Rheological Analysis of 913 Carbon Epoxy Laminates

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Abstract: **Autoclave curing process has been widely used for processing of impregnated composite prepregs. Applications of epoxy prepreg require understanding its rheological properties during the cure process. Like polymers, epoxy prepreg is a viscoelastic material. During a curing process under continuous sinusoidal stresses or strains, its viscoelastic characteristics change, which is reflected in the variations of rheological properties. Other changes that occurs during curing are chemical, physical, and mechanical changes like the cross linking between the fiber and resin. With the advancement of the cure process, crosslinking reaction occurs at a critical extent of reaction known as the gel point. At the gel point, epoxy resin changes from a liquid to a rubber state. It becomes very viscous and thus difficult to process; so the gelation has an important effect on the application process of epoxy prepreg. Hence there is a need to study the behavior of resin during curing process to set the optimum cure parameters.**

Earlier researchers have developed models on cure kinetics and on rheological behavior of different epoxy resins, by considering different empirical relationships. Since different resins exhibit different behaviors during curing, there is a scope to study the rheological characteristics of the 913 carbon epoxy material, which is widely used for advanced high strength aerospace structures.. In this work efforts were made to find the relationship between cure temperature and viscosity of 913 epoxy resin, and also an empirical relationship between cure temperature and degree of cure has been developed to know the amount of reaction that incurred at any instant of time. Also the empirical relation between degree of cure, viscosity, and cure temperature was developed. Efforts were made to find the relation between viscosity and glass Transition T_g, degree of cure and glass transition temperature T_g . The outcome of this work and the data helps designers in optimization of the cure cycles for curing of 913 carbon epoxy material.

Keywords: Autoclave, curing, epoxy, gelation, resin, rheology.

Nomenclature:

Tg = glass transition temperature.
α = degree of cure.
H=heat of reaction at any instant of time
HR= total heat generated, i.e. α=1.
U = activation energy for viscosity,
K= constant.
A = Arrenhnius constant

I. INTRODUCTION

Fiber reinforced composites are a class of composite materials consists of at least two chemically and physically distinct phases, suitably distributed to provide properties that are not obtainable with either of the individual phases. Design goals of fiber-reinforced composites often include high strength and/or stiffness on a weight basis [1]. In this study 913 epoxy resin prepreg was used as a raw material to carry out experiments. The rheology is the key chemical property commonly required in numerical simulations of polymer composite manufacturing processes. Rheological analysis has been used to study the cure process of epoxy resin (Kenny et al., 1991; Wang, 1997) and epoxy prepreg (Simon and Gillham, 1993) and is also essential to optimize cure cycles. Rheology provides information on viscosity change with temperature and time along with curing process, and therefore, is critical in modeling of resin flow in various composite manufacturing processes. To investigate the cure development numerically, cure kinetics models specific to the resin system used in the composite were developed. The chemical reactions involved in the cure of a resin such as 913 epoxy resin result in the generation of heat because the low molecular monomers are converted into highly cross-linked polymeric structure. The extent of the cure reactions is usually described by the degree of cure, α, which is quantified as the fraction of heat generated to that point relative to the total heat generated through the complete cure [2].

The Degree of cure (α) is given by (α) =H/HR, Where H=heat of reaction at any instant of time, HR= total heat generated, i.e. α=1.

Epoxy resins exhibit both viscous and elastic properties. During the curing process, their viscosity increases quickly in the gel region where the viscosity can be related to the degree

of cure. Earlier researchers have carried work on carbon/epoxy 8552 prepreg, where rheological measurements as a function of temperature and time were made for the impregnated prepreg system. The manufacturer's recommended cure cycle was evaluated and considered adequate to consolidate the studied system [3]. The chemo viscosity profile for 1080 resin under isothermal curing at a particular temperature was studied by Bloechle and can be represented by a dual Arrhenius expression [4]. Hinrichs [14], discussed the requirements for a rheological instrument to measure successfully the rheological properties of the polymer. The 50mm parallel plates are beneficial for low viscosity and the 25mm parallel plates are good for high viscosity. The viscosity of the polymer materials can be measured in the continuous rotation or oscillation mode.

