Nanostrength® Block Copolymers for Epoxy Toughening

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Introduction
Due to their high strength, excellent high temperature properties and good adhesion to many surfaces, epoxies are extremely valuable engineering materials in composite, adhesive, coating, and electronic applications. Epoxies, however suffer from a very low toughness. One approach to improve the toughness of epoxies is via flexibilization. Monofunctional or high MW difunctional epoxy molecules can react directly into the epoxy matrix, lowering its crosslink density. This improves the toughness of the material but does so by sacrificing strength and lowering the glass transition temperature of the network. Similarly, reactive rubber modifiers, such as carboxy-terminated butadiene acrylonitrile (CTBN), can react into the surrounding epoxy matrix. Again toughness is increased but with the sacrifice of strength and thermal properties.

A second approach to toughening is the inclusion of softer phase material which does not react into the matrix, either core-shell particles, typically with a PMMA shell surrounding a low Tg rubber core or thermoplastic spheres such as polysulfone (PSU). In core shells, upon an impact event or an approaching crack tip front, stress is concentrated in the low Tg rubber core, causing cavitation of the core. This cavitation then causes subsequent plastic deformation of the surrounding matrix (often referred to as shear banding), absorbing energy from the impact or crack front and thus toughening the epoxy. The difficulty with the use of core shells in epoxies relates to the problems of achieving a uniform dispersion; the highly crosslinked rubber cores do not allow for their dissolution in epoxy resins. (Core shells are typically used to toughen thermoplastics where extremely high shear and high temperatures aid dispersion during extrusion.)

Thermoplastic spheres suffer from having a much higher modulus. Thus, they are not effective as stress concentrators and cannot easily cavitate. They can only toughen the epoxy by physical mechanism such as crack pinning or crack deflection, less efficient mechanisms than the previously described cavitation and shear band formation mechanism. Due to this poor efficiency, they are often used at high concentrations, where they can have a detrimental effect on properties critical to processing such as viscosity.

In order to overcome the deficiencies associated with the aforementioned types of epoxy toughening agents, controlled radical polymerization has been used to design acrylic block copolymers under the trade name of Nanostrength® block copolymers. The structure of these block copolymers can be tuned to give excellent toughening to a wide range of epoxy systems without sacrificing strength or thermal properties.

**Nanostrength® Block Copolymers – A Self Assembling Technology**

One family of the Nanostrength® block copolymers are triblock polymers consisting of polymethylmethacrylate-b-polybutylacrylate-b-polymethylmethacrylate (MAM) family. The PMMA blocks give compatibility to epoxy resin, while the PBuA blocks provide an immiscible soft rubber phase for toughening. The MAM products (e.g. M51, M52 and M53) can easily be dissolved in a typical diglycidyl ether of bisphenol A (DGEBA) resin with the application of heat and a low amount of shear. When dissolved in DGEBA resin, the MAM block copolymer self-assemble into
nanostructures. The PMMA block will associate with the epoxy resin, forming an effective shell surrounding an immiscible PBuA core. (Figure 1) The Bates group has shown using non-acrylic block copolymers polymers that the size and shape of the self-assembled structures can be varied from spherical micelles to worm-like micelles to vesicles by increasing the ratio of epoxy immiscible block to epoxy miscible block.

The structuration present in the final cured epoxy using block copolymers depends on the chemical nature of the crosslinker (hardener) and the chemical composition of the block copolymer. Less polar crosslinking agents such as M-DEA (methylene-diethylaniline) have good compatibility with PMMA so the exact structuration present in the uncured DGEBA resin remains in the cured epoxy. With more polar crosslinking agents, the compatibility with PMMA is not as favorable. Upon addition of the hardener, the MW of the epoxy molecules begins to increase, making the enthalpic contribution to free energy more important than the entropic contribution. Unless good chemical compatibility is maintained, micro or macro aggregation of the block copolymer can occur.

In order to increase the compatibility of block copolymers with more polar hardeners, grades have been developed which incorporate dimethylacrylamide into the PMMA blocks. (e.g. M22N and M52N) Dimethylacrylamide has a higher $\chi$ parameter (22.7 (J/cm$^3$)$^{1/2}$) which increases the compatibility of the miscible block with more polar curatives such as dianinododecylsulfonate (DDS) ($\chi$). The DMA allows for better chemical compatibility and thus allows for nanostructuration, in the form of either spherical micelles or worm-like micelles, to remain in the cured epoxy.

