3.5. Blends of Thermoplastic Polymers with Vinyl Ester Resins

3.5.1. Introduction

The behavior and performance of a composite material cannot be explained only by the specific properties of its components (fibers and matrix). Mechanical properties of composite materials are also strongly dependent on the adhesion between fiber and resin. The interface between fibers and matrix transfers the stresses from the matrix to the fibers, so the interphase is important for tailoring the properties of the composite. For carbon fiber/vinyl ester composites, carbon fibers and vinyl ester are notably incompatible. The bond between carbon fiber and vinyl ester is poor[1]. One effective method to enhance the bonding between the carbon fiber and vinyl ester is to coat (size) the fiber with a thermoplastic polymer which is miscible with the vinyl ester and compatible with the fiber[2]. The sizing constitutes the interphase material. By molecularly engineering the chemical structure of the sizing, a thermoplastic sizing can incorporate the desirable mechanical properties into the composite. As part of the overall objective, optimizing interphase conditions and developing methods for improving the performance of carbon fiber/vinyl ester composites, this chapter summarizes some preliminary work on identifying potential sizing materials which are micible with vinyl ester resins. The emphasis has been placed on exploring blends of the vinyl ester with water-soluble and water dispersible polymers such as poly(N-vinylpyrrolidone), poly(ethenyl formamide), poly(ethyloxazoline), polyhydroxyether, and poly(ethylene oxide).

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[1] T. Juska, Carderock Div-SME-92-38, *Research and Development Report*, Jan., 1993.

[2] J. J. Lesko, A. Rau and J. S. Riffle, Proc. *10th Tech. Conf. of the Am. Soc. for Composites*, Oct. 1995.

3.5.2. Theory of Hydrogen Bonded Polymer Blends[3,4]

A necessary condition for miscible polymer blends is that the free energy of mixing is negative, as shown in equation 1.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0 \qquad (1)$$

For hydrogen bonded polymer blends, the free energy of mixing equation can be written as follows:

$$\frac{\Delta G_m}{RT} = \frac{\Phi_A}{M_A} \ln \Phi_A + \frac{\Phi_B}{M_B} \ln \Phi_B + c\Phi_A\Phi_B + \frac{\Delta G_H}{RT} ,$$

$$c = \frac{V_r}{RT}[d_A - d_B]^2 \qquad (2)$$

Where Φ_A and Φ_B are the volume fractions of polymer A and polymer B in the blend, and M_A and M_B are the degrees of polymerization. This equation consists of three major contributions: Combinatorial entropy, the first two logarithmic terms in the equation, is a very small, but favorable contribution to ΔG_{mix}; $\chi\Phi_A\Phi_B$ is an unfavorable contribution from the "physical" forces (disperse or van der Waals); the $\Delta G_H/RT$ is a favorable contribution derived from hydrogen bonding or so-called "chemical" forces (specific interaction). Miscibility depends primarily upon the balance between the contributions from the $\chi\Phi_A\Phi_B$ term and the $\Delta G_H/RT$ term. For non-hydrogen bonded polymer blends (in the Flory-Huggins case only dispersive forces present), miscible blends can be obtained only when the critical value of χ is < 0.002, and the solubility parameters of the two polymers must be within 0.1 $(cal.cm^{-3})^{1/2}$. For hydrogen bonded polymer blends, if there is a large favorable contribution from

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[3] M. M. Coleman, J. F. Graf, and P. C. Painter, *Specific Interactions and the Miscibility of Polymer Blends,* Technomic Publishing Co., 1990.

[4] M. M. Coleman and P. Painter, *Prog. Polym. Sci.,* 20, 1, 1995.

"chemical" forces, it is possible to obtain a miscible polymer blend even if the non-hydrogen bonded solubility parameter difference is about 2.4 $(cal.cm^{-3})^{1/2}$.

Experimentally, the least ambiguous criterion for polymer miscibility is the detection of a single glass transition temperature (T_g), which is intermediate between those corresponding to the two component polymers. Phase separation is judged by the existence of two distinct glass transition temperatures.

