

## PROCESSING OF THERMOPLASTIC MATRIX COMPOSITES

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### INTRODUCTION

In recent years considerable attention has been focused on the use of tough, high-temperature, solvent-resistant thermoplastic polymers as matrix materials for fiber-reinforced composites. Thermoplastic resin systems have shown potential for reducing manufacturing costs and improving the damage tolerance of composite structures. In order to produce high-quality composite laminates from continuous fiber-reinforced thermoplastic prepregs the processing temperature and pressure must be selected so that intimate contact (coalescence) at the ply interfaces is achieved resulting in the formation of strong interfacial bonds (consolidation).

The objectives of this investigation were to identify the mechanisms governing intimate contact and bond formation of thermoplastic ply interfaces during fabrication and to develop a first generation processing model to relate temperature and pressure to each of the mechanisms.

### AUTOHESION MODEL

During processing of thermoplastic composites, prepreg plies consolidate into a laminate by bonding at the interfaces. The interfacial bond strength has been shown to be a function of the processing temperature, contact pressure, and contact time. The theory of autohesion or self-diffusion can be used to explain strength development at the interface of two similar polymers in intimate contact. Schematically outlined in Fig. 1 is the autohesion phenomenon for an amorphous polymer above its glass transition temperature. Interfacial bond strength increases with time due to interdiffusion of mobile molecular chain ends across the interface. After long contact times, complete interpenetration and reentanglement of the polymer chains occurs and the interface can no longer be distinguished from the bulk material. Thus, the ultimate autohesive strength or the cohesive strength of the material is obtained.

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\*Now with Morton Thiokol, Inc., Brigham City, Utah.

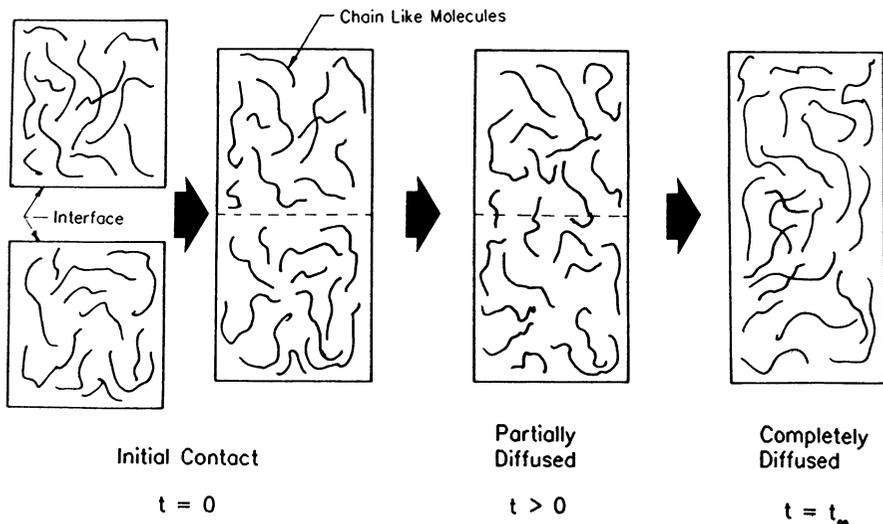


Fig. 1. Illustration of the autohesion phenomenon.

Analytical relationships for strength development at a polymer-polymer interface were developed by Wool [1-2]. Wool has shown that the autohesive strength is proportional to the fourth root of contact time, and if failure is by chain pull-out, the slope of the autohesive strength versus time curve provides a direct measurement of the self-diffusion coefficient. These relationships can be expressed as follows:

$$\sigma \sim t^{1/4} M^{-1/4} \quad (1)$$

$$\sigma_{\infty} \sim M^{1/2} \quad (2)$$

$$\sigma \sim \epsilon^{1/2} \quad (3)$$

where  $\sigma$  is the autohesive bond strength (tack stress),  $\sigma_{\infty}$  is the cohesive strength of the material,  $M$  is the molecular weight,  $\epsilon$  is the strain rate, and  $t$  is contact time. The self-diffusion coefficient ( $D$ ) of the polymer chains may be written as

$$D = A/M^2 \quad (4)$$

where  $A$  is a constant which can be determined from the slopes of the  $\sigma$  versus  $t^{1/4}$  and  $\sigma_{\infty}$  versus  $M^{1/2}$  curves. Wool's analysis provides a means of relating temperature and contact time to interfacial strength development of thermoplastic resins.

