Development of an Environmentally Friendly Solventless Process for Electronic Prepregs

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ABSTRACT: The most common commercial processes for manufacturing prepregs for electronic applications use solvent-based resin systems. Solvents are not environmentally friendly and contribute to voids in prepregs and laminates. The resin impregnation process is performed in an open resin bath. This low-pressure impregnation is conducive to voids in prepregs. Voids cause product variability, which is a major source of scrap in board shops. To eliminate these drawbacks, a solventless process, based on the concept of injection pultrusion, has been developed. The impregnation is performed in a die under pressure to minimize voids. In previous work, chemorheological and kinetic measurements were used to identify a potential epoxy-based resin system. In addition, flow visualization with model fluids was used to establish the basic flow mechanism. Here we use the previous results to develop a mathematical model for the B-staging process. A prototype B-staging die has been built and used to verify the mathematical model. The results show that the model agrees well with the experimental data for low pulling speeds and slightly underpredicts the runs at high pulling speeds. The properties of the prepregs, the dielectric constant (DK) and dielectric loss (DF), have also been measured in this research. The measurements show that the solventless prepregs have acceptable DK and DF values according to the Institute for Printed Circuits FR-4 designation (a permittivity and tangent loss standard). A microscope has been used to observe the void contents of the prepregs. The solventless prepregs have been compared against standard FR-4 prepregs and shown qualitatively to have fewer voids. Based on the mathematical model, two potential process alternatives for the manufacture of solventless prepregs have been developed and analyzed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1136–1146, 2004

Key words: differential scanning calorimetry (DSC); computer modeling; kinetics (polym.); rheology

INTRODUCTION

Printed circuit boards (PCBs) are the foundation of virtually all electronic products. They are the platforms upon which electronic components are mounted and interconnected. The substrates used for fabricating PCBs are commonly known as *copper-clad laminates.* They are made of organic laminated materials consisting of a particular resin, usually an epoxy or phenolic, embedded with some type of reinforcement, either glass or paper, and they have copper foil attached to the outer surfaces. When a multilayer PCB is manufactured, several PCBs are stacked and bonded together by prepregs, which basically consist of partially cured organic material impregnated in the reinforcement used to make the laminate.

The conventional process of manufacturing prepregs and laminates has several drawbacks. The first step in this process is impregnating fiberglass with an epoxy resin mixture.[1] The fiberglass is run through several rollers and dipped into an open epoxy resin bath. The epoxy is dissolved in a solvent, typically acetone or dimethylformamide. The solvents are used to lower the viscosity for improved impregnation and to dissolve the catalyst in the epoxy system. These solvents are not environmentally friendly. As a result, great care must be taken in their use and disposal. Moreover, these solvents are not healthy for employees. After the impregnation, the fiberglass is passed through a heating chamber, which is called a *treater,* to dry off the solvent and partially cure the resin. Not only is this not environmentally friendly, but because the glass impregnation is not performed under pressure, it is difficult to properly impregnate the glass bundles; this brings the possibility of voids inside the glass bundles, which are called *cigar voids.* In addition, if the resin is dried too quickly, the solvent boils and leaves spherical voids. Another related problem of this process is treater fires. The main cause of treater fires is the burning of organic material that accumulates in the treater wall (treater dust) because of solvent boiling. The treater dust also contributes to prepreg inconsistencies.

Voids produce product variability, which leads to the so-called internal registration problem. This is one of the major causes of scrap at a board shop. *Internal*

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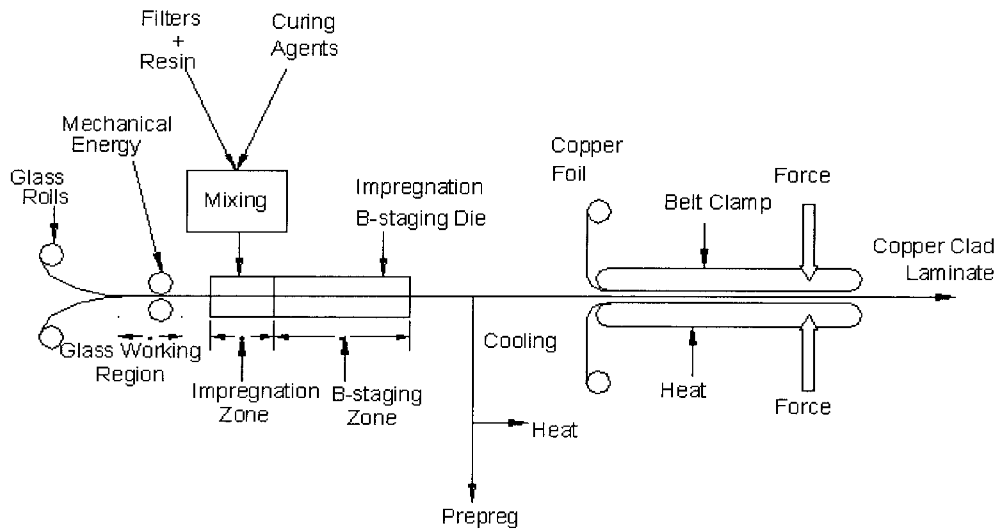

Figure 1 New solventless process.

registration basically refers to the misalignment of drilled holes and inner-layer circuit features. Another problem is that if the drilled holes hit a void, the copper solution used to plate the holes may flow into the void and cause a short circuit.