3.5.3. Miscibility of Vinyl Ester Blends

The vinyl ester resin that was used for the miscibility study was Derakane 441-400 (30 wt% styrene). PVP was first dissolved in the vinyl ester resin (ratio PVP/VE =10 wt% and 20 wt%) by stirring at temperature 25-40°C until a clear mixture was obtained. The initiators were added and stirring was maintained for 4 hours to ensure that the initiators were dissolved. Then the reaction mixtures were degassed for about half hour. Curing was carried out at 120°C in a convection oven for 1 hour. Other blends were prepared in the same manner. Miscibility of the blends was investigated by DSC (Perkin-Elmer DSC 7). Non-hydrogen bonded solubility parameters were estimated by group contribution methods using the MG&PC software (Miscibility Guide & Phase Calculator) according to equation (3):

$$\delta = \rho \Sigma\, F_i\, /\, M \tag{3}$$

where F_i is the molar attraction constant of the group being considered, ρ is the density of the polymer, and M is the molar mass of the polymer. The summation was carried over all structural features in the molecule.[5]

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[5] J. F. Graf, M. M. Coleman and P. C. Painter, *Miscibility Guide and Phase Calculator Software*, Technomic Publishing Co., 1991.

According to the data in Table 3.5.1, solubility parameters of poly(N-vinylpyrrolidone) (δ=11), poly(ethyloxazoline) (δ= 10) and poly(ethylene oxide) (δ=9.4) are close to that of the vinyl ester resin (δ=9.6), so they are potentially miscible with the cured vinyl ester/styrene network. However, poly(ethenylformamide) (δ=14.89) is unlikely to be miscible with the vinyl ester resin due to its much higher solubility parameter. Experimental results confirm that poly(N-vinylpyrrolidone) (PVP), poly(ethyloxazoline) (PEOZ) and poly(ethylene oxide) (PEO) are soluble in the vinyl ester resin, while poly(ethenylformamide) cannot be dissolved in vinyl ester resin at all. After the mixtures are cured, only one T_g was observed for PVP/VE blends and PEOZ/VE blends. The T_g versus composition graph for PVP/VE blends shows a maximum deviation from linearity which implies the existence of strong hydrogen-bonding