In the present investigation, the interfacial strength of thermoplastic polysulfone resin (Udel® P1700) samples bonded at different temperatures and contact times was measured. Autohesive bond strength was measured using an interfacial tensile test. The mechanical measurements were obtained at elevated temperatures (well above the  $T_g$  of the polysulfone resin,  $T_g = 194^\circ\text{C}$ ) and at a constant strain rate. These procedures were followed to insure that the failure mode was chain pull-out. It should also be noted that the mechanical tests were performed at the bonding temperature. A complete description of the experimental procedure is reported in reference 3 and will not be repeated here.

The results of the autohesive strength measurements are shown in Fig. 2 where the autohesive load is plotted as a function of the fourth root of contact time for different temperatures. From the figure it can be seen that the autohesive load increases linearly with the fourth root of contact time up to the cohesive domain as predicted by Wool. Also, as

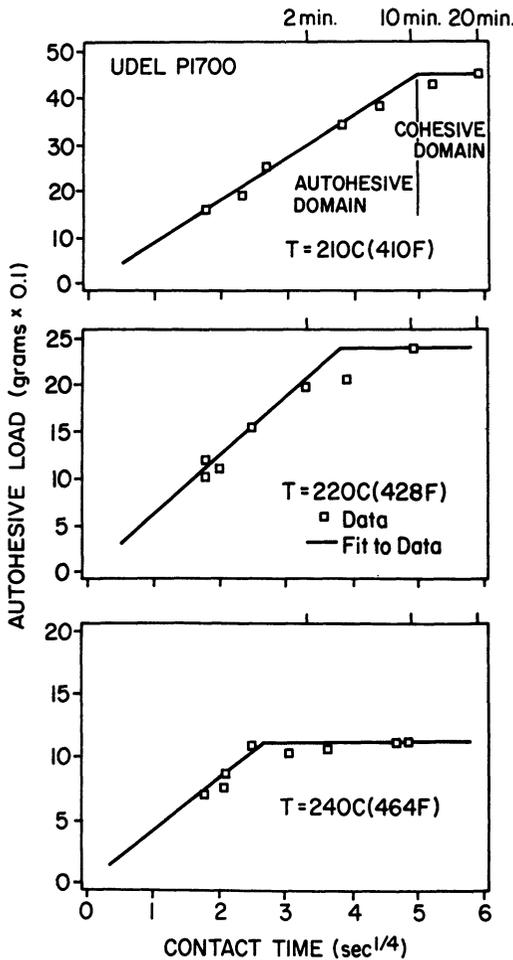


Fig. 2. Autohesive load as a function of the fourth root of contact time for polysulfone resin bonded at different temperatures.

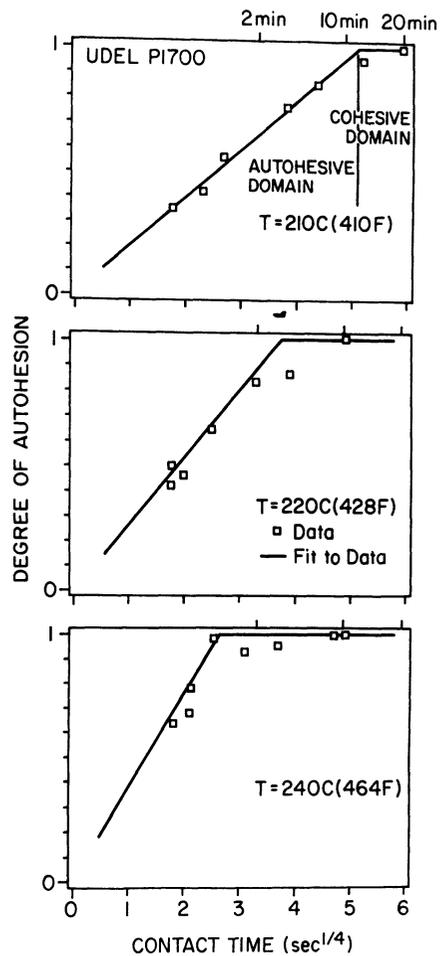


Fig. 3. Degree of autohesion as a function of the fourth root of contact time for polysulfone resin bonded at different temperatures.

the bonding temperature increases, the autohesive bond strength approaches the cohesive strength of the material at a higher rate.