The objective of our research is to design a new continuous solventless process based on the concept of injection pultrusion. The impregnation is performed by the injection of a solventless resin system into a die under pressure instead of the fiber being dipped into a solvent-based system in an open pan. This approach has the potential of eliminating cigar voids. Also, because no solvent is used, there will be no solvent boiling. From the die, the prepreg can be fed into a continuous lamination belt clamp to manufacture copper clad laminates, or it can just be stored. Figure 1 gives a schematic representation of the process.

There are several tasks that need to be accomplished before this solventless process is developed. First, a chemical system needs to be identified and characterized. The chemical system needs to have a low enough initial viscosity to make the impregnation possible through a closed die and to minimize the pulling force. A potential resin system for our new process was identified and characterized by Dehnke.[1] It consists of DER 383 [nonbrominated diglycidyl ether of bisphenol A (DGEBA)] and DER 542 (brominated DGEBA). As the curing agent, a resin based on phenolic novolac (Borden's SD-1731) is included. The catalyst is 2-ethyl-4-methylimidazole. Dehnke developed kinetic and chemorheological equations to predict the

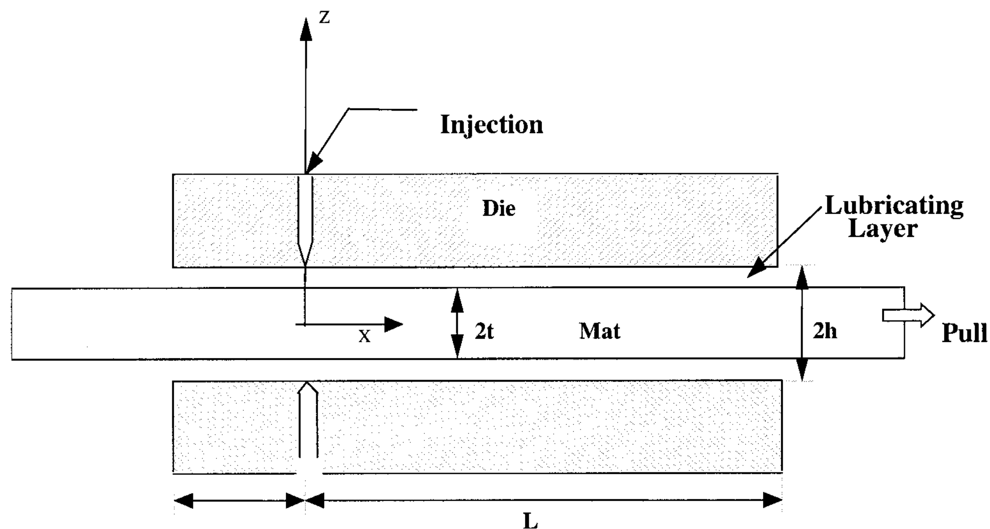

Figure 2 Schematic representation of the die.

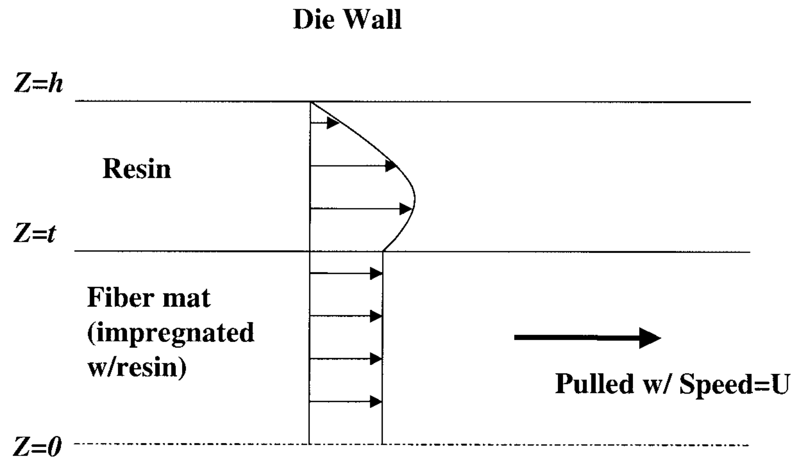

Figure 3 Die velocity profile.

reaction and rheological changes in the system. We use these equations here to develop a mathematical model for the process. The key findings of Dehnke's work include that the resin system melts at 105°C and that no reaction occurs below 110°C.

