# Technical Research

## The Effects of Inert Mineral Fillers on the Corrosion Resistance of Unsaturated Polyester Resins

INTERPLASTIC CORPORATION
Thermoset Resins Division

## ABSTRACT

Fillers have been used in corrosion resistant applications for many years. The main benefit of using an inert mineral filler is lowering the overall raw material cost of the composite, while maintaining suitable performance of the composite and service life.

This paper discusses some of the factors to consider in the screening of inert mineral fillers as well as the impact on the corrosion resistance of the cured composite. Composites made from a standard, unsaturated, isophthalic, corrosion resistant polymer and two inert mineral fillers were used in the study.

Three key factors to consider in using a filler in the composite are its ability to keep the material in suspension, its effect on gelation and how it affects the cure of the resin. In addition to those properties, this work compares the effect of these fillers on the corrosion resistance of reinforced composites and describes a technique of reviewing the corrosion resistance data for overall suitability of its use in corrosion applications.

The analysis includes a method to determine if the filler has a major impact on the corrosion resistance of the reinforced composite. This analysis looks at several combinations of the data to determine its performance in various environments and overall performance.

## INTRODUCTION

Fillers have been used for years in the manufacture of reinforced composites made with unsaturated polyester resins. Calcium carbonate and calcium sulfate are common fillers used in structural applications such as pick-up truck toppers, fiberglass tubs, showers and spas.

Alumina trihydrate and calcium sulfate are used to enhance the fire resistance of composites since both fillers have water bound in their structure. These products are designed to meet required building and/or transportation codes and regulations. Applications include everything from commercial showers to bowling ball cores, putties, marble casting, and solid surface countertops.

Using inert fillers for corrosion resistant composites was pioneered in the 1960's. This early application used sand, which is an inert silica-based material. Since a form of silica was already one of the raw materials used to manufacture fiberglass reinforcements, it did not compromise the corrosion resistance of the composite. However, sand has large heavy particles and provided specific challenges. Those included application techniques to incorporate the sand in the resin matrix and keep the particles evenly distributed once the fillers were incorporated into the resin matrix. Owens Corning Tank Division, now Containment Solutions, Inc., developed a manufacturing technique that allowed them to use treated sand successfully in composites and they continue to use it today.

Advances by the manufacturers of fillers to economically apply surface treatments have greatly expanded the use of fillers. Key developments have been fillers with hydrophobic coatings that enhance corrosion resistance in aqueous environments and the filler's ability to remain suspended in a resin mixture and reinforced composites.

Using treated alumina trihydrate (ATH) in corrosion resistant composites has been a commercial application since the 1990's. Using ATH lowers the overall cost of the composite, and it has minimal impact on corrosion resistance. Composites with ATH have higher flexural modulus, so a thinner composite can be used in applications where the modulus value is a design criteria.

## EXPERIMENTAL

All of the work was done with a single lot of a 1:1 isophthalic:maleic, all propylene glycol, unsaturated, polyester polymer commonly used in the corrosion industry. This was done to eliminate variations caused by differences in the polymer solution. The polymer was converted into a promoted thixotropic resin.

The resin and fillers were blended at a 80:20 ratio. Filler A is talc and Filler B is alumina trihydrate.

The thixotropic, unfilled resin was made and adjusted to viscosity, gel time, and cure development. Portions of this resin were then mixed with the fillers and the viscosities, gel and cure times were measured and recorded.

A Brookfield Viscometer, model LVT, spindle #3 at 6 and 60 rpm was used to check the viscosities of the resins at 77°F (25°C). The thixotropic index is the 6 rpm viscosity divided by the 60 rpm viscosity.

The gel time and cure were measured by placing a 100-gram mass in an 8-ounce (236 ml) paper cup, and adjusting it to 77°F (25°C). One gram of MEKP (DDM-9 by AtoFina) was added to the cup and the timer began when the mixing of the MEKP/resin started. It was mixed for 30 seconds and monitored for gelation. Once the mixture gelled, a thermocouple was placed in the center of the mass 1/8-inch (3.2 mm) from the bottom of the cup and the peak exotherm and cure time were measured.

The coupons for the corrosion testing were made according to ASTM C-581. A synthetic veil of Burlington Industries Nexus™ was used in place of the C-glass. This is especially critical for sodium hydroxide environments, where C-glass is not recommended because fiberglass is attacked quite rapidly by this environment. The coupons were cut into 5- by 4-inch (127 by 102 mm) rectangles and engraved in the upper right corner with identification.

They were then edge-coated and the engraving was sealed with the same resin to protect any exposed fiberglass ends from wicking the solutions into these areas of the coupon and negatively impacting the corrosion resistant testing.

The coupons were then post-cured. The post cure cycle consists of a four hour ramp up to 250°F (121°C), followed by two hours at 250°F (121°C) and then a 2-hour cool down to room temperature to minimize the thermal stresses.