In order to observe the effect of temperature on the autohesive strength and polymer diffusion coefficient, the data in Fig. 2 was normalized and replotted in Fig. 3. The degree of autohesion ( $D_{AU}$ ) is defined as

$$D_{AU} = \frac{\sigma(T, tc)}{\sigma_{\infty}(T)} \quad (5)$$

where  $\sigma$  is the autohesive bond strength and  $\sigma_{\infty}$  is the cohesive strength. The slope of the degree of autohesion versus fourth root of contact time curve is a measure of the polymer self-diffusion coefficient and increases with increasing temperature.

An empirical autohesion model for polysulfone resin was developed using the data obtained in the present investigation along with Wool's

model. The equation of the straight line in the autohesive domain can be written as

$$D_{AU} = D_{AU_0} + K(T) \cdot t_c^{1/4} \quad (6)$$

where  $D_{AU_0}$  is the initial degree of autohesion at  $t_c = 0$  (zero in this study) and  $K(T)$  is a temperature dependent parameter proportional to the polymer self-diffusion coefficient. The variation of  $K(T)$  with temperature is of interest in modeling. Assuming an Arrhenius temperature dependence,  $K(T)$  can be written as [4]

$$K(T) = K_0 \exp\left[-\frac{E_a}{kT}\right] \quad (7)$$

where the constants  $K_0$  and  $E_a$  are determined by plotting the natural log of  $K(T)$  (slopes of the  $D_{AU}$  vs  $t_c^{1/4}$  curves in Fig. 3) versus reciprocal temperature  $1/T$  (Fig 4).

The degree of autohesion calculated using equations (6) and (7) is compared with the measured degree of autohesion in Fig. 5. As can be seen from the figure, the model with an Arrhenius temperature dependence fits the data well.

#### INTIMATE CONTACT MODEL

The mechanisms by which a thermoplastic matrix composite consolidates to form a laminate has been identified as autohesive bond formation between plies. However, autohesion can occur only after the plies coalesce (i.e. are physically in intimate contact). During processing specific combinations of pressure, temperature, and time result in varying degrees of intimate contact of the laminate ply interfaces. At the present time a method for selecting the processing parameters so that complete intimate contact is achieved at all interfaces of a composite laminate does not exist.

In this investigation an approximate model was developed to relate the processing parameters to the degree of intimate contact. The formulation of the intimate contact model is described in detail in reference 3. Accordingly, only a brief outline of the model is given here.

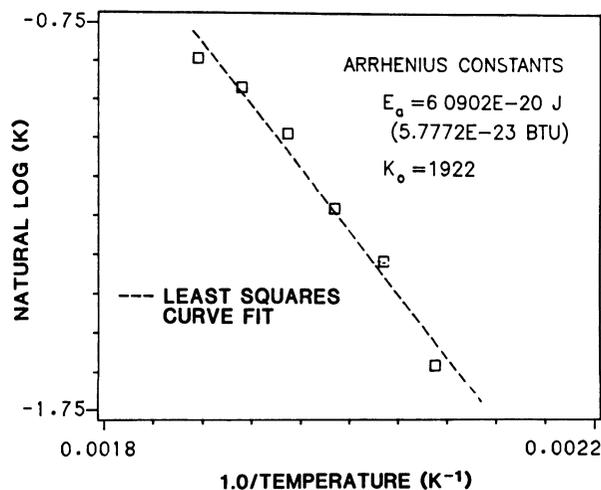


Fig. 4. Natural log of  $K(T)$  as a function of temperature.

