

Toughened and High Temperature Stable Vinyl Esters based on Fatty Acid Modifications for Liquid Molding Applications

by

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Liquid resins used for molding composite structures are a significant source of volatile organic compounds (VOC) and hazardous air pollutant (HAP) emissions. One effective method for reducing styrene emissions from vinyl ester (VE) resins is to replace some or all of the styrene with fatty acid-based monomers. In this investigation, the styrene was reduced to 20 wt% compared to 40-60 wt% associated with commercial products. In addition, fatty acid-based monomers can bring about other benefits like higher toughness, lower exothermal heat and low cure shrinkage. One disadvantage of these fatty acid-based VE resins, however, is the reduction in glass transition temperature (T_g) which limits their use in high temperature environments. Therefore, the specific focus of this work was to design high T_g fatty acid-based VE resins with low viscosities and high fracture properties. These high T_g resins were designed by blending fatty acid monomers with novolac vinyl esters. Various low viscosity formulations were established with T_gs as high as 147°C. Vinyl terminated poly(butadiene-co-acrylonitrile) (VTBN) and epoxy terminated poly(butadiene-co-acrylonitrile) (ETBN) were used as modifiers to these fatty acid vinyl ester resins. Though marked enhancement in fracture toughness was achieved without sacrificing T_g, further improvement in fracture toughness was limited due to the immiscibility of ETBN and VTBN with VE resins evaluated. The miscibility problem can be mitigated by using high acrylonitrile content carboxyl terminated poly(butadiene-co-acrylonitrile) (CTBN) but in this case a slight loss in T_g was detected. Thus modifiers having appropriate miscibility with VE resins to improve the fracture toughness without sacrificing T_g need to be identified by further work.

Introduction

Vinyl esters (VE) are one of the most popular resin systems used in polymer matrix composite fabrication for military and commercial applications due to their good properties, low weight and low cost. However, current commercial VE resins generally contain a high concentration of styrene to provide low viscosities suitable for composite fabrication via low cost liquid transfer molding techniques. Styrene is a hazardous air pollutant (HAP) and a volatile organic compound (VOC), and its use in composite manufacturing is being limited by the Federal Environmental Protection Agency of the United States of America [1]. Accordingly, fatty acid monomers have been developed and used to partially replace styrene in VE resins because of their low cost, low volatility, and because they are derived from renewable resources. These monomers allow for the production of high performance composites while using ~20 wt% styrene, compared to 40-60 wt% styrene associated with commercial products [2,3]. Additionally, the use of fatty acid monomers in VE resins can result in other beneficial properties, such as high toughness, low exothermal heat and low cure shrinkage.

One disadvantage associated with the use of fatty acid monomers as reactive diluents is the low T_g (<0°C) of their homopolymers compared with that of styrene (~100°C). This limits their use in producing VE resins for high temperature applications. The use of multifunctional novolac VE resins was explored to partially counteract the loss of T_g resulting from fatty acid monomers and to produce high temperature, low VOC VE resins. Aside from their high styrene content (33%) relative to fatty acid-based vinyl esters, commercial multifunctional novolac VE systems, such as Derakane 470-300 and 470HT-400, possess low fracture toughness due to their high crosslink densities. Though the presence of fatty acid can diminish this problem, other effective modifiers have to be employed to improve fracture toughness further.

Fracture toughness of VE resins can be improved by the addition of liquid rubber modifiers[4-7]. Vinyl terminated poly(butadiene-co-acrylonitrile) (VTBN) and epoxy terminated poly(butadiene-co-acrylonitrile) (ETBN) provide significant improvement in certain VE resins, provided that the liquid rubber forms a miscible system with VE monomers prior to cure and precipitates completely from the resins resulting in a second phase after cure [4].

The goal of this study is to make low VOC, high performance VE resins by using fatty acid to modify current commercial novolac VE resins. Ideally, the resulting resins will have low viscosities suitable for liquid molding, T_gs after hydrothermal conditioning (wet T_g) over

120°C, and fracture properties greater than those of commercial novolac VE resins.

