

*(Meth)Acrylate Functional Monomers  
Part 1 – Additives for Enhanced  
Composite Performance*

**Introduction**

The tremendous growth of activity in the composites industry continues to create a need for materials that meet the tough demands for environmental compliance and high performance at an economical cost. Much of this activity has been focused on composite systems based on unsaturated polyester resins (UPRs) and vinyl esters (VEs) utilized in laminating, gel coat and free-flowing molding applications.

Both UPRs and VEs are typically dissolved in styrene monomer to aid in processing and assist in the curing of the resin itself. More recently, other monomers such as vinyltoluene, divinylbenzene and (meth)acrylate esters have been used to crosslink the resin system and reduce emissions (VOC) associated with the use of styrene. In addition, UPR and VE composite systems typically contain a significant amount of reinforcing and non-reinforcing fillers, pigments and other additives to reduce costs and enhance performance. Many of these materials are compounds that provide hardness, strength and high temperature performance. However, these materials tend to raise viscosity and are typically inert, so they do not contribute to the curing of the resin.

**Summary**

In this paper we studied the effect of adding a unique class of materials designated (meth)acrylate functional solid monomers to UPR and VE systems. The objective of the study was to determine the influence of these solid monomers or “reactive fillers” on the rheology of these systems, their curing and resulting physical properties.

The results indicated that certain (meth)acrylate functional monomers can be used to lower viscosity and control thixotropy of highly filled systems. This benefit may provide the formulator the ability to reduce the styrene monomer content in the system, thereby lowering emissions (VOC). In addition, the monomers of this study were observed to be co-reacted upon curing of the resin providing improved high temperature performance at low levels. The monomers were further observed to increase glass transition temperature (T<sub>g</sub>) and heat distortion temperature (HDT). They were also observed to improve flexural properties at elevated temperatures. Overall, it was observed that addition of low levels of (meth)acrylate functional monomers can provide a means of addressing environmental issues through rheology modification as well as provide high performance through reinforcement via crosslinking.

**Experimental**

Two (meth)acrylate functional monomers, **SR705** and **SR708**, were added to a variety of polyesters and vinyl esters in a variety of composite formulations. Comparative studies were performed with and without the additive for viscosity, gel or cure time and physical properties (i.e., tensile properties, flexural properties, hardness).

Zero, 2 and 5 parts by weight of **SR705** and **SR708**, respectively, were added to 100 parts by weight of a 1) dicyclopentadiene/orthophthallic anhydride polyester, 2) isophthallic anhydride polyester and 3) vinyl ester as described in Table 1. All of these resins were pre-promoted with accelerators such as organometallic driers or tertiary amines such as di-methyl-p-toluidine. They were used as received commercially and therefore, the accelerator type and amounts are unknown.

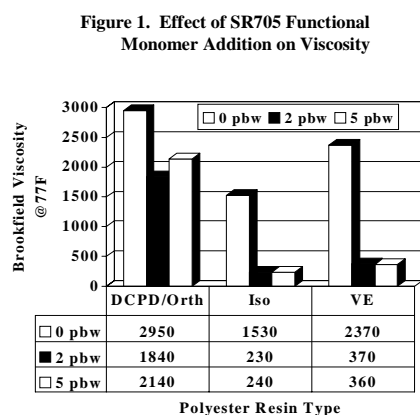


Table 1. (Meth)Acrylate Functional Monomer Modified UPR/VE -Formulations

| FORMULATION #   | PARTS BY WEIGHT |     |     |     |     |
|---|-----------------|-----|-----|-----|-----|
|   | 1A              | 2A  | 3A  | 4A  | 5A  |
| DCPD/Ortho Polyester Resin<br>(Ashland Aropol FRP A220)<br>SR705<br>SR708 | 100             | 100 | 100 | 100 | 100 |
|   |                 | 2   | 5   | 2   | 5   |
| FORMULATION #   | 1B              | 2B  | 3B  | 4B  | 5C  |
| Iso Polyester Resin<br>(CCP Stypol 40-4339)<br>SR705<br>SR708             | 100             | 100 | 100 | 100 | 100 |
|   |                 | 2   | 5   | 2   | 5   |
| FORMULATION #   | 1C              | 2C  | 3C  | 4C  | 5C  |
| Vinyl Ester Resin<br>(Reichold PolyLite 33350)<br>SR705<br>SR708          | 100             | 100 | 100 | 100 | 100 |
|   |                 | 2   | 5   | 2   | 5   |