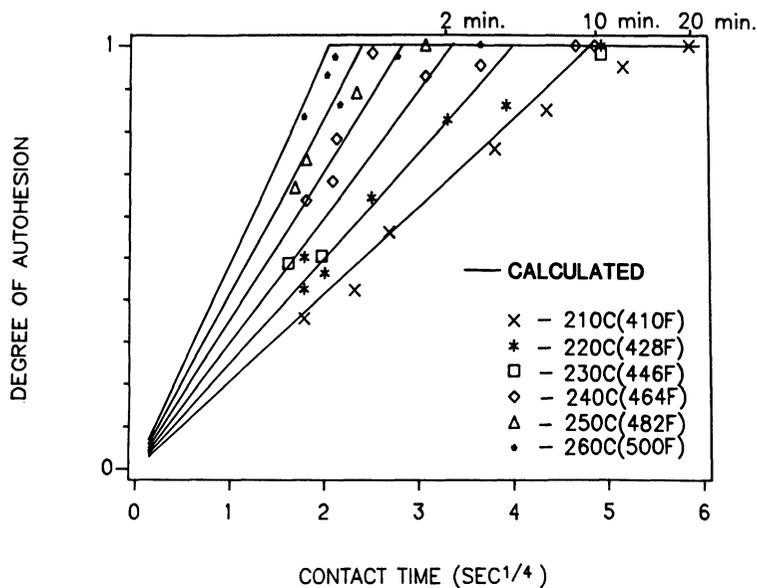


Fig. 5. Comparison between the measured degree of autohesion and the degree of autohesion calculated using Eq. (6) and assuming an Arrhenius temperature dependence.

The intimate contact model is composed of three sub-models. The first sub-model is used to describe the prepreg tow height nonuniformity across the width of a prepreg. A prepreg is made up of single tows laid side by side. The tows have constant cross-sectional areas and fiber/matrix fractions. However, the tow thickness varies across the width of the prepreg. Thus, when the prepreg plies are stacked on top of each other, spatial gaps are present. Unlike thermosetting matrix composites, which rely on low viscosity flow and wetting ability of the resin to coalesce the ply interfaces, thermoplastic matrix composites must be physically deformed to cause coalescence. Intuitively, one would expect that prepreps with nonuniform tow height distributions will take longer to achieve intimate contact at the ply interfaces than prepreps with very uniform tow height distributions.

The measured tow heights across the width of a prepreg sheet are used to construct a histogram representing the percentage of tows within an interval of tow heights. A histogram of tow height data for a graphite fiber, polysulfone resin prepreg is shown in Fig. 6. A Weibull distribution function was fit to the tow height data for use in the model calculations.

The second sub-model is a mechanics model simulating the viscoelastic response of a single tow subjected to a uniformly distributed compressive load (Fig. 7). The model relates the applied pressure to the rate of deformation of the resin impregnated fiber tows. In the model formulation it was assumed that deformations are slow, steady, and small (steady simple shear flow); the tows act independently concerning the disruption of flow, and the resin impregnated fiber tows can be treated as a homogeneous fluid. With these assumptions the formulation of the tow deformation sub-model simplifies to a squeezing flow of a homogeneous fluid between two infinitely long parallel plates.

The final sub-model is an assumed constitutive relationship for the resin, as well as, an assumed relationship simulating the influence of the fiber on the resin viscosity. In the present model formulation it was assumed that the resin can be modeled as a generalized Newtonian fluid and the power law formula was used to calculate the non-Newtonian resin

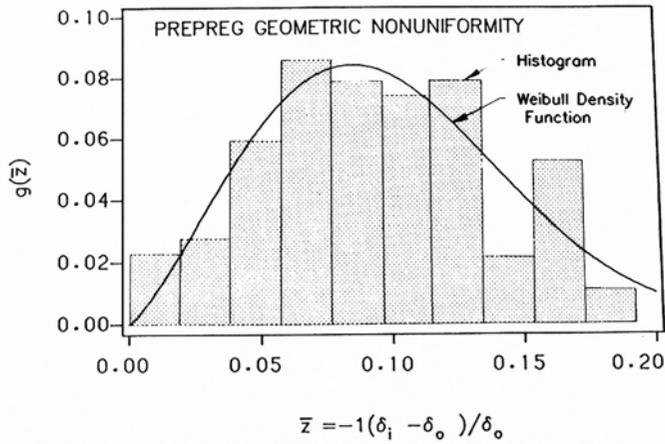


Fig. 6. Histogram of tow height data. A two parameter Weibull density function  $g(\bar{z})$  was fit to the data for use in the model.  $\bar{z}$  represents the tow heights  $\delta_i$  normalized to the largest tow height  $\delta_0$ .

