A New Class of Metal Organic Thickeners for Sheet Molding Compound

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Abstract

A key requirement in the manufacture of sheet molding compound (SMC) is controlling the rheology throughout the production processes. The role of the thickening agent is to provide the required increase in viscosity of the resin paste mixture at a controlled rate during compounding, maturation (storage), and molding. Magnesium oxide (MgO) has been the most commonly used thickening agent for polyester based SMC. Due to MgO's high affinity to moisture, the rheological behavior is not always met and additional moisture control is required to achieve constant maturation time. Another challenge in using MgO thickeners can be an upward drift in viscosity over time that will push the compound beyond the targeted molding viscosity.

Novel thickening agents have been developed for SMC based on aluminum complex crosslinkers. The new metal organic thickeners eliminate the influence of moisture, therefore making it possible to achieve constant maturation timeline for every batch of polyester SMC produced. Viscosity studies demonstrate the new thickening agents provide stable viscosity with minimal drift once the targeted molding viscosity is achieved. Further mechanical characterization of the glass-polyester SMC, compounded with the new thickener formulation, showed equivalent or higher mechanical properties in comparison to conventional SMC.

Introduction

Sheet molding compound (SMC) is an important manufacturing process for the production of composites. Due to its good flow-ability and class-A surface finish, SMC have been in use for many secondary structure applications. Furthermore, the use of polyester and vinyl ester resins in the production of SMC is well documented.

SMC is a versatile long fiber thermoset composite process where fibers of 0.5 inch to 2 inch are randomly oriented and sandwiched between two thin layers of resin spread over carrier films. With the aid of a compression force, the fibers are impregnated with the resin paste mixture for complete wet out of the fibers. During compounding, the viscosity of the paste should not exceed certain limits or the fibers will not wet-out. The sandwich mixture (resin paste plus fibers) will continue to increase in viscosity during the compounding step resulting in a formable solid. The compounded material is staged until the target viscosity for molding is achieved (maturation), typically between 2 to 5 days.

Historically and currently, the primary thickening agents for polyester and vinyl ester based sheet molding compounds have been magnesium oxide (MgO) and magnesium hydroxide

($Mg(OH)_2$). Two of the challenges in using these common thickeners are moisture sensitivity and viscosity drift. A new class of aluminum organic thickeners has been developed to address the issues of viscosity drift and moisture sensitivity. The new class of aluminum thickeners has predictable viscosity control through the compounding, maturation, and molding stages. Once the targeted molding viscosity is achieved, the viscosity of the SMC remains stable without the upwards drift observed with other thickeners. The new class of aluminum thickeners is not moisture sensitive with respect to performance thus insuring the thickening process is predictable for time and viscosity.

Background

Aluminum organic compounds including aluminum alkoxides, aluminum acylates, and aluminum chelates are used as rheology modifiers and thickeners for resins and oils. The aluminum organic compounds provide thickening by forming covalent and coordinate linkages with hydroxyl and carboxyl functionalities. The covalent and coordinate linkages provide structure and body in numerous applications including lithographic ink vehicles, overprint varnishes, and rheology modifiers for coatings. Aluminum organic thickeners have been used to build structure in oils and resins through crosslinking for use in carrier systems. Aluminum organic thickeners are an adaptable method of controlling rheology or viscosity in applications where the requisite hydroxyl and carboxyl functionalities are present.

To develop new applications for the aluminum organic chemistries, search options include thickeners, viscosity modifiers, rheology modifiers, crosslinkers, and gellants. Previously, aluminum organic compounds have been demonstrated as thickeners for polyester resins. One example includes US Patent 4,265,975 “Polyester Resin Composition Containing Oxy Aluminum Acylates”.[1] This patent illustrates the thickening capability of aluminum acylates. US Patent 4,049,748 “Unsaturated Polyesters Combined with Organoaluminum Compounds” focusses on the reactivity of Aluminum Alkoxides.[2] US Patent 7,888,521 “Aluminum Chelates” focuses on a complex aluminum chelate for use as gellants.[3]

