CRP Tougheners for Use in Composite Systems

by

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Abstract

Composite toughening remains one of the most difficult challenges facing the industry today. Although many systems for altering the flexibility or toughness of a composite system exist, most are difficult to incorporate into formulations and deliver varied results such as loss in modulus, processability or Tg. A new series of toughening systems based on nanotechnology has been developed using a series of block copolymers that self-assemble into nanodomains within the composite matrix. Of the various copolymers available, several have demonstrated interest in this continually developing field. These copolymers are primarily based around 1) triblock copolymers with alternating hard and soft segments that incorporate and nanostructure simultaneously and 2) single block polymers that chemically react into the polymer matrix and create nanostructuration within the composite. This paper will focus on the two different mechanisms available and show some of the practical results achieved with this novel technology.

In addition, the use of a nitroxide mediated controlled radical polymerization trap has previously been demonstrated to alter the curing kinetics of UPR resins, giving advantages such as reactivity control, increased pot-life and longer time for wet-out of fibers (while keeping cure time constant). The increased reactivity control also leads to a higher degree of crystallinity and less polydisperse thermoset network, which is shown to increase mechanical properties such a shear strength.

Introduction

The use of thermoset polymers in composites has major advantages including the high strength of the materials, corrosion/solvent resistance and stability at high temperatures. A major weakness of thermosetting resins, however, is their lack of toughness.

Traditional options for toughening unsaturated polyester resin (UPR) or vinyl ester resin (VER) composites typically come with certain tradeoffs. For example, the backbone chemistry of the resin can be altered, increasing toughness but at a cost of lower strength. Reactive rubber modifiers can also increase toughness but with similar detrimental effects on modulus and T_g. Core shell technology, traditionally used to toughen thermoplastic systems, is incompatible with thermoset composites as the core shell polymers compete for solubility with the fibers and filler materials. Block copolymers such as SBS have been used but carry with them the trade-off of yellowing and poor thermal stability. Finally, a rather inefficient toughness can be achieved by the addition of extra fiber reinforcement, but this carries with it a high penalty in terms of weight of the finished part.

In order to overcome the deficiencies associated with the aforementioned types of composite toughening agents, controlled radical polymerization (CRP) and anionic polymerisation have been used to design triblock copolymers under the trade name of Nanostrength® block copolymers and reactive single block polymers under the trade name of FlexiBloc®. The composition, functionality and structure of these polymers can be tuned to give excellent miscibility and toughening to a wide range of UPR and VER systems without sacrificing strength or thermal properties.

Another major need in the composite arena is the ability to reduce the weight of parts without adversely effecting the strength and stiffness of the finished product. The use of a controlled radical polymerization trap allows for the creation of a more ordered, less polydisperse thermoset matrix. The increases in strength are then realized due to the chemical ordering of the material, allowing for design of parts with lower fiber content.

Controlled Radical Polymerization and Nanostructuration for the Mechanical Properties of Composites

Using nitroxide mediated controlled radical polymerization (NM-CRP), polymer intermediates with trapped free radicals can be created. As seen in figure 1a, due to the presence of the nitroxide trap (designated as SG-1) at the end of the propagating chain, this polymer can be thought of as 'living'. It is able to re-initiate and polymerize once an activation temperature

is reached. In this way, the polymer can react directly into a composite resin, polymerizing with the styrene monomer. With controlled conditions, nanostructuration of the additive polymer, can be achieved, as demonstrated by the small polybutyl acrylate (PBA) domains in a polystyrene matrix, (figure 1b.) NM-CRP can be used to polymerize a wide variety of monomers including acrylates, methacrylates and styrene.

The architecture and functionality of polymers can be controlled with excellent precision using NM-CRP. Functionality such as acids, hydroxyl, amine or glycidyl groups can be added at precise locations in a polymer backbone. Such functionality can be used to react into the matrix, tune the solubility parameter of a block for better miscibility with a host matrix or cause non-reactive (hydrogen bonding) interactions with components of a formulation. This has a major advantage in composite applications as it is often desirable to have the toughening agents associate with the fiber or filler particles. Incorporation of acid groups into the polymer chain leads to better compatibility with the highly filled resin systems.