Table 3.5.1. Miscibility of sizing materials with vinyl ester resins

| Polymers	Repeat unit	Solubility in vinyl ester resin	Solubility parameter cal cm-3
Poly(N-vinyl pyrrolidone)		yes	11.01
poly(ethyl oxazoline)		yes	10.03
Polyhydroxyether		yes	10.23
poly(ethylene oxide)		yes	9.42
poly (ethenyl formamide)		no	14.89
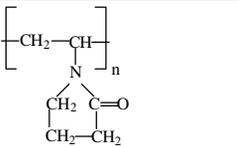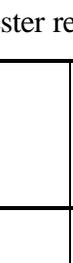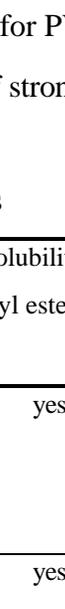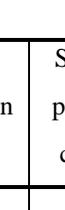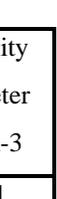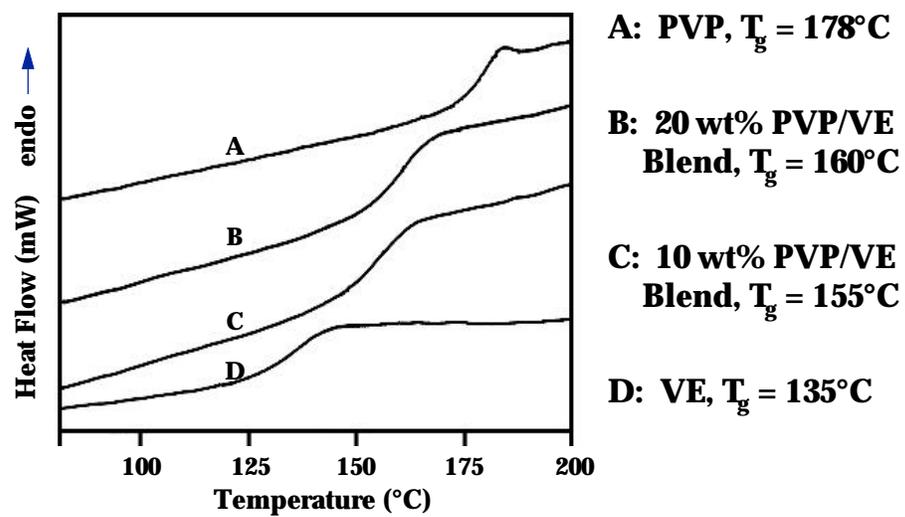
Figure 3.5.1. DSC diagrams of pure PVP, vinyl ester resin, and their blends.
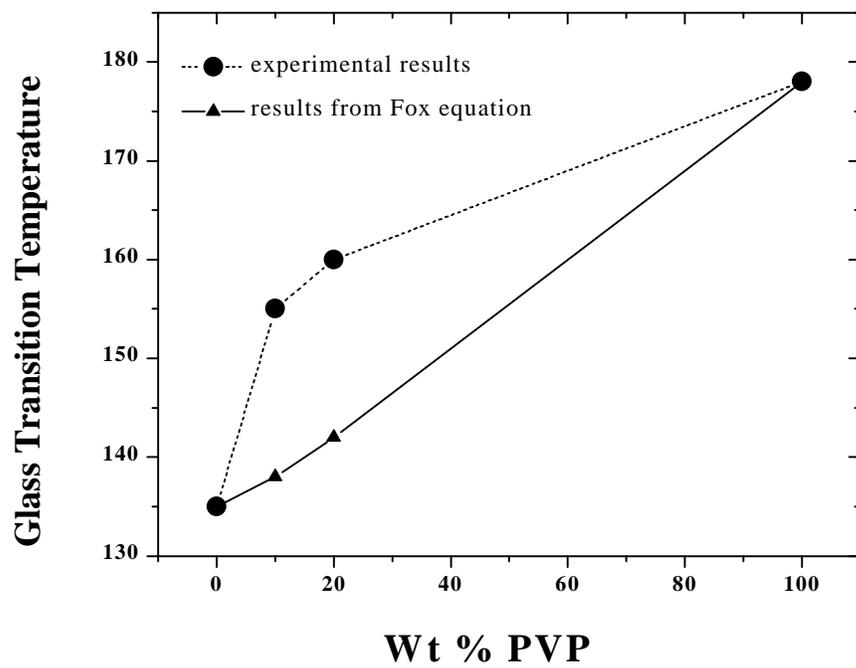
Figure 3.5.2. Glass transition temperatures as a function of PVP weight percentage in PVP/VE blends.
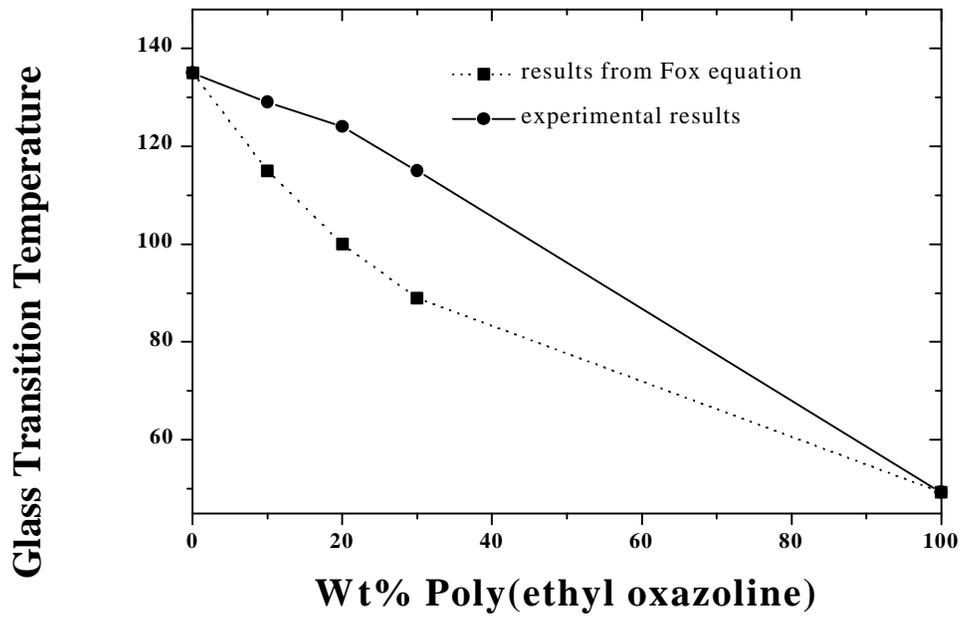
Figure 3.5.3. Glass transition temperatures as a function of weight percentage of poly(ethyloxazoline) in poly(ethyloxazoline)/vinyl ester resin blends.

between poly(N-vinylpyrrolidone) and the vinyl ester network (Figures 3.5.1 and 3.5.2). Figure 3.5.2 also shows that the result can not be explained by the Fox equation ($1/T_g = W_1/T_{g1} + W_2/T_{g2}$). A similar deviation from linearity is also observed for PEOZ/VE blends, as shown in Figure 3.5.3. In the case of PEO/VE blends, the value for T_g could not be determined by DSC although this is likely to be a miscible system.

