FORMULATOR'S CORNER

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Technologies for Improving the Durability

Coatings are encountered on a daily basis, both in our personal lives, such as flooring and interior paints, and in specialized industrial applications, such as pipe line coatings and marine coatings for commercial and cargo ships. The performance expectations of coatings are high; requirements might include long-term adhesion to the substrate, ozone- and lightfastness, moisture and solvent resistance, gloss, and overall durability of the coating. Durability requires not only scratch, abrasion, and mar resistance, but the ability of a coating to resist cracking and damage from impact with another object. Certain coating chemistries have excellent engineering properties and resistance to solvents and chemicals, but contain deficiencies in other areas—such as drying speed for two-part waterborne polyurethane coatings or impact resistance with certain unmodified epoxies. Crosslinked epoxies are amorphous, and the structure of this type of thermoset leads to a relatively brittle material, with poor resistance to crack initiation and growth.[1]

Researchers have developed several different methods to improve the impact resistance of coatings while retaining the beneficial properties. It is important for coating formulators to understand the different technologies available to improve the durability and impact resistance of coatings, as all technologies have their inherent strengths and weaknesses. Although these technologies apply to a variety of polymer systems, for the purposes of this article, epoxies are primarily used to demonstrate the differences of how each approach can deliver improved performance.

METHODS FOR IMPROVING IMPACT RESISTANCE

Impact to a coating causes aesthetic damage, at the very least, but can also cause more serious damage, such as cracking, delamination from the substrate, and even flaking of the coating from the substrate. Impact can be an important consideration in almost any coating application, but for applications such as fusion bonded epoxy (FBE) coatings for water, gas, and oil pipelines, impact resistance is critical. Installation and handling of the pipe can lead to impact damage of the coating, and damage of the coating can cause the pipeline to fail performance expectations in key areas such as solvent resistance. In residential applications, the integrity of coatings is key to meeting high customer expectations of long product lives, despite conditions that subject coatings to repeated impact damage.

Although improving the impact resistance of coatings can be a challenge to achieve, coatings manufacturers now have the option to use several recently developed methods to improve impact resistance of coatings, particularly epoxies, so that the coatings can meet their product expectations. For epoxies, improving impact resistance often involves the introduction of well dispersed particles of nanometer to micron size. The second phase particles can increase impact resistance through a variety of mechanisms, including enhanced coating ductility, particle bridging, crack deflection, and crack pinning, to name a few. Dispersed second phase particles can either form during the curing process, or they can be added to the coating formulation pre-formed. These particles can take the form of elastomers, nanosilicas, block copolymers, or rigid thermoplastics.

This article focuses on improvements in impact resistance for coatings, which is a complicated measure of toughness due to the fact that impact resistance results can be affected by various intrinsic and extrinsic effects. Studies have shown, though, that when all variables are maintained, the introduction of the second phase particles significantly improves the impact resistance of coatings. The ability of the epoxy to be toughened will also depend on its degree of crosslinking and ductility, with relatively ductile epoxies being good candidates for toughening by inclusion of rubbery particles, and high-T_g, less-ductile epoxies being more efficiently toughened with the addition of rigid thermoplastics.[2] The ductility of the cured epoxy is dependent on a number of factors, including epoxy structure, equivalent weight, and functionality, as well as curative structure and stoichiometry. In a systematic study by Pearson and Yee, it was demonstrated that varying the molecular weight of the epoxy changed the matrix ductility in a controlled manner, with the more ductile formulations being more efficiently toughened with the addition of reactive liquid polymer.[3] The following sections will provide a brief overview of each technology, highlighting their strengths and weaknesses.

