ΠΡΑΚΤΙΚΑ ΤΗΣ ΑΚΑΔΗΜΙΑΣ ΑΘΗΝΩΝ

ΜΗΧΑΝΙΚΗ. — **Basic Principles for Viscoelastic Development of Composite Materials,** by *James C. Seferis*, Corresponding Member of the Academy of Athens and *Frédéric U. Buehler**, Polymeric Composites Laboratory University of Washington.

ABSTRACT

Model prepreg with various degrees of impregnation and resin content was produced and tested. The creep of these materials at different temperatures was used to viscoelastically characterize the prepregs. Previously it was found that power of impregnation correlated well with prepreg tack. Accordingly, viscoelasticity was examined from a power point of view and was determined by measuring the power required to force the material to creep. In this investigation, we elaborated a model to understand and describe how viscoelasticity is developed in prepreg systems. Consequently this work addresses a fundamental question as to how viscoelasticity develops in the production of composite materials.

INTRODUCTION

Over the past decade, advanced composites have taken a more significant role in many areas such as the sporting goods and aerospace industries.

Although the manufacturing process of advanced composites has been fairly well established, some of the fundamental properties of the prepreg (i.e. viscoelasticity, anisotropy, and heterogeneity) are not yet fully understood and have not been thoroughly investigated [1].

The first step in the production of fiber reinforced composites is prepegging [2-5]. Prepregging can be viewed as a unit operation during which the reinforcing fibers are combined with a matrix resin to produce a uniform lamina structure as summarised in Figure 1. Ideally the viscous matrix resin wets the entire elastic fiber bed and creates an even distribution of fibers in the matrix resin, resulting in a viscoelastic prepreg.

PREPREG

VISCOELASTIC MATERIAL DEVELOPMENT

MATRIX RESIN	REINFORCING FIBERS
(VISCOUS FLUID)	(ELASTIC SOLID)

PREPREG SYSTEM

• VISCOELASTIC
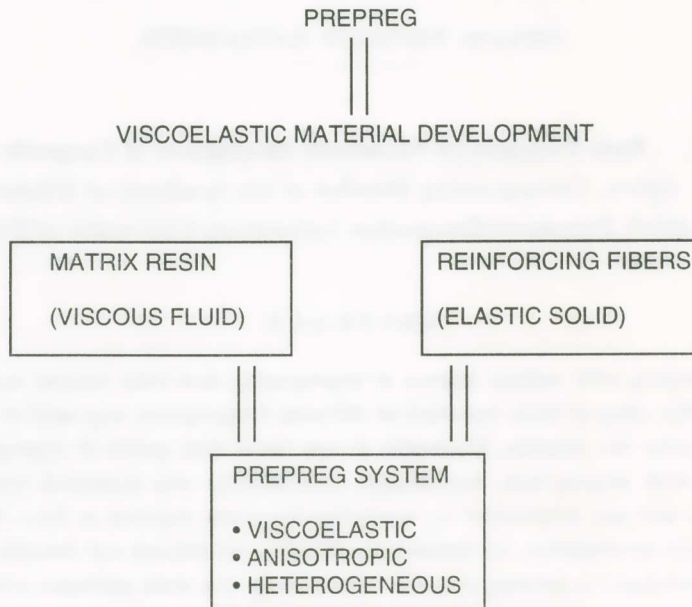• ANISOTROPIC
• HETEROGENEOUS

Figure 1. Formation of viscoelastic prepreg by combining viscous
matrix resin and elastic reinforcing fibers.

