

Viscosities of Unsaturated Polyester Resins: Combining Effects of Prepolymer Structure, Resin Composition, and Temperature

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SYNOPSIS

The effects of temperatures, styrene concentration, and molecular composition of unsaturated polyester (UP) prepolymers on the viscosity of UP-styrene systems are studied. The viscosity of UP resins follows the Arrhenius-type expression with resin temperature as well as with the styrene molar fraction of the resin. The two Arrhenius correlations can be combined into a simple dual-Arrhenius equation by combination rule. This dual-Arrhenius equation comprises pseudo viscosity parameters of styrene monomer and UP prepolymer, respectively. The pseudo viscosity parameters of styrene monomer are experimentally found constant; while those of UP prepolymer seem to be number-average molecular weight correlated rather than weight-average molecular weight correlated. The UP prepolymers having different molecular structures show different pseudo viscosity parameters due to their own molecular interaction parameters. The pseudo viscosity parameters of UP prepolymers should be determined experimentally for the time being. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Unsaturated polyester (UP) resin is probably the most widely used thermoset resin for polymeric composites.¹ The typical applications include glass-fiber laminates, paper laminates, bulk molding, impregnation castings, and, in recent years, bulk molding compounds (BMC) and sheet molding compounds (SMC).² In all the applications, the viscosity of the raw UP resin is an important factor to be considered for material handling and compound preparation. Moreover, the viscosity of the UP resin in the synthesis process affects several operation controls such as reaction kinetics, final temperature, and agitation controls. It should also be well controlled in the final styrene dilution stage to have homogeneous products.

The generally used UP resin is a solution of unsaturated polyester prepolymer in styrene monomer. During the curing process, the styrene monomer reacts with the vinylene groups of UP prepolymer and forms linkage among the UP molecules. It acts

as a crosslinking agent to create polymer network. While, before curing, styrene behaves as a solvent which dissolves the UP prepolymer to have good handling property, because the UP prepolymer, at room temperature, is either a highly viscous liquid or a sticky solid.

The viscosity of a polymer solution depends on four factors. Those are (i) temperature, (ii) solvent or solute content, (iii) polymer molecular weight, and (iv) polymer miscibility. Among them, the temperature effect on the solution viscosity has been known to follow Arrhenius equation for UP resin,³ epoxy resin,⁴ and other polymer solutions.^{5,6} For an immiscible system or a colloid solution, the effect of solvent (or solute) content on the solution viscosity may follow Batchelor equation⁷ for colloid solution, $\eta_r = 1 + 2.5\phi + 6.2\phi^2$, where, η_r is relative viscosity and ϕ is colloid volume fraction. For a miscible polymer solution (such as polystyrene-dioctyl phthalate⁸ and polyisobutylene-toluene⁹ solutions), a power law equation,¹⁰ $\eta_z = KM_w^a C^b$, expresses the effects of solute content and polymer molecular weight. In the power law equation, η_z is zero-shear viscosity, M_w is polymer molecular weight, C is polymer concentration, and K, a, b are constants.

Simply, the zero-shear viscosity is often correlated with the polymer molecular weight by the power law, $\eta_z = K'M_w^a$,¹¹ where a is either between 2.5 and 1.0 for M_w below critical molecular weight, M_c , or between 3.3 and 3.6 for M_w above M_c .¹² In fact, the power index a varies from polymer to polymer. That is believed to be caused by the polymer structure which influences the solution miscibility.

Although many efforts have been made for the effects of the four factors on the viscosity of polymer solution, there are few works studying the four factors together particularly for the unsaturated polyester resins. As mentioned above, the resin viscosity is an important parameter in industry application, either resin synthesis or polymer processing, a wide study on the viscosity of UP resins would be practically worthwhile. This work studies the parameters on the viscosities of several model UP resins and tries to derive a simple rule for predicting viscosity.

EXPERIMENTAL

Materials

Several model unsaturated polyester prepolymers were used in this work. The notations and the molecular characteristics of the prepolymers are listed on Table I. The A group (i.e., A1, A2 and A3) is the UP prepolymer synthesized from maleic anhydride and propylene glycol, while the B group contains isophthalic component which makes the prepolymer structure less flexible and increases the miscibility with styrene. The C group, composed of maleic anhydride, di-ethylene glycol, and neo-pentyl glycol, was also used to investigate the glycol effect on the resin viscosity by comparison with the A group. Their molecular weights are also listed on the Table

I. The prepolymers were diluted in styrene monomer at the desired concentration for viscosity studies.

Chromatography

A gel permeation chromatography (GPC, Perkin Elmer, series 10) was used to measure the polymer molecular weight at room temperature with the following column combinations: 50, 100, 500, 1000 Å and a mix column of average size 500 Å. A differential refractometer (RI) detector in the flow direction was used to determine the molecular weights of all the species. All the GPC curves were analyzed by using the calibration curve obtained with standard samples of monodispersed polystyrene to estimate the molecular weight.

