3.3. Rheological Behavior of Vinyl Ester Resins

3.3.1. Introduction

Rheology is the study of the deformation and flow of matter[1]. There has been significant appreciation of the importance of the rheological behavior of materials in chemical processing industries. While the rheological behavior of polymers involves several widely different phenomena, such as viscous flow, rubberlike elasticity, viscoelasticity, and Hoohea., n/bn elasticity, this chapter only focuses on the viscosity of vinyl ester resins in steady shear. Such a study is important since viscosity is traditionally regarded as one of the most important material properties. A practical study of material response must first investigate the material's viscosity.

Viscosity is the measurement of a fluid's resistance to flow. For a liquid under shear, the rate of deformation, or shear rate, is proportional to the shearing stress. Newton's law states that the ratio of the stress to the shear rate is a constant. That constant is viscosity. The common units for viscosity are poise (P), grams per centimeter second g/(cm.s), or dyne seconds per square centimeter (dyn.s)/cm^2). The centipoise (cP), one hundredth of a poise, is the most common unit. The SI units of viscosity is Pascal seconds (Pa.s and mPa.s)(1 mPa.s = 1cP)[2-3].

Viscosity is an important parameter for the on-line process to make vinyl ester/carbon fiber composites. Vinyl ester resins need to have a low viscosity in order to flow into the fibers and to permit good wetting of the carbon-fibers. Styrene was used as diluent to decrease the viscosity of the vinyl ester resins. Thus, the styrene concentration is an important factor which controls the viscosity of vinyl ester resins. Concurrently, viscosity is highly sensitive to

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[1] P. C. Hiemenz, *Polymer Chemistry*, Markcel Dekker, Inc., 1984.

[2] *Encyclopedia of Polymer Science and Technology*, Vol 14, 455, N. M. Bikales, G. C. Overberger, and G. Menges, Eds., Wiley Publications, New York, 1988.

[3] B. Gaur and J. S. P. Rai, *Eur. Polym. J.*, 29 (8), 1149, 1993.

changes in temperature, and the molecular weight of the vinyl ester oligomers also affects viscosity significantly. All these factors need to be studied and understood so that the viscosity of the vinyl ester resins can be controlled. The effect of temperature and the effect of styrene on viscosity of vinyl ester resins have been reported in literature[4, 5].

Rheological behavior can be investigated by a variety of methods, including simple capillary viscometers, extrusion rheometers, and rotational viscometers.[6] In this chapter, the rheological behavior of vinyl ester resins was studied by using a Brookfield digital viscometer. The effect of temperature, the effect of styrene content and the molecular weight of the vinyl ester oligomers on the viscosities of the vinyl ester resins were examined. The relationship between viscosity, processing temperature and glass transition temperature is also discussed in this chapter.

3.3.2. Results and Discussion

3.3.2.1. Effect of Styrene Contents

The viscosity of the initial resins must be low to provide efficient flow of the resin into the fiber preforms in an on-line process. A Brookfield digital viscomter was used to measure the viscosities of vinyl ester resins. The zero shear viscosity was determined by direct extrapolation of low-shear data from the plot of the viscosity vs. shear rate. The viscosities were measured for a series of resins (vinyl ester molecular weight = 690 g/mol) with increasing styrene concentrations at room temperature (Figure 3.3.1). Figure 3.3.1 shows the effect of styrene concentration on viscosity. The viscosity of vinyl ester resins decreases with

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[4] R. E. Young, in *Unsaturated Polyester Technology*, P. E. Bruins, Ed., Gordon and Breach, New York, p.315, 1976.

[5] I. K. Varma, B. S. Rao, M. S. Choudhary, and D. S. Varma, *Die Angewandte Makromol. Chem.*, 130, 191, 1985.

[6] J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, *Viscosity and Flow Measurement, A Laboratory Handbook of Rheology*, Wiley-Interscience, New York, 1963.

increases in styrene concentration and can be calculated using the equation obtained from the curve fits in Figure 3.3.1:

$$\log\eta = 7.45 - 0.187(\%St) + 0.00143(\%St)^2 \qquad (1)$$

Vinyl ester resins with varying styrene concentrations provide a system with a wide range of viscosities which are suitable for different applications. Vinyl ester resins with higher styrene concentrations offer improved resistance to acids and alkalias while those with lower styrene concentrations afford better resistance to solvents[4].