The initial flexural strengths for calculating retention were established by testing thick, medium and thin coupons. Fifteen specimens were tested for each of the resin combinations.

Following are the corrosive environments used for the study: 1% nitric acid (pH 0.9), 5% nitric acid (pH 0.2), 10% phosphoric acid (pH 0.9), 5% sulfuric acid (pH 0.3), 10% sulfuric acid (pH 0.1), 1% ammonium hydroxide (pH 11.0), 40mg/l sodium hydroxide (pH 11.0), 1% sodium hydroxide (pH 12.0), 5% sodium hydroxide (pH 12.0), 1% sodium hypochlorite (pH 11.0), 0.1% detergent (pH 10.0), 0.1% soap (pH 7.0), 100% fuel C, 100% vegetable oil, and 100% tap water (pH 7.0) at 77°F (25°C). Samples were pulled out of the solutions and tested at periods of one, three, six and twelve months.

When the samples were pulled from the solutions, they were stored in a sealed container for conditioning at room temperature for 24 to 40 hours before testing for flexural strength and modulus. The specimens were tested within two days after the conditioning period.

## RESULTS & DISCUSSION

**Viscosity:**

The data is compiled in Table 1. Each of the fillers increased the viscosity as expected. However, Filler A significantly lowered the thixotropic index (0.39) compared to a slight increase (0.10) with “As Is.” Both materials should be sprayable through atomization and impingement style spray guns at their present viscosities and thixotropic indices, but Filler B would have better sag resistance when applied to a vertical surface than the mix made with Filler A.

**Gel Time and Cure:**

The data is compiled in Table 2. The unfilled and filled resins all cured well in this test. The filler did not significantly affect the gel time and the gel-to-peak time was shortened, which is likely due to the increase in the MEKP level, which was 1.5 compared to 1.0, based on the resin content in the 100 gram mass gel times.

The peak exotherm was significantly lowered with the incorporation of the filler. The filler acts as a heat sink so it will absorb energy as the resin/filler mixture exotherms. The drop in exotherm between the two resin/filler mixtures were comparable, 48°F (27°C) versus 55°F (31°C) respectively.

**Corrosion Resistance:**

The retention of flexural strength at one, three, six and twelve months for the three systems are compiled in Tables 3, 4 and 5. The retention of flexural moduli at one, three, six and twelve months are compiled in Tables 6, 7 and 8.

All of the resins did poorly in the basic environments - sodium hydroxide and sodium hypochlorite. This is typical performance for an isophthalic unsaturated polyester resin in these media. The sodium hypochlorite results are shown in Figures 1a, b and c. Filler A had better retention of properties at six and twelve months compared to the other composites. It had 8% greater retention of properties compared to the unfilled composite and 14% greater than Filler B.

All of the composites had an acceptable retention of properties in the other corrosive environments. Each of the mixtures retained at least 75% of their properties for each of the environments after twelve months of exposure.

Rating the three systems (“As Is”, 20% Filler A, 20% Filler B) was the next focus of this analysis, which involved grouping chemicals into families. The chemicals were broken down into four groups: Acid, Base, Solvent and “Other.” The groups of chemicals are listed in Table 9.

An average retention of flexural strength and flexural moduli for the three, six and twelve month readings are compiled in Tables 10 and 11 respectively. The readings from month one were not included because the samples showed very little change and would have dampened the overall results of the filler for the remaining test period.

The retention of flexural strength for the coupons made with Filler B were the best in Acid, Base and "Other" environments. The "As Is" sample did have better retention in the solvent environment. The coupons with Sample A had the lowest retention in all cases. The data

is plotted in Figure 2.

The retention of flexural modulus for the coupons made without filler, "As Is", were the best in the Acid, Base and "Other" environments. Filler A had a slightly higher retention than Filler B in the solvent environments. "As Is" had 2.8 lower retention than Filler A and 2.1 lower than Filler B. The data is plotted in Figure 3.

The average of the flexural strength and moduli for each of the chemical groups is listed in Table 12. Figure 4 graphically displays this data. The Acid, Solvent and "Other" chemical groups show the "As Is" and Filler B samples within 0.3 units of each other. The Base environment shows Filler B with 1.6 higher rating than "As Is." Filler A had the lowest rating in all four environments, ranging from 0.7 to 4.1 units lower.

The final analysis of the data is broken down into three categories: Strength, Modulus and Overall (all of the data). It is plotted in Figure 5 and listed in Table 12. Filler B had the highest rating (91.8) for the Strength category followed closely by "As Is" (91.1) and then Filler A (88.8). The Modulus category had "As Is" being the best (93.3) followed by Filler B (91.8) and Filler A (91.1). The Overall Rating of 92.2 by "As Is" was the highest rating and Filler B was very close at 91.8. Filler A had a rating of 90.0.