Instrumentation

A Haake viscosimeter, model RV2, was used to measure the resin viscosity at different temperature. A thermal bath (Haake F3) was used to control the system temperature. The resin was loaded in the gap between the cup and the rotor and rested there for several minutes to equilibrate the temperature at isothermal condition. The viscosities were measured by the shear stress on continuously changing the shear rate from 0 to 705 s⁻¹.

RESULTS AND DISCUSSION

Figure 1 shows measured shear stress (τ) versus shear rate ($\dot{\gamma}$) for A1 prepolymer in styrene solution (A1/styrene = 60/40 by weight) at different temperatures. The viscosity can be obtained by the ratio of shear stress to shear rate. All the curves on Figure 1 are linear, which indicates that the viscosity of A1

Table I Model UP Prepolymers Used in This Work

Notation	Molecular Components ^a	M_n	M_w	D_p^b	$f_s, \text{ max RT}$ (wt %)
A1	MA, PG	1387	5421	3.91	60
A2	MA, PG	1718	5293	3.08	72
A3	MA, PG	3350	10720	3.2	62
B1	MA, PG, IPA	3470	11533	3.32	90
C1	MA, DEG, NPG	2450	4680	1.91	58
C2	MA, DEG, NPG	3190	8166	2.56	60
C3	MA, DEG, NPG	4370	35047	8.02	63

^a MA: maleic anhydride, PG: propylene glycol, IPA: iso-phthalic acid, DEG: di-ethylene glycol, NPG: neo-propylene glycol.

^b $D_p = M_w/M_n$.

^c $f_s, \text{ max RT}$: maximum styrene weight fraction in UP resin to maintain homogeneous mixture at room temperature.

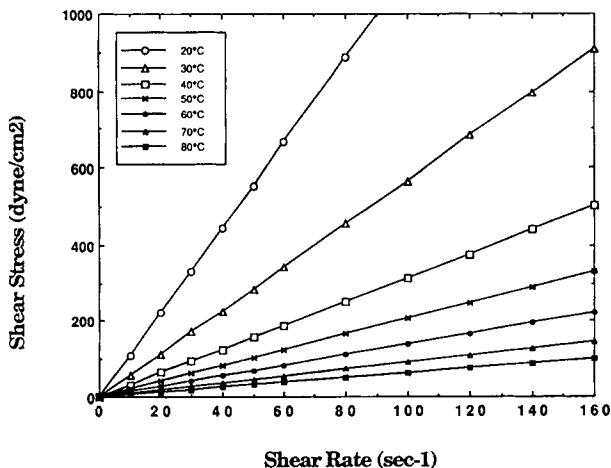


Figure 1 Shear stress versus shear rate of the UP resin (40 wt % styrene with 60 wt % A1 prepolymer) at various temperatures.

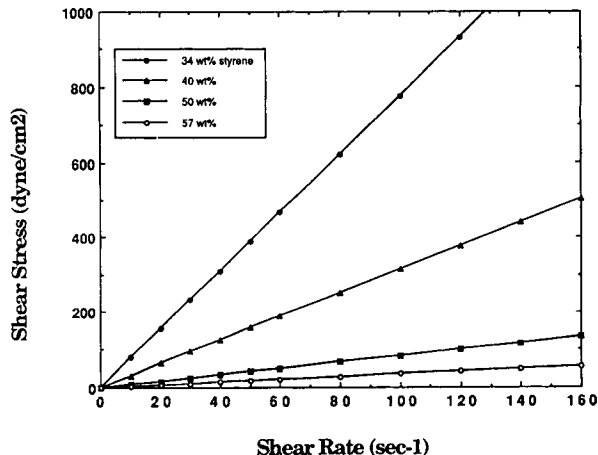


Figure 2 Shear stress versus shear rate of the UP resin (A1 prepolymer with styrene) at 40°C with various styrene composition.

resin is shear rate independent within a wide temperature range. Similarly, Figure 2 shows shear stress vs. shear rate for A1 prepolymer with different styrene content at 40°C. Again, all the curves are linear. It represents that the viscosity is also shear rate independent within a wide styrene concentration range. For all the prepolymers listed on Table I, results similar to Figures 1 and 2 are also obtained. One, then, can conclude that the viscosity of UP resin is shear rate independent.

The viscosity of A1 resin with different styrene concentration is drawn vs. temperature as shown on Figure 3 (a). A well-known method to correlate the viscosity of polymer solution with temperature is Arrhenius equation [3]:

$$\eta_0 = \eta_\infty e^{E/RT} \tag{1}$$

where, η_0 is resin viscosity, η_∞ is infinite viscosity, E is activation energy of the resin, $R = 8.314 \text{ J/mol } ^\circ\text{K}$ and T is temperature in $^\circ\text{K}$. Therefore, the results of Figure 3 (a) are rearranged as $\ln(\eta_0)$ vs. reciprocal of temperature, following the form of eq. (1). The points are experimental data and the lines are linear regression results. The results show that the A1 resin viscosity follows very well the Arrhenius equation for all the resin composition. The slope of the line represents the resin activation energy and the Y-axis intercept shows the logarithmic of infinite viscosity, $\ln(\eta_\infty)$. One obtains that, on Figure 3, both the infinite viscosity and resin activation energy are resin composition dependent.