REACTIVE LIQUID POLYMERS

Reactive liquid polymers are synthetic rubber with chemical functionality—low molecular weight butadiene or butadiene-acrylonitrile copolymers with reactive groups at the ends of the polymer chains, allowing the incorporation of rubber properties such as impact resistance, resilience, and adhesion into coatings. Because they have low

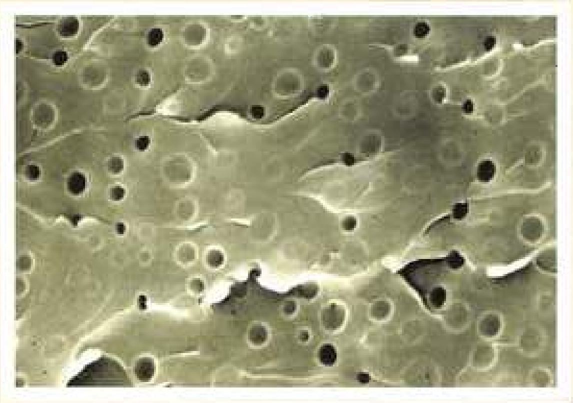


Figure 1—SEM of a cured epoxy matrix containing reactive liquid polymers.

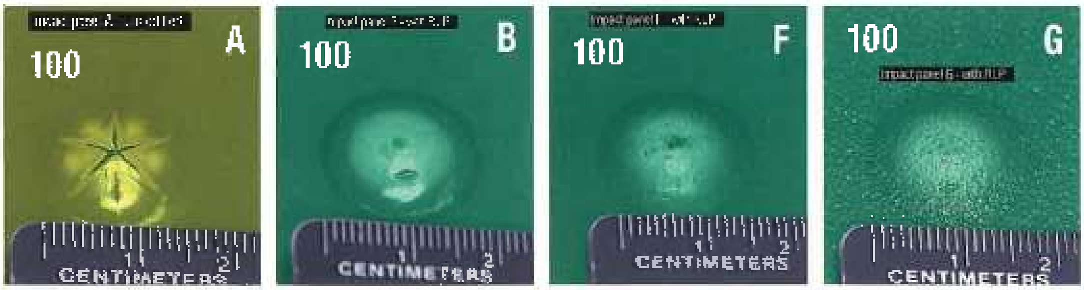
molecular weight, they are viscous liquids at room temperature, making them easy to incorporate into coating formulations. The butadiene-acrylonitrile (BN) copolymers have one of several different terminal reactive groups, including carboxyl terminated (CTBN), epoxy terminated (ETBN), amine terminated (ATBN), hydroxyl terminated (HTBN or HTB), or vinyl/methacrylate terminated (VTBN), and are chosen based on the specific type of coating and curative chemistry that is selected. Initially, the reactive liquid polymer will be miscible in the coating, but as the coating cures and the molecular weight grows, the polymer will phase separate into discrete, spherical domains on the size order of 0.5 to 1.0 µm. An SEM showing the morphology of an epoxy with phase separated reactive liquid polymers is provided in *Figure* 1.

Selection of the correct reactive liquid polymer—guided by the formulation—is crucial. The polymer must have a reactive group that allows the polymer to react into the matrix, leading to phase separation and formation of the spherical second phase. The acrylonitrile level of the polymer must also allow the polymer to be soluble in the coating matrix before curing, allowing for a stable formulation and consistent morphology post-cure.

This technology can be applied to a multitude of coating chemistries such as acrylics, vinyl ester, epoxy, unsaturated polyester, and polyurethane polymer formulations. The impact resistance can be significantly improved, mostly through the ability of the phase-separated elastomeric particles to allow brittle coatings such as epoxies to have enhanced shear deformation. *Figure* 2 shows the result of incorporating several different CTBN reactive liquid polymers; in a 100 lb-in reverse impact test, an unmodified epoxy sample was punctured by impact, whereas the three CTBN-modified epoxies remained intact.

A very small portion of the reactive liquid polymer will remain soluble in the matrix, which can lead to a slight decrease in matrix properties such as T_g and modulus. The typical concentration of these reactive liquid polymers in coatings is 5–15 parts, and the increase in toughness can be optimized with respect to the slight T_g decrease, as shown in *Figure* 3.

