J Mater Sci (2007) 42:9822–9826
DOI 10.1007/s10853-007-1990-2

Impact of hygrothermal aging on the dynamic mechanical properties of Sheet Molding Compound

Ryan Mills · Douglas Gardner · Adriaan van Heiningen

Received: 13 March 2007 / Accepted: 11 July 2007 / Published online: 21 August 2007

Abstract Sheet Molding Compound, (SMC), is a composite material comprised of an unsaturated crosslinked polymer, reinforcing fiber such as glass, thermoplastic processing aids, mineral fillers, and lubricant (release agent). Mechanical properties for service requirements are developed through fiber reinforcements randomly aligned in between two polymer sheets. Service requirements for the SMC material are necessary for specified amounts of time. For example, SMC used for automotive parts have upwards of a 10 year service life; therefore, the study of how the SMC material changes with time and environmental exposure is of interest. In the current study, hygrothermal aging is used to accelerate normal environmental aging and dynamic mechanical thermal analysis (DMTA) is used to study the mechanical and chemical changes as a function of temperature and aging time. Results from the current study show through high performance liquid chromatography (HPLC) analysis that poly(vinyl acetate) (PVAc) does not chemically react with water in the SMC material and DMTA data show that water has two roles in the thickening reaction in the SMC between MgO and carboxylic acid functional groups adding an additional step to what has been previously reported.

Introduction

The initial motivation for this work was to replicate work in the literature with standard glass reinforced SMC. The replicated results would be used to compare to SMC fabricated with biobased fiber reinforcement to evaluate how well a biobased SMC competes with glass reinforced SMC. Hygrothermal aging analysis has been previously done with a class A SMC and serves as the experimental protocol for the biobased fiber study.

SMC in this study is a material comprised of an unsaturated polyester resin, PVAc low profile additive, MgO thickening agent, $CaCO_3$ filler, peroxide catalyst, and zinc stearate mold release agent. This material has been used for some time in the automotive and building product industries. The mechanical properties of the composite may be engineered through changes in the relative percentages of the components. However, most service applications for the material are external and the material is exposed to heat and moisture variations over long periods of time. SMC has been shown to develop microvoids when exposed to humidity and deteriorates over time in humid environments, [1, 2]. Previously, DMTA analysis was used to study class A SMC that had been exposed to hygrothermal aging, [3]. Results indicated that PVAc was hydrolyzed to poly(vinyl alcohol) (PVOH) and water is necessary for the reaction of carboxylic acid functional groups and MgO.

Objective

The objective of this work was to repeat and verify the results previously found [3] and compare glass to natural fiber reinforced SMC. Glass based SMC was compounded and denoted by AOC Resins. The final crosslinked SMC

R. Mills (✉) · D. Gardner
School of Forest Resources, and Advanced Engineered Wood
Composites Center, University of Maine, Orono, ME 04469,
USA
e-mail: Ryan.Mills@umit.maine.edu

A. van Heiningen
Department of Chemical Engineering, University of Maine,
Orono, ME 04469, USA

was fabricated at the University of Maine Advanced Engineered Wood Composites Center (AEWC).

Most findings from the hygrothermal aging analysis agreed with previous results [3]. However, HPLC was run on the aging solution to determine whether acetic acid was found in the leachate, which would support the hypothesis of Mendoza-Patlan et al. that PVAc hydrolyzes during aging and none was found. Also, DMTA data indicates that water has two functions in the MgO polyester thickening reaction.

Experimental procedure

The SMC consisting of polyester resin, PVAc, MgO, glass reinforcement, mold release agent, styrene, and catalyst was obtained from AOC resins, Valparaiso Indiana. A compression mold made of carbon steel was designed and fabricated to produce a Sheet Molding Compound (SMC) composite of approximately 18 cm by 18 cm. To make the molded SMC, an industrial B-stage SMC was acquired from AOC Resins. The B-stage SMC was successfully compression molded into C-stage SMC at 1000 psi, 150 °C and 3 min cure time. Samples of 7 mm × 3 mm × 45 mm were cut from the SMC. These samples were sanded to 1.8 mm thickness and then dried to constant weight at 70 °C and 103 °C.