The existence of strong hydrogen-bond interaction between vinyl ester resin and sizing materials can be further confirmed by FTIR. Because PVP and PEOZ are water soluble polymers and can easily absorb moisture, the neat vinyl ester ($M_n = 690$ g/mol) without styrene was also examined for the H-bonding study. The neat vinyl ester blend was dried in a vacuum oven at 60°C overnight. Figure 3.5.4 shows scale-expanded infrared spectra in the carbonyl stretching region (1740-1620 cm^{-1}) for pure PVP and a 50:50 blend of neat vinyl ester resin with PVP recorded at room temperature. Pure PVP is characterized in this region by a rather broad band at 1677 cm^{-1}. The relatively low frequency for PVP compared to the usual carbonyl frequencies can be explained by the mixed contributions from the carbonyl stretching and N-C stretching vibrations.[6] Upon mixing with vinyl ester resin, a second band is observed at 1659 cm^{-1} and can be assigned to hydrogen-bonded PVP carbonyl groups. The formation of hydrogen-bonding weakened the strength of the carbonyl bond of PVP in the blend, shifting the carbonyl stretching vibration to a lower frequency.[7-8] Figure 3.5.5. shows the corresponding hydroxyl stretching region (3700-3100 cm^{-1}) for pure vinyl ester resin and a 50:50 blend of vinyl ester resin with PVP recorded at room temperature. Upon blending with PVP the self-associated OH stretching frequency band at 3452 cm^{-1} is shifted to the lower frequency side, 3351 cm^{-1}. Similar results have also been observed for

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[6] A. Martinez, J. J. Iruin, and M. J. Fernandez-Berridi, *Macromolecules,* 28, 3707, 1995.

[7] Q. Guo, J. Huang, and X. Li, *Eur. Polym. J.*, 32, 423, 1996.

[8] I. Janarthanan and G. Thyagarajan, *Polymer*, 33, 3593, 1992.

the blends of neat vinyl ester resin with PEOZ and are shown in Figures 3.5.6 and 3.5.7. Figure 3.5.8 shows the FTIR spectra of Derakane 441-400 and a 50:50 blend of Derakane 441-400 with PVP recorded at room temperature. Although the sample in this case cannot be dried before FTIR experiments due to the presence of styrene, the shifting of the self-associated OH stretching frequency band to the lower frequency is again observed. However, the presence of styrene may dilute the concentration of hydrogen bonding in the resin, resulting in a smaller shift.