Zhuofeng Liu et al. [6], reported the chemo rheological behaviors of a low viscosity epoxy resin system (Huntsman 1564/3486) for vacuum infusion moulding process (VIMP) with viscosity experiments. Dusi et al. [10] measured and modeled the cure kinetics and viscosity of Fiberite 976 Resin. Shanku et al. [11] reported the rheological characteristics and cure kinetics of Epon 862/W epoxy resin for pultrusion use, the viscosity expression used in previous investigations was modified to a quadratic form in this case. C.Garschke et al. [2], reported the cure kinetics and rheology of an amine-cured TGMDA resin film, i.e. the effort was made to predict the viscosity-time-temperature behavior of the toughened resin film M18-1 (Hexcel, France) using chemo-rheological modelling under resin film infusion (RFI) process conditions. The model parameters to describe the resin curing kinetics and rheology of the amine-cured epoxy resin film were obtained using differential scanning calorimetry (DSC) and rheometry.

G. Liang et al. [7], investigated the cure kinetics and rheology of a novel soy-based resin system by means of DSC and viscometer measurements. The rheology was measured with a Brookfield viscometer and was characterized using neural network. The study on the rheological properties of epoxy asphalt concrete was carried out by using the Huet-Sayegh model [8]. L. Rosu et al. [9] reported the curing of vinyl ester resins and rheological behavior, in that the viscometric measurements were carried out on a rheotest viscometer, using a cone and plate device at a constant shear rate. With the advancement of the cure process, a crosslinking reaction occurs at a critical extent of reaction. This is the onset of formation of networking and is called the gel point. At the gel point, epoxy resin changes from a liquid to a rubber state. It becomes very viscous and thus difficult to process; so the gelation has an important effect on the application process of epoxy prepreg. Although the appearance of the gelation limits greatly the fluidity of epoxy resins, it has little effect on the cure rate; so the gelation cannot be detected by the analysis of cure rate, as is the case in the DSC. The gel time may be determined by a rheological analysis of the cure process. Besides the gel time, another important parameter is the glass transition temperature (Tg). The Tg is the temperature region where the amorphous polymer changes from one state to another when the temperature changes, either from glass to rubber phase or from rubber to glass phase. The application temperature range of epoxy prepreg depends on its Tg. Many empirical relations are available in literature for different epoxy resin system, none of viscosity model available in literature that can describe the rheological characteristics of the 913 epoxy resin system. For a specific resin system, it may turn out that all the available empirical models can not fit the test data accurately.

II. EXPERIMENTAL WORK:

Materials used: The commercial 913 resin G801 carbon/epoxy resin prepreg, which has the fiber volume ratio of 60 %, was used as the sample in this study .

From literature survey Rheological properties of epoxy prepreg are closely related to the cure process. And the viscosity of a curing resin system can be determined by two factors: the degree of cure and the temperature. With the development of the cure reaction, gelation occurs and epoxy prepreg becomes difficult to process i.e. as the temperature increases viscosity of resin decreases and at particular temperature cross linking between resin and fiber occurs. Since the degree of cure α is a function time, the viscosity can be expressed in terms of α. The viscosity as a function of α is given in Fig. 1.

Much work has been done to develop appropriate mathematical models for the descriptions of the viscosity advancements at various thermosetting resins during cure. The following empirical model finds the most common applications. The empirical relationship between viscosity, degree of cure and temperature is used to calculate viscosities at any temperature [12]. The correlation is as follows

$$\mu = \mu\infty \, exp\left(\frac{U}{RT} + K\alpha\right) \qquad \text{..... (1)}$$

Where μ∞ is a constant for a given epoxy resin system, U is the activation energy for viscosity, and K is a constant which is independent of temperature.

The constants in equation are determined as

$$\ln\mu = A + K\alpha \quad \text{-----} \quad (2)$$

$$\text{where, } A=\ln\mu\infty+U/RT \text{ ---} \quad (3)$$

The constant K and the parameter A were found by fitting a linear least square curve to the μ versus α data generated at a constant temperature.