Aging experiments

Aging experiments were done according to previous work in the literature [3]. Samples were cut using a diamond cutting saw, and polished to 7 mm × 1.8 mm × 45 mm and dried. After drying, the samples were placed into the water using a honeycomb type network to keep track of the different samples. The samples were hygrothermally aged at 70 °C. After the proper aging time elapsed, a sample was removed, weighed, and tested using DMTA analysis. An aliquot of aging solution was kept to be run using HPLC analysis.

Dynamic Mechanical Thermal Analysis

The tan δ for the hygrothermally soaked samples was determined by DMTA and was used to make a hypothesis about the possible chemical reactions taking place in the SMC matrix. The hygrothermal tests simulate an accelerated exposure of the SMC to the environment.

The hygrothermal aging was done as has been described previously [3]. The samples were sanded to 1.8 mm after drying then were placed in a honey comb like structure to keep track of the samples and were aged at 70 °C for the appropriate time, then removed and weighed. The samples were tested to prove that the material was homogenous demonstrating proper fabrication technique. Water sorption was determined gravimetrically to demonstrate pseudo saturation for the material.

DMTA analysis was done to determine the storage (elastic) modulus (E′) and loss (inelastic) modulus (E″) and loss tangent tan δ. The elastic modulus and inelastic modulus relate to the tan δ by E′/E″. The DMTA experiments were run isochronally in three point bending mode with a temperature range of −50–260 °C at 1 Hz frequency and 1 °C per minute ramp rate with an MKIV-Rheometrics DMTA. Strain settings were 1% to assure operation in the linear viscoelastic range. Liquid nitrogen was used to achieve the low temperature testing. All DMTA analysis was done at a frequency of 1 Hz and thermal heat ramps of 1 °C per minute to compare to previous results [3]. The aging times used were 3, 168, and 1032 h. Dried references were used to compare to the aged samples and to determine repeatability.

HPLC analysis

The aging solution was analyzed by high performance liquid chromatography (HPLC) to determine whether any of the SMC components leach into the water. Samples were analyzed using a Shimadzu HPLC equipped with a refractive index detector on a BioRad HPX-87H organic acid analysis column. The mobile phase was 0.5 mM sulfuric acid at 0.6 mL/min, run at 60 °C.

Results and discussion

Water uptake as a function of time

After polishing, the samples were aged and gravimetrically determined the water weight content as a function of time (Fig. 1).

Water sorption for the material approaches saturation at 1032 h of aging and the sorption has a Fickian behavior (Fig. 1b) agreeing with previous diffusion studies of the material. Equation 1 is used to determine the diffusion coefficient for the SMC [4].

$$M = M_m \left[\frac{4}{\pi} \sqrt{\frac{Dt}{e^2}} \right] \qquad (1)$$

where M is the mass of water absorbed, M_m is the mass at saturation, D is the diffusion coefficient and e is the thickness of the material. The diffusion coefficient works out to be 8.64×10^{-13} m^2/s.