In conclusion, PVP/VE and PEOZ/VE are miscible blends - at least over the composition ranges investigated. PEO/VE may also be miscible blends but this needs to be confirmed.
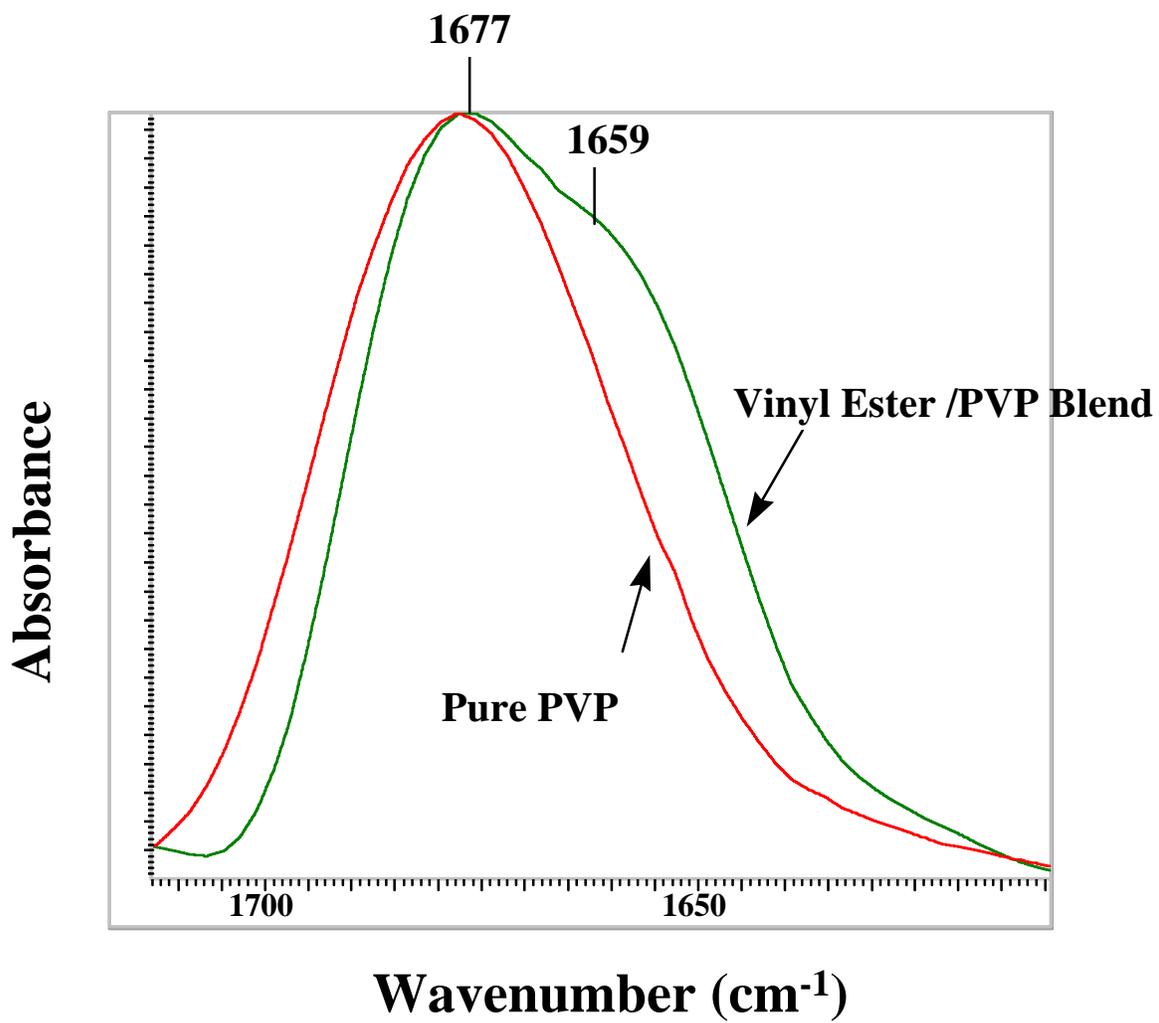
Figure 3.5.4. FTIR spectra of pure PVP and 50:50 