**Nanostrength® Block Copolymers in Epoxy**

Block copolymers allow for unique property sets to be achieved in epoxy systems, opening the door for new epoxy applications. Due to their non-reactive backbone, block copolymers can provide increases in toughening without sacrificing Tg or modulus. Due to nanostructuration, block copolymers provides superior toughening as compared to reactive rubber flexibilizers or core shell toughening agents. In fact, Nanostrength® block copolymers can be used at significantly lower use levels than competitive products to reach the same toughening levels. Additional advantages of block copolymers include the ability to dissolve these polymers in epoxy resin (no need for time consuming and inconsistent dispersion). The small size of the self-assembled structures allows for its use in composites with small inter-fiber spacing or thin bond line adhesives.

DGEBA epoxies were studied with several different hardeners, M-DEA, polyetheramine (PA), dicyandiamide (DICY) and diaminodiphenylsulfone (DDS). The cured epoxy bars were evaluated for toughening by testing the $K_{IC}$, (ASTM D5045-99) or the ability for the epoxy to stop crack growth. The Tg of the epoxy was measured by dynamic mechanical analysis. The properties of block copolymer modified epoxies were compared to neat epoxy systems and those modified with

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CTBN. Tapping Mode Atomic Force Microscopy (TM-AFM) phase imaging was used to observe the morphology of the modifiers in the cured epoxy.

In the DICY cured DGEBA epoxy systems, block copolymers with dimethylacrylamide (M52N) shows substantial improvements in toughening as compared to equivalent loadings of CTBN (grade CTBN X13, with 74% butadiene). (See Table 1) These polymers also show better Tg retention than CTBN. Furthermore, equivalent levels of toughening can be achieved using only 5% loading of M52N vs. 10% CTBN. At this loading ratio, the block copolymers have even larger advantages in Tg (with additional advantages in modulus and viscosity). When an identical formulation was cured at lower temperatures, the advantage of M52N over CTBN became even greater (10% loading results in a K1C of 2.40 and a Tg of 118 with 10% M52N, while 10% CTBN gives a K1C of 1.88 and a Tg of 112).

Figure 1: (Top) Schematic of Arkema’s MAM Nanostrength® block copolymers products self-assembling in epoxy resin. (Bottom) TEM images of self-assembled nanostructures in epoxy resin.
Table 1: Comparison of toughening with Nanostrength<sup>®</sup> block copolymers and CTBN in a DICY cured DGEBA epoxy.

<table>
<thead>
<tr>
<th>Loading Level</th>
<th>K1C</th>
<th>Tg</th>
<th>K1C</th>
<th>Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.88</td>
<td>148.1</td>
<td>0.88</td>
<td>148.1</td>
</tr>
<tr>
<td>2.50%</td>
<td>1.32</td>
<td>146.4</td>
<td>1.03</td>
<td>TBD</td>
</tr>
<tr>
<td>5.00%</td>
<td>1.64</td>
<td>144.2</td>
<td>1.32</td>
<td>139.1</td>
</tr>
<tr>
<td>10.00%</td>
<td>1.82</td>
<td>135.4</td>
<td>1.62</td>
<td>129.2</td>
</tr>
</tbody>
</table>

It is interesting to look at the structure/property relationship for block copolymers in epoxy. In the DICY system, a traditional MAM with no DMA (such as M53) at 10% loading undergoes micro-macrophase separation, resulting in a poor $K_{IC}$ (1.35). M52N which forms worm-like micelles in this system shows outstanding toughening ($K_{IC}=1.82$ with 10% loading). These worm-like micelles are very asymmetric, 10-50 nm in width but several hundred nm in length. An experimental grade with even better compatibility to the epoxy matrix gives spherical micelles and a good but not outstanding toughening ($K_{IC}=1.54$ with 10% loading). (Figure 2)

A study at Lehigh University has recently shown that the toughening of epoxies with MAM block copolymers increases as the epoxy equivalent weight (EEW) of the DGEBA backbone of the epoxy increases. This study showed that M52N in a dicy system exhibited superior fracture toughness to either grade of CTBN (X13 or X8 with 82% butadiene) for both low and high EEW resins. (Figure 3)

High speed impact testing (CEAST Fractovis Dart Drop) was also carried out to see the ability of a modified epoxy to absorb impact energy. CTBN was compared to block copolymer grade M52N in the same DICY system as tested above (10% loading of the modifier). Again, Nanostrength<sup>®</sup> block copolymers show superior ability in impact testing as compared to the neat resin and CTBN, absorbing more than twice the energy at failure as shown in figure 4.
The differences in toughening between competitive technologies are even more significant in a lower Tg polyetheramine cured epoxy. In this system with a more PMMA friendly crosslinking agent, the greatest improvements in toughening are seen with a traditional MAM (M53).