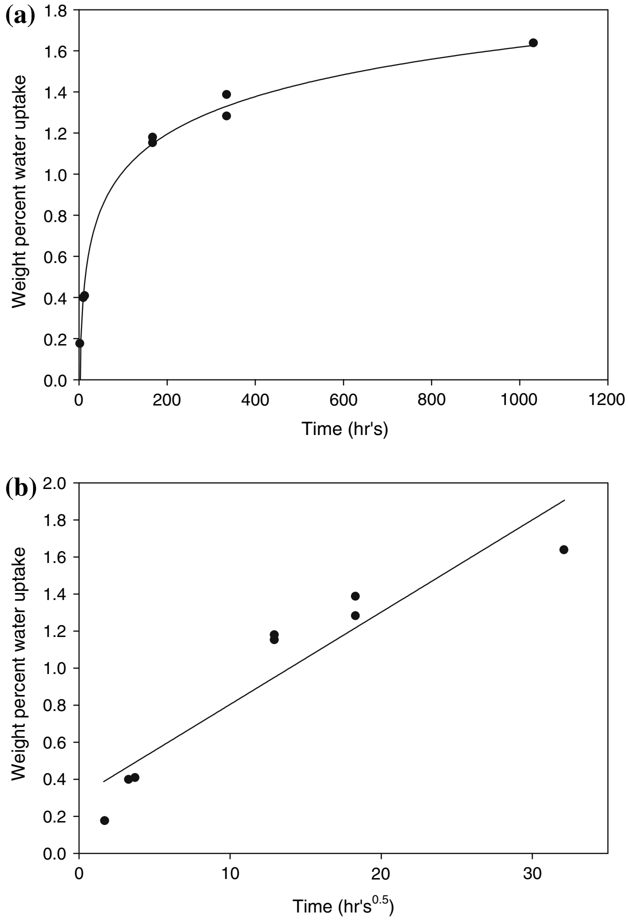

Fig. 1 Dry weight percent water uptake during aging, (**a**) as a function of time, and (**b**) as a function of the square root of time

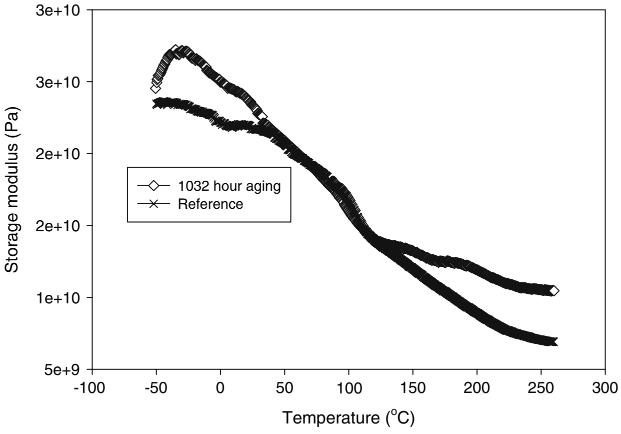

Fig. 2 Storage modulus for reference × and 1032 h aged sample ◇

Material storage modulus response

As Patlan et al. reported, the storage modulus of the material doesn't change with aging in magnitude, (Fig. 2), but the glass transition peaks do change. This leads to an analysis of the tan δ peaks of the material to understand the changes occurring in the material as a function of aging time.

DMTA repeatability

Multiple heat ramps with the DMTA were necessary to get reproducibility with the same SMC sample perhaps demonstrating irreversible thermally induced internal relaxation for the material (Fig. 3.). Each sample has a slightly different tan δ in magnitude, but show the same glass transition peaks for the individual components in the composite. These slight differences are very small considering the magnitude of the inelastic and elastic modulus and are a result of small differences in the samples. The glass transitions of the individual components impact the elastic and inelastic modulus magnitudes and can be seen as peaks in the tan δ plots. Comparison of the qualitative magnitudes of the peaks is an indication of the quantity of the material in the sample. By comparing the aged samples to a reference sample, differences in the relative magnitudes of glass transition peaks may give insight into the impact of exposure to heat and humidity. By aging samples for short, intermediate, and long time periods, a complete cycle analysis of the aging of the material may be deduced. Table 1 lists the chemical and corresponding temperature for the glass transition seen in DMTA analysis.