3.3.2.2. Effect of Temperature

The viscosity of most materials decreases as temperature increases. The Andrade equation relates the viscosity to temperature as follows:

$$\eta = A \cdot 10^{B/T} \qquad (2)$$

$$\log \eta = \log A + B/T \quad , \qquad (3)$$

where A and B are constants characteristic of the polymer or other material and T is the absolute temperature. The viscosity of a polymer at a given temperature can be estimated by knowing the viscosity at two other temperatures. This knowledge allows calculation of the constants A and B and subsequent determination of viscosities at other temperatures. The Andrade equation holds for many polymer solutions and polymer melts well above their glass-transition temperatures.[7]

The concentrated vinyl ester resins (low styrene content) with two different molecular weights (M_n = 690 g/mol and M_n = 1000 g/mol) were measured at temperatures of 25 °C, 35 °C, 50 °C and 75 °C. Plots of $\log\eta$ vs 1/T are shown in Figure 3.3.2. It was found that $\log\eta$ vs 1/T was a straight line for all tested resins for temperatures ranging from 25 - 75°C, which are well above their T_g. The constants A and B were also determined and listed in Table

3.3.1. As styrene content increases, the viscosity of the vinyl ester resins became less dependent on temperature, as indicated by the decrease in both log A and B.

3.3.2.3. Effect of Molecular Weight

Unlike dilute solutions, concentrated polymer solutions show a great deal of interaction between the macromolecules. For a concentrated solution, properties above and below M_e**,** the critical molecular weight for chain entanglement, may be quite different. The dependence of viscosity on molecular weight, changes from around unity below M_e to around 3.4 - 3.5 above M_e, as indicated in equations (4) and (5).[8-10]

Table 3.3.1. Constants A and B in the Andrade equation for various vinyl ester resins.

Vinyl ester resins with M_n = 690 g/mol		
Wt% Styrene	log A	B
20	-9.198	3995
25	-8.540	3660
30	-6.89	2983
Vinyl ester resins with M_n = 1000 g/mol		
30	-7.99	3752
35	-8.67	3795
40	-6.13	2758

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[7] G. W. Scott Blair, *Elementary Rheology*, Academic Press, Inc., New York, 1969.

[8] G. V. Vinogradov and A. Ya. Malkin, *Rheology of Polymers*, Springer-Verlag, New York, 1980.

[9] T. G. Fox, S. Gratch, and S. Loshaek in *Rheology*, F. R. Eirich ed., Vol. 1, Academic Press, Inc., New York, 1956.

[10] G. Berry and T. G. Fox, *Adv. Polym. Sci*., 5, 261, 1968.

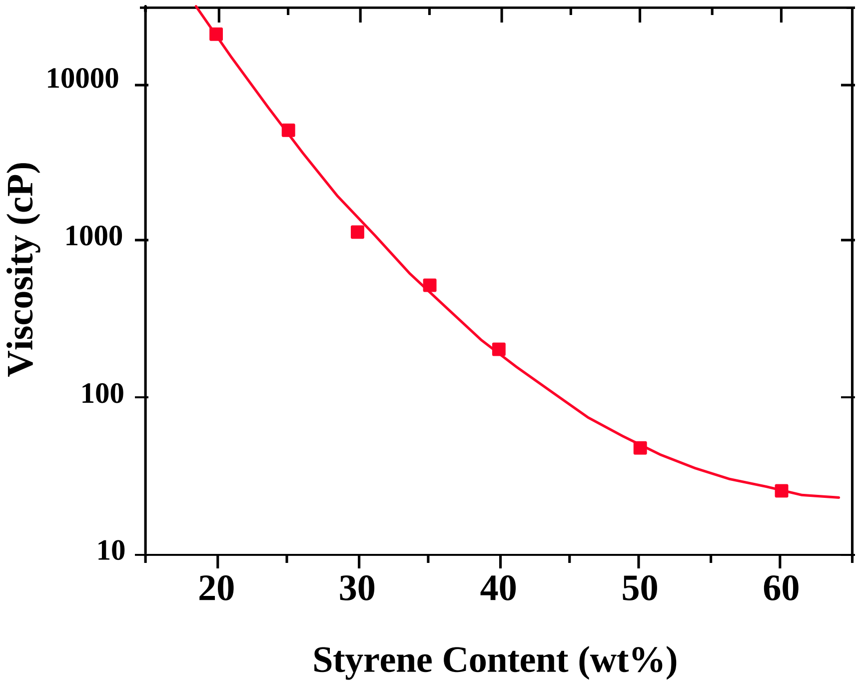

Figure 3.3.1. Viscosity of uncured vinyl ester resins at 25°C. (M_n = 690 g/Mol).