## CONCLUSIONS

1. The proper selection of a filler, ATH and talc have a slight impact on the gel, cure and viscosity properties of the resin.

2. The fillers lower the overall corrosion resistance of the composite.

3. The proper selection of filler can enhance the corrosion performance of the composite.

4. The talc filler gave better overall corrosion resistance performance than ATH filler.

5. The talc filler's overall corrosion resistance was similar to the unfilled resin (“As Is”).

## REFERENCE

This work is based on the original technical paper of the same title, published in 2005 by David J. Herzog, Anthony J. Bennett, David Jay Lampert, and Jason D. Schiro on behalf of Interplastic Corporation. It is available from the American Composites Manufacturing Association (ACMA).

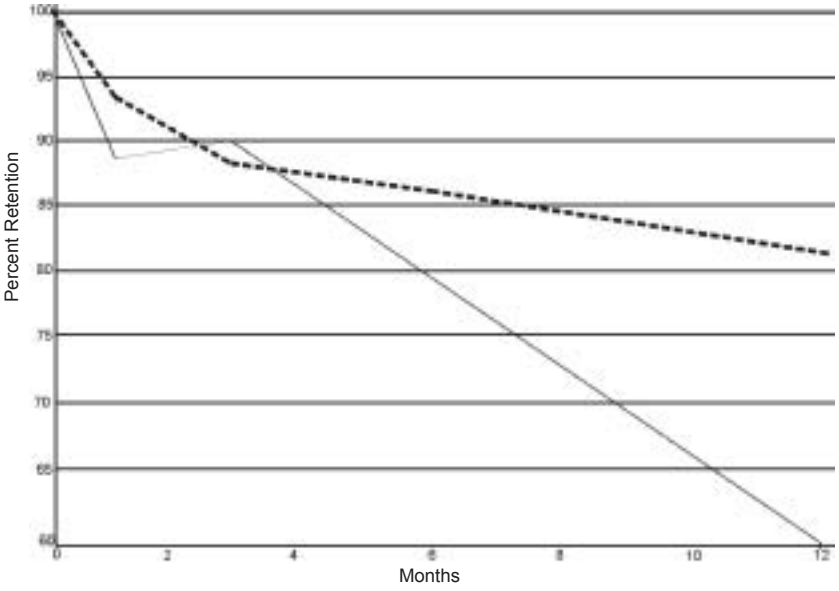
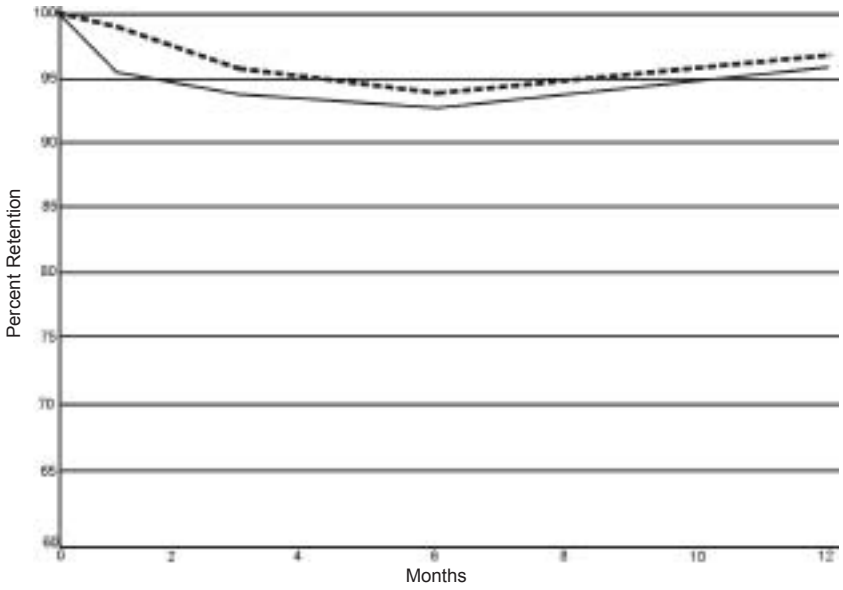
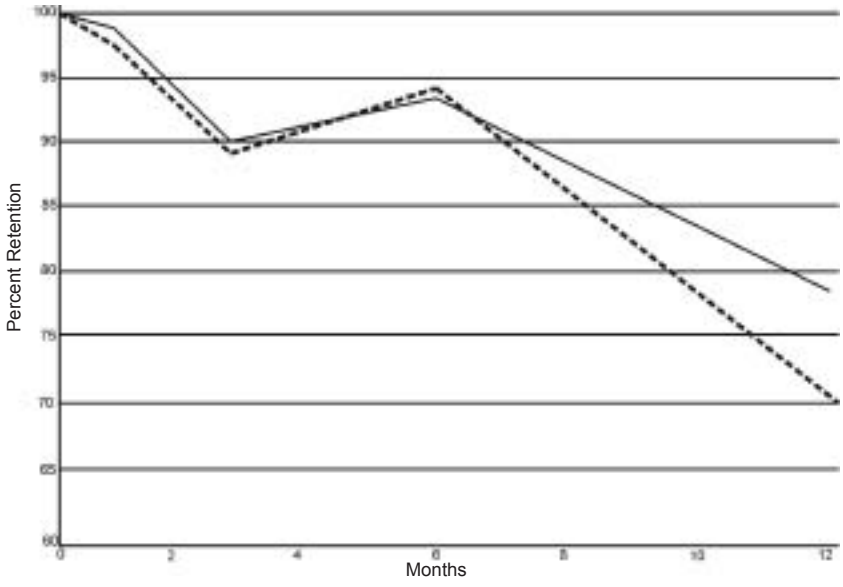