DMTA glass transition analysis

Table 1 summarizes the following: that the reaction of carboxylic functional groups and the magnesium oxide create a complex that has a glass transition peak in the

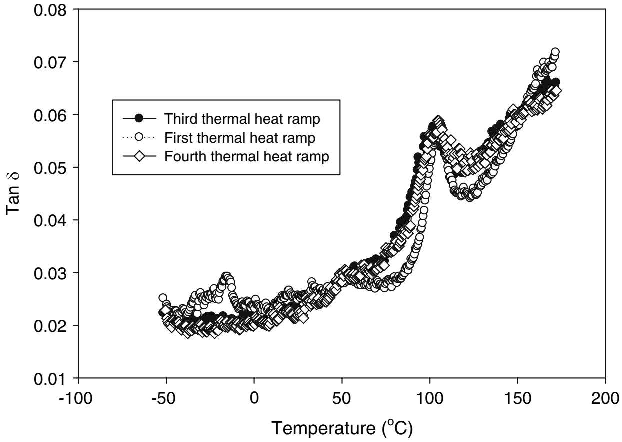

Fig. 3 Multiple DMTA thermal ramps on the same SMC sample, Initial heat ramp, ○ third heat ramp, ■, fourth heat ramp, ◇

Table 1 Temperature corresponding to tan δ peaks

Temperature, °C	Chemical pertaining to Tan Delta peak
25	RCOOH-Mg^{2+}–HOOCR, [3]
50	Poly(vinyl acetate), [3]
85	Poly(vinyl alcohol), [10]
110	Unsaturated polyester, (UPE), [5]
150–250	Cross linked polyester network, (PE), [3]

range of 15–30 °C ; the low profile additive PVAc has a glass transition in the range of 45–55 °C; the glass transition for PVOH is in the range of 80–90 °C; unsaturated polyester resin has a glass transition in the 100–120 °C range; and the crosslinked polyester network has a glass transition from 140–260 °C range. These peaks are the basis of the DMTA analysis.

A set of graphs were made with DMTA curves at all the different aging times for comparison of the relevant glass transition peaks (Fig. 4).

Previously, Mendoza-Patlan et al. reported that the metal carboxylic acid functional complex produced a peak in the range of 25 °C [3]. This peak is also observed with the SMC material in this study. However, where the previous researchers only saw the peak after aging, in this study the peak is found for samples that had no accelerated aging. The proposed mechanism for metal oxide coordination polymers reported by Mendoza-Patlan et al. was first presented by Vansco-Szmercsanyi et al. [6–9]. This mechanism requires water to initiate the formation of the metal carboxylate. Mendoza-Patlan et al. dried their sample in the range of 68–72 °C and in this study the samples were dried at 72 °C and 103 °C. The increased drying temperature was used in an attempt to drive off all the water to inhibit the thickening reaction. Even with all the samples dried at 103 °C the peak at 25 °C is still apparent.

One difference between Mendoza-Patlan et al. samples and the samples in this study is the presence of unsaturated polyester after crosslinking indicating that there is more mobility in our samples. Vansco-Szmercsanyi et al. reported that only trace amounts of water are necessary to initiate the metal carboxylate reaction. Drying to constant weight at 72 °C doesn't remove all the water. Even drying to constant weight at 103 °C doesn't remove all the water and the thickening reaction should take place unless the metal carboxylate complex isn't mobile enough to form the proper geometry for the reaction to occur. By aging the SMC in solution, the polymers may over time orient in such a way with the metal oxide so the thickening reaction takes place. This would explain the difference between Mendoza-Patlan et al. results and the results presented here. Therefore, water is necessary for both the reaction to take place and also contributes to increased molecular mobility in the SMC material allowing for proper molecular orientations.