Viscosity Screening

Both commercial and experimental aluminum organic thickeners were screened with polyester SMC paste in laboratory viscosity studies. The SMC paste is a representative formulation (polyester resin, filler, initiator, and inhibitor) and commercial grade MgO was used as the control. The role of the thickening agent is to control the viscosity of the formulation throughout the production processes: compounding, maturation, and molding. The thickening agent is added to the paste formulation beginning the thickening process. It is imperative the viscosity of the paste does not increase too quickly or the fibers will not wet out. This will lead to weakness and delamination. Target viscosity for wetting out the fibers is less than 80,000 cP for 20 to 30 minutes. The target molding viscosity is typically between 12,000,000 to 25,000,000 cP. The target molding viscosity should be achieved in 2 to 5 days.

For the viscosity studies the viscosity of the paste was measured at 15 minutes, 1 hour, 3 hours, 1 day, 2 days, and so on. During the viscosity studies, it was realized that several of the commercial aluminum organic compounds were not suited for SMC applications. The increase in viscosity was too rapid, greater than 1,000,000 cP in 15 minutes. During the screening, there were aluminum organics with initial viscosity build comparable to the MgO control. Additional studies looked at concentration and moisture effects on the viscosity. The viscosity studies were evaluated over several weeks. The MgO control would drift upward beyond 30,000,000 cP with time. The aluminum organic thickeners would plateau once the targeted viscosity was achieved. Moisture added to the samples did not affect the viscosity build of the aluminum organic thickeners. Machine trials with the commercial aluminum organic thickeners were successful for compounding and molding, however mechanical testing of the molded parts did not meet the performance targets of the parts prepared with the MgO control. The carrier oils required for the solubility of the aluminum organics are compatible with most industrial coating applications; however, these oils appeared to be detrimental to the tensile properties for the SMC.

It was evident that a new class of aluminum organic thickeners was required that were specifically designed for SMC applications. Viscosity screening with the new class of aluminum thickeners had comparable results to the commercial aluminum organic thickeners. The initial viscosity build was similar to MgO to insure proper compounding. The maturation met the targeted molding viscosity in the required time and the viscosity plateaued once the targeted viscosity was achieved. Figure 1 shows the viscosity comparison for the experimental aluminum organic thickeners XP 480 and XP 482, the commercial aluminum organic thickener (standard), and the MgO control. The viscosities were recorded with a Brookfield HB5 viscometer with T-Bar set up. Based on the lab viscosity evaluations, compounding and molding trials were planned at Fraunhofer Project Centre with two experimental aluminum organic thickeners, one commercial aluminum thickener (Standard), and MgO as a control.