blend of vinyl ester resin with PVP in C=O stretching region.
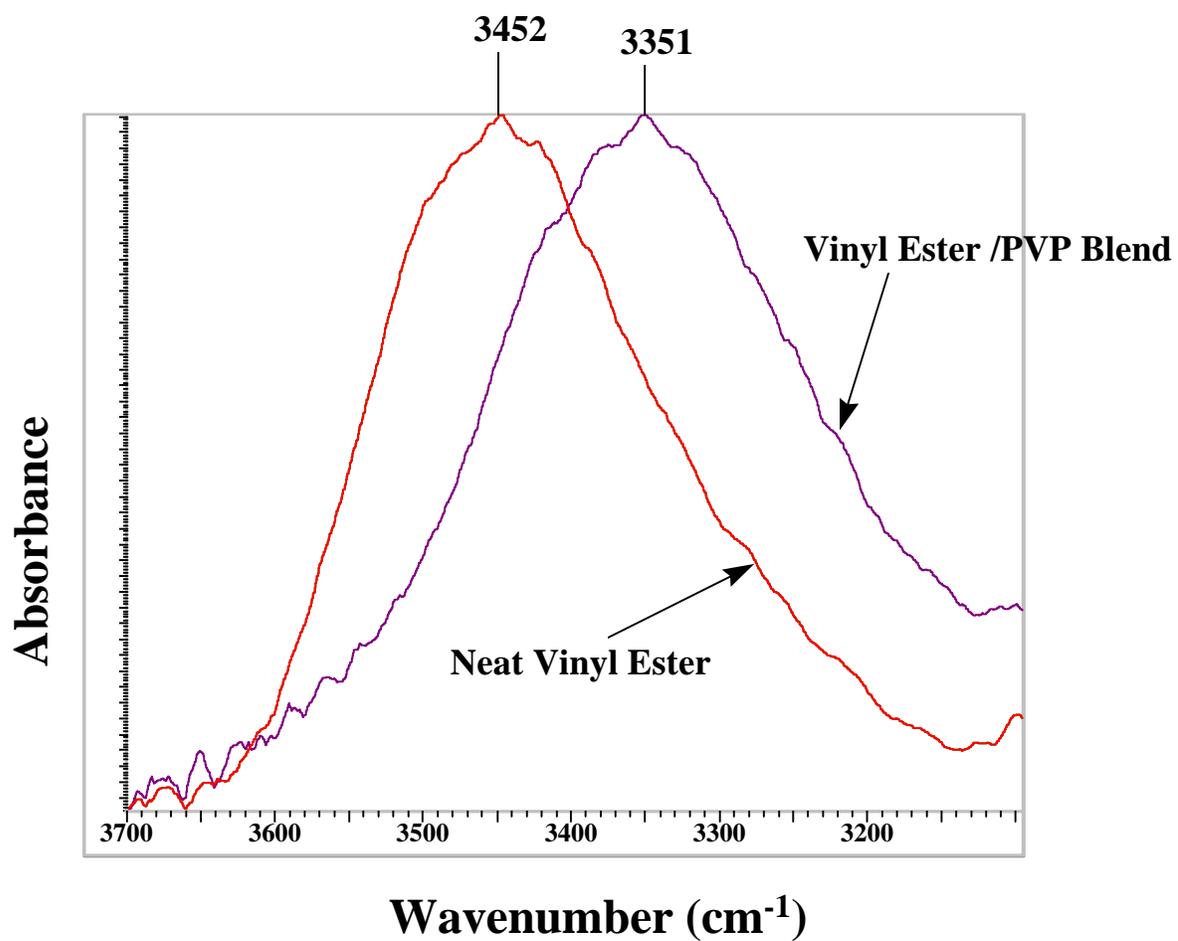
Figure 3.5.5. FTIR spectra of a neat vinyl ester resin (dimethacrylate of diglycidyl ether of Bisphenol A, Mn = 700 g/mol) and 50:50 blend of the neat vinyl