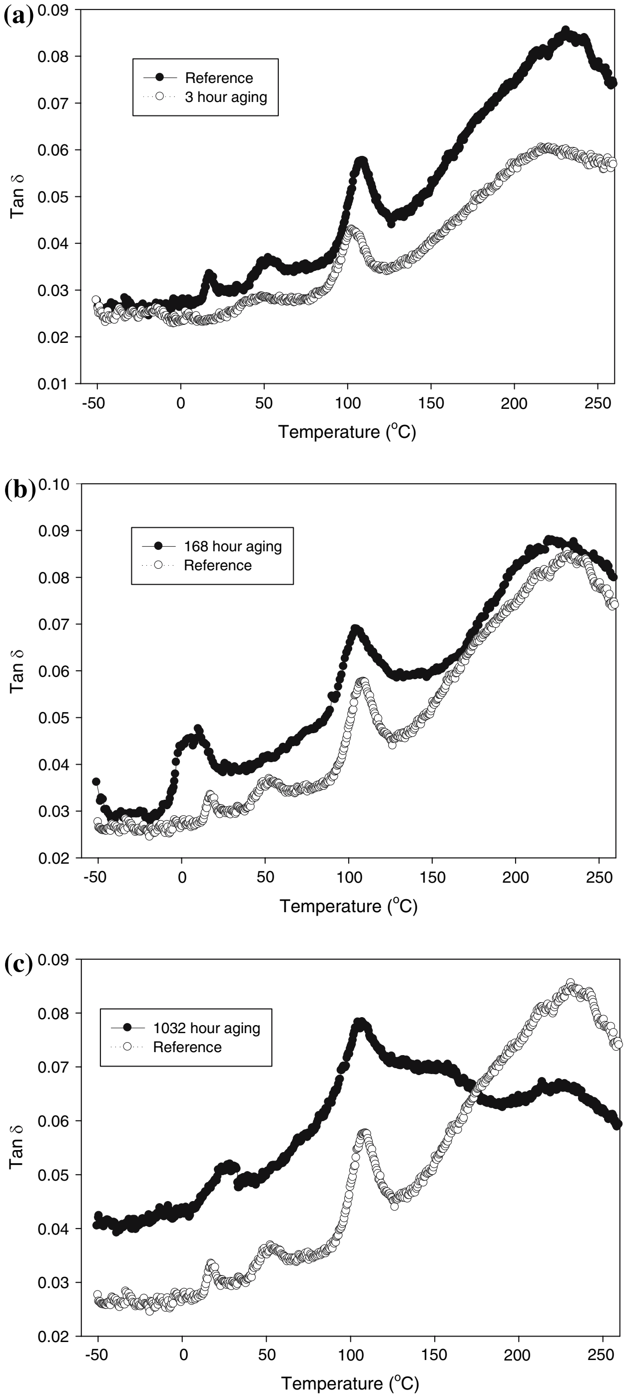

Fig. 4 Tan δ for reference and aged samples, (**a**) 3 h, (**b**) 168 h, and (**c**) 1032 h

Mendoza-Patlan et al. also reported that PVAc was hydrolyzed to PVOH and acetate during aging. To investigate this further, the aging solution used to age all the samples was analyzed by HPLC analysis.

HPLC analysis

For the HPLC analysis, the *Y*-axis units are uRIU, or micro refractive index units. This value is the difference between the current refractive index and the value when the instrument was calibrated with the mobile phase. In the top scan, (Fig. 5) for the aging solution, three peaks are seen at 6.5 min, 10.8 min, and an inverted peak at 22.5 min. The standard samples are in the lower scan to compare with the aging solution. If poly(vinyl acetate) is converted to poly(vinyl alcohol), acetic acid should be produced. An acetic acid sample, concentration of 2 g/L, was run with fucose, concentration of 2.3 g/L, as a standard reference. Two peaks are seen with fucose at 10.9 min and acetic acid at 15.2 min. The acetic acid peak at 15.2 min doesn't correspond to any of the peaks in the aging solution indicating that acetic acid is not present in the aging solution. Based upon the composition of the SMC, styrene was hypothesized to be one of the chemicals leaching from the SMC during aging. Therefore, another HPLC run with styrene, concentration of 50 g/L, using the same column was performed. An inverted peak at 22.5 min is seen for the styrene. Comparison with the chromatograph of the aging solution therefore suggests that styrene is one of the molecules being leached out of the SMC. The other two peaks in the aging solution are still unidentified but are thought to be PVAc and residual or unreacted polyester, as these molecules may have a retention time similar to fucose. A HPLC chromatograph was not generated for PVAc because the exact PVAc used in the composite was not available to run as the SMC received from AOC resins was in compounded form and couldn't be run on the column to determine retention time. However, the decrease in intensity for the PVAc glass transition peak from DMTA analysis seen in both Mendoza-Patlan et al. and the current investigation during aging would be consistent with PVAc being leaching out of the SMC during aging. Further analysis of the DMTA curves shows no glass transition peak for PVOH. PVOH would be the product of the hydrolysis of PVAc. Glass transition peaks for PVOH in DMTA analysis have been determined to be in the range of 85 °C, [10]. Analysis of Mendoza-Patlan et al. DMTA curves also show no glass transition peaks for PVOH [3].