For 913 epoxy resin system the values of U, A, and K were calculated from the dynamic scanning DSC experiments and plotting the values using Kissingers and Ozawa plot. The values are as follows.

Activation Energy U = E = 78.65 kJ/mol,
Arrhenius Constant A = 2.31×109 min-1,
Constant K = 0.27 min-1.

The viscosities at various cure temperatures are calculated using equation (1) and the values are given in Table 1. Then an empirical relationship between viscosity and cure temperature has been developed using linear curve fitting technique, thereby the viscosity of the resin during curing can

be calculated at any particular cure temperature. The empirical relation is as follows

$\ln\mu = 9.0566\times10^{3} X - 21.743$
with $R^2 = 0.9997$ …… (4)
where $X = 1/T$ K^{-1}

Isothermal DSC (Differential Scanning Calorimeter) analysis has been carried out in order to develop an empirical relationship between degree of cure and temperature; the values are given in Table 2. From these values following correlation has been developed between the DOC(degree of Cure) and the cure temperature 'T' using linear curve fitting technique.

$\alpha = 2.0349\ln T - 11.319$ for $T > 370K$ --------- (5)
$\alpha = 0.0077\ln T - 2.4713$ for $T \leq 370K$ ----------(6)

Efforts are made in this study to establish a relationship between glass transition temperature (Tg) and the degree of cure. From the literature reviews it is found that the Tg increases with the increment of degree of cure. Wisanrakkit et al [15]. There exists a unique relationship between the Tg and degree of cure regardless of the cure temperature and cure path.

The phenomena of both gelation and vitrification may occur in the cure process of epoxy prepreg. Depending on the epoxy prepreg systems, gelation occurs at a special conversion point (Barton et al., 1992; Flory, 1953), where the epoxy resin changes from a liquid state to a rubber state. The phenomenon of vitrification of the cure process is closely related to Tg. When Tg is lower than the cure temperature, the cure process is controlled by kinetics. Based on corresponding state principles, a theoretical equation relating Tg to the degree of cure was introduced by DiBenedetto [16]. The DiBenedetto equation cannot be applied to some polymer systems, especially for highly cross-linked systems. Pascault and Williams (1990) introduced the maximum glass transition temperature T of the system (attained when $\alpha = 1$ in the DiBenedetto equation) and further extended the DiBenedetto equation as follows:

$$Tg = \frac{(1-\alpha)\mathrm{Tg0} + \lambda\alpha\mathrm{Tg}\infty}{[\,(1-\alpha)+\lambda\alpha\,]} \quad \text{------ (7)}$$

Where Tg0 is the glass transition temperature when $\alpha = 0$, and λ= Fx/Fm, is an adjustable structure dependent parameter between 0 and 1, Fx/Fm is the ratio of segmental mobilities.

From equation (7) we can develop an empirical relation between Tg and degree of cure α. thereby knowing the degree of cure at any particular temperature glass transition temperature can be calculated.
The values of glass transition temperatures at various degrees of cure are given in Table. 3 and the glass transition Tg curve with degree of cure is shown in Fig 5. the relation between the glass transition temperature Tg and the degree of cure has been developed as shown below.

$Tg = 56.572\alpha^2 + 40.105\alpha + 27.764$…….. (8)
with $R^2 = 0.9999$

As the Tg value varies with degree of cures, viscosity also varies with Tg hence it is important to develop the valuable empirical relationship between viscosity and Tg.

The values of viscosities at various Tg points are caluculated and mentioned in Table 4 , the viscosity curve has been plotted at various Tg points and a relation (eq.9) is developed by linear curve fitting, from this relation the viscosity at any glass transition temperature can be easily calculated.

$\mu = 3E{+}68Tg^{-26.18}$ with $R^2 = 0.9992$ ……. (9)

III. RESULTS AND DISCUSSIONS

The empirical relationship developed between viscosity and temperature is verified with the experimental data sheets provided by the manufacturers. The experimental data values are found in a good agreement with the theoretical values obtained by the developed equation no.1..

The following values are utilized to calculate the viscosity at various temperatures.