Block copolymer additive allow for excellent toughening of thermosets. One block can be selected for optimal compatibility with the UPR or VER system, while the other block can be selected to be the soft rubber phase, which will contribute to the toughening of the composite. As these are linear block copolymers, they can easily be dissolved in polystyrene, UPR or VER. Upon curing, the block copolymer self-assembles into nano-micelles, with the immiscible rubbery domains forming the interior core while the miscible block forms the compatible shell. By tuning the compatibility of the miscible block and the ratio of miscible block to immiscible block, a wide range of different types of nanostructuration can be achieved. Figure 2 shows different nanostructures achieved in a dicyandiamide cured bisphenol A epoxy using NM-CRP block copolymer technology.

In addition to NM-CRP, using anionic polymerization, triblock polymers, styrene-butadiene-methylmethacrylate (SBM) can be synthesized. The SBM has the aforementioned advantages of block copolymers along with the additional advantage a butadiene rubbery block, allowing for lower temperature impact resistance. Additionally, lower MW SBM block copolymers can be prepared resulting in less effect on viscosity and processability. Anionic polymerization has been used to create SBM block copolymers modifiers (such as grade E41) for

toughening of UPR and VER resins without loss in Tg and modulus.

The introduction of a nitroxide into a traditional free radical type of polyester resin cure creates a "living" element to the resin curing system. This has two immediate effects, the first being to change the kinetics of the polymerization in a way that stabilizes very fast reacting systems at room temperature. This effect is unique in the fact that the radicals produced by premature initiator decomposition do not disappear, but rather become blocked to an inactive species until sufficient energy is put into the system to activate the disassociation of the nitroxide/polymer chain couple. In styrene based systems, this is relates to an initiation temperature of $60^{o}C$. This effect can be seen in figure 1a.

The second effect that occurs is that the way that the polymerization proceeds is changed. Because of the presence of "living" radicals in the cure system, premature termination that presents itself in normal free radical cures is dramatically reduced. The characteristics of living radical systems is that they build at a uniform, linear rate, with a much smaller than normal polydispersity index (distribution of chain lengths and therefore molecular weights). Since resin cures lead to a network type of polymerization, the outcome is to "homogenize" the size and molecular weight of the polystyrene crosslinks.

Since this homogenization has occurred, the effect is to reduce the free volume "errors" that occur within the resin matrix. Thus, with an elimination in free volume errors and discontinuities, the resin tends to become more ordered in nature. This effect can be seen by a change in the DMA curve, the result from the change in order of the crosslinked network. Another benefit from this polymerization technique is an increase in the Tg of the overall composite by a few degrees.

Tables 3 and 4 show the changes in short beam shear strength seen with different loadings of nitroxide, as well as the changes in T_g from the DMA curves. It appears that there is an upper limit above which a detrimental effect can be seen on all properties. This behavior is also the case with the reactivity control, where above 600 ppm CRP additive, the entire system kinetics seem to slow down. Whether these effects are due to the limited number of chains in a highly crosslinked network, or to some other as of yet unpredicted behavior is unclear.

Compatibility, Structuration and Toughening of Composite Systems

A series of living single polymer blocks, living acid functionalized single polymer blocks, living diblock copolymers were synthesized for screening in UPR and VER applications. One of the first systems evaluated for improvements in toughening is a DCPD UPR system. Initially blends were made without filler and glass fiber to allow for AFM imaging. AFM imaging revealed that polymethylethylacrylate (PMEA) was completely miscible in the resin while polybutylacrylate (PBA) underwent microphase separation resulting in 10-20 micron rubber spheres as shown in figure 3.

A formulation with DCPD resin, calcium carbonate, glass fiber, zinc stearate and peroxide was used as a model formulation for sheet molding of a UPR resin. These formulations were cast into discs for high speed impact testing using a Dynatup dart drop tester. Energy absorbed before failure was the primary method of measuring toughness. Figure 4 demonstrates that immiscible PBA living low Tg polymer give greater improvement in toughening than miscible polymers. Superior toughening can be achieved by incorporating acid into the backbone of the PBA polymer (grade FlexiA12), likely due to for increased compatibility to filler and fiber particles.