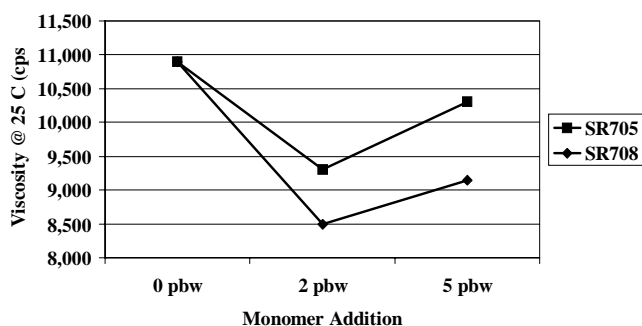
## Rheology

Viscosity measurements for the **SR705** modified formulations were made using a Brookfield RVT viscometer equipped with specified spindles at specified temperatures and shear rates. Resulting viscosities are plotted in Figure 1.



In a separate study, 40 parts by weight of Aluminum Trihydroxide (ATH), a common filler for many composite applications, was added to 100 parts by weight of each of the **SR705** and **SR708** modified vinyl ester formulations. Viscosity measurements were again measured using a Brookfield RVT Viscometer with specified spindles at specified shear rates. The results of this study are plotted in Figure 2.

Figure 2. Viscosity of Highly Filled (Meth) Acrylate Functional Modified Vinyl Esters Systems



## Cure Performance

1.25 parts by weight of methyl ethyl ketone peroxide initiator were added to each of the **SR705** modified formulations in Table 1. Gel time was measured on 100 gram samples by immersing a glass stirring rod into the sample and recording the time the rod was immersed to the time the rod did not move freely. Gel times of 20-75 minutes are desirable for most applications. Therefore, gel time adjustments were made to some formulations by addition of accelerators so that comparative testing of physical properties could be conducted. The initial gel times and the adjusted gel times with amount of accelerator required are reported in Table 2.

Table 2. (Meth) Acrylate Functional Monomer Modified UPR/VE – Gel Times

| FORMULATION #  | 1A | 2A  | 3A  |
|--|----|-----|-----|
| Initial Gel time (mins)                              | 64 | 155 | 165 |
| + 0.20% Cobalt Octoate; 0.15% Dimethylacetoacetamide | NA | 69  | 72  |
| FORMULATION #  | 1B | 2B  | 3B  |
| Initial Gel time (mins)                              | 27 | 170 | 270 |
| + 0.25% Cobalt Octoate; 0.15% Dimethylacetoacetamide | NA | 58  | 65  |
| FORMULATION #  | 1C | 2C  | 3C  |
| Initial Gel time (mins)                              | 42 | 248 | 252 |
| + 0.18% Cobalt Octoate; 0.13% Dimethylacetoacetamide | NA | 68  | 61  |

## Physical Properties

1.25 parts by weight of methyl ethyl ketone peroxide were added to each of the adjusted formulations in Table 2 for preparation of clear castings and laminates to test for tensile properties, flexural properties, heat distortion temperature, glass transition temperature and hardness.

## Clear Castings

Clear castings were prepared by pouring the formulation between two pieces of tempered glass sprayed with mold release and separated by a 1/8” thick spacer. The formulations were then left to gel at 77°F for 2 hours. The clear castings used for testing tensile properties, flexural properties and hardness were post-cured for 2 hours at 150°F.

Tensile properties were determined following ASTM D638 using Type I specimens. Tensile property results for the **SR705** modified formulations are reported in Table 3.

Flexural properties were determined following ASTM D790 (Method I, Procedure A, L:d = 16:1). Flexural property results for the clear castings of the **SR705** modified formulations are reported in Table 3.

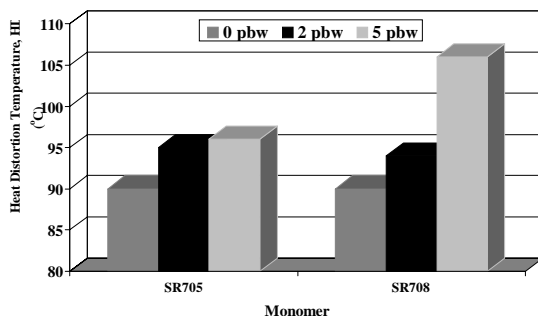
Hardness was determined following ASTM D2583 using a Barcol Impressor. Barcol hardness results for the **SR705** modified formulations are reported in Table 3.