E = 78.65 kJ/mol, A = 2.31×109 min-1,
K = 0.27 min-1, and μ = 10 Pa.s

From the Table. 1 and Fig. 1, it is noticed that, as the temperature increases the viscosity decreases and the excess resin material flows and the cross linking between occurs.
it is found that as the cure temperature increases the degree of cure increases. The predicted viscosities have very good agreement with the experimental data, even in the gel region. It seems clear that the viscosity profile at each temperature can be better described by the proposed viscosity model i.e. obeys equation (4).

Table 1. Details of viscosities and degree of cure at different temperatures.

Temp K	Degree of cure, α	Viscosity (Theoretical) (Pa.s)	Viscosity (Experimental Data) (Pa.s)
432	0.99	0.442	0.459
424	0.98	0.667	0.68
412	0.97	1.275	1.27
396	0.926	3.186	3.08
392	0.89	4.02	3.89
384	0.84	6.56	6.30
380	0.76	8.33	8.086
372	0.603	13.63	13.47
363	0.36	23.99	24.68
358	0.23	33.3	34.97
343	0.145	103.4	105.75

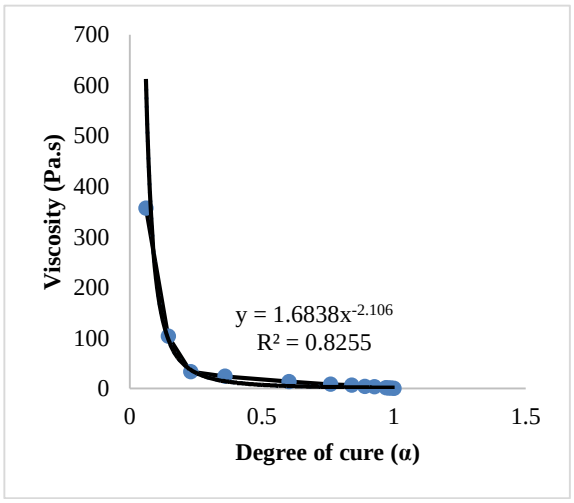

Fig.1 shows the behavior of resin viscosity as a function of degree of cure.

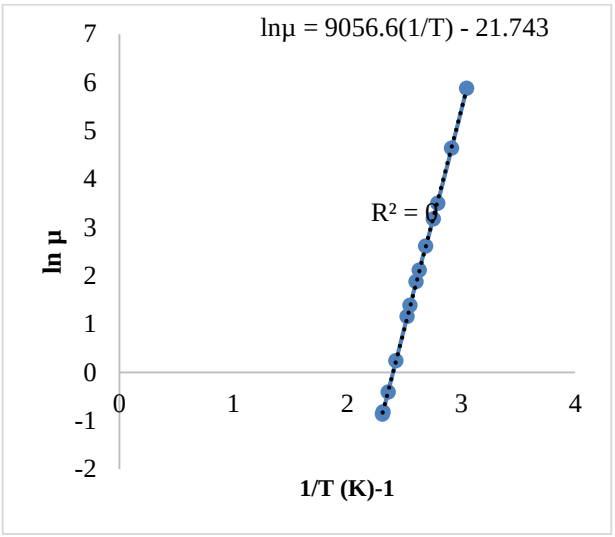

Fig. 2. Shows the resin viscosity behavior with cure temperature.

The values of degree of cure at any time can be calculated by either by equation (5) or (6) according to given temperature value. The values of degree of cure at various temperatures are calculated and tabulated as shown in the below table 2.

Table 2. Comparison of degree of cure obtained from model and experiments.