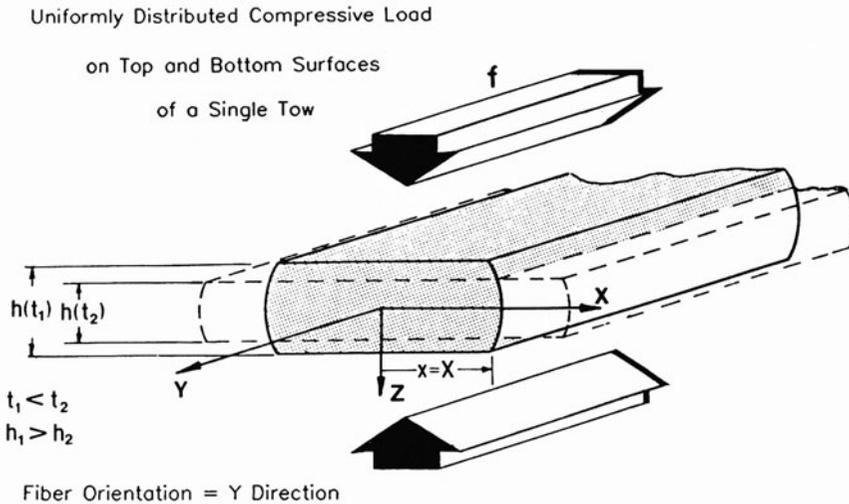


Fig. 7. Illustration of the deformation of a resin impregnated tow.

viscosity. The effect of fiber reinforcement on the neat resin viscosity is assumed to take the following form as a first approximation. At a given temperature and concentration of fiber ( $\phi$ ), the ratio of fiber filled resin viscosity to the neat resin viscosity is constant [5] and can be expressed as

$$C(T, \phi) = \frac{\eta(T, \dot{\gamma}, \phi) \text{ (fiber filled resin)}}{\eta(T, \dot{\gamma}, 0) \text{ (neat resin)}} \quad (8)$$

where  $C$  is defined as the reinforcement/viscosity influence factor,  $\eta$  is viscosity,  $\phi$  is fiber concentration, and  $\dot{\gamma}$  is the shear rate.

Graphite/polysulfone (Hercules AS-4 fiber and Udel® P1700 polysulfone resin) laminates, with a  $[0,90,0]_T$  stacking sequence, were compression molded using different processing cycles. The cross-ply stacking sequence was selected because it provides a worst case situation in that no nesting of the tows occurs as in the case of unidirectional laminae. After processing, the ply interfacial contact area (degree of intimate contact) was measured using the ultrasonic C-scan technique. The test procedures and interpretation of the C-scan results used to measure the degree of intimate contact of the cross-ply laminates are discussed in reference 3.

A comparison of the intimate contact model with the experimental data for AS-4/P1700 cross-ply laminates is shown in Fig. 8. The degree of intimate contact plotted in the figure represents the interfacial area in contact normalized with respect to the total interface area. Because of the lack of experimental data for the shear viscosity of fiber-reinforced polysulfone resin, values of C (reinforcement/viscosity influence factor) and n (slope of the viscosity versus shear rate curve), cannot be uniquely determined from the present model formulation. To observe the influence of pressure and temperature on the degree of intimate contact, n was arbitrarily set to one for the lowest test pressure (172 kPa). Values for C at each temperature condition were obtained by fitting the model to the data. Assuming that C is a function only of temperature and fiber concentration, the value of n was adjusted to fit the data at higher processing pressures. At the present time the model cannot be used to determine the degree of intimate contact under a set of arbitrary processing conditions. However, the variations of C and n with temperature and pressure appear reasonable.