Materials and Experimental Procedure

Materials: Derakane 470HT-400 vinyl ester resin was obtained from Ashland and was used without modification. Epon Resin 160, a novolac epoxy, and Epon 828, a diglycidyl ether of bisphenol A (DGEBA), were purchased from Hexion Specialty Chemicals and were used to synthesize vinyl ester resins. Methacrylic acid was purchased from Aldrich chemicals and was reacted with the epoxy monomers to produce vinyl ester (Figure 1). Two commercial DGEBA vinyl ester resins with $n \sim 0.1$ and containing no styrene, CN 151 and RDX 26936, were obtained from Sartomer and Cytec Surface Specialties Inc., respectively. Octanoic acid is a fatty acid with eight carbon chain length. Methacrylated octanoic acid (MOct) was produced by Applied Poleramic, Inc. and was used without modification. The liquid rubbers used for the toughening study were vinyl terminated poly(butadiene-*co*-acrylonitrile) (Hycar 1300×33), epoxy terminated poly(butadiene-*co*-acrylonitrile) (Hycar 1300×40) and carboxyl terminated poly(butadiene-*co*-acrylonitrile) (Hycar 1300×13) provided by Noveon Solutions.

Vinyl Ester Resins Preparation: Vinyl ester monomers were prepared by reacting methacrylic acid with Epon 160 ($n=0.5$) and Epon 828 ($n=0.098$) to produce VE 160 and VE 828, respectively (Figure 1). The reaction was catalyzed by 1 wt% AMC-2 (Aerojet Chemicals, Rancho Cordova, CA), which is a mixture of 50% trivalent organic chromium complexes and 50% phthalate esters. In order to maintain stability and prevent gelation, 0.01 wt% or 100 ppm hydroquinone was added as an inhibitor. Typically, the reaction was allowed to proceed for 2 hours and a green liquid product was obtained. Acid number below 4 and disappearance of the epoxy peak (917cm^{-1}) were used as two indicators for the end of the reaction

Room Temperature Cure of VE Resins: VE resin systems were initiated using Trigonox 239A (Akzo Nobel Chemicals, Chicago, IL), containing 45% cumene hydroperoxide, and cobalt naphthenate (CoNap) (Aldrich) as a catalyst to promote room temperature cure. The Trigonox and CoNap concentrations were 1.5% and 0.375%, respectively, of the total resin mass. All resins were allowed to cure at room temperature for 16h. Post-cure was realized by heating at $130^\circ\text{C} \sim 150^\circ\text{C}$ for 2 h.

Water Absorption Study: Samples with dimensions $30 \times 12 \times 1.5\text{ mm}^3$ were exposed to a controlled humidity environment (60°C and 79% relative humidity) until saturation was reached. The samples were periodically removed and weighed, and then re-introduced to the humid environment. Saturation was achieved when

the sample weight no longer changed with exposure time. Immersion in boiling water for 24 h was also used as a method of sample conditioning.

Fourier Transform Infrared Spectroscopy (FTIR) was used to monitor water absorption of samples. A Thermo Nicolet Nexus 670 FTIR spectrometer was used. Near IR spectroscopy was conducted in transmission mode at 16 cm^{-1} with 32 scans per data point.

Dynamic mechanical analysis (DMA) was performed using a TA instruments DMA 2980 at a frequency of 1 Hz and at a heating rate of $2^\circ\text{C}/\text{min}$. Specimens of dimensions $30 \times 12 \times 3\text{ mm}^3$ were tested in single cantilever beam loading configuration. The temperature at which the maximum in the loss modulus occurs was considered the T_g of the material. The conditioned samples were also tested using DMA and the T_g obtained immediately following conditioning are designated as wet T_g .

Viscosity Measurements: The viscosities of designed resin systems were evaluated using a Brookfield digital viscometer. Viscosity was measured at 30°C .

Results and Discussion

Design of High T_g Formulation: Fatty acid based resin with dry T_g of 140°C and wet T_g of 120°C is required for certain DoD applications. With this aim, novolac vinyl esters with multiple functional groups were employed in this study to improve the T_g of fatty acid based resins. Consequently, Derakane 470HT-400 (simplified as Der470HT in this study) was selected because it has the highest T_g among the commercial available VE resins. The goal was to reduce the styrene content in this resin from 33 wt% to 25 wt% or less by replacing styrene with methacrylated octanoic acid, while achieving good performance and processibility. To compensate for the loss of vinyl ester monomer when reducing the amount of styrene, DGEBA based vinyl ester (VE 828) was added to the system. As summarized in Table 1, formulations were designed by adjusting the weight fraction of MOct and Styrene in order to achieve both the performance and processibility at the minimum loading amount of styrene. As can be seen, the formulation of 75.8 wt% Der 470HT, 14.2 wt% VE 828 and 10 wt% MOct gave the best combination of the highest T_g (147°C) as well as the lowest viscosity (388 cP at 30°C). At the same time, the styrene content in formulation was reduced to 25% compared to the original level of 33%. This formulation is marked as FAVE-O-HT for the convenience of further discussion. The material is in the glassy state at low temperatures, goes through a glass transition at moderate temperatures, and is a rubber at high temperatures.