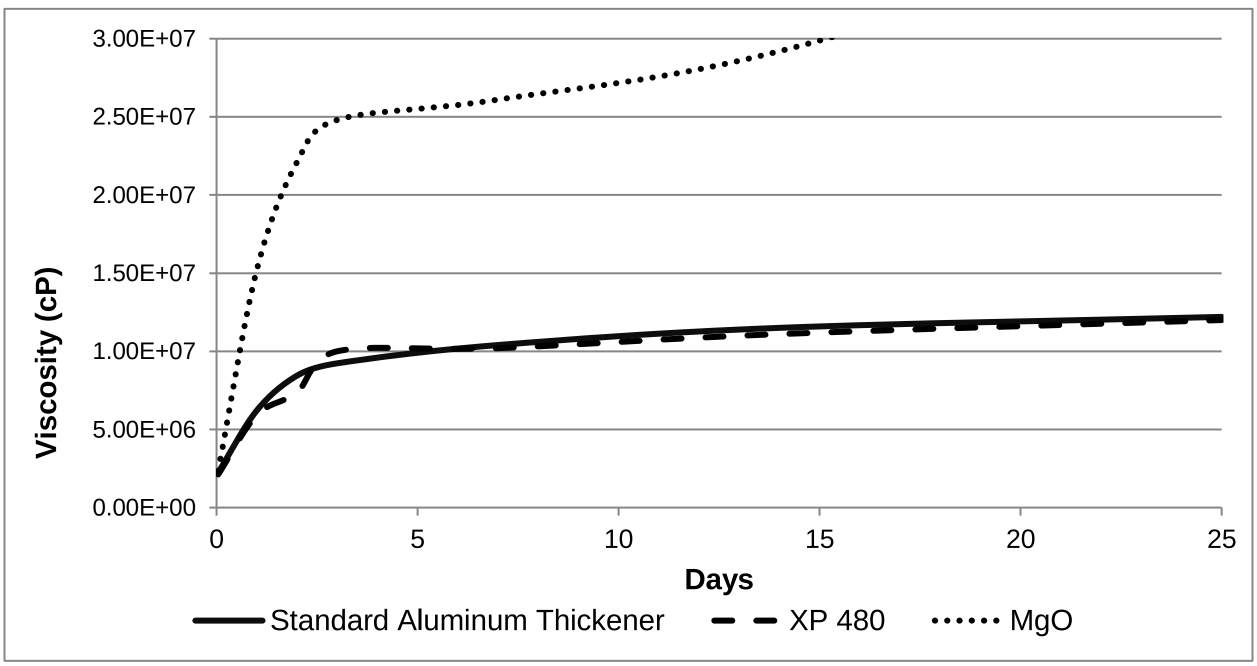

Figure 1: Viscosity screening of SMC paste comparing aluminum organic thickeners and MgO

Experimental section

SMC Compounding

For the machine trials, 6 different formulations were prepared. Four with the new class of aluminum organic thickeners at two different concentrations (XP 480 & XP 482), one formulation containing a commercial aluminum organic thickener (FedChem), and one commercially available MgO (Luvatol). Polyester resin (from Reichhold) was used in these formulations with 27% percent by weight of glass fiber (2400Tex glass fiber from Johns Manville). The thickener concentrations are shown in the Table 1.

Table 1: Thickener concentrations used in the trial

Thickener	Concentration 1 (phr)	Concentration 2 (phr)
XP 480	3.30	3.85
XP 482	3.85	4.40
Standard Aluminum Thickener	4.40	-
MgO	3.00	-

The compounding for the six formulations was completed on Day 1. The rolled SMC material was allowed to mature for 48 hours before molding. The rolled samples were then placed in a warm environment (28 – 30°C) to aid the maturation process.

Compression Molding

After 48hours of maturation, the sheets were cut to required dimensions in order to mold the material. A Dieffenbacher Compress Plus, 2500T press was used for compression molding. The mold was a 457 x 457 mm hard chrome plated shear edge tool used to make the plaques. The SMC sheets were cut to 250 x 250 mm sheets and stacked to layers of 4 and 5. The stacked up SMC charges were placed at the centre of the mold with about 30% mold coverage. Two plaques of each were manufactured and tested. The mold temperature was set to 150ºC (top mold – 147ºC and bottom mold – 148ºC) and cured for 300 sec. Samples are detailed as shown below.

Mechanical Testing

Tensile and Flexural tests per ISO 527 and ISO 14125 were performed on the plaques that were manufactured. Two samples of each kind were cut out from the plaques using water-jet cutting process. Figure below shows the location of the specimens from the plaques.