The objective of the present study is to model the formation of viscoelasticity during the unit operation of prepregging, as well as to understand the relationship between viscoelasticity, anisotropy, and heterogeneity in scaling from fundamental basic science to material utilization. These three concepts are the fundamental building blocks for scaling between properties, processing, and structure to design, manufacturing, and performance, as shown in Figure 2 [6].
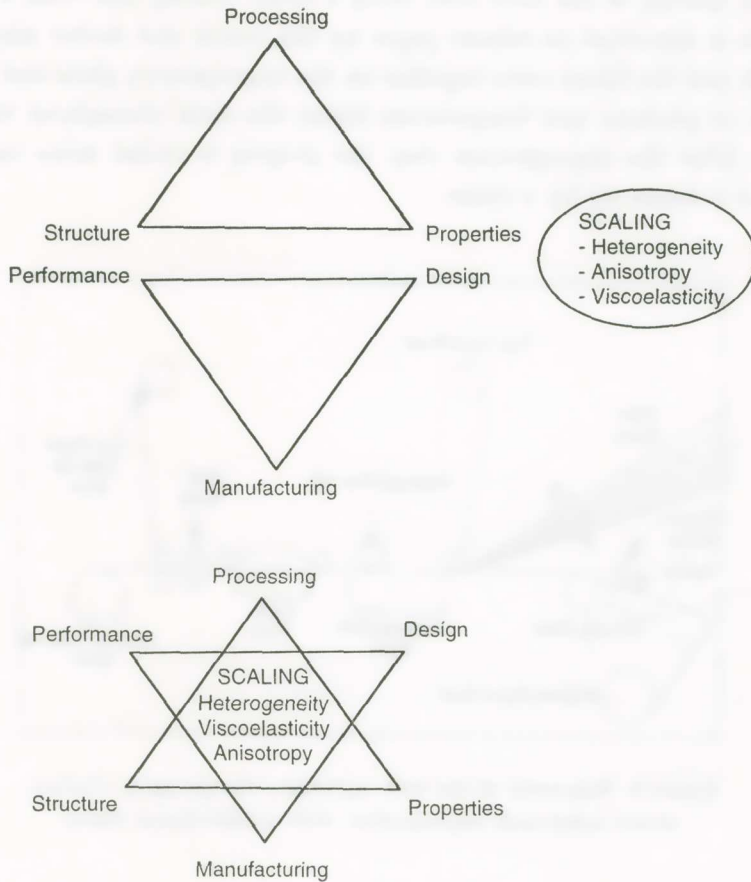
Processing

Structure

Properties

SCALING
- Heterogeneity
- Anisotropy
- Viscoelasticity

Performance

Design

Manufacturing

Processing

Performance

Design

SCALING
Heterogeneity
Viscoelasticity
Anisotropy

Structure

Properties

Manufacturing

Figure 2. Trinity concept showing the integrating principle of scaling
and the interrelation between processing, properties, structure, visco-
elasticity, anisotropy and heterogeneity.

BACKGROUND

Prepregging can be thought of as a unit operation consisting of combin-
ing reinforcing fibers with a host matrix. The reinforcing material is usually
either a woven fabric or unidirectional fibers. The matrix can be either a ther-
moset or a thermoplastic and the impregnation is done either by hot-melt or
by solution dip [5]. Figure 3 shows a schematic of a hot-melt prepregging pro-
cess with unidirectional fibers. In such a process, the first step is the align-

ment and spacing of the fiber tows using a comb. During this time, a matrix resin film is deposited on release paper by the coater and doctor blade. The resin film and the fibers come together on the impregnation plate and the application of pressure and temperature forces the resin throughout the fiber bundles. After the impregnation step, the prepreg is cooled down on a chill plate and is taken up by a roller.
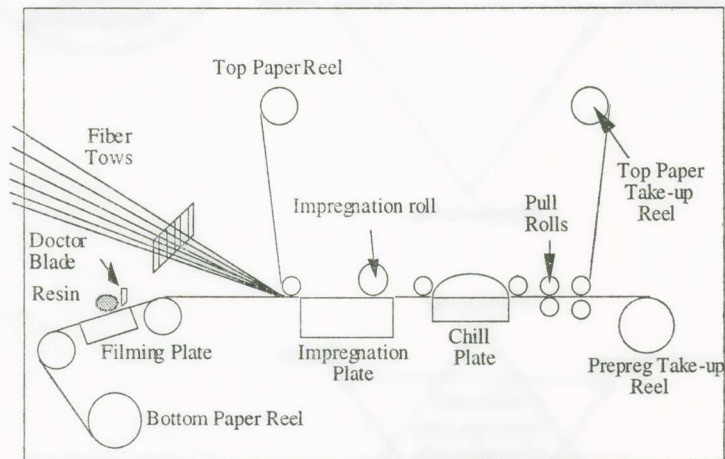

Figure 3. Schematic of the unit operation of prepregging. Process shown is hot-melt impregnation with unidirectional fibers.