At higher levels, usually greater than 20 parts of reactive liquid polymer per 100 parts of epoxy, the inclusion of reactive liquid polymers can significantly increase the flexibility of the coating, which is desirable in applications where coatings are subjected to bending. Due to the low T_g of the reactive liquid polymer, the low temperature impact resistance is also significantly improved, and the flexibility at low temperature for higher concentrations is excellent. Overall, reactive liquid polymers have decades of proven



Unmodified Epoxy #1 | **Epoxy Modified with Hypro™ 1300X8 CTBN** | **Epoxy Modified with Hypro™ 1300X9 CTBN** | **Epoxy Modified with Hypro™ 1300X13 CTBN**

Figure 2—100 lb-in reverse impact test at R.T.

performance in coatings to improve impact resistance and can also improve other performance properties of the coating, such as adhesion to the substrate.

CORE SHELL POLYMERS

Core shell rubbers are a second method to introduce elastomeric second phase particles into a coating to improve impact resistance. Core shell rubbers contain an inner core that is usually elastomeric in nature with a low T_g, surrounded by a shell that is compatible with the coating matrix. The particles are pre-formed at a consistent particle size and therefore do not rely on phase separation to generate the second phase and morphology. A pictorial representation of a core shell particle cross section is shown in *Figure* 4.

Core shell particles toughen different coating chemistries, such as epoxies, vinyl esters, and unsaturated polyester resins, by many of the same mechanisms that are observed in the use of reactive liquid polymers: particle cavitation ahead of the crack tip leading to plastic void growth, termination of cracks, relieving of internal stresses during cure, and microcrack prevention. The core is designed to be the portion of the particle that provides impact resistance and therefore will usually consist of a low T_g polymer, such as butadiene-styrene copolymers, polybutadiene, polysiloxane, or acrylic polymers. The shell is designed to be compatible with the coating matrix so that the particles evenly disperse throughout the coating and do not agglomerate, and it can be composed of a variety of different polymers.

Because the particle is pre-formed, it must first be dispersed in the epoxy or added to the epoxy as a concentrate of core shell pre-dispersed in epoxy. This can sometimes be a disadvantage due to the fact that the formulators must either disperse the core shell particles themselves or use a portion of epoxy from the concentrate that may not be desirable in the formulation. However, because the particle is pre-formed, there is very little T_g depression since the elastomeric core does not solubilize in the matrix. As the particle size of the

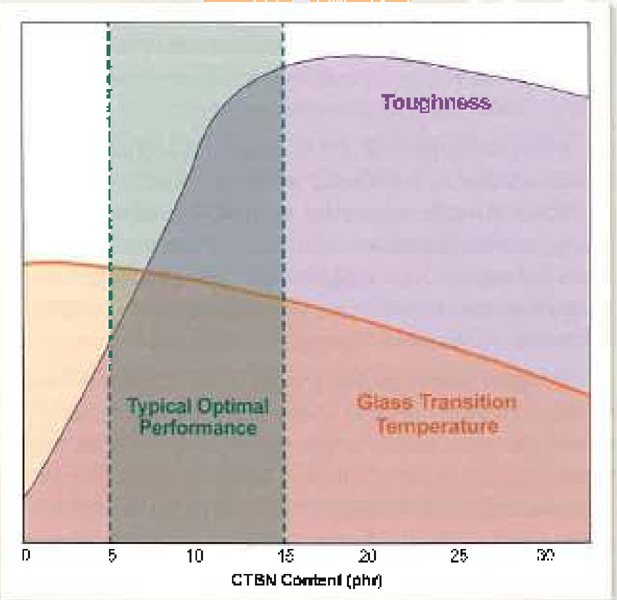


Figure 3—Optimization of reactive liquid polymers in formulations.

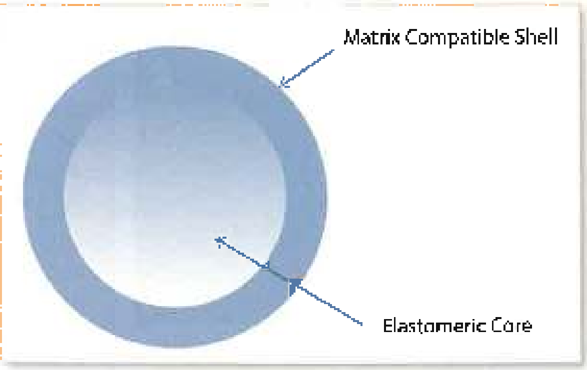


Figure 4—Cross section of typical core shell particle.