Figure 3: Fracture toughness of dicy cured epoxies with different EEW resins.

Figure 4: High speed impact energy of toughened epoxies.
Table 2: Comparison of toughening with Nanostrength® block copolymers and CTBN in a polyetheramine cured DGEBA epoxy.

<table>
<thead>
<tr>
<th>Loading Level</th>
<th>M53</th>
<th>CTBN X8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K1C</td>
<td>G1C</td>
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<tr>
<td>0%</td>
<td>0.76</td>
<td>183</td>
</tr>
<tr>
<td>10.00%</td>
<td>2.78</td>
<td>3437</td>
</tr>
</tbody>
</table>

Again the comparison of morphology shows that a “spider web” structure, asymmetric interconnected modifiers, (this time with M53) is superior to the nanosphere morphology that M52N gives in this system.

Figure 5: AFM Tapping modes images of 10% loading of M53, K1C=2.78 (left) and M52N (right), K1C=1.88 in a polyetheramine cured DGEBA epoxy.

The finding that asymmetric interconnected morphologies give better toughening in comparison to perfectly dispersed modifiers is supported in the literature both with block copolymer³ and core shell modifiers⁴.

Nanostrength® block copolymers in Epoxy Composites and Epoxy Adhesives

The enhanced fracture toughness and impact performance with minimal sacrifice of thermal properties using block copolymers modified epoxies makes them potentially valuable in several types of end use applications. Application specific testing has been carried out to confirm the value of MAM block copolymers in advanced epoxy composites and epoxy adhesives.

The use of block copolymers in RTM6, an epoxy resin/ hardener system used for resin transfer molding in the aerospace industry, was studied in collaboration with Dr. Fabris at Bayreuth University. Fracture toughness was also studied internally on DGEBA resins cured with M-DEA and cured with DDS.

In higher Tg systems common for composite applications, the maintenance of Tg and strength is critical. In these systems, hard thermoplastic spheres are often used as toughening agents to avoid the detrimental effect of CTBN on Tg. In these rigid

systems, plastic deformation of the matrix is difficult; so toughening is accomplished with crack pinning and bridging mechanisms. While the low Tg soft PBuA blocks of MAM block copolymers allow for cavitation and shear band formation toughening, the hard thermoplastic PMMA blocks in these polymers allow it to also participate in crack pinning and deflection in these high Tg systems while giving almost perfect maintenance of Tg. (Figure 6) MAM block copolymers out-perform polysulfone (PSU) in toughening, viscosity, and Tg in RTM6.

For validation of the use of block copolymers in adhesive applications, lap shear testing has been carried out at an independent adhesive testing facility in France, Rescoll laboratories. Testing was carried out on epoxy resins cured with DICY, polyetheramines (Jeffamine D230) and diethylene triamine (DETA). Lap shear tests primarily test the adhesion of the aluminum substrates to the epoxy resin but can also give some information on the toughening the resin.

**Figure 6: Evaluation of Nanostrength® block copolymers in high Tg epoxy systems for composite applications.**
Block copolymers showed equivalent performance to CTBN in modifying the DICY (modified with M52N) and polyetheramine resin (modified with M53), confirming that it does not interfere with adhesion in these systems. In the DETA system (modified with M52, a lower MW version of M53 for reduced viscosity) MAM block copolymers significantly outperformed CTBN, suggesting that it substantially increased the toughness of this system. High and low temperature lap shear and T peel testing are planned to further evaluate block copolymers for adhesive applications.

![Figure 7: Lap shear testing shows that Nanostrength® block copolymers maintains adhesion in DICY and polyetheramine cured systems and gives significant improvements in DETA cured systems.](image)

**Conclusion**

Acrylic block copolymers have been used to successfully toughen epoxies. Due to its block copolymer structure and unique nanostructured morphologies, Nanostrength® block copolymers provide exceptional toughening to epoxies without sacrificing thermal properties. The use of co-monomers in the epoxy miscible block, allows for these excellent properties to be achieved in a wide range of epoxy systems. The improved properties offered by MAM block copolymers will open up new applications for epoxies in electronics, adhesives, coatings and composites.