Table 1: Representative formulations of VE resins

Sample No.	Der470HT (wt%)	VE828 (wt%)	MOct (wt%)	Styrene (wt%)	T _g (°C)
1	60.6	29.4	10	20	147
2	60.6	24.4	15	20	138
3	75.8	14.2	10	25	147
4	75.8	9.2	15	25	136

Table 2: Viscosity of designed resins compared with commercial VE resins

Resin	Viscosity (cP) at 30°C
Formulation 1	780
Formulation 2	540
Formulation 3	388
Formulation 4	296
Der 470HT	290

Water Absorption Study: Two conditions, boiling water for 24 h and 60°C humid air with 79% R.H. until saturation, were employed in this study to determine the effect of moisture on the thermomechanical properties of fatty acid-based resins. A representative VE resin system of VE 160/MOOct/St (70-5-25) was investigated with respect to water absorption and its influence on T_g. The typical DMA results for 100°C water uptake are given in Figure 2. T_gs before and after (wet T_g) water uptake are 152°C and 133°C respectively which means water uptake imparts a 19°C decrease in T_g. However, the second and third DMA runs of this sample (Figure 3), demonstrate that the T_g recovers completely after full removal of water. This indicated no hydrolysis occurred during water absorption by VE resins. DMA spectra of sample exposed to 60°C water vapor for 5 days produced similar results.

Near infrared (NIR) spectroscopy was employed to monitor the water uptake of the sample exposed to 60°C (RH=79%) on a daily basis for seven consecutive days. The spectra are shown in Figure 4. Results show a marked increase in the water peak at ~5100 cm⁻¹. No other changes were observed, and the material is unchanged according to NIR after complete water removal. The NIR results also show that after DMA runs, the water can be fully removed as reflected in the disappearance of water peak in NIR spectra given in Figure 5.

The weight gain during water absorption experiments at 60°C (RH=79%) is shown in Figure 6. It can be seen that after 5 days, saturation is reached; the equilibrium water absorption in this case is 1.74%. In another set of experiments, weight change of samples at two stages, after water uptake and after DMA first scan, was measured with results given in Table 3. Water absorptions for 24 h boiling water and 60°C (RH=79%) after 5 days are 2.25% and 1.62% respectively. These results show that the sample at 100°C will absorb more water and will be correspondingly subject to greater loss in T_g. Accordingly, it can be deduced that water uptake at 100°C for 24 h is a more critical method to evaluate the VE resins' resistance to water absorption. The T_gs following exposure to boiling water for 24 h were measured for some commercial VE resins as well as our designed resin system and the results are given in Table 4. FAVE-O-HT has a moderate wet T_g of 124°C relative to the commercial resins. The T_g is above our goal value of 120°C.

Table 3: The relation between water absorption and T_gs of a formulation containing 70 wt% VE 160, 5 wt% MOOct, and 25 wt% styrene.

75VE160-5MOct-25St	Initial	100°C water 24 h	after 2 nd DMA run	60°C (RH=79%) water 5 days	after 2 nd DMA run
T _g (°C)	152	133	154	138	153
Water Absorption (%)	0	2.25	0	--	--
	0	--	--	1.62	0

Table 4: Wet T_g of designed resin and commercial VE resins

Resin	Wet T _g after 100°C 24 h (°C)
Derakane 8084	103
Derakane 441-400	125
Derakane 470-300	139
Der 470HT	155
FAVE-O-HT	124

Commercial Resin Selection: As reported in the previous section, the designed resin has excellent properties, but uses a vinyl ester that has been prepared at the laboratory bench scale. To meet DoD and commercial applications, the appropriate commercial VE monomer resin as a replacement for VE 828 must be identified. CN151 and RDX 26929, both of them based on methacrylated diglycidyl ether of bisphenol A epoxy, were consequently tested in our formulations with regard to their impact on T_g and other properties. Though both of these resins can produce fatty acid based resin with slightly different T_g, when mixed with 33% styrene respectively,

the RDX 26939 monomer produced a resin with a significantly higher T_g (153°C) than the CN151-based resin (132°C), as illustrated in Figure 7. Note that postcure of CN151 was realized by heating at 90°C for several days while the RDX 26926 sample was postcured at 90°C for 10 minutes. The difference in T_g of these two resins is likely due to lower methacrylate functionality in CN-151 and this difference can be eliminated by introducing high functionality novolac VE resin.