ester resin with PVP in OH stretching region.
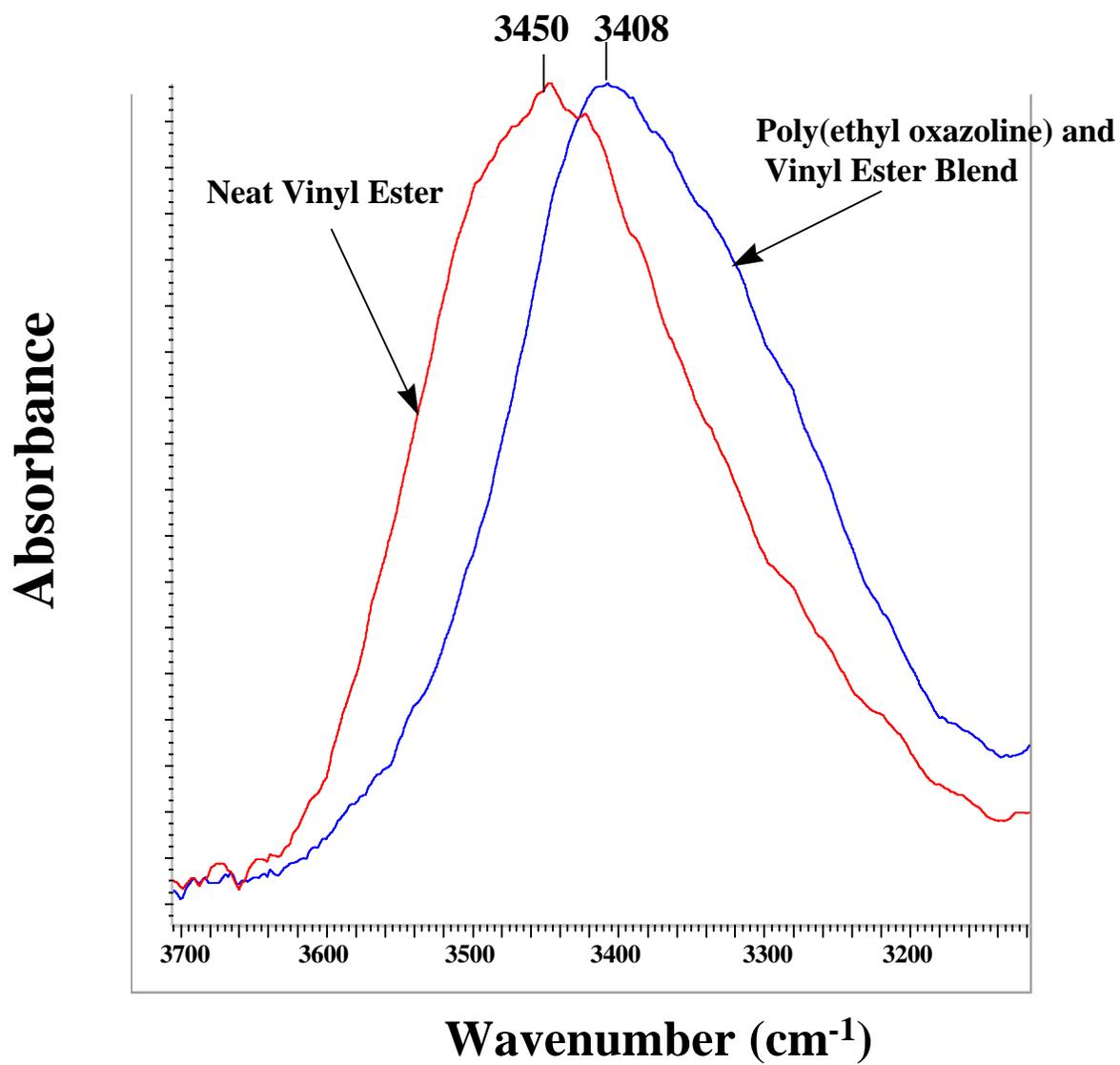
Figure 3.5.6. FTIR spectra of vinyl ester resin and 50:50 blend of vinyl ester resin with PEOZ in OH stretching region.
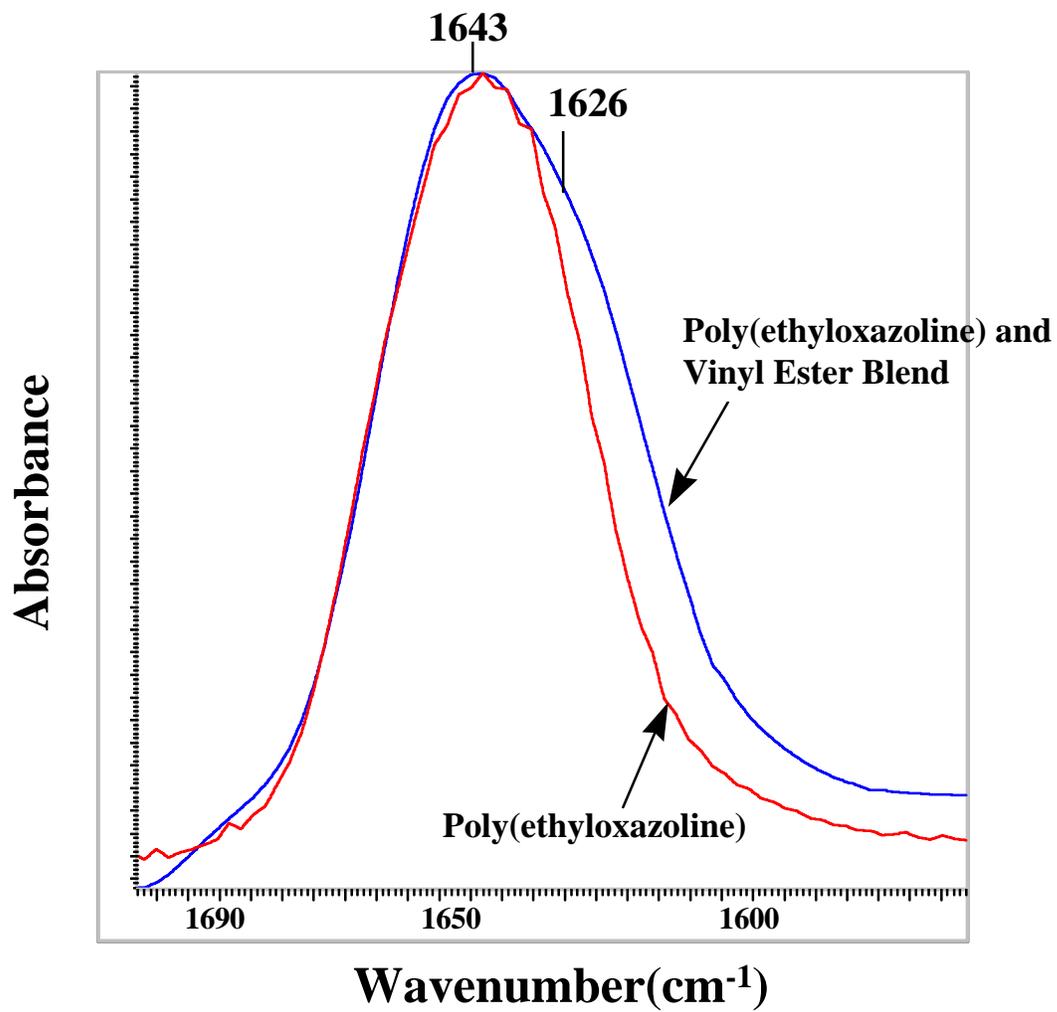