Hogade et al.[2] demonstrated the existence of a lubricating layer between the mat and the die surface. They showed that, as long as the lubricating layer was greater than 2.54×10^{-5} m, the mat could be assumed to be a rigid surface for modeling the fluid flow in the die. Hogade et al. also developed and experimentally tested an isothermal model for the die flow without a chemical reaction. This model has been used as the basis for developing a complete nonisothermal model, including the chemical reaction, for the die.

NONISOTHERMAL MATHEMATICAL MODEL

In the best case scenario, there are two injection gates, one on the top and one on the bottom of the die, through which the resin can be injected, as shown in Figure 2. During the process, the die is heated to a certain temperature, the mat is pulled at a certain speed (U), and the resin is injected at a certain flow rate (Q) and temperature. The model consists of fluid mechanics and heat-transfer equations along with the chemical reaction. Because the system is symmetric, only the top half is modeled. Figure 3 shows the flow inside the die. Next we present the mathematical model for the die.

Resin layer, from $z = t$ to $z = h$

It is assumed that

- The velocity is only in the X direction ($V_y = 0$ and $V_z = 0$).
- The thermal conductivity (k), heat capacity (C_p), and density (ρ) are constant.
- The boundary condition is no-slip.

Integrating the equation of motion and taking into consideration that the viscosity is not constant, we obtain the following:[3]

$$V_x = U\left(1 - \frac{\int_t^z \frac{1}{\eta}\,dz}{\int_t^h \frac{1}{\eta}\,dz}\right) + \frac{dP}{dx}\left(\int_t^z \frac{z}{\eta}\,dz - \frac{\int_t^h \frac{z}{\eta}\,dz \int_t^z \frac{1}{\eta}\,dz}{\int_t^h \frac{1}{\eta}\,dz}\right) \quad (1)$$

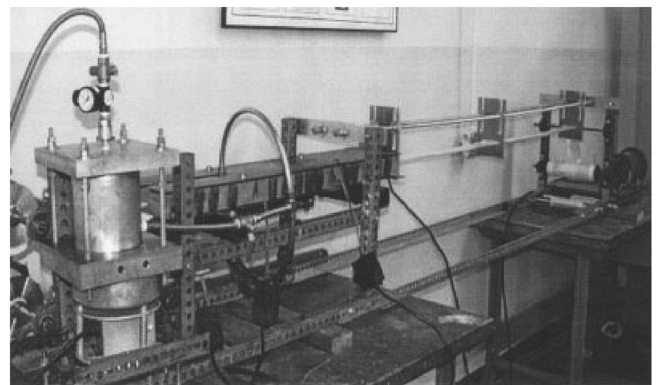

Figure 4 Experimental setup.

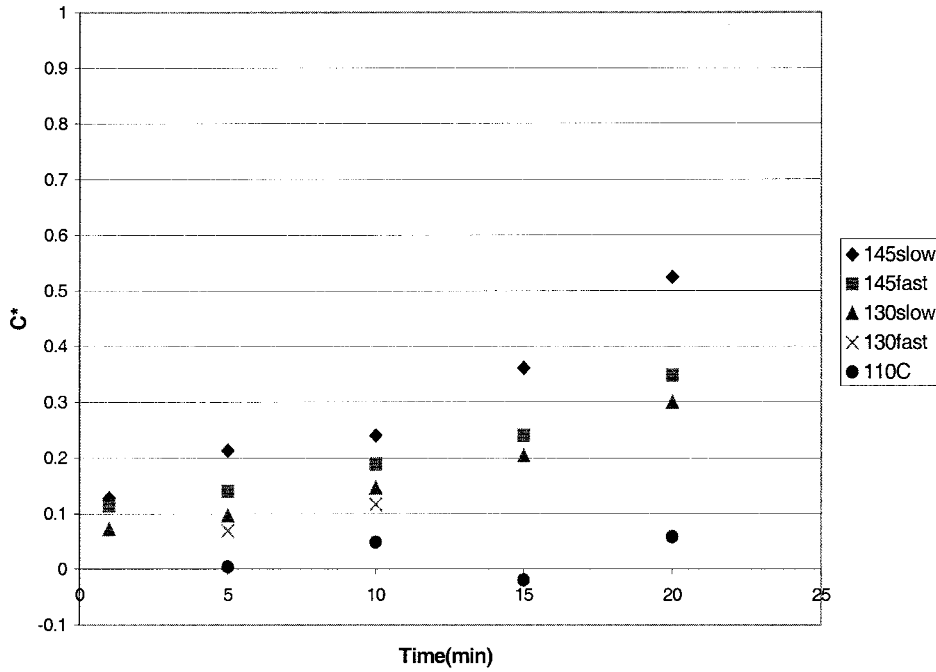

Figure 5 Measured extent of reaction versus time.