The dependence of the infinite viscosity and the resin activation energy on the resin composition has

not been investigated scientifically. The logarithmic infinite viscosity and the resin activation energy obtained from Figure 3 (b) are drawn vs. mole fraction

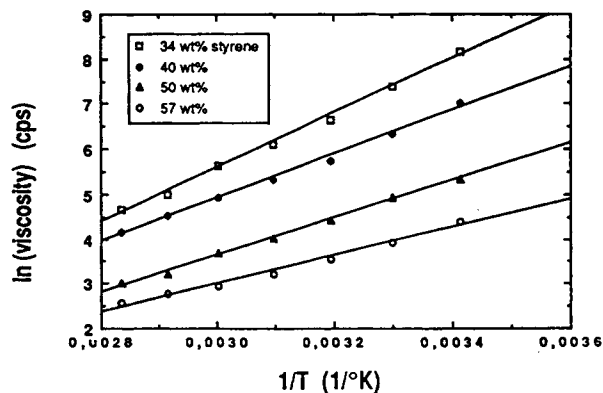
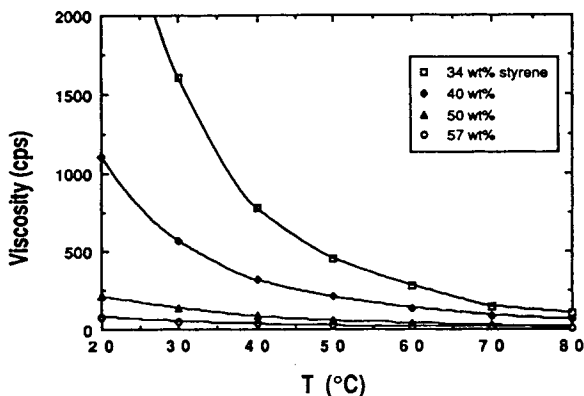


Figure 3 (a) Viscosity versus temperature and (b) logarithmic viscosity vs. reciprocal of temperature of the A1-styrene resin.

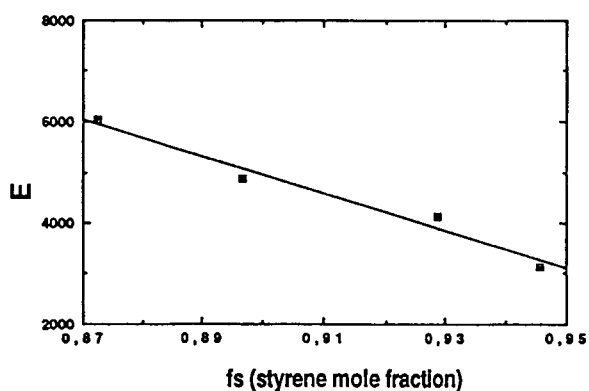
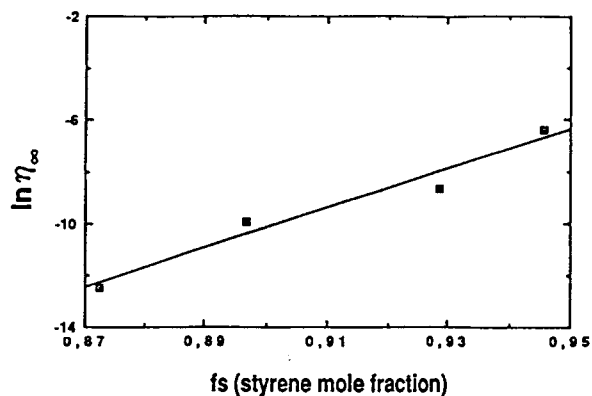


Figure 4 Correlations of (a) infinite viscosity and (b) activation energy with styrene mole fraction for the A1-styrene resin after correlation with temperature on Figure 3.

of styrene monomer in the resin, shown in Figure 4, (a) and (b), respectively. Both of them are linearly correlated with mole fraction of styrene (or UP prepolymer) in the resin. The results mean that the logarithmic infinite viscosity and the resin activation energy can be empirically expressed as a function of composition as follows:

$$\ln \eta_{\infty} = a_1 + a_2 f_s \quad (2)$$

$$E = E_1 + E_2 f_s \quad (3)$$

where a_1 , a_2 , E_1 , and E_2 are parameters that can be determined by the Y-axis intercept and the slope of Figure 4, (a) and (b); f_s is styrene mole fraction. For A1 resin, a_1 , a_2 , E_1 and E_2 are -78.07 , 75.32 , 320.7 KJ/mol and -310.1 KJ/mol, respectively.