Temperature (K)	Degree of cure (Theoretical) α	Degree of cure (Experimental) α
432	0.99	1.02
424	0.98	0.99
412	0.97	0.933
396	0.926	0.85
392	0.89	0.83
384	0.84	0.79
380	0.76	0.76
372	0.603	0.72
363	0.36	0.32
358	0.23	0.285
343	0.145	0.169

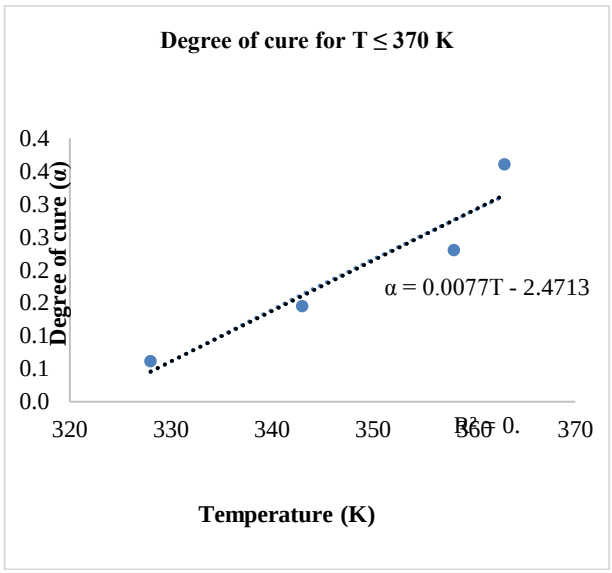

Fig 3. Degree of cure versus cure temperature plot.

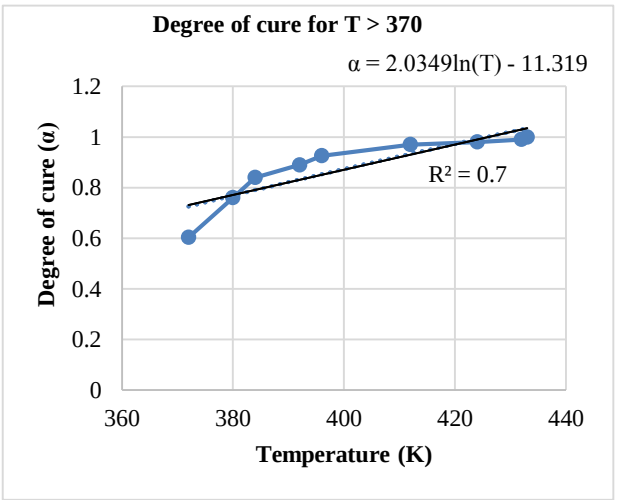

Fig 4. Degree of cure versus cure temperature plot (for cure temperature T>370 K.

From Table.2, Fig.3 and Fig. 4, it can be observed that as the temperature increases the degree of cure increases. In other words at higher temperatures the reaction occurs at faster rate, this is because as the temperature increases the activation energy decreases hence reaction occurs at faster rate. The relationship obeys equations (5) and (6).

An empirical relation between degree of cure and glass transition temperature has been developed for 913 resin system considering the following values.

$Tg0 = 25\ 0C,\ Tg\infty = 125\ 0C,\ \lambda = 0.6\ (0 \leq \lambda \leq 1)$

Also the relationship between the viscosity and glass transition temperature is developed in order to determine viscosity at any given cure temperature or the corresponding Tg.

Table 3. Glass transition temperatures with degree of cure.

Temperature K	Degree of cure α	Glass Transition Temp. T_g (^{0}C)
432	0.99	123.3
424	0.98	121.7
412	0.97	120.09
396	0.926	113.24
392	0.89	107.91
384	0.84	100.90
380	0.76	90.51
372	0.603	72.68
363	0.36	50.23
358	0.23	40.19
343	0.145	34.23

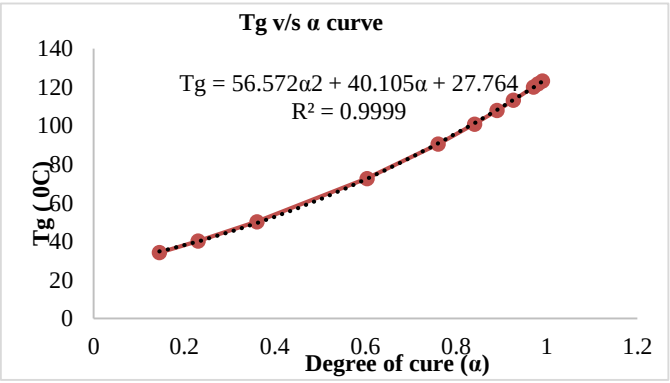

Fig.5. Plot shows the behavior of Glass transition Tg with Degree of Cure.