Table 3. (Meth) Acrylate Functional Monomer Modified UPR/VE – Clear Castings

| FORMULATION #           | 1A     | 2A     | 3A     |
|-------------------------|--------|--------|--------|
| Tensile Strength (psi)  | 5,028  | 4,279  | 4,735  |
| Elongation @ Break (%)  | 1.01   | 0.82   | 0.95   |
| Tensile Modulus (mpsi)  | 0.487  | 0.524  | 0.475  |
| Flexural Strength (psi) | 8,313  | 8,102  | 8,101  |
| Flexural Modulus (mpsi) | 0.532  | 0.558  | 0.548  |
| Barcol Hardness         | 40     | 42     | 42     |
| FORMULATION #           | 1B     | 2B     | 3B     |
| Tensile Strength (psi)  | 7,920  | 6,824  | 6,450  |
| Elongation @ Break (%)  | 2.00   | 1.52   | 1.50   |
| Tensile Modulus (mpsi)  | 0.419  | 0.438  | 0.442  |
| Flexural Strength (psi) | 16,652 | 14,495 | 11,593 |
| Flexural Modulus (mpsi) | 0.460  | 0.483  | 0.469  |
| Barcol Hardness         | 40     | 42     | 42     |
| FORMULATION #           | 1C     | 2C     | 3C     |
| Tensile Strength (psi)  | 9,360  | 9,972  | 9,945  |
| Elongation @ Break (%)  | 2.98   | 3.08   | 3.01   |
| Tensile Modulus (mpsi)  | 0.429  | 0.444  | 0.440  |
| Flexural Strength (psi) | 12,384 | 16,644 | 13,247 |
| Flexural Modulus (mpsi) | 0.465  | 0.493  | 0.488  |
| Barcol Hardness         | 35     | 39     | 36     |

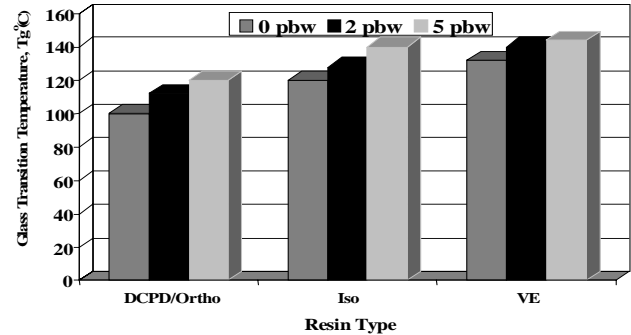
Heat distortion temperature (HDT) was determined following ASTM D648 using 264 psi load. The clear castings used for testing HDT were post-cured for 1 hour at 70°C, 1 hour at 90°C and 1 hour at 120°C. The HDT results for the **SR705** and **SR708** modified Isophthalic polyester are plotted in Figure 3.

Figure 3. Effect of (Meth) Acrylate Functional Monomers on Iso Polyester Heat Distortion Temperature (HDT)



Glass transition temperatures (Tg's) were determined using Dynamic Mechanical Thermal Analysis. The clear castings used for Tg testing were post-cured for 1 hour at 70°C, 1 hour at 90°C and 1 hour at 120°C. The Tg results are for the **SR708** modified formulations are plotted in Figure 4.

Figure 4. Effect of SR708 Addition on Glass Transition Temperature (Tg) by DMA Analysis



### Laminates

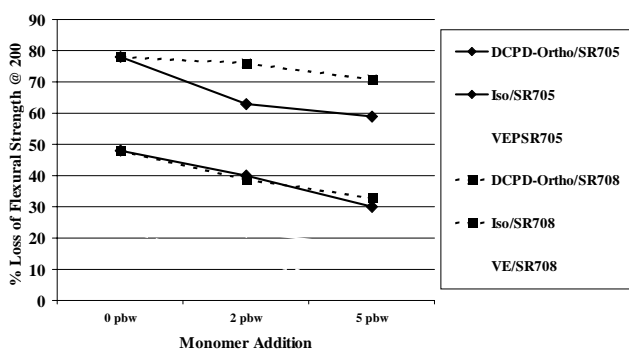
Laminates were fabricated by hand lay-up using 3 plies of 0/90 knit fiberglass matting with the initiated formulations applied between each layer. The finished laminate panels were post-cured for 2 hours at 150°F.

Flexural properties were determined following ASTM D790 (Method I, Procedure A, L:d = 16:1). Laminate testing was done in the 0° reinforcement axis with the load placed on the mold (CS) face. Laminate testing was conducted at 77°F and 200°F. Flexural property results for the **SR705** and **SR708** laminates are plotted in Table 4. The percent loss of flexural strength from 77°F to 200°F is plotted in Figure 5.