Substituting Equations (2) and (3) into Eq. (1), one obtains:

$$\eta_0 = e^{(a_1 + a_2 f_s)} e^{(E_1 + E_2 f_s)/RT} \quad (4)$$

or

$$\eta_0 = e^{(a_1 + E_1/RT)} e^{(a_2 + E_2/RT) f_s} \quad (5)$$

or

$$\eta_0 = \eta_E e^{\beta f_s} \quad (6)$$

with

$$\ln \eta_E = a_1 + E_1/RT \quad (7)$$

and

$$\beta = a_2 + E_2/RT \quad (8)$$

where, η_E is defined as pseudo bulk viscosity and β is gradient factor.

Equation (6) is an analogue of eq. (1), and it implies that the resin viscosity also follows the Arrhenius-type expression with styrene mole fraction. To prove this derivation, an opposite approach from eq. (6) to eq. (4) backward is discussed hereafter.

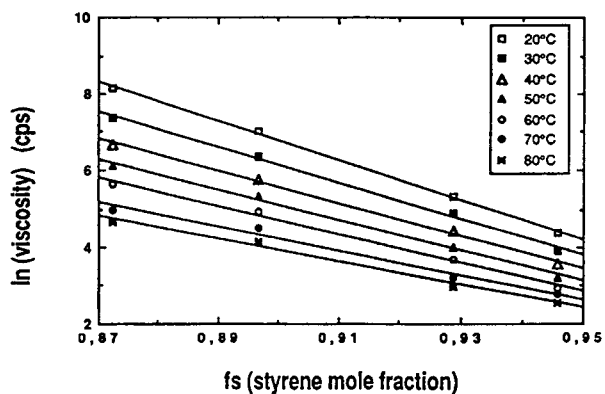
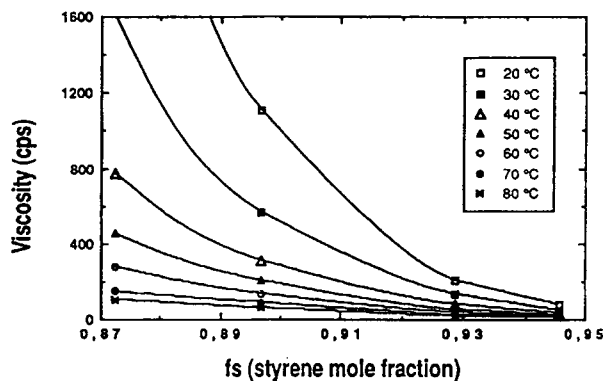


Figure 5 (a) Viscosity and (b) logarithmic viscosity of the A1 styrene resin vs. styrene mole fraction at various temperature.

Figure 5(a) shows resin viscosity, η_0 , vs. styrene mole fraction, f_s , at different temperature; while Figure 5(b) shows logarithmic resin viscosity vs. styrene mole fraction. The points are experimental data and the lines are linear regression results. It shows that the resin viscosity is expressed very well by the Arrhenius expression of eq. (6) within wide range of temperature. The Y-axis intercepts, $\ln \eta_E$, and the slopes, β , obtained from Figure 5(b) are certainly temperature dependent. According to eqs. (7) and (8), the logarithmic pseudo bulk viscosity and the gradient factor are correlated with the reciprocal of system temperature, shown as Figure 6, (a) and (b). The linear correlations are quite good. The values of a_1 , a_2 , E_1 , and E_2 of eqs. (7) and (8) are obtained from Figure 6 as -78.04 , 75.28 , 320.3 KJ/mol and -309.6 KJ/mol, respectively. They are very close to those obtained from Figure 4. These comparisons show that the viscosity of UP resins shows double Arrhenius expression behavior for temperature and styrene concentration. A simple form of

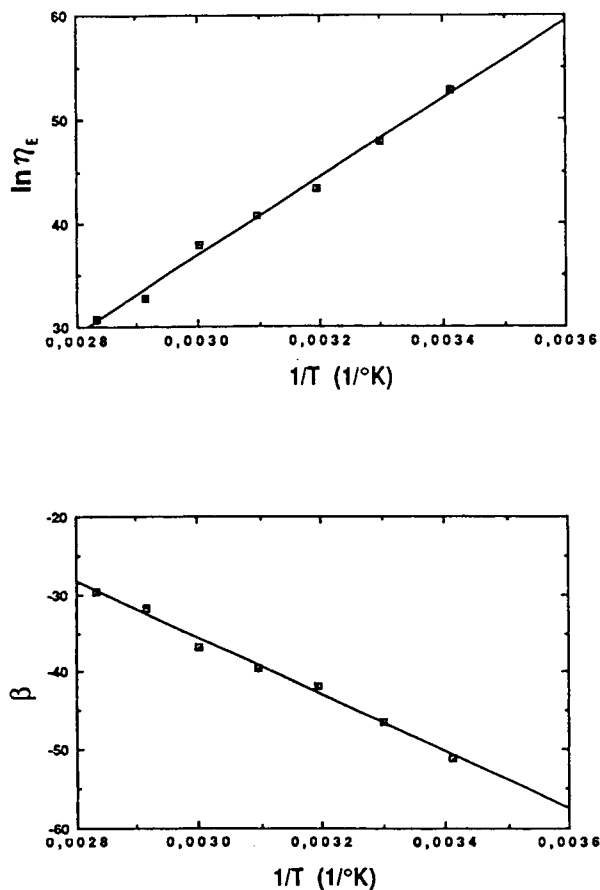


Figure 6 Correlations of (a) infinite viscosity and (b) activation energy with temperature for the A1 styrene resin after correlation with styrene mole fraction on Figure 5.