Figure 1:
1% Sodium Hypochlorite
Flexural Strength & Modulus

Neat Formula (“As Is”)




Filler A




Filler B

Figure 2: Flexural Strength Ratings in Various Media Families

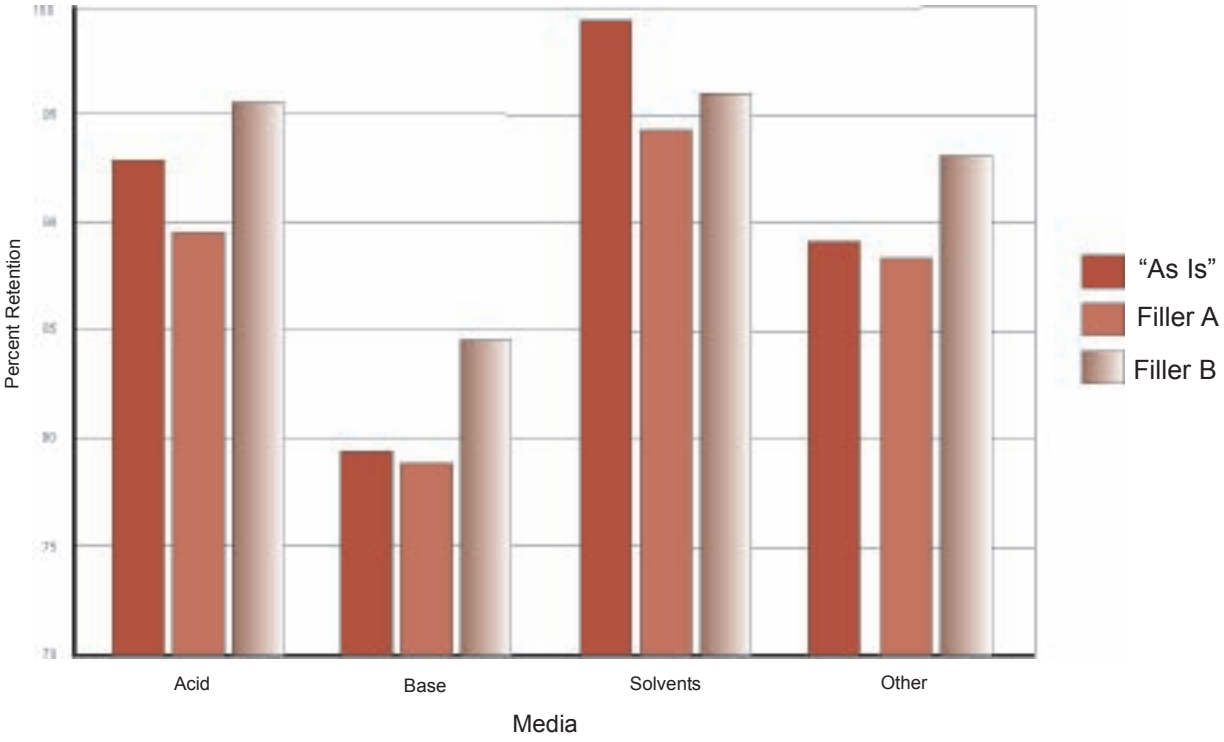



Figure 3: Flexural Modulus Ratings in Various Media Families

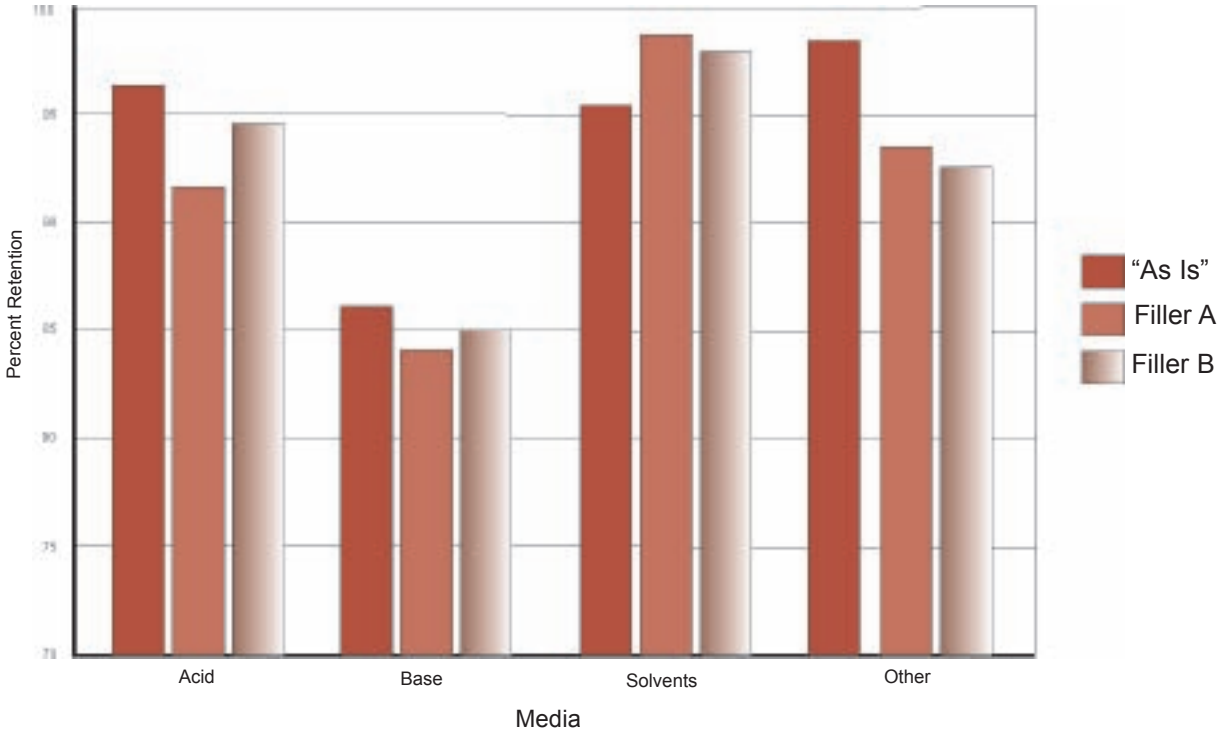


Figure 4: Ratings of the Combination Flexural Properties in Various Media Families

