performance and, at times, lower cost.

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