eq. (4) or eq. (5) reveals the double Arrhenius equations. All the parameters in eq. (4) or eq. (5) can be obtained by the correlation order of (i) temperature-styrene fraction or (ii) styrene fraction-temperature. The two correlation orders give similar results.

With the aid of eq. (4) or (5), one can easily simulate the resin viscosity with different styrene content at different temperature. Figure 7 shows the 3D simulation results of the viscosity of A1 prepolymer with respect to temperature and styrene mole fraction. It clearly shows the resin viscosity is significantly high at low storage temperature and with low styrene content. However, one can not extend eq. (4) or (5) to all the ranges of styrene content due to the miscibility limit. At certain temperature, there is always a maximum styrene content for a resin to have a homogeneous mixture. Above the maximum styrene content, the resin becomes immiscible and phases out into two phases. In the two-phase region, one can not apply eq. (4) or (5) to calculate the resin viscosity. The extreme styrene content can be determined from the cloud point curve of phase diagram¹³ of the resin system. For example, the extreme styrene fraction for A1 prepolymer at room temperature is 58% by weight. Table I also lists the extreme styrene fraction for all the studied UP resin. The study of extreme styrene fraction due to the phase miscibility is out of the topics and will be discussed elsewhere.

Eq. (4) or eq. (5) can be derived further based on the styrene mole fraction, f_s , and the UP prepolymer mole fraction, $f_u = 1 - f_s$, as follows:

$$\begin{aligned} \ln \eta_0 &= (a_1 + a_2 f_s) + (E_1 + E_2 f_s)/RT \\ &= [a_1(1 - f_s) + (a_2 + a_1)f_s] \\ &\quad + [E_1(1 - f_s) + (E_2 + E_1)f_s]/RT \quad (9) \end{aligned}$$

if

$$\begin{aligned} a_1 &= a_u, \quad a_2 + a_1 = a_s, \quad E_1 = E_u, \\ &\quad \text{and } E_2 + E_1 = E_s, \quad (10) \end{aligned}$$

Eq. (9) becomes

$$\ln \eta_0 = [a_u + E_u/RT](1 - f_s) + (a_s + E_s/RT)f_s \quad (11)$$

i.e.,

$$\begin{aligned} \eta_0 &= e^{(a_u + E_u/RT)(1 - f_s)} e^{(a_s + E_s/RT)f_s} \\ &= [\eta_{u_0} e^{E_u/RT}]^{(1 - f_s)} \cdot [\eta_{s_0} e^{E_s/RT}]^{f_s} \\ &= (\eta_{u_0})^{(1 - f_s)} \cdot (\eta_{s_0})^{f_s} \quad (12) \end{aligned}$$

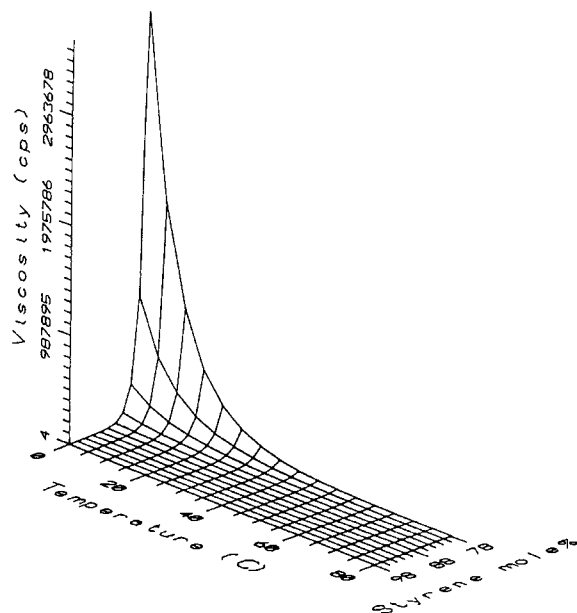


Figure 7 Influence of styrene mole fraction and resin temperature on the viscosity of A1 styrene resin.

or

$$\ln \eta_0 = (1 - f_s) \ln \eta_{u_0} + f_s \ln \eta_{s_0} \quad (13)$$

where

$$\begin{aligned} \eta_{u_\infty} &= e^{a_u} \\ \eta_{s_\infty} &= e^{a_s} \\ \eta_{u_0} &= \eta_{u_\infty} e^{E_u/RT} \\ \eta_{s_0} &= \eta_{s_\infty} e^{E_s/RT} \end{aligned} \quad (14)$$

Because both η_{u_0} and η_{s_0} have the same form of Arrhenius-type viscosity equation as eq. (1) and they are separately located in the UP side and the styrene side on eq. (11), they may be defined as “pseudo viscosities” of UP prepolymer and styrene monomer, respectively.