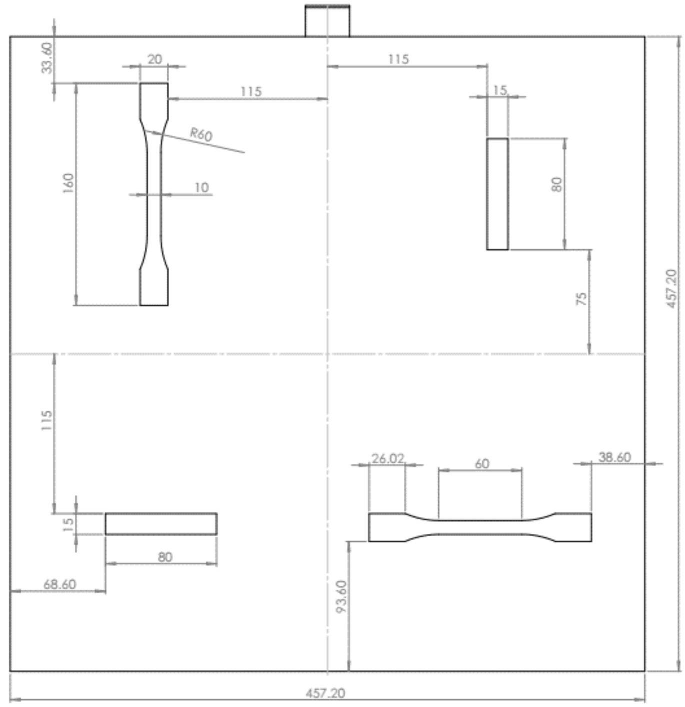

Figure 2: Schematics of the section of the plaque from which the specimens were cut out

Results and Discussions

Mechanical Test Results

1. Tensile Test

For each formulation 8 samples in total were tested. The tensile and flexural results reported in this paper. In all the graphs presented, the first 4 bars in blue represents the new thickener systems in development, followed by the standard aluminum based thickener from FedChem and finally MgO based thickener from Luvatol.

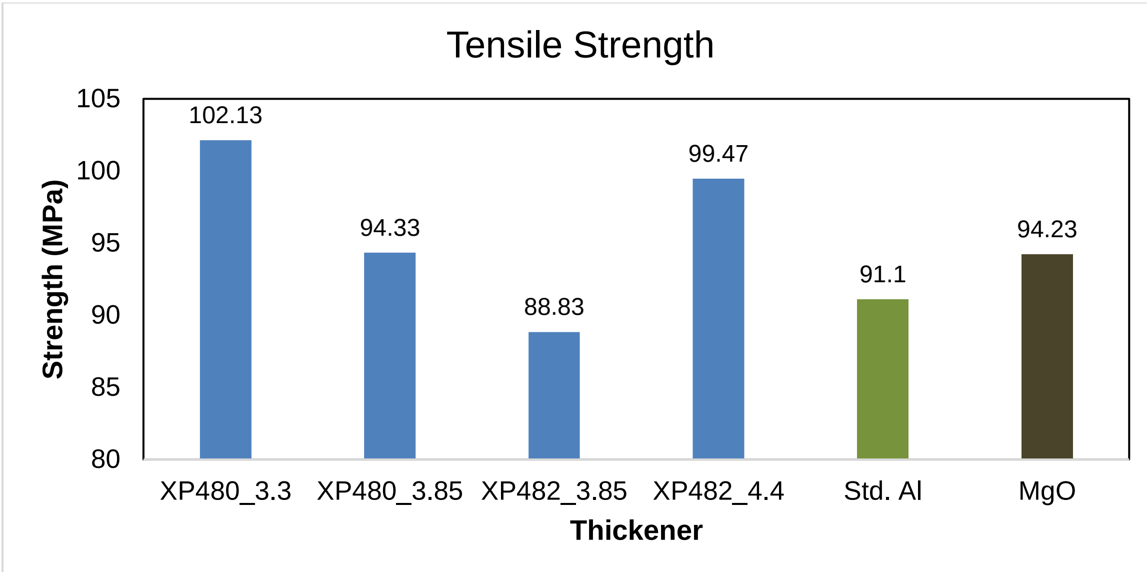

Figure 3: Tensile Strength of the samples after taking average of the samples tested