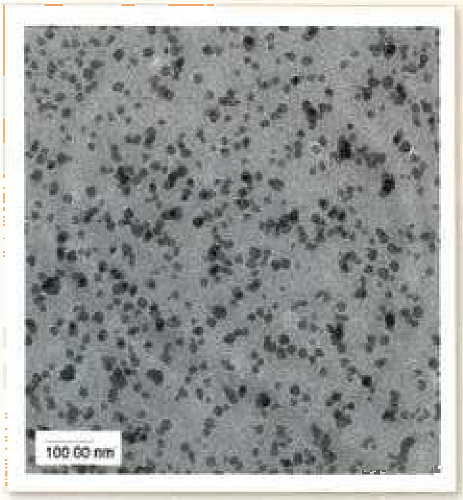


Figure 5—SEM of nanosilica dispersed in epoxy resin.

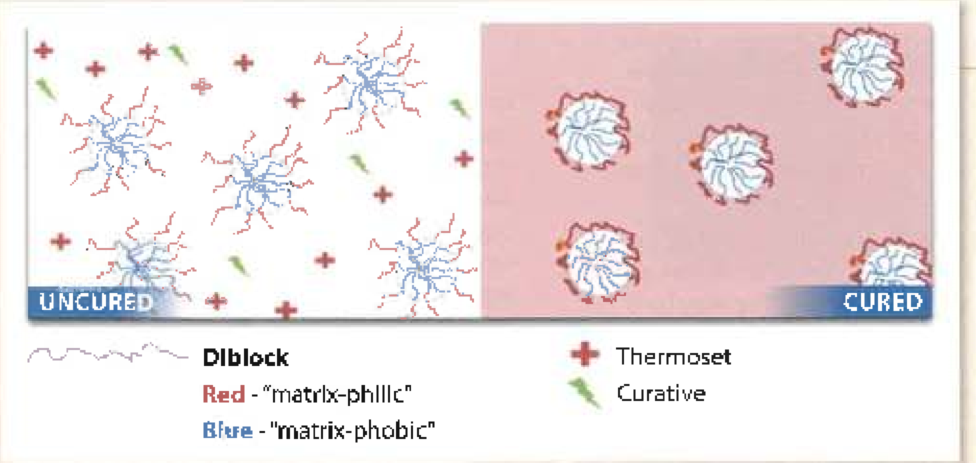


Figure 6—Phase separation of diblock copolymer in thermoset matrix.

core shell rubbers is lower, coatings or parts prepared with this toughener are more transparent than those prepared with reactive liquid polymers, which can be opaque. Synergistic improvements are seen with core shell particles when combined with other tougheners such as reactive liquid polymers.

NANOSILICA

Improvements to impact resistance made with nanosilica are very similar to the improvements seen with core shell technology. Nanosilica are surface-modified silica that are uniformly dispersed in epoxy, with a particle size of approximately 20 nm and containing a very uniform particle size distribution. Although pre-dispersions are available in epoxies, nanosilica can also be dispersed in other matrices such as acrylics to improve scratch resistance. A typical SEM of nanosilica dispersed in epoxy is shown in *Figure* 5.

Because the silica nanoparticles have a very small particle size and do not agglomerate, there is minimal impact to the viscosity of the coating formulation. Typical use concentrations range from 5–15%, with optimal properties usually being achieved at the lower concentrations. Similar to core shell particles, the addition of nanosilica particles to a coating formulation will have little effect on the overall T_g. The nanosilica particles toughen the coating by methods similar to those mentioned above, with particle debonding from the matrix being an important exception. Ahead of a crack, nanosilica particles can debond from the matrix, creating a void within the matrix. These voids can then grow in size similar to rubber particle cavitation and hole growth, thereby allowing plastic deformation of the matrix.