In addition, the FlexiA12 and the E41 SBM triblock polymer were incorporated into a typical isophthalic pultrusion resin at 5 phr loading and cast into 3" by ½" by ¼" bars. The hazy appearance of the FlexiA12 bars suggest that the FlexiA12 modifier reacted into the resin, again demonstrating both regions of micro and nanostructuration. In contrast E41 modified bars are perfectly transparent, suggesting a rubber particle size of 30-100 nm.

Fracture toughness measurements (following ASTM D 5045- 99) were done on these bars and the results are summarized in Table 1. As seen, 5 phr FlexiA12 results in a 22% increase in K1C and a 40% increase in G1C while 5 phr E41 shows a 40% gain in K1C and a 58% gain in G1C. Important to note is that the toughening is not simply achieved by flexibilizing the resin, as the modulus of the bars tested in fracture toughness is similar within experimental error. Instead of flexibilizing the resin, the nano-phase separated domains toughen the material without effecting modulus, increasing the resistance to crack propagation.

E41 and FlexiA12 were also incorporated into pultruded composites made at the University of Mississippi. These resins were then pultruded into a 2 inch wide by 1/8 inch thick flat panel using a continuous pull pultrusion machine with 72 ends of fiberglass and die conditions of 300 front end zone, 350 mid zone, and 325 finish zone. Typical pull speeds were 18-24 inches/minute and pull forces of 1500 to 2000 psi. These parts were used for all subsequent testing of reinforced parts..

Short beam shear and dynamic mechanical analysis were used to evaluate the beams. Short beam shear measurements (Table 2) showed that even with the addition of 5 phr of rubbery based additives, strength only dropped by 7-10%. Dynamic mechanical analysis (Fig 5) indicated that Tg as measured by tan delta showed almost no decrease: 110.5 °C for the neat resin; 107.3 °C for the FlexiA12 modified resin and 108.7 °C for the E41 modified resin.

Conclusion

We have shown the use of functionalized living single block polymers, and triblock polymers as toughening agents in UPR and Vinyl Ester Resins. These materials made by controlled radical polymerization and anionic polymerization represent a potential new class of toughening agents for the composites industry, where excellent toughening can be achieved without the sacrifice of other key properties. In addition the use of a radical trap can increase the ordering in UPR systems, resulting in improved thermal and mechanical properties. These polymers and molecules represent a toolbox for UPR/VER composites for improved mechanical properties.
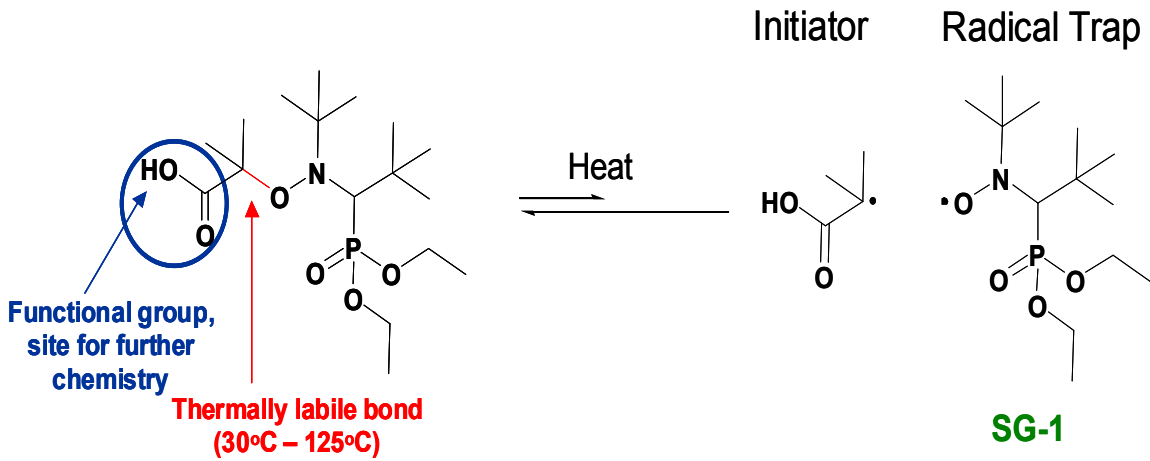
Figure 1: A)