Table 4. (Meth) Acrylate Functional Monomer Modified UPR/VE – Laminate Testing

| FORMULATION #               | 1A     | 2A     | 3A     | 4A     | 5A     |
|-----------------------------|--------|--------|--------|--------|--------|
| Flexural Properties @ 77°F  |        |        |        |        |        |
| Flexural Strength (psi)     | 57,093 | 41,564 | 42,487 | 57,973 | 60,484 |
| Flexural Modulus (mpsi)     | 1.715  | 1.448  | 1.289  | 1.730  | 1.692  |
| Flexural Properties @ 200°F |        |        |        |        |        |
| Flexural Strength (psi)     | 12,623 | 15,445 | 17,302 | 13,966 | 17,742 |
| Flexural Modulus (mpsi)     | 0.589  | 0.762  | 0.816  | 0.669  | 0.742  |
| FORMULATION #               | 1B     | 2B     | 3B     | 4B     | 5B     |
| Flexural Properties @ 77°F  |        |        |        |        |        |
| Flexural Strength (psi)     | 56,730 | 49,619 | 46,464 | 64,931 | 63,364 |
| Flexural Modulus (mpsi)     | 1.751  | 1.686  | 1.583  | 1.848  | 1.879  |
| Flexural Properties @ 200°F |        |        |        |        |        |
| Flexural Strength (psi)     | 29,402 | 29,591 | 32,652 | 39,844 | 42,602 |
| Flexural Modulus (mpsi)     | 1.196  | 1.078  | 1.233  | 1.371  | 1.315  |
| FORMULATION #               | 1C     | 2C     | 3C     | 4C     | 5C     |
| Flexural Properties @ 77°F  |        |        |        |        |        |
| Flexural Strength (psi)     | 51,993 | 47,471 | 48,189 | 64,507 | 60,066 |
| Flexural Modulus (mpsi)     | 1.662  | 1.663  | 1.787  | 1.807  | 1.715  |
| Flexural Properties @ 200°F |        |        |        |        |        |
| Flexural Strength (psi)     | 39,937 | 36,227 | 40,085 | 57,843 | 56,121 |
| Flexural Modulus (mpsi)     | 1.386  | 1.301  | 1.347  | 1.881  | 1.891  |

**Figure 5. (Meth) Acrylate Functional Monomer - Effect on Loss of Flexural Properties**



## Conclusions

This paper demonstrates that (meth)acrylate functional monomers can be formulated into peroxide curable UPR and VE composite systems at additive levels to aid in processing and to improve performance.

Specifically, **SR705** was found to reduce viscosity as much as 80% at less than 5 parts by weight addition to 100 parts of neat pre-promoted resin for a dicyclopentadiene-orthophthallic anhydride based polyester, an isophthallic anhydride based polyester and a bisphenol A based vinyl ester. This result could allow formulators to achieve higher filler loadings for applications requiring higher strength or lower cost.

**SR705** monomer was also found to significantly increase the gel time for these three resin systems at less than 5 parts by weight addition. Therefore, it may be used as a cure retarder in applications requiring a longer working time. The increased gel time effect can be overcome by the use of additional promoters or accelerators such as cobalt driers or dimethyl- aniline.

No significant detrimental effect on physical properties such as tensile strength, elongation, tensile modulus and hardness was observed when up to 5 parts by weight of **SR705** was added to the UPR and VE formulations of this study. Some decrease in flexural strength was observed for the isophthallic anhydride based resin system although flexural strength was improved for the bisphenol A vinyl ester based system and flexural modulus was slightly improved for all three resin systems tested.

The major benefit resulting from addition of (meth) acrylate monomers to UPR and VE based systems as shown by this study was improvement in heat resistance or thermal properties of both the cured resin and a laminated composite made from these resins. **SR708** addition at 5 parts by weight to the isophthallic anhydride based polyester increased the heat distortion temperature (HDT) from 90°C to 106°C. The addition of 5 parts by weight of **SR708** monomer also increased the glass transition temperature (T<sub>g</sub>) of the cured resin 20°C for the DCPD/ortho polyester, 20°C for the Iso polyester and 12°C for the bisphenol A vinyl ester. More importantly, the T<sub>g</sub> was increased enough for the general purpose DCPD/ortho polyester that it approached the T<sub>g</sub> of the higher performance iso polyester and the T<sub>g</sub> of the iso polyester was increased to where it approached the T<sub>g</sub> of the high performance vinyl ester. This improvement could be very useful for high temperature applications such as under-the-hood automotive composites or electronic components.

When the **SR705** and **SR708** monomer modified resins were used to prepare a laminate typical of a marine craft application the flexural properties of the laminate were significantly improved as it was subjected to elevated temperatures. The loss in flexural strength as the laminate was aged from 77°F to 200°F decreased as much as 24% for the DCPD/ortho polyester laminate, 37% for the Iso polyester laminate and 69% for the vinyl ester laminate. These results indicate that (meth)acrylate functional monomers would be very useful as additives for applications where thermal cycling or thermal shock is important.

## ACKNOWLEDGEMENT

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