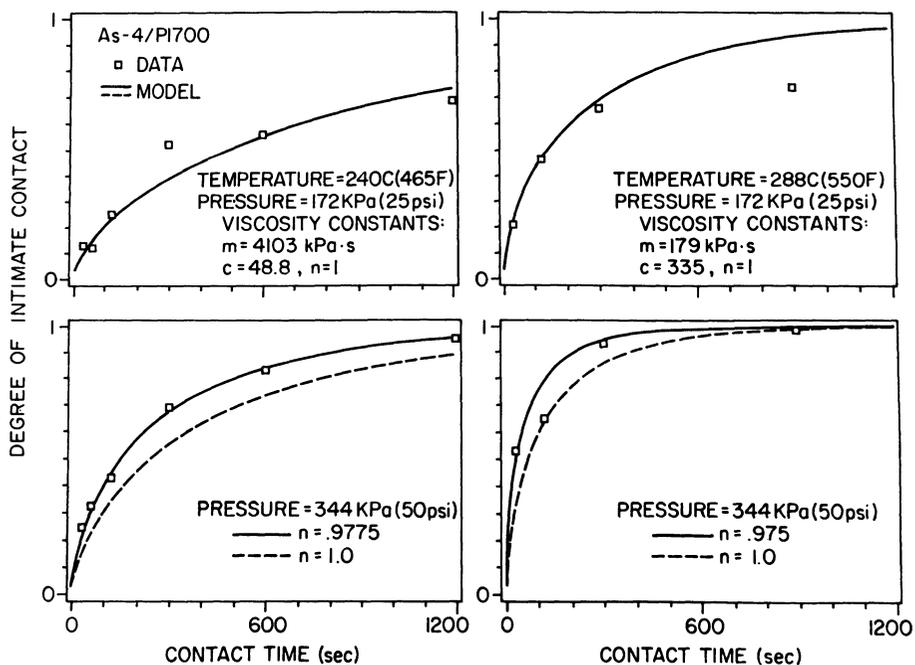


Fig. 8. Predicted and measured results for intimate contact of graphite-polysulfone  $[0,90,0]_T$  laminates.

## SUMMARY

The mechanisms governing intimate contact and bond formation at the ply interfaces of a thermoplastic composite during processing have been identified. The theory of autohesion is used to explain interfacial bond strength development during processing. A viscoelastic mechanics model simulating the compression of resin impregnated tows was developed to explain the phenomenon by which the prepreg ply interfaces achieve intimate contact.

Based on the results of this investigation it is clear that further work is needed to obtain a better understanding of the influence of fiber reinforcement on the resin viscosity. Also, the effect of the fiber reinforcement on the interfacial bond formation needs to be examined.

## ACKNOWLEDGEMENT

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## DISCUSSION

From the Floor: It might be in your second slide, but could you speculate on what is the effect on crystallinity on the autohesion phenomenon?

Mr. Loos: I have not looked at semicrystalline materials and I'm not exactly sure if the autohesion phenomenon would be significant at all. I have not addressed the effects of crystallinity on autohesion, but it is known that crystallinity will prevent the interdiffusion process. Furthermore, semicrystalline thermoplastic matrix composites, such as PEEK resin matrix composites, are usually processed above the melt temperature of resin. Therefore, the mechanisms explaining the consolidation process during processing of a semicrystalline resin composite are going to be different than the mechanisms governing consolidation of an amorphous resin composite.

From the Floor: So you expect your model to be valid for amorphous resin composite and not for a crystalline resin composite?

Mr. Loos: Right now, we expect the model to be valid for an amorphous material.

Dr. Bruce Thompson, Ames Lab: I believe you said you measured the degree of intimate contact with a C-scan measurement. I was curious, in what way you interpret the data to obtain this numerical prediction and the degree of contact?

Mr. Loos: I assume you are primarily wondering what we did with the two interfaces, right?

Dr. Thompson: Let me make it more specific. If you interface large areas of non-contact and large areas of contact, are you going to do it on a microscopic basis with small contacts, a small amount of contacts? And you might interpret the data differently in those two regimes. I was just curious how.

Mr. Loos: What we did for this study was make C-scan measurements as a function of position over the top surface of small three inch by three inch laminates. These measurements gave the locations of areas of contact and areas of non-contact at the interfaces over the entire width and length of the specimen.

We decided to use the C-scan measurement as a preliminary technique to measure the percentage of interfacial area in intimate contact as a function of time for a given processing temperature and pressure. Does that answer your question?

Dr. Thompson: Yes. There have been some things developed that might be worthwhile talking about.

Mr. Loos: One of the reasons why I put up the last slide, was that I was hoping to get some suggestions on how to measure the degree of intimate contact at each interface of a multilayer composite laminate.

Dr. Thompson: I didn't say I had any suggestions about that.