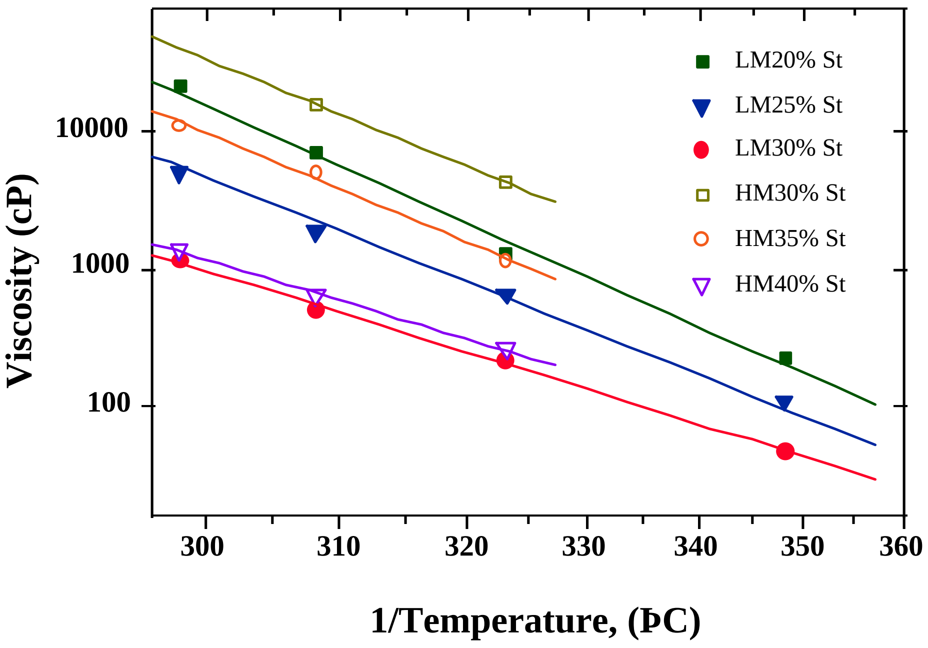

Figure 3.3.2. Plot of Log η vs 1/T for different vinyl ester resins.

$$\eta = KM \qquad \text{below } M_c \tag{4}$$

$$\eta = KM^{3.4\text{-}3.5} \qquad \text{above } M_c \tag{5}$$

The M_e, above which entanglement occurs, is usually thought to be on the order of 5,000 - 20,000 g/mol, depending on the chemical structure of the polymer. However, in highly concentrated polymer solutions, dependence of viscosity on molecular weight with exponents larger than 1 may occur at low molecular weights. Although there are no detailed studies on the effect of molecular weight on viscosity, it can be found in the vinyl ester resin system discussed here, that the viscosity of vinyl ester resins increases significantly when the molecular weight of the vinyl ester oligomers increases from 690 g/mol to 1000 g/mol. For example, at 35 wt.% styrene concentration at room temperature, the viscosity of the VER with M_n = 690 g/mol is 521cP, while that of the VER with M_n = 1000 g/mol is 10500cP. The high dependency of viscosity on the molecular weight of the vinyl ester resins of low molecular weight is probably due to hydrogen bonding between the vinyl ester molecules, increasing the effective chain length.

3.3.2.4. Relationship Between the Viscosity, Processing Temperature and Glass Transition Temperature

The glass transition temperature of the VER with M_n = 690 g/mol was determined by DSC. It was found that the vinyl ester resins only have one T_g. The T_g of the vinyl ester resins decreases linearly as styrene concentration increases (Figure 3.3.3). For concentrated polymer and oligomer solutions, the Williams-Landel-Ferry (WLF) equation can be used to relate the viscosity with the glass transition temperature.[11] In general, the WLF equation holds in the temperature range T_g to (T_g +100°C).

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[11] M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, 77, 3701, 1955.

$$\log(\eta/\eta_{Tg}) = \frac{-17.4(T - T_g)}{51.6 + (T - T_g)} \quad (6)$$

For the vinyl ester/styrene system, a similar relationship exists between the testing temperature, the T_g, and viscosity. In the 20 wt.%, 25 wt.% and 30 wt.% styrene resins, the plots of $\log\eta \sim (T-T_g)^{-1}$ (Figure 3.3.4) fall on the same line, suggesting that the viscosity of the vinyl ester/styrene mixtures are associated with the difference between T_g and the measurement temperature. The curve fits give the equation:

$$\log \eta = \frac{253.2}{T - T_g} - 0.2427 \quad (7)$$

Since low viscosity is a processing necessity, the styrene content variations must be carefully tailored to viscosity. The viscosity decreases significantly with temperature increases. On the other hand, good resin stability can only be maintained under 50°C due to the existence of a free radical initiator. Experimental results in this system suggest that when $T-T_g$ is above 70°C, the low viscosity necessary (under 2000cP) for processing can be achieved.