Figure 1: A.) Structure of NM-CRP agent used to make functional and block copolymers.
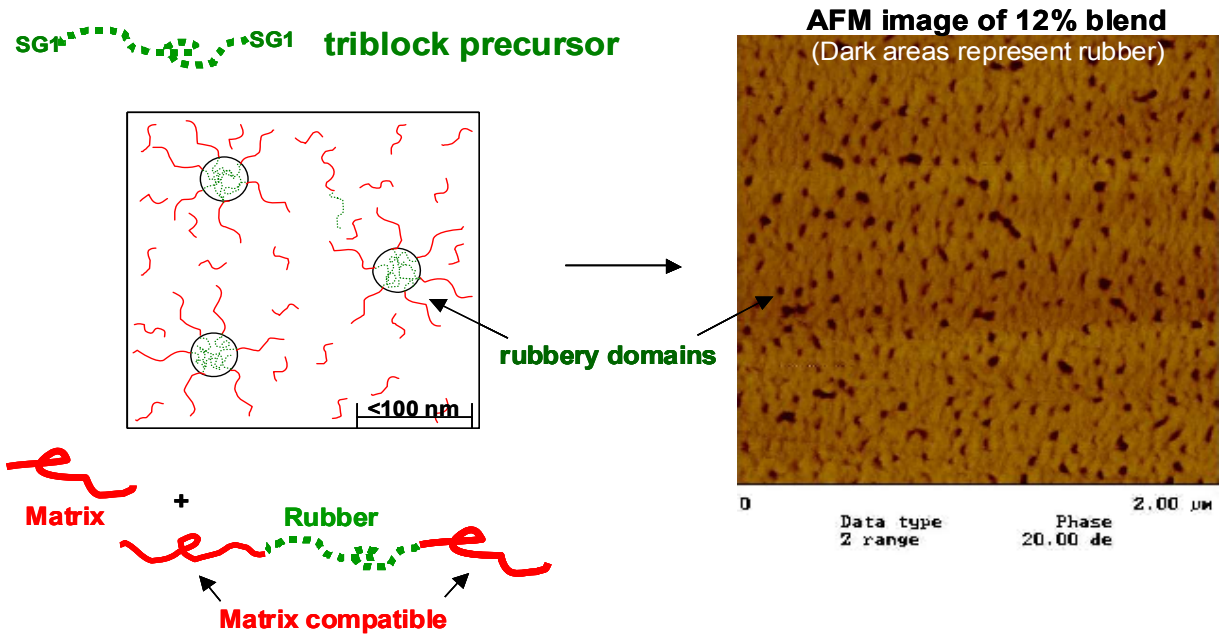
Figure 1: B)

Figure 1: B.) Schematic and Atomic Force Microscopy Tapping Mode (TM-AFM) image of living butyl acrylate polymer reacting into styrene matrix to form nanostructured domains.
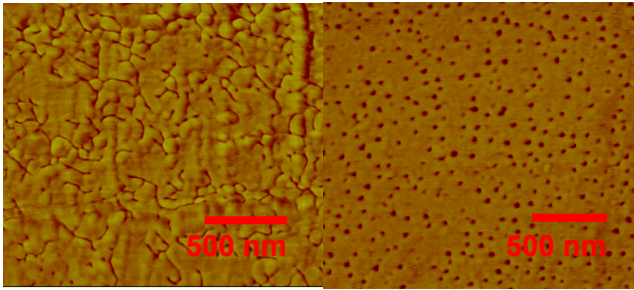
Figure 2