Figure 3.5.7. FTIR spectra of PEOZ and 50:50 blend of vinyl ester resin with PEOZ in carbonyl stretching region.
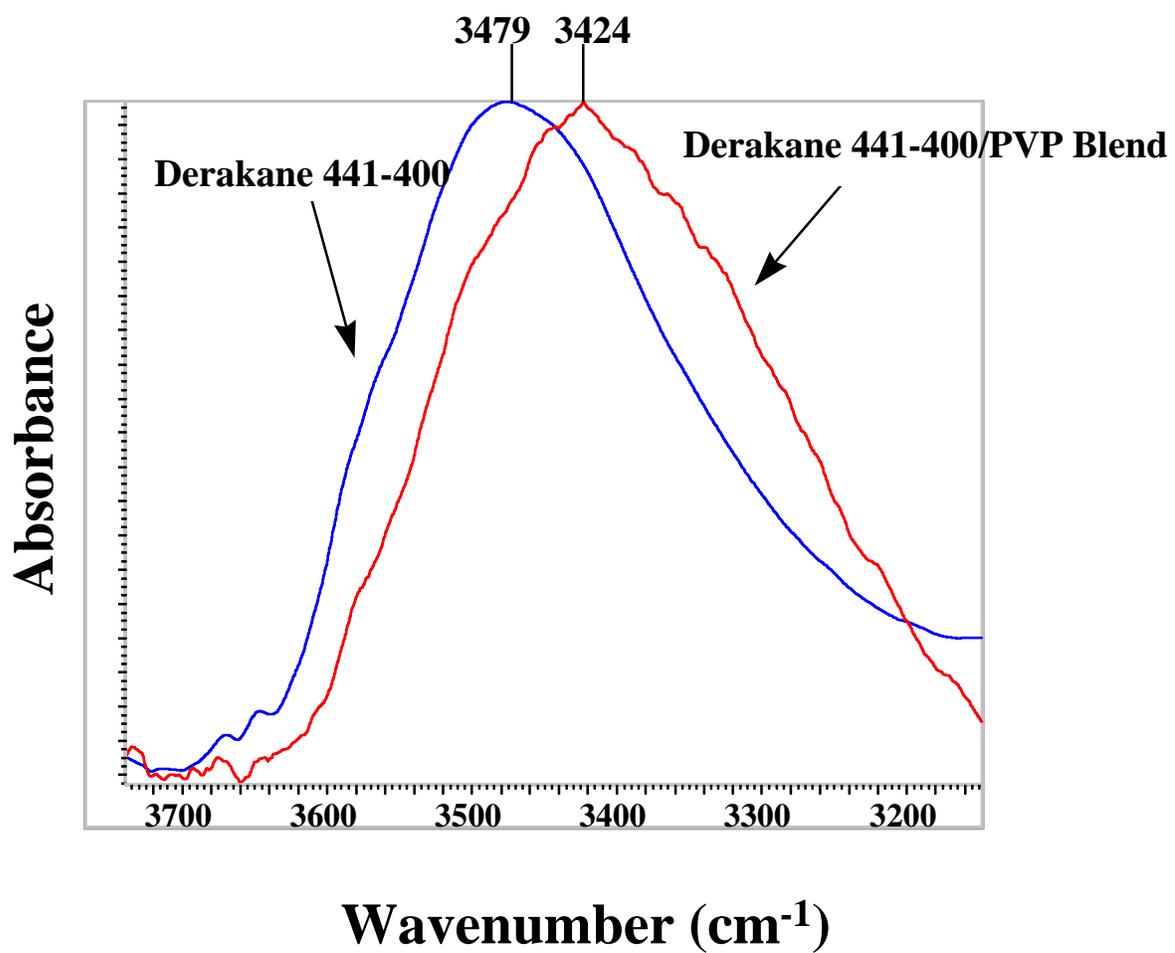
Figure 3.5.8. FTIR spectra of Derakane 441-400 and 50:50 blend of Derakane 441-400 with PVP in the OH stretching region.