Seferis and co-workers have investigated the prepregging process and developed a dimensionless Prepreg Flow Number (PFN) which can also be used to characterize the prepregging process [2, 3]. The PFN is defined as:

$$PFN = \frac{KP_e}{\mu VY_f} \tag{1}$$

where

K = collimated fiber bed permeability [m²]

P_e = effective pressure under the roll [Pa]

μ = viscosity of the impregnating resin [Pa s]

V = production line speed [m/s]

Y_f = fiber bed thickness [m]

The PFN characterizes the process of prepregging, and is an indicator of the quality of the final material. Quality of prepreg can often be a subjective notion. However, the end-user usually attributes a great importance to tack. The importance of tack has been studied in depth by Seferis and co - workers, and tack values from compression to tension cycles have been correlated with tack as determined by manufacturing personnel [7]. More recently, tack measured as compressive power per unit volume was found to strongly correlate with power of impregnation (Figure 4) [1].
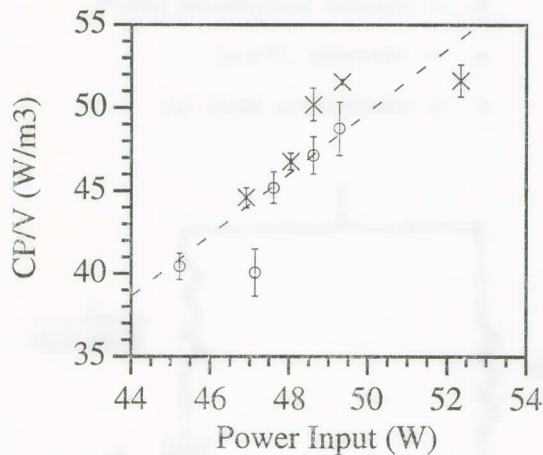

Figure 4. Compressive power per unit volume versus pull roll motor power input. Crosses are gap controlled data points and circles are pressure controlled data points. Dashed line is best least square fit and error bars are standard deviations.

The correlation beween power and tack motivated the present study, which is an attempt to better understand the formation of viscoelasticity during prepregging by looking at the power involved during a creep experiment. The approach selected to reach this objective is to describe viscoelastic behavior by creep power based on a mechanical model analog. The selected model, known as the standard linear solid (SLS) model, is schematically illustrated in Figure 5. The following stress-strain relationship can be derived from the SLS-model:

$$\sigma + \tau \frac{d\sigma}{dt} = \frac{1}{J_r} \varepsilon + \frac{1}{J_u} \tau \frac{d\varepsilon}{dt} \tag{2}$$

where

$$\tau = \frac{\eta}{\dfrac{1}{J_u} - \dfrac{1}{J_r}}$$

J_u = unrelaxed compliance [Pa^{-1}]

J_r = relaxed compliance [Pa^{-1}]

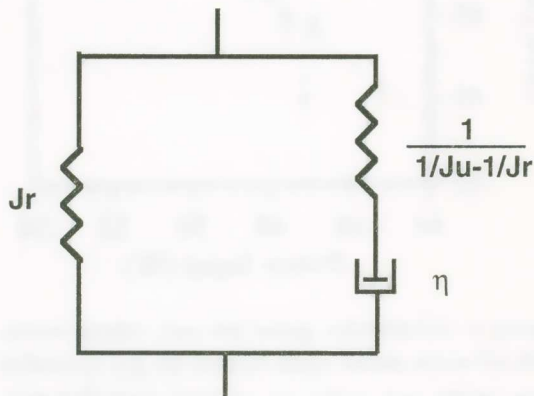η = viscosity [Pa-s]

τ = retardation time [s]

Figure 5. Schematic of the standard linear solid model.
J_r = relaxed compliance, J_u = unrelaxed compliance, η = viscosity.

If a constant stress is applied (creep), the derivative of the stress with respect to time vanishes to yield:

$$\sigma = \frac{1}{J_r} \varepsilon + \frac{1}{J_u} \tau \frac{d\varepsilon}{dt} \tag{3}$$

solving for strain knowing with $\varepsilon = 0$ at $t = 0$ yields:

$$\varepsilon(t) = \sigma_0 J_r \left(1 - \exp\left(-\frac{J_u t}{J_r \tau} \right) \right) \tag{4}$$

The creep power P can be obtained by realizing that power is an expression of force multiplied by velocity:

$$P = Fv = \sigma A \frac{d\,(\varepsilon l_0)}{dt} = \frac{\sigma A l_0 J_u}{\tau} \exp\left(-\frac{J_u t}{J_r \tau}\right) \tag{5}$$

The temperature dependence on the retardation time τ can be calculated using an activation energy approach with the Andrade Equation viz:

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right) \tag{6}$$

where

τ = retardation time [s]

τ_0 = retardation time at a reference temperature [s]

E_a = activation energy [J/mol]

R = gas constant [J/mol–K]

T = temperature [K]

Therefore, a plot of $\ln(\tau)$ vs. $1/T$ allows the activation energy to be determined.