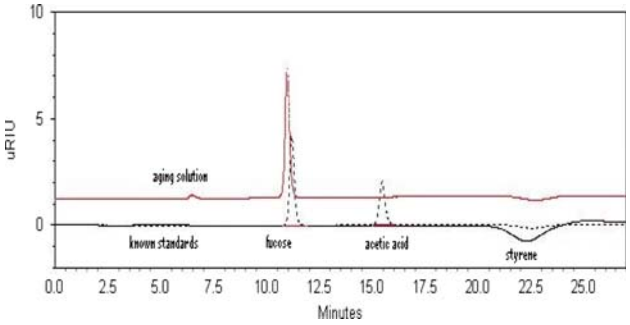

Fig. 5 HPLC scan of aging solution for SMC, fucose and acetic acid, and styrene

Conclusions

Hygrothermal aging of SMC has impacts on the chemical make up and mechanical properties of SMC. The accelerated aging by hydrothermally soaking the SMC at 70 °C gives insight as to how the material may change over longer periods of time exposed to heating and drying combined with humidity cycles. One of the most significant impacts is the plasticization of the material allowing for the molecular motion of polymeric chains resulting in proper orientation for complexation reactions. This is shown by the presence of the MgO thickening reaction even after drying to constant weight at 103 °C hypothesized to be a result of a lower degree of crosslinking compared to previous studies [3]. The low profile additive that is not covalently linked to the polyester matrix may leach into the aging solution over time and explains the decrease in the PVAc peak. The PVAC doesn't react with water to form PVOH as there is no peak for PVOH in the DMTA scans and no acetic acid found in the aging solution.

Acknowledgements The DOE IFPR grant number DE-FC36–046014306 and the National Science Foundation under Grant No. EPS-0554545 are acknowledged as providing financial support for this project, Sara Walton for the HPLC analysis, and AOC resins for the B stage SMC.

References

1. Chan-Park MB, McGarry FJ (1996) Polym Composite 17:537
2. Saito R, Kan WMJ, Lee LJ (1996) Polymer 37:3567
3. Mendoza-Patlan N, Martinez-Vega JJ, Revellino M (2001) J Mater Sci 36:1523
4. Ghorbel I, Valentin D (1993) Polym Composite 14(4):324
5. Saratomer Corporation, "Saratomer composites concepts, vol. 1" http://www.sartomer.com/TechLit/3025.pdf, as on 1 March 2007
6. Vancso-Szmercsanyi I, Szilagya A (1974) J Polym Sci Pol Chem Ed 12:2155
7. Szilagya A, Izvekov V, Vancso-Szmercsanyi I (1980) J Polym Sci Pol Chem Ed 18:2803
8. Vancso-Szmercsanyi I, Szekely-Pecsi ZS (1983) J Polym Sci Pol Chem Ed 21:1901
9. Alvey FB (1971) J Polym Sci A1 9:2233
10. Cendoya I, Lopez D, Alegria A, Mijangos C (2001) J Polym Sci Pol Phys 39:1968