It is found that the resin viscosity drastically reduces as the cure temperature increases with the proportionate increase in glass transition Tg. It has been observed a major viscosity shift in between the cure temperature of 363 to 380 K. thereafter the viscosity reduces gradually up to 396 K and then the viscosity remains more or less constant, which depicts the complete resin vetrification.

From the plot as shown in the Fig.5 the resin viscosity as any point of cure temperature can be calculated and the viscosity curve indicates that the 913 resin can be cured at the minimum cure temperature of 412 K (139 o C) so as to accomplish better quality and compaction, it is observed that the resin properties are not affected with the raise in cure temperature from 412 K and this can be raised up to 432 K.

Table 4. Resin Viscosities at different glass transition temperatures.

T_g (^{0}C)	T_g (K)	Viscosity (Theoretical) (Pa.s)	Viscosity (Experimental) (Pa.s)
123.3	396.3	3.18	2.89
121.7	394.7	3.497	3.21
120.09	393.0	3.84	3.60
113.24	386.2	5.82	5.68
107.91	380.9	8.133	8.15
100.90	373.9	12.77	13.25
90.51	363.5	25.78	27.74
72.68	345.6	95.13	104.05
50.23	323.23	592.32	599.93
40.19	313.1	1474.1	1380.8
34.23	307.2	2573.8	2272.2

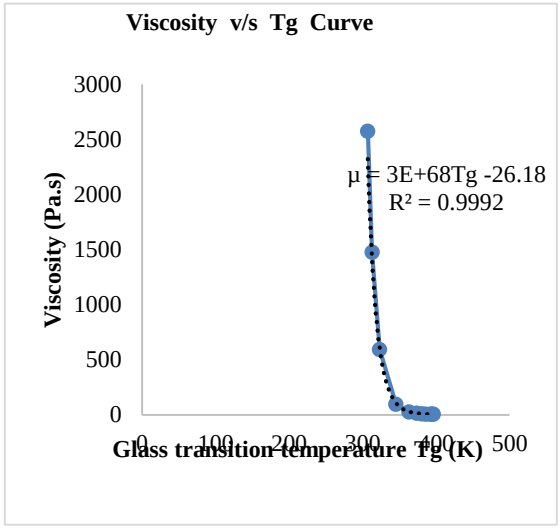

Fig. 5.Resin viscosity behavior at various glass transition temperatures

IV. CONCLUSIONS

In this research work, rheological studies of 913 epoxy resin was carried out to find out the empirical relationship between degrees of cure, viscosity, and cure temperature. Efforts were also made to find the relationship between viscosity and glass transition temperature (T_g) , degree of cure (α) and glass transition temperature(T_g).

It is found that the resin viscosity drastically reduces as the cure temperature increases with the proportionate increase in glass transition temperature Tg. It has been observed a major viscosity shift occurs between the cure temperature 363 to 380 K. thereafter the viscosity reduces gradually up to 396 K and then the viscosity remains more or less constant, which depicts the complete curing of resin at this stage.

The viscosity curve indicates that the 913 resin has to be cured at a minimum cure temperature of 412 K (139 ^{o} C) with a hold time of minimum 45 mins, so as to accomplish better quality and compaction, Hold time can be varied from 45 mins to 75 mins depend upon the thickness of the component and the thermal gradient between the lead and lag thermocouples during curing. It is observed that the resin properties are not affected with the raise in cure temperature from 412 K and this can be raised up to 432 K.

The results depict that, as the cure temperature increases the degree of cure increases. In other words at higher temperatures the reaction occurs at faster rate, this is because as the temperature increases the activation energy decreases hence reaction occurs at faster rate. Later at some point the reaction is controlled by the diffusion and the reaction stops, which indicates the complete curing process. This stage happens at 433 K for the 913 resin system, Hence these 913 reisn prepeg materials can be cured from 410 K to 433 K to accomplish better quality and strength.

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