The term “pseudo” means that they may not actually be viscosities of UP prepolymer and styrene monomer because eq. (11) is rather an empirical equation than a theoretical equation. Consequently, η_{u_∞} and η_{s_∞} are defined as “pseudo infinite viscosities” of UP and styrene, a_u and a_s are “pseudo logarithmic infinite viscosities,” and E_u and E_s are “pseudo activation energies” of UP and styrene. All the parameters, E_u , E_s , a_u , a_s on eq. (11), can be determined experimentally.

The discussion above has been found to be true for all the systems studied in this work. The pseudo activation energies and the pseudo logarithmic infinite viscosities of the systems, for UP prepolymers and styrene, obtained by data fitting are listed on Tables II and III.

The results show that all the experimental values of the pseudo activation energies and the pseudo logarithmic infinite viscosities are independent of the correlation order between temperature and styrene mole fraction. The error between the two correlations is relatively small.

In eq. (12), one defined η_{s_0} and η_{u_0} as the pseudo viscosities of styrene monomer and UP prepolymer. It implies that η_{s_0} should be independent of the system studied, while η_{u_0} is dependent on the UP prepolymer. According to this implication, a_s and E_s must be intrinsic properties of styrene only. Table II shows that the average data of a_s and E_s are slightly scattered. They, however, are randomly

Table II Pseudo Logarithmic Infinite Viscosity (a_s) and Pseudo Activation Energy (E_s) of Styrene Monomer Studied in This Work

Resin System	a_s (cps)			E_s (KJ/mole)		
	Method 1 ^a	Method 2 ^b	Average	Method 1 ^a	Method 2 ^b	Average
A1-styrene	-2.756	-2.738	-2.747	10.641	10.559	10.600
A2-styrene	-3.358	-3.358	-3.358	12.055	12.055	12.055
A3-styrene	-2.873	-2.872	-2.872	9.145	9.030	9.088
B1-styrene	-2.520	-2.540	-2.530	11.806	11.806	11.806
C1-styrene	-2.425	-2.215	-2.320	11.723	10.923	11.323
C2-styrene	-2.384	-2.185	-2.285	9.062	9.561	9.312
C3-styrene	-2.368	-2.460	-2.414	9.312	10.199	9.756
			(-2.647 ± 0.381)			(10.563 ± 1.207)

^a Values obtained by eqs. (1), (2), (3), and (10), i.e., data fitted by correlation order of temperature and, then, styrene mole fraction.

^b Values obtained by eqs. (6), (7), (8), and (10), i.e., data fitted by correlation order of styrene mole fraction and, then, temperature.

scattered and are not dependent on the resin characteristics. The mean values of a_s and E_s are -2.647 cps and 10.563 KJ/mol, respectively. The experimental error is about 13%, which may be due to insufficient data points on styrene mole fraction. Nevertheless, the result shows that the pseudo logarithmic infinite viscosity and pseudo activation energy are reasonably constant.

If $f_s = 1.0$, η_0 in eq. (12) is simply equal to the pseudo styrene viscosity η_{s0} . Substituting a_s and E_s by the obtained mean values, one obtains $\eta_0 = \eta_{s0} = 5.02$ cps at 25°C . In literature, the styrene viscosity at 25°C is 0.715 cps.¹⁴ The difference of order of 1 may be due to narrow range of styrene fraction (0.89–0.96 mol % or 35–60 wt %) studied in this work or due to molecular interaction with UP prepolymer. That is the reason why a_s , E_s , η_{s0} , and η_{s0} are defined as pseudo properties of styrene monomer instead of real intrinsic properties.

Different from the pseudo logarithmic infinite viscosity and the pseudo activation energy of styrene shown on Table II, those of UP prepolymers shown on Table III seem to be dependent on the molecular weight of UP prepolymer. Figure 8 shows the results of (a) pseudo logarithmic infinite viscosity versus number-average molecular weight and (b) pseudo activation energy vs. number-average molecular weight for UP prepolymers studied in this work.

The data points of the A group UP prepolymers (Table I) are located on a straight line. Those of the C group prepolymers are located on another line. It means that the pseudo parameters of the UP prepolymer can be correlated well with its number-average molecular weight. For A group prepolymer (MA-PG type UP prepolymer), the correlations obtained from Figure 8 are as follows:

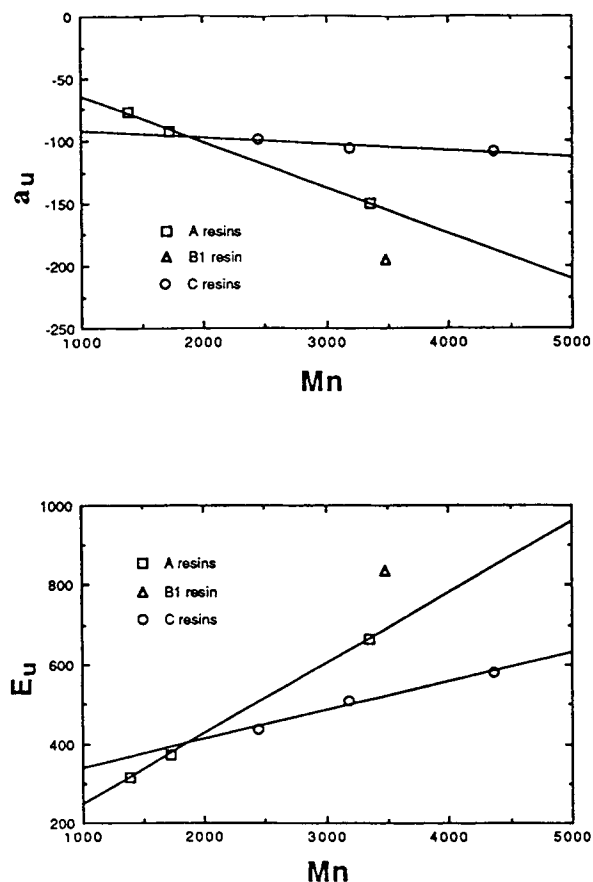


Figure 8 Correlations of (a) pseudo logarithmic infinite viscosity, a_u , and (b) pseudo activation energy, E_u , with number-average molecular weight of UP prepolymer.

$$a_u = -87.43 - 0.00505 M_n$$

$$E_u = 262.47 + 0.0736 M_n \quad (15)$$

Table III Pseudo Logarithmic Infinite Viscosity (a_u) and Pseudo Activation Energy (E_u) of UP Prepolymers Studied in This Work

Resin System	a_u (cps)			E_u (KJ/mol)		
	Method 1 ^a	Method 2 ^b	Average	Method 1 ^a	Method 2 ^b	Average
A1-styrene	-76.498	-76.498	-76.498	314.269	313.937	314.103
A2-styrene	-93.164	-93.164	-93.164	371.470	371.470	371.470
A3-styrene	-150.570	-150.571	-150.570	663.873	663.873	663.873
B1-styrene	-196.016	-194.152	-195.084	838.883	833.894	836.388
C1-styrene	-99.504	-96.976	-98.24	435.986	435.737	435.862
C2-styrene	-115.593	-94.785	-105.189	508.069	511.145	509.607
C3-styrene	-106.743	-110.683	-108.713	599.735	570.068	579.902

^a Values obtained by eqs. (1), (2), (3), and (10), i.e., data fitted by correlation order of temperature and, then, styrene mole fraction.

^b Values obtained by eqs. (6), (7), (8), and (10), i.e., data fitted by correlation order of styrene mole fraction and, then, temperature.

For C group prepolymers, the correlations are

$$a_u = -27.30 - 0.0369 M_n$$

$$E_u = 65.72 + 0.1785 M_n \quad (16)$$

The linear correlation lines are represented as the solid lines shown on Figure 8. The different correlation results of eqs. (15) and (16) are believed due to the different molecular structures of A group and C group prepolymers. Changing the glycol component from PG (for A group) to DEG/NPG (for C group) may change the molecular movement and the molecular interaction parameters of the UP prepolymer. Therefore, the dependence of a_u and E_u on the molecular weight is significantly different, shown on Figure 8. The data points of B1 prepolymer, however, are not located on the straight lines of A group and C group prepolymers on Figure 8 because the molecular structure of B1 prepolymer (MA-IPA-PG type UP prepolymer) is different from those of A and C group prepolymers. Consequently, its pseudo logarithmic infinite viscosity and pseudo activation energy are deviated from the correlations with number-average molecular weight for Group A and C prepolymers.

Similar to Figure 8, Figure 9 shows the results of (a) pseudo logarithmic infinite viscosity and (b) pseudo activation energy vs. weight-average molecular weight of UP prepolymer. The data points are so scattered that the correlations with weight-average molecular weight are not as good as those with number-average molecular weight. It may be due to different polydispersity of the UP prepolymer shown on Table I. By comparing Figure 9 with Figure 8, the correlations of pseudo logarithmic infinite viscosity and pseudo activation energy seems to be better with number-average molecular weight than with weight-average molecular weight.

Figure 8 clearly shows that the pseudo parameters of the UP prepolymer are not only dependent on its molecular weight but also dependent on its molecular structure. For UP prepolymers, the factor of molecular structure includes the components of di-acids (or co-acid anhydrides) and di-alcohols used for prepolymer synthesis, the composition of each component contributed in the prepolymer molecules, and the branchings on the molecules.¹⁵ The correlation between the pseudo parameters and the molecular structure is so complicated that it will be discussed further elsewhere.