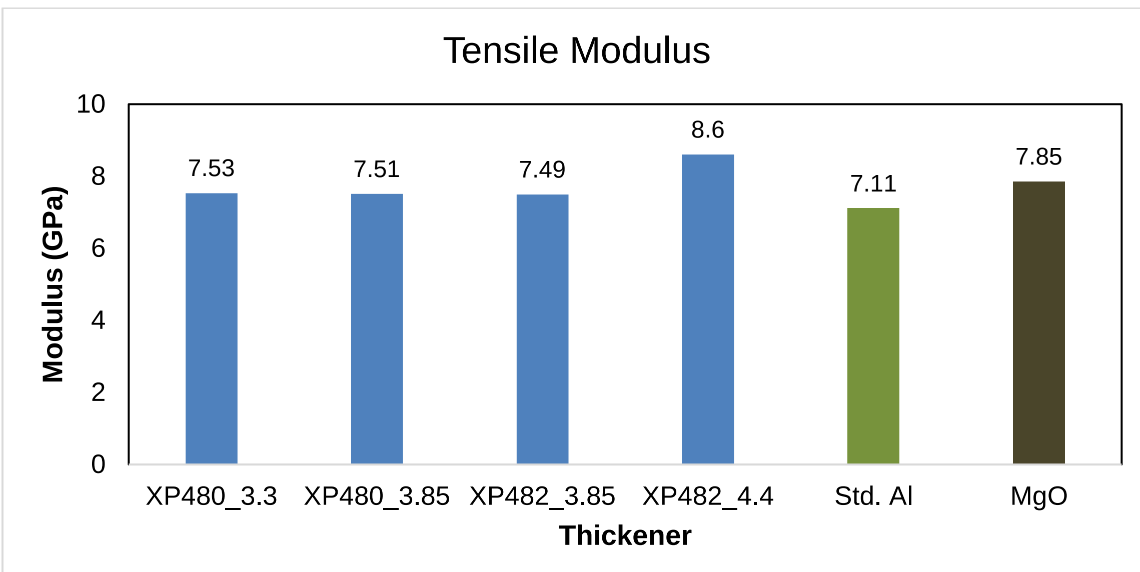

Figure 4: Tensile Modulus of the sample after taking average of the samples tested

As demonstrated by the graphs in Figures 3 and 4, both the new class of aluminum organic thickeners performed comparably with the commercially available MgO thickener. Even for the concentration which did not do as well as the others, the drop in properties are within 5% relative to MgO specimens.