In order to describe prepreg viscoelastic properties from fiber and resin properties, both parallel and series combinatorial models are examined. For a rule of mixture approach, prepreg viscoelastic behavior is assumed to be bound between that of the neat resin and that of the dry fiber bed. When fiber and resin properties are combined together to describe prepreg behavior, a parallel combination of properties should represent a lower bound and a series combination should represent an upper bound.

A parallel combination model of creep power values would give:

$$\frac{1}{P} = \frac{A}{P_r} + \frac{1-A}{P_f} \tag{7}$$

While a series combination model would be accomplished viz:

$$P = AP_r + (1 - A)P_f \tag{8}$$

where

A = model parameter

P = creep power of prepreg (W)

P_f = creep power of the fibers (W)

P_r = creep power of the neat resin (W)

The model parameter A in equations 7 and 8 is dependent on the resin content, the spatial distribution of the resin, the degree of impregnation, and the resin degree of cure. In an ideally impregnated system A would be equal to the resin content.

EXPERIMENTAL

The model resin used in the study consisted of a combination of a tetra-functional epoxy resin, a difunctional epoxy resin, a thermoplastic tough-ener, and a curing agent. The tetrafunctional epoxy used was tetraglycidyl diamino diphenyl methane (TGDDM), MY 720 manufactured by Ciba Geigy. The difunctional epoxy, diglycidyl ether of bisphenol A (DGEBA), was pro-vided by Shell Chemical Co. (Epon® 828). The thermoplastic toughener was polyether sulfone (PES), 5003P PES, manufactured by Imperial Chemical Industries. Diamino-diphenylsulfone (DDS), from Ciba Geigy (HT 976) was used as the curing agent.

Unidirectional prepreg was manufactured using a California Graphite® hot-melt prepreg machine described by Hoisington et al. [8]. Toray T800 12K sized carbon fibers were impregnated with the previously described resin. Prepreg samples were processed using impregnation temperatures of 40, 60, 80, 100, and 120°C, and the final prepreg had degrees of impregnation of 0.65, 0.73, 0.80, 0.86, and 0.95 respectively. Degree of impregnation was calculated from the initial prepreg thickness and a calculated ideal, void-free prepreg thickness.

Creep experiments were performed for each prepreg sample at several testing temperatures of -10, 10, 30, and 50°C. Five prepreg plies 5.08 by 5.08 cm (2 in by 2 in) were placed between square metal platens mounted on a mechanical testing frame (Instron Model 4505). A constant load of 267 N (60 lb) was applied for ten minutes for each test by loading at a rate of 0.0254

cm/min (0.01 in/min). The change of displacement was measured as a function of time during the constant loading. Each creep experiment was performed at constant temperature ($\pm 1^{\circ}$C) in an environmental chamber (Instron Model 3111).

RESULTS AND DISCUSSION

Load-displacement — time data was initially collected on the Instron and processed to yield strain versus time. Figure 6 shows the strain versus time for neat resin, carbon fibers, and prepreg at different degrees of impregnation.
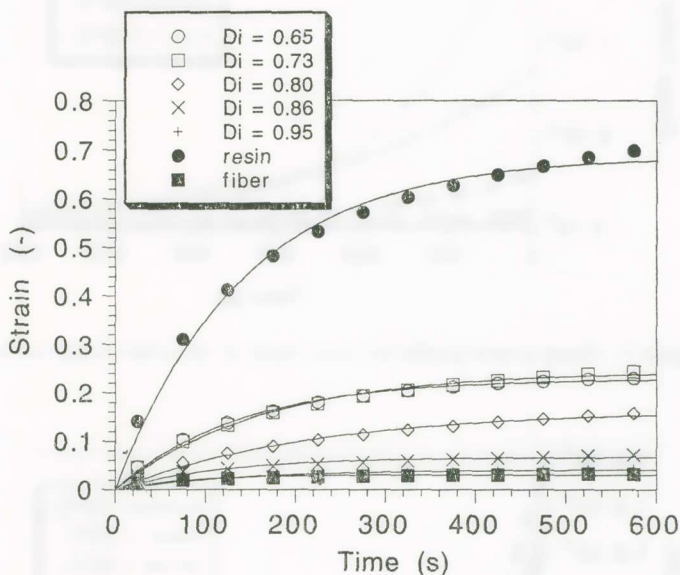