Substituting eq. (15) into eq. (12), one can simulate the resin viscosity of styrene with A-type UP prepolymer with respect to temperature, styrene

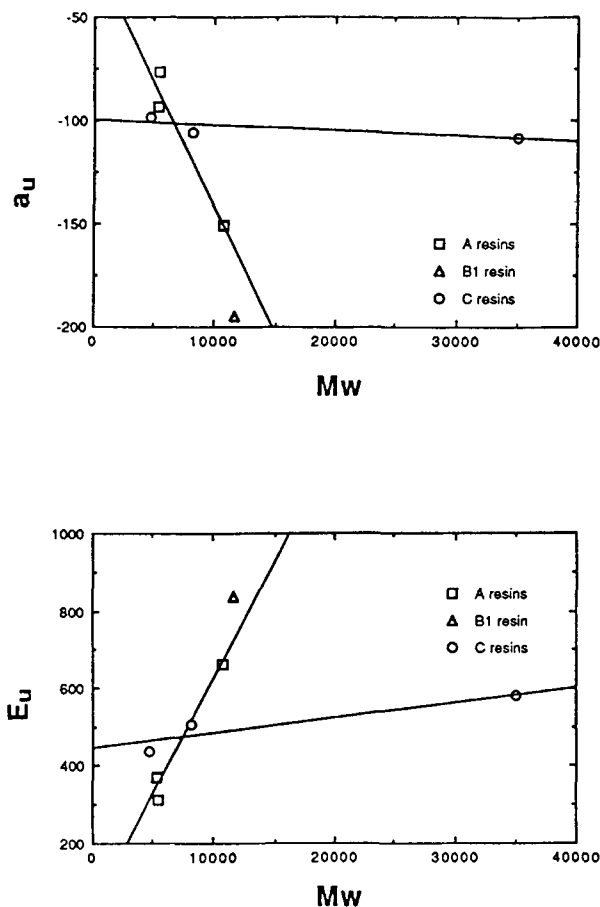


Figure 9 Correlations of (a) pseudo logarithmic infinite viscosity, a_u , and (b) pseudo activation energy, E_u , with weight-average molecular weight of UP prepolymer.

fraction, and number-average molecular weight of UP prepolymer. It is impossible to present all the factors above on the resin viscosity on a single figure because it will be a 4-D plot. A 3-D plot of resin viscosity with respect to styrene fraction and prepolymer molecular weight for the A-type prepolymer at 25°C is shown on Figure 10 as an application example of the empirical equations obtained in this work.

Although the correlation equations obtained in this work are rather empirical than theoretical, they are still practically useful. They can be applied for optimizing the resin viscosity in synthesis and on storage. They are also useful for estimating the initial resin viscosity before the curing process instead of measuring the viscosity every time.

CONCLUSION

The viscosity of unsaturated polyester resin follows the Arrhenius-type expression with resin tempera-

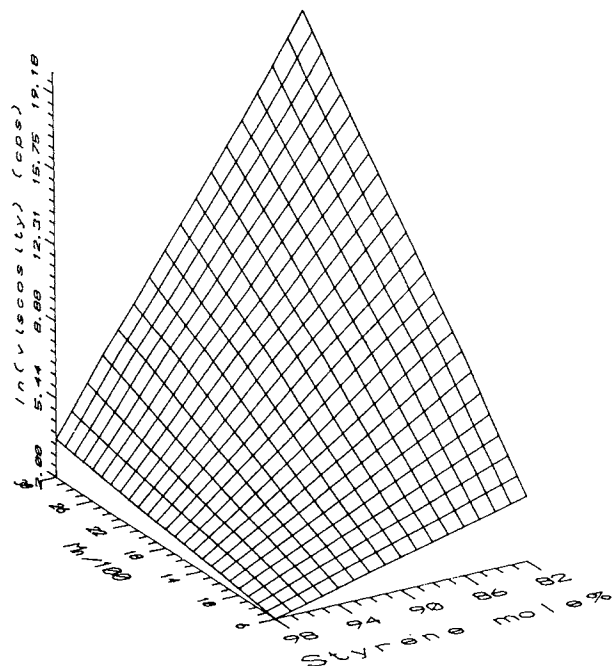


Figure 10 Influence of styrene mole fraction and number-average molecular weight of A1 prepolymer on the resin viscosity at 25°C.

ture as well as with the styrene mole fraction of the resin. The two Arrhenius correlations can be combined into a simple equation, analogous to combination rule, which is determined by the pseudo viscosities of styrene monomer and UP prepolymer, and their composition. The pseudo viscosity parameters of styrene monomer are found constant experimentally, while those of UP prepolymer are number-average molecular weight correlated rather than weight-average molecular weight correlated. The UP prepolymer having different molecular structure shows different pseudo viscosity parameters which must be experimentally determined for the time being. It is concluded that the resin viscosity

can be easily simulated with respect to resin temperature, styrene mole fraction, and UP prepolymer's number-average molecular weight. The correlation equations obtained in this work are rather empirical than theoretical and should be applied within the composition range of good phase miscibility. The extrapolation of the correlation equations out of the miscibility limit must be done carefully with enough experimental data.

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