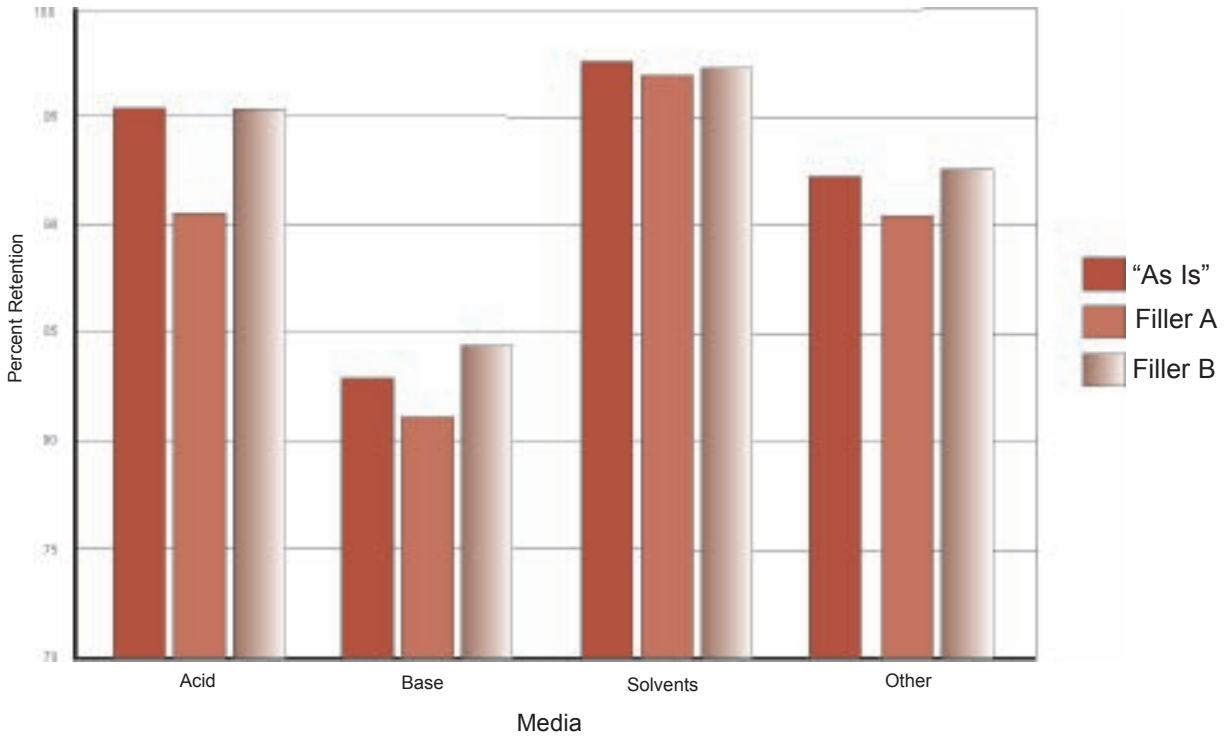
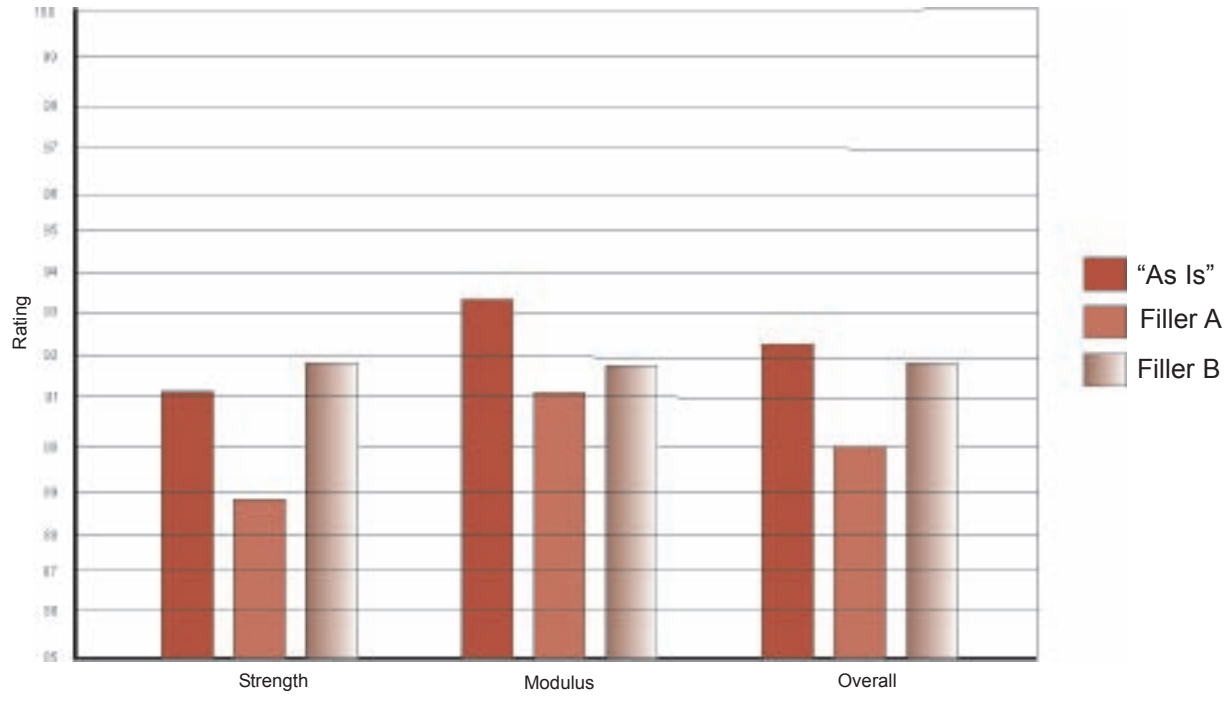



Figure 5: Overall Ratings of Corrosion Resistance



## Table 1: Viscosity Measurements

| Sample | "As Is" | Filler A | Filler B |
|---|---|---|---|
| Viscosity, cps | 392 | 550 | 600 |
| Thixotropic Index | 2.50 | 2.11 | 2.60 |

Samples mixed with 80% resin and 20% filler. Readings taken at 77°F/25°C.

## Table 2: Gel and Cure Measurements

| Sample | "As Is" | Filler A | Filler B |
|---|---|---|---|
| Gel Time - Minutes | 15.80 | 14.88 | 19.18 |
| Cure Time - Minutes | 28.91 | 25.67 | 28.92 |
| Gel-to-Peak Time - Minutes | 13.11 | 10.79 | 9.74 |
| Peak Exotherm °F/°C | 378/192 | 330/166 | 323/162 |

Data run with 1.0 grams of MEKP to 100 grams of resin/filler mixtures.