Figure 6. Strain versus time at 50°C for neat resin, carbon fibers, and prepreg with different degrees of impregnation. Solid curves are model fit.

The solid lines show the model fit represented by equation 4. The fit was nearly perfect, showing that the model gives a good mathematical representation of creep at the macromechanical level.

Figure 7 shows the creep power as a function of time for neat resin. Creep power was lower at low temperature, and as the temperature increased, creep increased and so did creep power. The next figure (Figure 8) shows creep power for carbon fibers at five different temperatures. No strong dependence

of creep on temperature was observed in the case for the carbon fibers. The power of creep for the fibers was roughly temperature independent due to the inert, non-reactive, and temperature resistant nature of the carbon fibers.

Values of J_r and τ/J_u obtained from the model equations were plotted versus the reciprocal of temperature using a semi-log plot (Figures 9 and 10). The results show that the resin relaxed compliance had a strong dependence
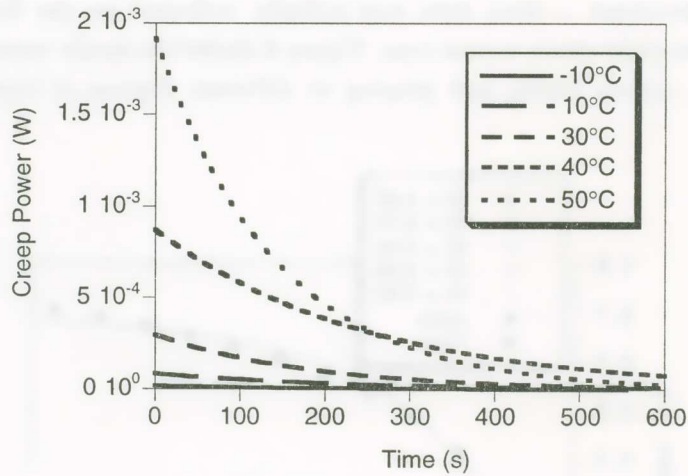

Figure 7. Creep power profile for neat resin at different temperatures.
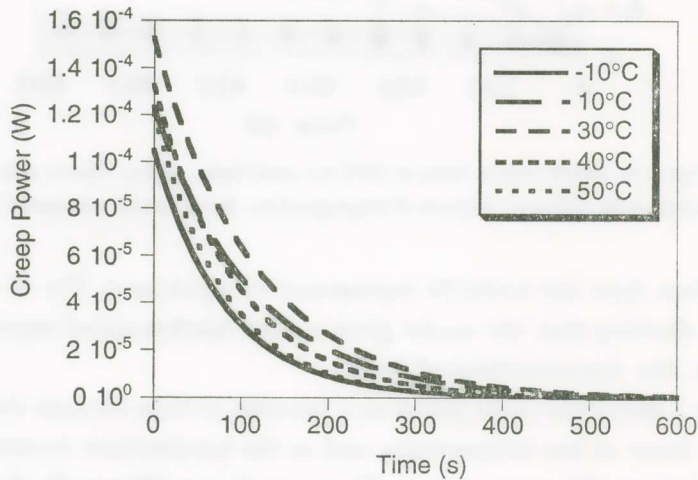
Figure 8. Creep power profile for carbon fibers at different temperatures.