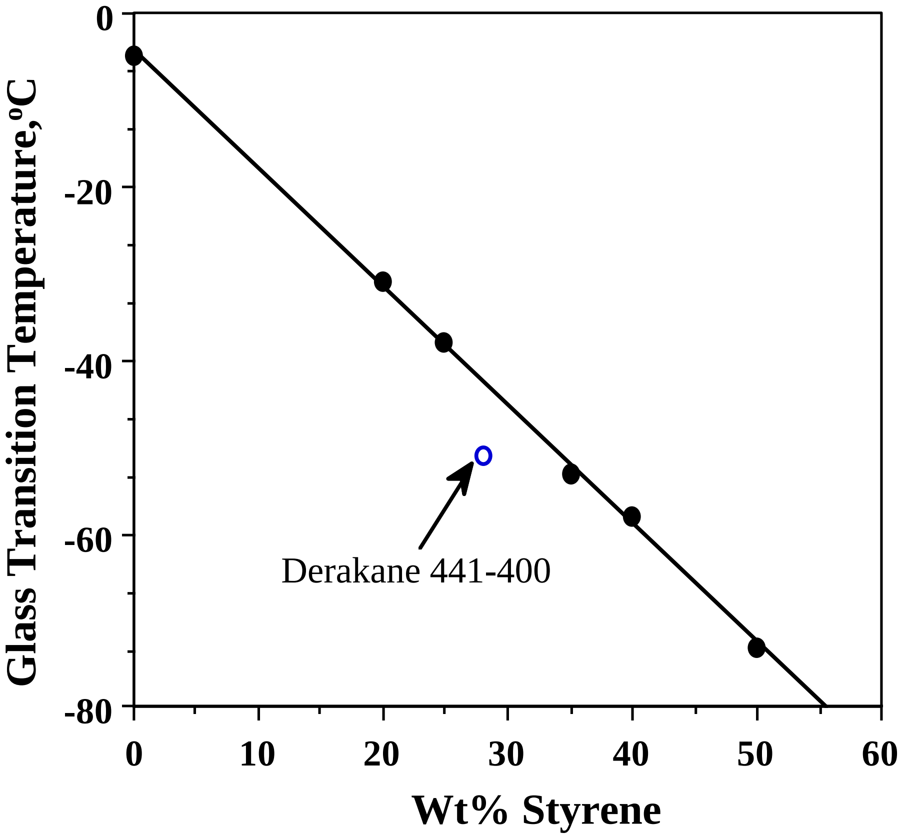

Figure 3.3.3. Glass transition temperature of VER with M_n = 690 g/mol.

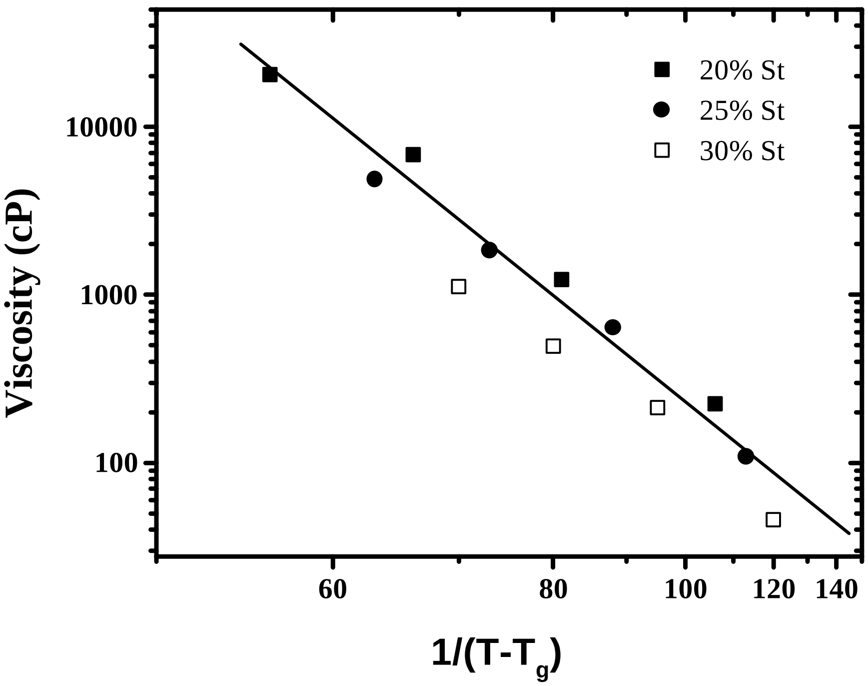

Figure 3.3.4. Plot Log η vs. T-T_g for 20 wt.%, 25 wt.% and 35 wt.% styrene of vinyl ester resin with M_n = 690 g/Mol.