## Table 3: Flexural Strength on Unfilled Resins ("As Is")

| | Months | | | |
|---|---|---|---|---|
| Environment | 1 | 3 | 6 | 12 |
| 1% Nitric Acid | 100 | 100 | 100 | 100 |
| 5% Nitric Acid | 100 | 100 | 100 | 100 |
| 10% Phosphoric Acid | 100 | 100 | 99 | 93 |
| 5% Sulfuric Acid | 87 | 90 | 85 | 86 |
| 10% Sulfuric Acid | 100 | 86 | 78 | 79 |
| 1% Ammonium Hydroxide | 98 | 91 | 90 | 80 |
| 40 mg/L Sodium Hydroxide | 100 | 96 | 100 | 94 |
| 1% Sodium Hydroxide | 92 | 92 | 80 | 78 |
| 5% Sodium Hydroxide | 100 | 72 | 52 | 40 |
| 1% Sodium Hypochlorite | 88 | 90 | 78 | 60 |
| 0.1% Detergent | 100 | 94 | 95 | 100 |
| 0.1% Soap Solution | 82 | 82 | 85 | 74 |
| 100% Fuel C | 100 | 100 | 100 | 100 |
| 100% Tap Water | 83 | 100 | 100 | 91 |
| 100% Vegetable Oil | 100 | 100 | 100 | 100 |

| Environment | Months 1 | 3 | 6 | 12 |
|---|---|---|---|---|
| 1% Nitric Acid | 97 | 90 | 89 | 96 |
| 5% Nitric Acid | 98 | 100 | 97 | 90 |
| 10% Phosphoric Acid | 97 | 94 | 86 | 80 |
| 5% Sulfuric Acid | 93 | 82 | 89 | 77 |
| 10% Sulfuric Acid | 98 | 97 | 86 | 96 |
| 1% Ammonium Hydroxide | 92 | 87 | 87 | 84 |
| 40 mg/L Sodium Hydroxide | 96 | 94 | 92 | 96 |
| 1% Sodium Hydroxide | 91 | 88 | 75 | 85 |
| 5% Sodium Hydroxide | 84 | 61 | 42 | 35 |
| 1% Sodium Hypochlorite | 99 | 82 | 83 | 87 |
| 0.1% Detergent | 97 | 88 | 85 | 84 |
| 0.1% Soap Solution | 91 | 84 | 95 | 88 |
| 100% Fuel C | 92 | 89 | 92 | 90 |
| 100% Tap Water | 100 | 96 | 100 | 94 |
| 100% Vegetable Oil | 94 | 97 | 91 | 100 |

Table 4: Flexural Strength on Resin with Filler A

| Environment | Months 1 | 3 | 6 | 12 |
|---|---|---|---|---|
| 1% Nitric Acid | 94 | 92 | 92 | 98 |
| 5% Nitric Acid | 100 | 93 | 99 | 100 |
| 10% Phosphoric Acid | 100 | 88 | 90 | 99 |
| 5% Sulfuric Acid | 88 | 93 | 96 | 96 |
| 10% Sulfuric Acid | 100 | 95 | 100 | 96 |
| 1% Ammonium Hydroxide | 100 | 94 | 100 | 92 |
| 40 mg/L Sodium Hydroxide | 99 | 90 | 100 | 93 |
| 1% Sodium Hydroxide | 96 | 90 | 93 | 75 |
| 5% Sodium Hydroxide | 93 | 49 | 53 | 42 |
| 1% Sodium Hypochlorite | 98 | 90 | 94 | 79 |
| 0.1% Detergent | 100 | 89 | 96 | 89 |
| 0.1% Soap Solution | 100 | 93 | 96 | 98 |
| 100% Fuel C | 100 | 91 | 100 | 100 |
| 100% Tap Water | 99 | 92 | 89 | 100 |
| 100% Vegetable Oil | 98 | 96 | 100 | 99 |

Table 5: Flexural Strength on Resin with Filler B

| Environment | Months 1 | 3 | 6 | 12 |
|---|---|---|---|---|
| 1% Nitric Acid | 100 | 97 | 100 | 100 |
| 5% Nitric Acid | 93 | 91 | 93 | 91 |
| 10% Phosphoric Acid | 99 | 94 | 97 | 99 |
| 5% Sulfuric Acid | 98 | 98 | 100 | 98 |
| 10% Sulfuric Acid | 96 | 100 | 99 | 99 |
| 1% Ammonium Hydroxide | 99 | 96 | 96 | 89 |
| 40 mg/L Sodium Hydroxide | 97 | 96 | 100 | 99 |
| 1% Sodium Hydroxide | 95 | 100 | 95 | 87 |
| 5% Sodium Hydroxide | 97 | 83 | 67 | 42 |
| 1% Sodium Hypochlorite | 94 | 88 | 87 | 76 |
| 0.1% Detergent | 96 | 95 | 95 | 95 |
| 0.1% Soap Solution | 88 | 100 | 100 | 100 |
| 100% Fuel C | 97 | 96 | 94 | 88 |
| 100% Tap Water | 94 | 94 | 98 | 98 |
| 100% Vegetable Oil | 99 | 98 | 94 | 97 |