on temperature and could be expressed with an Arrhenius-like relationship. On the other hand, the carbon fibers did not exhibit a temperature-dependent
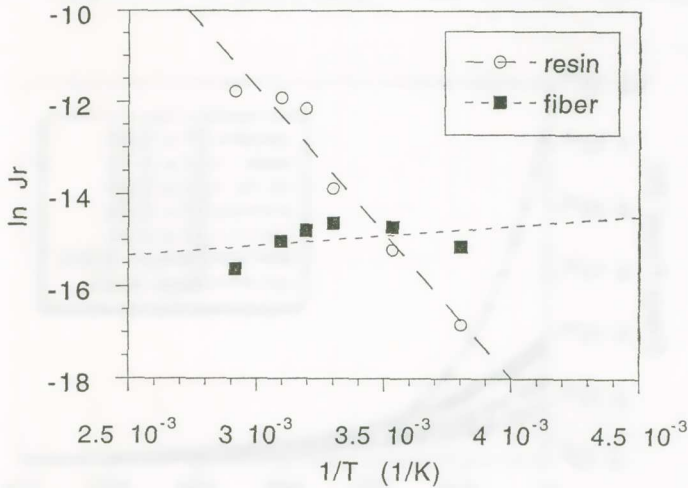

Figure 9. Temperature dependence of the relaxed compliance for neat resin and carbon fibers. Dashed lines are best linear fits.
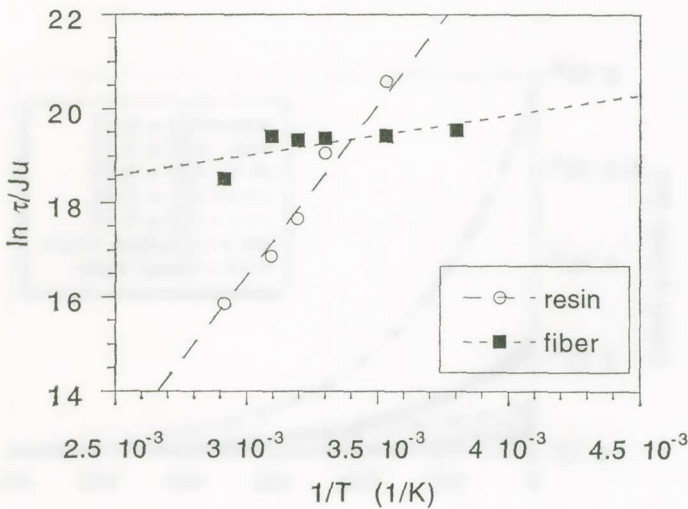

Figure 10. Temperature dependence of the ratio of relaxation time to unrelaxed compliance for neat resin and carbon fibers. Dashed lines are best linear fits.

relaxed compliance and no strong temperature dependence of τ/J_u was found for carbon fibers (Figure 10).

However, τ/J_u for the resin followed an Andrade equation expression (Figure 10), where τ/J_u increased exponentially as the temperature increased.
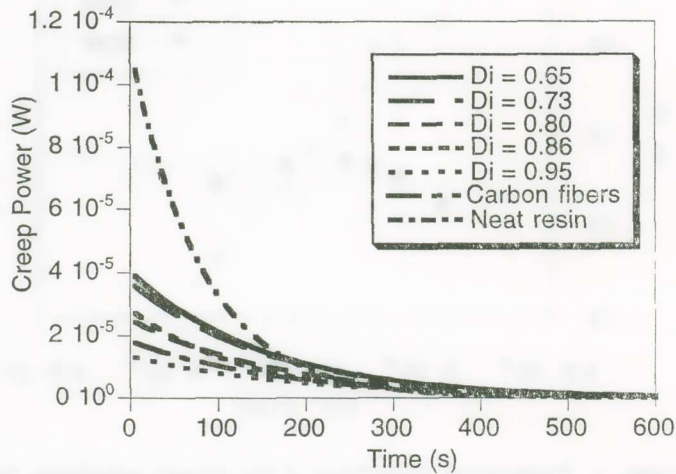

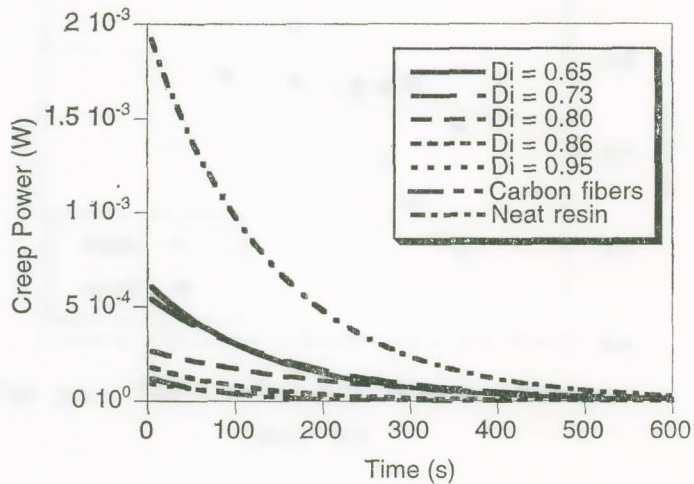Fifure 11. Creep power profile at -10°C for neat resin, carbon fibers, and prepreg at different degrees of impregnation.