Figure 2: TM-AFM images showing the ability to form either nano-worm like micelles or nanospheres with a 10% loading of different block copolymers in a dicyandiamide cured epoxy.
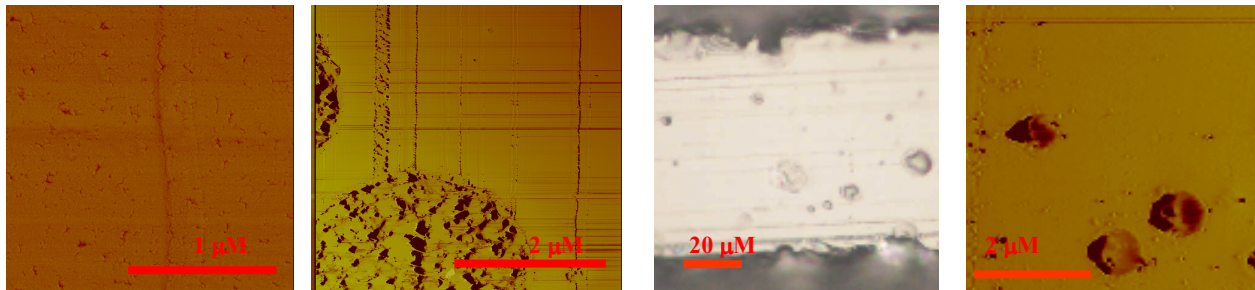
Figure 3

Figure 3: UPR DCPD belnds with 10% of miscible PMEA (far left TM-AFM image) and immiscible PBA(center left TM-AFM image). In an isopthalic resin, both micro and nanostructuration is seen with the acid modified flexibloc (center right optical image, far right TM-AFM image) .
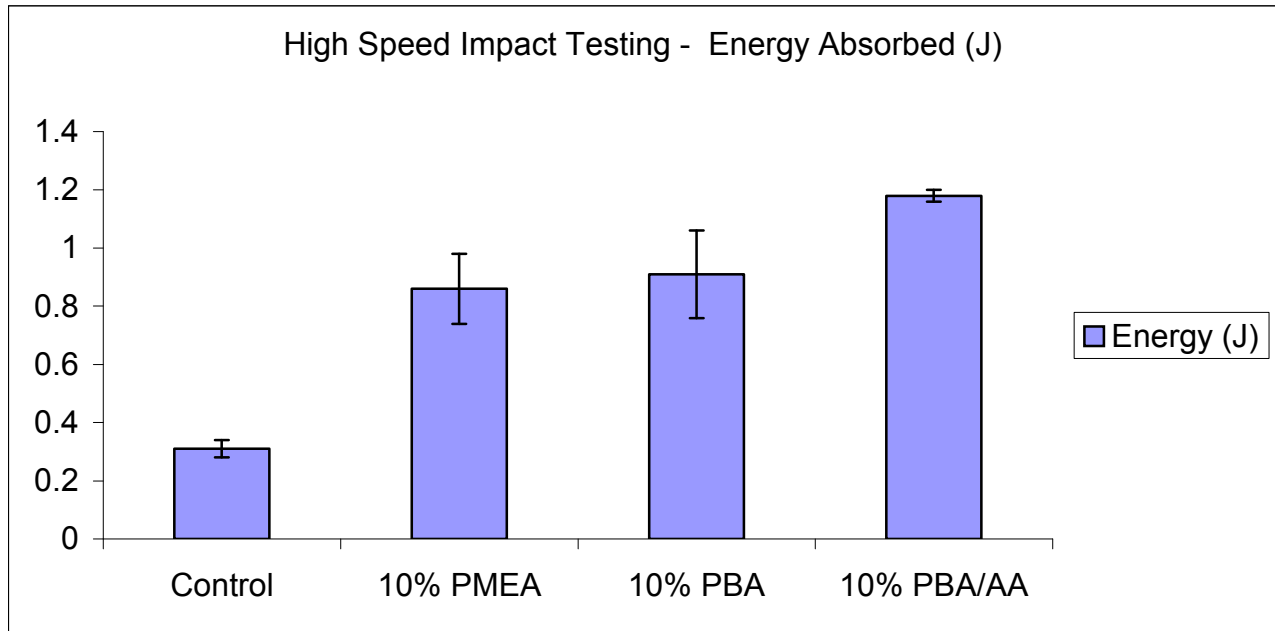
Figure 4

High Speed Impact Testing - Energy Absorbed (J)

Control: 0.31
10% PMEA: 0.86
10% PBA: 0.91
10% PBA/AA: 1.18

Legend: Energy (J)

Figure 4: High speed impact testing shows the advantages in toughening of incorporation of functional groups.