Table 6: Flexural Modulus on Unfilled Resin (“As Is”)

Table 7: Flexural Modulus on Resin with Filler A

| Environment | Months 1 | 3 | 6 | 12 |
|---|---|---|---|---|
| 1% Nitric Acid | 100 | 100 | 97 | 96 |
| 5% Nitric Acid | 99 | 89 | 85 | 75 |
| 10% Phosphoric Acid | 94 | 93 | 94 | 91 |
| 5% Sulfuric Acid | 94 | 90 | 89 | 87 |
| 10% Sulfuric Acid | 98 | 96 | 91 | 87 |
| 1% Ammonium Hydroxide | 97 | 98 | 96 | 92 |
| 40 mg/L Sodium Hydroxide | 99 | 96 | 93 | 97 |
| 1% Sodium Hydroxide | 94 | 96 | 96 | 84 |
| 5% Sodium Hydroxide | 88 | 78 | 50 | 39 |
| 1% Sodium Hypochlorite | 100 | 96 | 88 | 84 |
| 0.1% Detergent | 95 | 98 | 94 | 98 |
| 0.1% Soap Solution | 89 | 93 | 94 | 95 |
| 100% Fuel C | 99 | 95 | 98 | 92 |
| 100% Tap Water | 100 | 100 | 100 | 100 |
| 100% Vegetable Oil | 94 | 96 | 98 | 99 |

Table 8: Flexural Modulus on Resin with Filler B

| Environment | Months 1 | 3 | 6 | 12 |
|---|---|---|---|---|
| 1% Nitric Acid | 98 | 93 | 93 | 94 |
| 5% Nitric Acid | 97 | 90 | 92 | 90 |
| 10 % Phosphoric Acid | 95 | 94 | 95 | 95 |
| 5% Sulfuric Acid | 97 | 100 | 100 | 94 |
| 10% Sulfuric Acid | 99 | 93 | 96 | 96 |
| 1% Ammonium Hydroxide | 100 | 93 | 91 | 90 |
| 40 mg/L Sodium Hydroxide | 96 | 94 | 96 | 92 |
| 1% Sodium Hydroxide | 92 | 88 | 81 | 82 |
| 5% Sodium Hydroxide | 100 | 66 | 57 | 43 |
| 1% Sodium Hypochlorite | 97 | 89 | 95 | 70 |
| 0.1% Detergent | 99 | 92 | 94 | 91 |
| 0.1% Soap Solution | 96 | 90 | 96 | 94 |
| 100 % Fuel C | 100 | 100 | 100 | 96 |
| 100% Tap Water | 92 | 93 | 93 | 95 |
| 100% Vegetable Oil | 99 | 99 | 100 | 100 |

Table 9: Chemical Groups

| | |
|---|---|
| Acid | Nitric, Phosphoric, Sulfuric Acids |
| Base | Sodium Hydroxide, Ammonium Hydroxide, Sodium Hypochlorite |
| Solvents | Tap Water, Fuel C, Vegetable Oil |
| Other | Soap Solution, Detergent |

Table 10: Analysis of Flexural Strength Retention Data

| Media | "As Is" | Filler A | Filler B |
|---|---|---|---|
| Acid | 93.3 | 89.8 | 95.6 |
| Base | 79.5 | 78.5 | 84.7 |
| Solvents | 99.0 | 94.3 | 96.3 |
| Other | 88.3 | 86.8 | 93.6 |

Table 11: Analysis of Flexural Modulus Retention Data

| Media | "As Is" | Filler A | Filler B |
|---|---|---|---|
| Acid | 97.1 | 92.8 | 94.8 |
| Base | 86.7 | 84.2 | 8.0 |
| Solvents | 95.2 | 98.0 | 97.3 |
| Other | 97.5 | 93.9 | 92.8 |

Table 12: Overall Ratings of the Combination of Flexural Strength and Modulus Retention Data

| Media | "As Is" | Filler A | Filler B |
|---|---|---|---|
| Acid | 95.2 | 91.3 | 95.2 |
| Base | 83.1 | 81.4 | 84.8 |
| Solvents | 97.1 | 96.1 | 96.8 |
| Other | 92.9 | 90.4 | 93.2 |

Table 13: Overall Ratings

| Media | "As Is" | Filler A | Filler B |
|---|---|---|---|
| Strength | 91.1 | 88.8 | 91.8 |
| Moduli | 93.3 | 91.8 | 91.8 |
| Overall | 92.2 | 90.0 | 91.8 |

INTERPLASTIC CORPORATION
Thermoset Resins Division

1225 Willow Lake Blvd., St. Paul MN 55110-5145
651.481.6860 800.736.5497 fax: 651.481.9836
www.interplastic.com