Fracture Toughness Improvement: 5% and 9% weight fraction of vinyl terminated poly(butadiene-co-acrylonitrile) (VTBN) and epoxy terminated poly(butadiene-co-acrylonitrile) (ETBN) were used to improve the fracture toughness (G_{Ic}) of the designed resin system. The results are summarized in Table 5 along with the fracture toughness of other commercial VE resins for comparison. The rubber modifiers used in this study did not show good miscibility with our fatty acid-based resin system. The toughness as measured by G_{Ic} of these systems effect was not as good as the commercial toughened vinyl ester resin (Derakane 8084). Nonetheless, marked improvement was achieved with no loss of T_g. The poor miscibility of VTBN and ETBN is also detrimental to long term storage of the resin. Thus, CTBN with high content of acrylonitrile, 26% compared to the 18% of VTBN and ETBN, was chosen as a toughener. The results showed the miscibility is highly improved and a transparent solution can be obtained. However, the T_g of the FAVE-O-HT with 10% CTBN is 136°C, exhibiting a slight decrease compared to VTBN and ETBN toughened resin systems.

Table 5: Fracture toughness (G_{Ic}) of liquid rubber modified and commercial VE resins

VE Resins	T _g (°C)	G_{Ic} (J/m ²)
Derakane 8084	118	680
Derakane 470HT-400	173	56
FAVE-O-470HT	145	102
5 wt% ETBN FAVE-O-HT	145	135
9 wt% ETBN FAVE-O-HT	151	141
5 wt% VTBN FAVE-O-HT	146	--
9 wt% VTBN FAVE-O-HT	147	167
10 wt% CTBN FAVE-O-HT	136	--

Conclusions

Fatty acid based monomers of methacrylated fatty acids were employed in combination with novolac VE resin to achieve high temperature resistance, low VOC resin systems. A T_g of 147°C was achieved along with low styrene content and good processibility. DMA analysis shows the high temperature resistance of VE resin is reduced by water absorption but the loss is reversible after removal of water. Equilibrium water uptake on exposure to 60°C, 79% RH humid air was found to be 1.7%. Conditioning for 24h in boiling water was found to be a more severe test. Under such conditions T_g was reduced to 124°C. This value is greater than our wet T_g goal of 120°C. Additionally, using fatty acid based monomers as a replacement for styrene, fracture toughness improvements were observed. Further improvement is possible with the addition of rubber modifiers.

Acknowledgements

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Figures

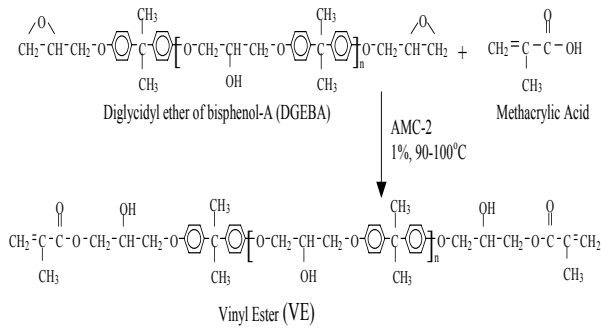


Figure – 1. The Reaction of DGEBA and Methacrylic Acid to Produce Vinyl Ester.

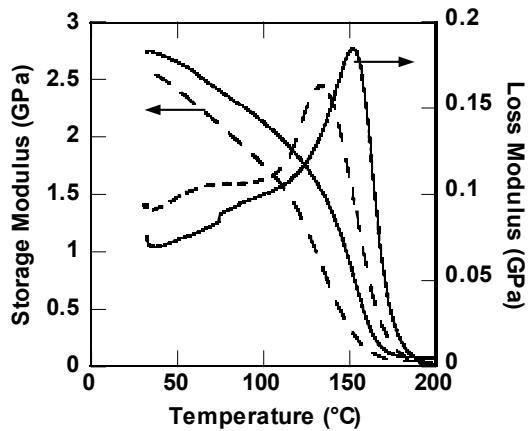


Figure – 2. DMA Scans of VE 160/MOOct/St (70-5-25) Before (Solid Line) and After (Dashed Line) 24 h Boiling Water Exposure.

