

LOWER USPE EMISSIONS BY VINYL TOLUENE MODIFICATIONS

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ABSTRACT

As a result of the 1990 Clean Air Act amendments, the Environmental Protection Agency (EPA) is developing a Maximum Available Control Technology (MACT) standard for the regulation of Hazardous Air Pollutant (HAP) emissions by the thermosets composites industry. Styrene, the most important diluent for unsaturated polyester resins, will be the focus of the emissions problem for the open-molding composites industry. Styrene is widely used because of its good performance, low cost, and worldwide availability.

In its attempt to reduce styrene emissions, the EPA has proposed that the total styrene monomer content in corrosion resins be limited to less than 35%. If this proposal is incorporated into the MACT, isopolyester resins made from Amoco Purified Isophthalic Acid (PIA) used in open molding fabrication processes will be directly impacted. Thus, all of the industry's workhorse isopolyester corrosion resins are threatened and could potentially be legislated out of the market place.

In order to comply with the proposed EPA styrene limitations, BP Amoco initiated a program to lower the styrene content of Isopolyester corrosion resins. Successful styrene reduction methods include substituting monomers such as vinyl toluene which has a much lower vapor pressure. Also, because of its lower volatility, vinyl toluene will increase the flash point of the resin in addition to reducing the total volatile organic emissions of the resin. Although it is more expensive than styrene, it has been shown in the current study to be effective at low levels and is commercially available from Deltech Corporation.

The data show that vinyl toluene could be substituted for styrene monomer in a corrosion resin without a loss in corrosion properties. The resin blend containing 15% vinyl toluene performed at a level consistent with the all styrene control.

INTRODUCTION

The objective of this project was to determine if vinyl toluene monomer could be substituted for styrene monomer at various levels, in an isopolyester resin, without a loss of physical properties or a reduction in its corrosion resistance. An isopolyester corrosion resin was synthesized in our pilot plant and dissolved in styrene monomer, vinyl toluene monomer, and blends of both monomers. Liquid resins and clear cast properties were determined by conventional SPI and ASTM test methods. Composites (using ASTM C581 construction) of these resins were prepared and one year immersion testing in five different media was initiated. One year testing of these composites has been completed.

EXPERIMENTAL

The standard (1/1) isopolyester corrosion resin for this study was synthesized by the two-stage method to a high number average molecular weight in the pilot plant ten-gallon reactor. The formulation and some properties are shown in [Table 1](#). This resin was dissolved in styrene monomer (control), vinyl toluene monomer (sample D), and blends of both monomers; 70:30 (B) and 50:50 (C) styrene:vinyl toluene mixtures (see [Table 2](#)). Liquid resin properties of each blend were determined, [Table 3](#). As the percent of vinyl toluene monomer in the resins increased, several changes in the liquid properties were observed. First, the Brookfield solution viscosity increased and, second, the SPI Gel time was reduced. The most significant property change, however, occurred in the Volatile Organic Emissions. As the vinyl toluene content was increased, the emission levels were reduced. As expected, the lower vapor pressure of the vinyl toluene dramatically reduced the total organic emissions of the resins. This reduction was critical to meet the proposed MACT for styrene emissions.

The four resins were cast, post cured (two hours at 105 °C) and evaluated for physical properties. [Table 4](#) shows the physical properties of the unreinforced resins. There is a trade off in resin viscosity and HDT as the vinyl toluene content is increased. Solution viscosity increased and the Heat Distortion Temperature decreased as the vinyl toluene content is increased.

The composites for corrosion testing are prepared according to ASTM C 581. The resultant composites were 24 weight percent reinforcement (2 plies of 1.5 oz glass mat surfaced with 10 mil "C" veils) and 76% resin. Each resin used a gel system of Lupersol DDM promoted with cobalt octoate adjusted to give a pot life of about twenty minutes. The laminates were cured at room temperature overnight. Coupons were cut to size, 4 inches by 6 inches, and engraved in the corner for the future identification. The edges of the coupons were coated and the engraving was sealed with the same resin used in the composite. Sealing the edges of the coupons protected the fiberglass ends that were exposed when the panels were cut, so that wicking of the solutions into these areas of the coupon would not be a factor in the corrosion resistant testing. The coupons were then post cured at 105 °C for two hours and allowed to cool to room temperature. The cure development of the C581 composites was monitored by differential scanning calorimetry (DSC). All four of the resin systems had very similar cure times. The total glass reinforcement content of each composite was determined according to ASTM procedures. Internal flexural properties and Barcol Hardness (Instrument 934-1) were determined by testing ten specimens of each resin formulation and data are reported in [Table 5](#).

The test coupons were weighed and Barcol Hardness determined prior to being totally immersed in the test media. Test coupons were exposed in the following media: distilled water, 10% sodium carbonate, and 25% sulfuric acid at 71 °C; coupons were also exposed in ASTM Fuel C and gasoline with 10% methanol at 22 °C. Representative coupons were taken and tested at one, three, six, and twelve months. When coupons were taken from the aqueous solutions, they were rinsed with deionized water and wiped dry with a paper towel. After drying, all coupons were weighed and the Barcol hardness was determined before placing them in air-tight polyethylene bags. Four test specimens were prepared from each coupon and tested for flexural strength and modulus. The percent retained flexural strength, flexural modulus, and Barcol Hardness are reported to the nearest percent.

As described in Amoco Bulletin IP-49, analysis of data is traditionally done after one-year testing. Many experts believe that the resin deterioration occurs at a decreasing rate that is approximated by a logarithmic function. If so, when the first year's data are plotted on a log-log grid, the best straight line through them can be extended to predict retention of properties in the future. The properties measured are hardness, flexural strength, and flexural modulus. To access relative performance of the resin, an average retention value of the three key properties is plotted in Figures I-V below. This value is an arithmetic mean of the flexural strength, flexural modulus, and Barcol Hardness retention values.

RESULTS AND CONCLUSIONS

All of the resin blends were similar in liquid properties. Significantly, as the percent of vinyl toluene was increased from 15 to 50% of the resin composition, the volatile emissions of the resins were reduced 22-53 percent. The clear cast properties showed a modest reduction in flexural strength and heat distortion temperature as the levels of vinyl toluene increased. The effects of the vinyl toluene in the liquid and clear cast properties become more discernible as the level increases.

The corrosion data reflect a similar performance for all of the resin formulations in all of the test media except those samples aged in the gasoline/methanol blend. In the gasoline/methanol blend, the corrosion resistance of the resins dropped off significantly as the vinyl toluene content of the resin increased. The performance of the 15% blend (B) in this media, however, was similar to the all styrene control.

Based on the results of the one year corrosion resistance testing, a 15% vinyl toluene, 35% styrene blended resin is a suitable replacement for the all styrene resin in most corrosion applications.

ILLUSTRATIONS

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BIOGRAPHIES

Jim Van Fleet is a Research Technologist at the BP Amoco Research Center, Naperville, IL. Jim has been with BP Amoco for the past 11 years focusing on the applications of composite materials. His research areas are catalysts research, corrosion resistant resins, polymer concrete, and composites testing. His recent efforts have been directed at reducing styrene emissions from unsaturated polyester resins.

Mel Duhon is the Product Manager for Deltech Corporation in Baton Rouge, LA. Deltech is the sole world supplier of para-methylstyrene, vinyl toluene, and tertiary butyl styrene. Mel manages new business development, new applications, and the product specific technical concerns for Deltech Corporation as well as providing technical service to Deltech customers.