Transparency of coatings can be maintained, again because of the extremely small particle size. One disadvantage, similar to the core shell particles, is that the nanosilica must either be dispersed by the formulator or be used as a concentrate in epoxy. Several studies have shown very synergistic improvements in toughness when nanosilica is used in combination with reactive liquid polymers. When used at 4–5% each, nanosilica combined with reactive liquid polymers show improvements in fracture toughness and impact resistance that are not attainable when either technology is used singularly.

BLOCK COPOLYMERS

Block copolymers for use in coatings to improve impact resistance consist of a block that is compatible with the matrix and a second block that is incompatible. The block copolymers can be diblock or triblock copolymers, with the triblock copolymers containing two end blocks that are compatible with the coating matrix and a middle block containing matrix-incompatible material. Either before or after epoxy curing, the block copolymers will generate a specific morphology depending on their respective compatibility with the matrix. The blocks that are not compatible ("matrix-phobic") will associate and be surrounded by the blocks that are compatible with the matrix ("matrix-philic"). A general representation of this concept is shown in *Figure* 6, showing formation of spherical micelles.

Depending on concentration and compatibility, the block copolymer can form other morphologies, such as vesicles or wormlike micelles. The size of the domains formed is typically less than 100 nm, and use concentrations are 5–10%. Because of the small particle size, optical clarity is maintained for the most part, and there is minimal effect on T_g.

The ultimate increase in toughness will depend on the morphology that is generated, which will be dependent on the overall coating formulation. This may be a disadvantage due to the fact that positive results may not translate directly from system to system. The block copolymers can be difficult to disperse in thermosets such as epoxy and are often supplied as masterbatches in epoxy. Viscosity of a coating formulation is minimally affected by the addition of block copolymers. Low temperature impact resistance is also not as effectively increased with the use of block copolymers compared to the use of a low T_g elastomeric second phase.

KEY THERMOPLASTIC

The technologies above effectively toughen lightly to moderately crosslinked thermosets but do not efficiently toughen very high T_g, highly crosslinked thermosets. Rigid particle thermosets have been introduced as a solution to this problem. The thermoplastic is dissolved in hot epoxy, sometimes with a copolymer to assist in dispersion, and upon cooling, the thermoplastic will precipitate out of solution to form second phase particles at addition levels of 5–20%. Some examples of thermoplastic materials that can be used are poly THF/nylon 11 block copolymers and ethylene vinyl acetate copolymers, polyether sulfones, or polyimides. The addition of thermoplastics can be difficult to employ, and the ultimate morphology can be difficult to control and often relies on specialized techniques to generate the proper morphology for improving impact resistance. The degree of toughening is strongly dependent on the morphology of the resultant polymer blend; therefore, the morphology must be optimized to achieve the highest degree of toughening.

EMERGING TRENDS

Nanoparticle addition is emerging as another potential technology to increase the impact resistance of coatings, in addition to other properties such as scratch resistance. These nanoparticles could include carbon nanotubes and nanofibers, graphene, or montmorillonite organoclays. The research in this field is beginning to show improvements in the toughness properties of coatings, but significant challenges are still present, such as dispersion of the nanoparticles without agglomeration and optimization of properties to achieve the degree of improvement seen with traditional toughening technologies. Reactive liquid polymers are sometimes used as additives to help disperse and bind the nanoparticles into the matrix.

CONCLUSIONS

Improving the durability and impact resistance of coatings can be achieved through a variety of different technologies. All technologies involve the introduction of discrete second phase particles. The second phase particles can be formed by phase separation during curing or cooling of an epoxy, or they can be added pre-formed. Different materials can make up the second phase, including elastomers, nanosilica, block copolymers, and thermoplastics, each material with its own unique advantages and disadvantages. The coating formulator is therefore presented with a variety of options with which to maximize the impact resistance of their formulation to meet the growing demands of coatings.

References

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