Figure 12. Creep power profile at 50°C for neat resin, carbon fibers, and prepreg at diferent degrees of impregnation.

   Creep power for the prepreg versus time at different temperatures and
degrees of impregnation is illustrated in Figures 11 and 12. The general trend
in these figures was that creep power decreased as the degree of impregnation
increased. With the resin content being the same in each of these prepregs,
this behavior can only be explained by the degree of impregnation of the re-
sin and the spatial distribution of the resin. The higher the degree of impreg-
nation, the higher the degree of B-staging (because of higher impregnation tem-
perature). A higher degree of B-staging results in higher viscosity and there-
fore lower power of creep. On the other hand, a prepreg with a low degree of
impregnation has more space for resin to flow into, which gives a higher creep
power. Therefore, it is expected that highly impregnated prepregs would
show a lower creep power, which was observed in Figures 11 and 12.

   In order to understand the impact of resin content on the power of creep,
prepregs of different resin content were produced and tested. Figure 13 shows
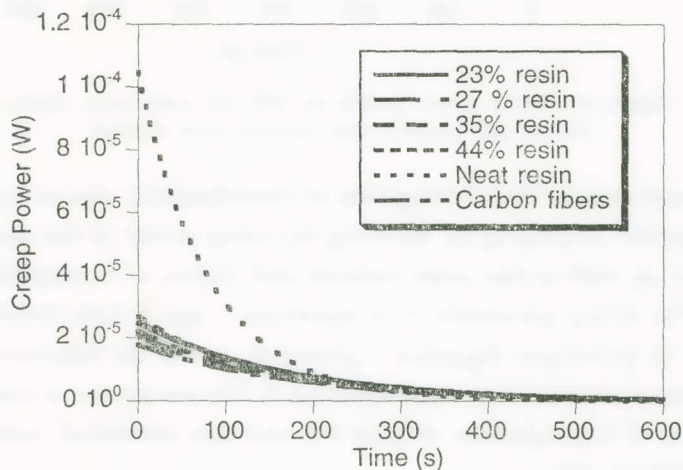
Figure 13. Creep power profile at -10°C for neat resin, carbon
fibers, and prepreg with various resin content.

that at -10°C the creep power of prepreg did not change appreciably when the
resin content was increased from 23% to 44%. At this temperature, the resin
viscosity was high and the creep power was low. Not many differences can be
observed between the prepregs because of the low temperature which causes
the resin viscosity to be very high. When the creep temperature was increased

to 50°C (Figure 14), for the highest resin content a higher creep power was observed. A larger resin content results in more contribution of the resin matrix to creep, and therefore a higher creep power since the resin has a higher power of creep than the reinforcing fibers.
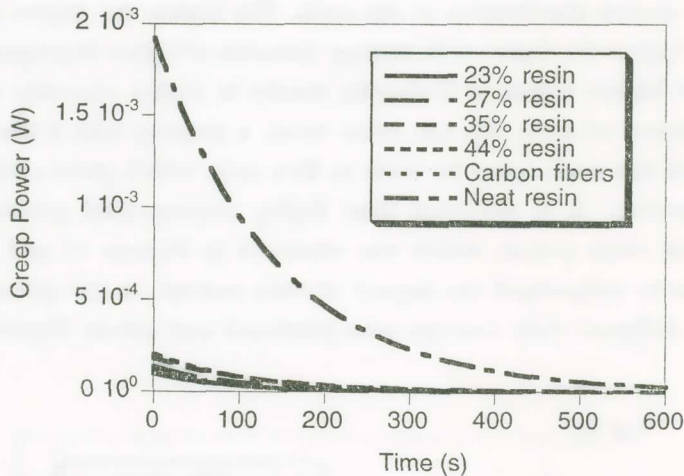

Figure 14. Creep power profile at 50°C for neat resin, carbon fibers, and prepreg with various resin content.