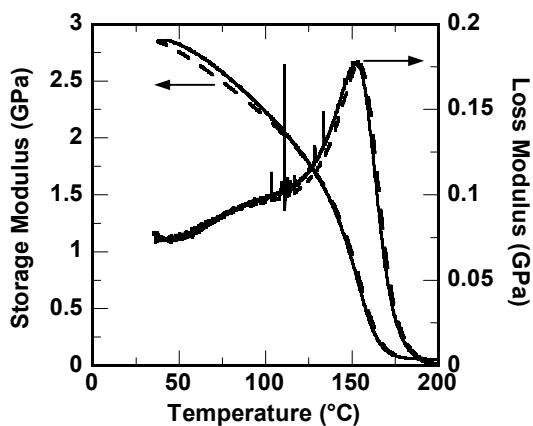


Figure – 3. Second (Dashed Line) and Third (Solid Line) DMA Scans of VE 160/MOOct/St (70-5-25) Conditioned for 24 h in Boiling Water.

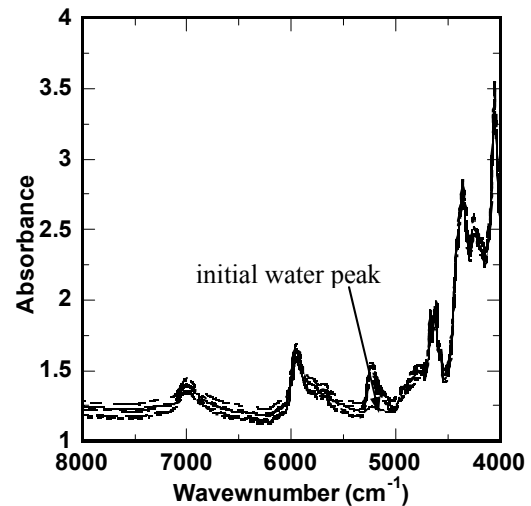


Figure – 4. NIR Spectra of VE 160/MOOct/St (70-5-25) Before and After Conditioning in 60°C Humid Air with RH=79% for 7 days.

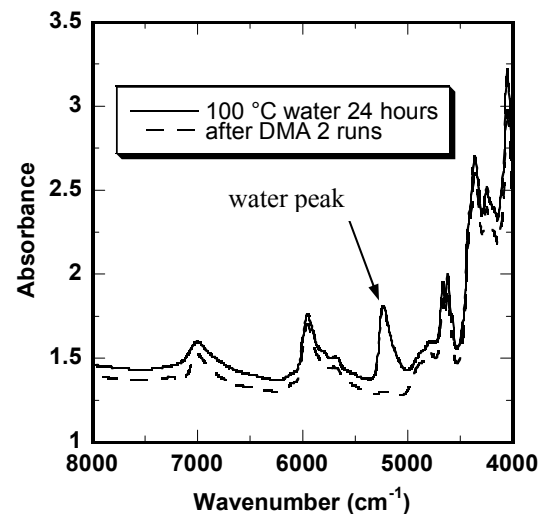


Figure – 5. NIR Spectra of VE 160/MOOct/St (70-5-25) After Conditioning in Boiling Water for 24 h (Solid Line) and After DMA Runs (Dashed Line).

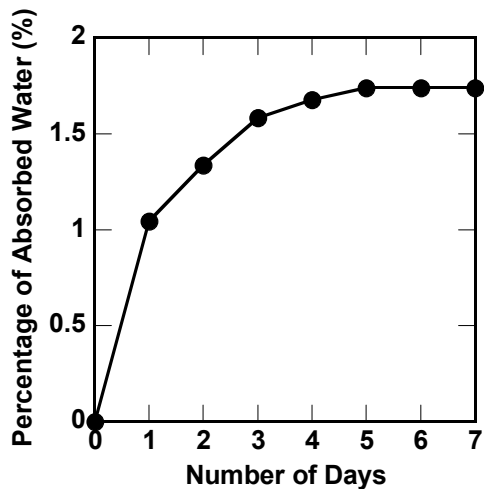


Figure – 6. Weight Change of Sample Conditioned in 79% RH, 60°C Humid Air.

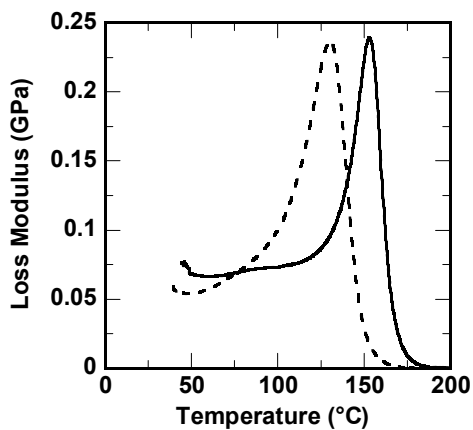


Figure – 7. DMA Spectra for CN151 and RDX 26936 with 33% Styrene. RDX 26936 (Solid Line), CN151 (Dashed Line).

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