2. Flexural Test

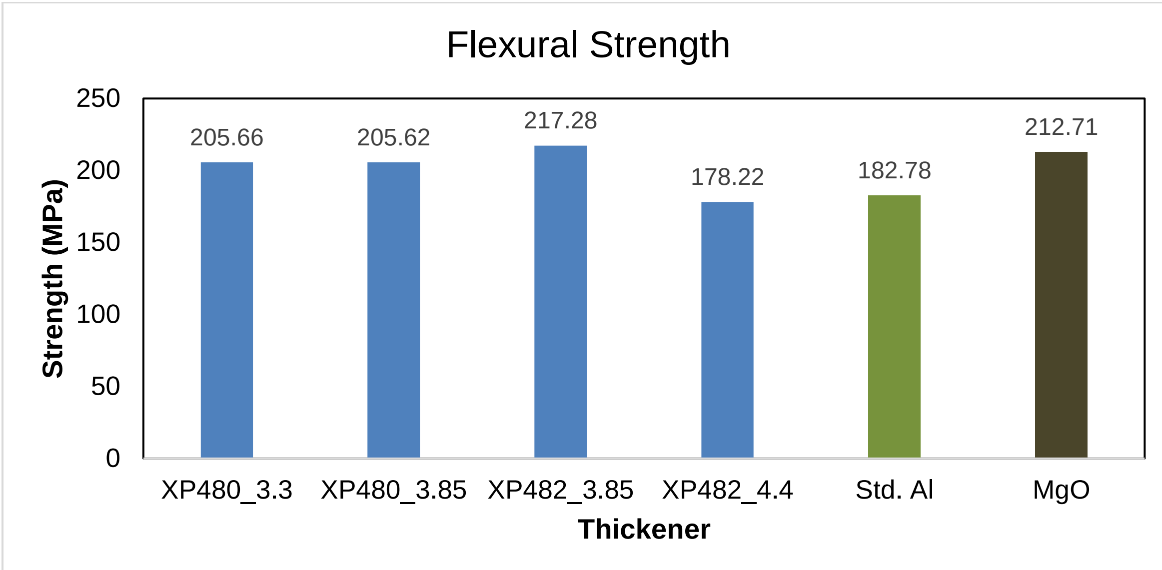

Figure 5: Flexural Strength of the samples after taking average of the samples tested

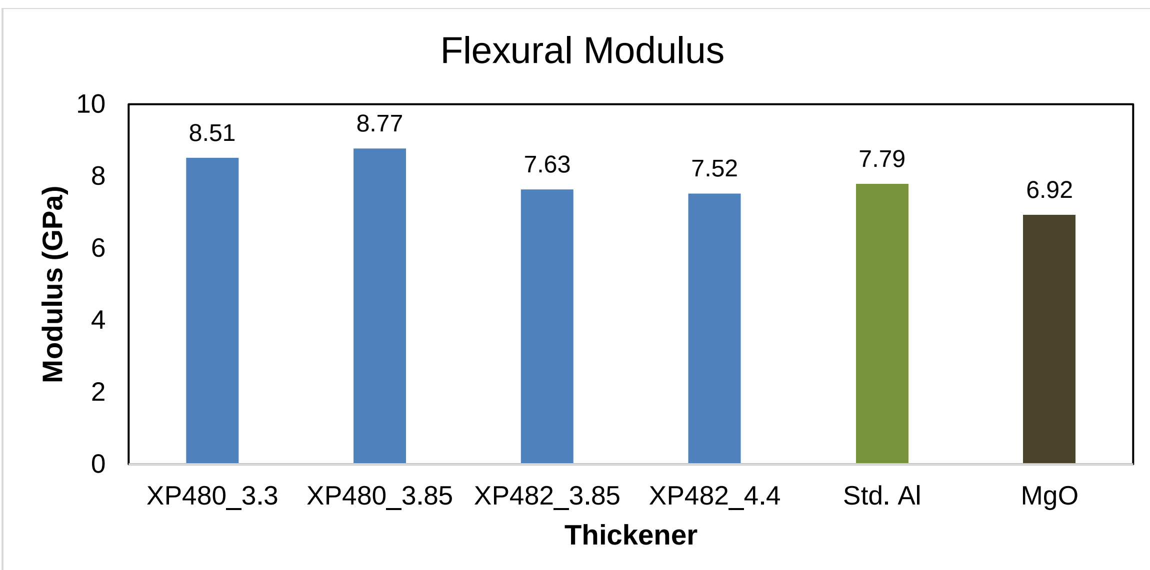

Figure 6: Flexural Modulus of the samples after taking average of the samples tested

Flexural strength of the formulations made using the new aluminum organic thickeners were in comparison to that of MgO. The 4.4 phr concentration of XP482 had a 16% reduction in strength relative to MgO but with 3.85 phr concentration, it outperformed the MgO thickeners. Modulus of the samples were found to be slightly higher for all the new generation thickeners.

Conclusion

A new class of aluminum organic thickeners has been developed for polyester and vinyl ester SMC applications. The liquid based thickeners can readily be metered into the resin paste mixture for ease of handling. Viscosity studies have shown the aluminum organic thickeners provide the required viscosity control through all stages of production and are stable with respect to viscosity drift. The new aluminum organic thickeners are not moisture dependent unlike the commercially available MgO based thickeners. The new full scale study which is reported here shows that the thickeners had predicable viscosity build required for compounding and molding. Mechanical testing of the molded parts showed comparable tensile and flexural properties relative to parts prepared with the MgO thickener. The new class of aluminum organic thickeners are a viable alternative for SMC viscosity control.