The next step in the investigation of viscoelasticity was to try to predict the creep power of prepreg by knowing the creep power of the neat resin and pure fibers, as well as the resin content and degree of impregnation for the prepreg. The fitting parameter A in equations 7 and 8 were determined by a non-linear fit technique. Equation 7 proved to model the behavior of the prepreg in a more accurate way than equation 8. The parameter A correlated well with degree of impregnation (Figure 15) and also correlated well with resin content (Figure 16).

It was found that below 23% resin content, the contribution of the resin to the prepreg viscoelasticity was insignificant. Prepreg with 23% resin content behaved like carbon fibers, and therefore, A should be set to zero for such prepregs.

Parameter A showed strong correlation to both degree of impregnation and resin content, but other variables contributing to its value have not been determined in the present work. Void content, degree of cure of the resin, as well as spatial distribution of the resin may have an influence on A.
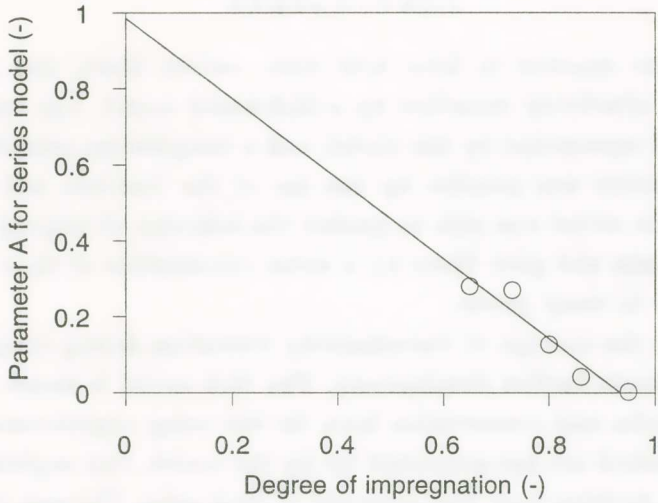
Figure 15. Correlation between the parameter A of equation 7
and the degree of impregnation of the prepreg. Temperature of
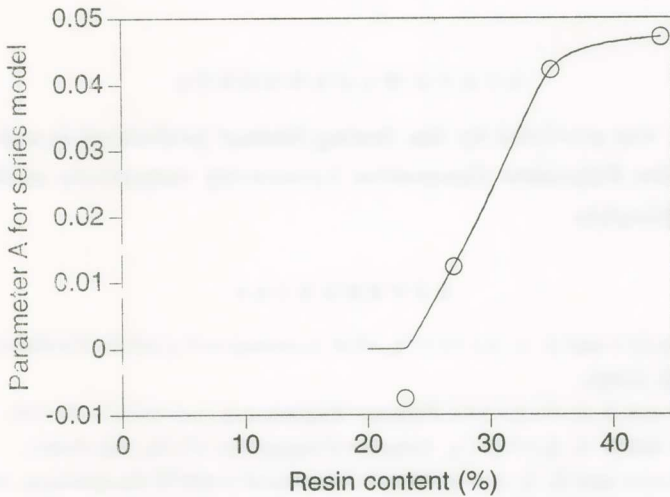creep was 50⁰C. Solid line is least square fit.

Figure 16. Correlation between the parameter A of equation 7
and the resin content of different prepregs. Temperature of creep
was 50⁰C. Solid line is an educated interpolation to the data
points.

CONCLUSIONS

The power required to force neat resin, carbon fibers, and prepreg to creep can be effectively described by a SLS-based model. The experimental data was well represented by the model, and a temperature prediction of the model parameters was possible by the use of the Andrade and Arrhenius equations. The model was able to predict the behavior of prepreg from that of the neat resin and pure fibers by a series combination of their individual contributions to creep power.

However the concept of viscoelasticity formation during composite manufacturing needs further development. The SLS model is based on conservation principles and conservation laws. In real creep experiments there are dissipations which are not accounted for by the model. This explains why the parameter A deviates from that expected in ideal cases. Through the analysis of prepreg as a viscoelastic material, an understanding of the fundamental development of the constituents (resin and fibers) of the unit operation can be modeled. This study has just begun to phenomenologically lead the way to a new approach of the development of viscoelasticity in composite materials.

ACKNOWLEDGMENTS

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