DMA analysis chart — Tan Delta vs Temp (C)

Legend:
- Neat UPR
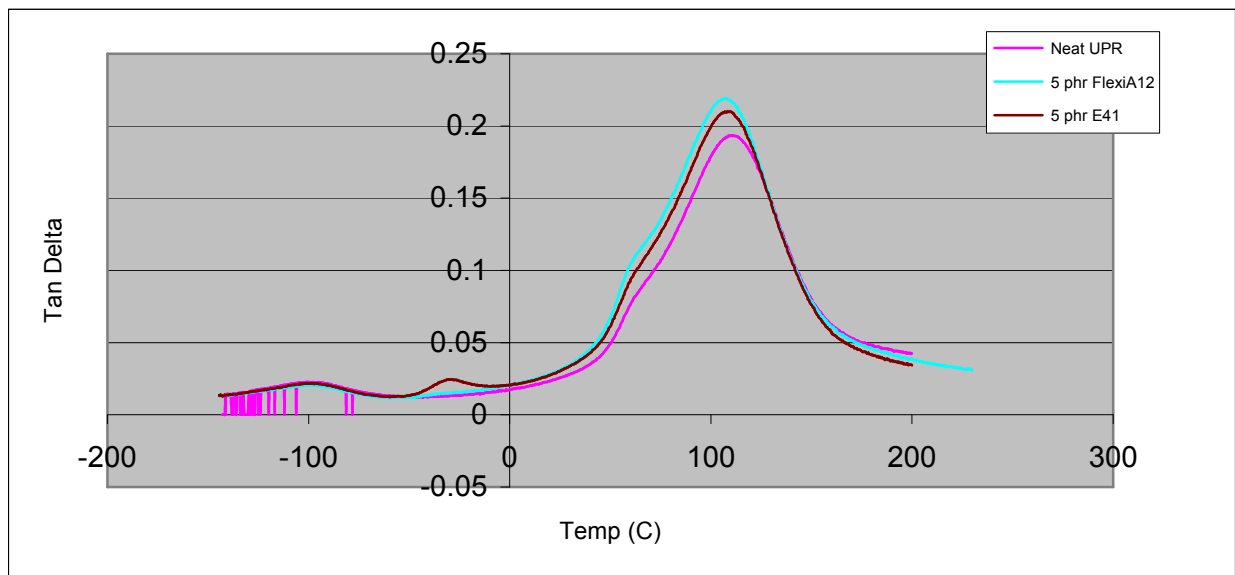- 5 phr FlexiA12
- 5 phr E41

Figure 5: DMA analysis of modified pultruded UPR composites

Table 1 Fracture toughness of unfilled resin

	K_{1C} (MPA* $m^{1/2}$)	G_{1C} (J/m^2)
Neat UPR resin	0.68 ± 0.12	273 ± 51
UPR + 5 phr FlexiA12	0.83 ± 0.06	382 ± 9
UPR + 5 phr E41	0.95 ± 0.12	432 ± 71

Table 2 Short beam shear of rubber modified composite

	Short Beam Shear Composite Samples Peak Stress (ksi)
Neat UPR resin	7.3
UPR + 5 phr FlexiA12	6.8
UPR + 5 phr E41	6.6

Table 3 Short beam shear of nitroxide modified composite

	Short Beam Shear Composite Samples Peak Stress (ksi)
Neat UPR resin	7.3
UPR + 0.4 phr RC-50	7.7
UPR + 1.0 phr RC-50	7.8
UPR + 1.5 phr RC-50	7.4

Table 4 Thermal data from DMA of nitroxide modified composite

	T_g from DMA curves, °C
Neat UPR resin	111.3
UPR + 0.4 phr RC-50	113.8
UPR + 1.0 phr RC-50	112.3
UPR + 1.5 phr RC-50	108.9