The boundary conditions are as follows:

$$Z = t \quad V_x = U$$

$$Z = h \quad V_x = 0$$

The pressure drop equation can be obtained from the calculation of Q:[3]

$$\frac{dP}{dx} = \frac{-\frac{Q}{W} - U\left(t - \frac{\int_t^h \frac{z}{\eta} dz}{\int_t^h \frac{1}{\eta} dz}\right)}{\left(\int_t^h \frac{z^2}{\eta} dz - \frac{\left(\int_t^h \frac{z}{\eta} dz\right)^2}{\int_t^h \frac{1}{\eta} dz}\right)} \tag{2}$$

Dehnke et al.[4] developed the following equation for the viscosity:

$$\eta = \eta_0(c_g^*/c_g^* - c^*)^B \tag{3}$$

$$\eta_0 = 979.07 * e^\wedge(-0.0231T) \tag{4}$$

$$c_g^*(T) = -1.5477 + 0.0057T \tag{5}$$

$$B(T) = 6.2256 - 0.0132T \tag{6}$$

The equation of energy is

$$\rho C_p\left(\frac{\partial T}{\partial t} + V_x \frac{\partial T}{\partial x}\right) = k\left(\frac{\partial^2 T}{\partial z^2} + \frac{\partial^2 T}{\partial x^2}\right) + \rho H_R R \tag{7}$$

and the equation of the chemical reaction is

$$\left(\frac{\partial C}{\partial t} + V_x \frac{\partial C}{\partial x}\right) = R \tag{8}$$

where[5]

$$R = (k_1 + k_2 C^{*m})(C_\infty^* - C^*)^n \tag{9}$$

$$K_1 = K_{o1e}^{(-E1/RT)} \tag{10}$$

$$K_2 = K_{o2e}^{(-E2/RT)} \tag{11}$$

Fiber mat layer, from $z = 0$ to $z = t$

In this layer, the resin impregnates the fiber mat and moves together with it. As a result, U is constant. The equation of energy is

$$\rho_e C_{pe}\left(\frac{\partial T}{\partial t} + U \frac{\partial T}{\partial x}\right) = k_e\left(\frac{\partial^2 T}{\partial z^2} + \frac{\partial^2 T}{\partial x^2}\right) + \rho_e H_{Re} R \tag{12}$$

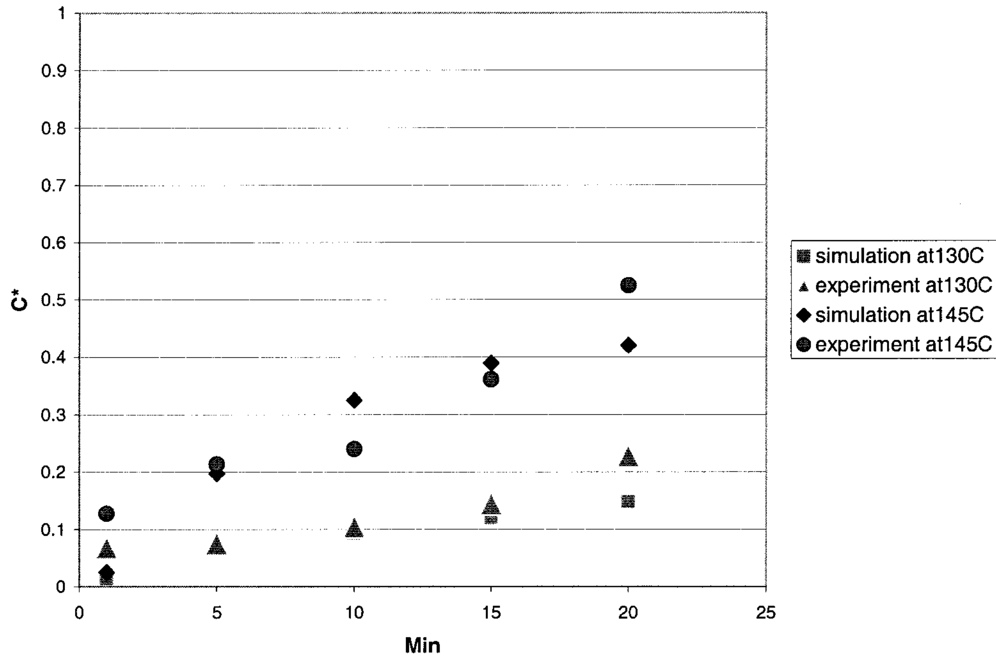

Figure 6 Experimental data versus the simulation results for a pulling speed of 0.0025 m/s.

$$\frac{1}{\rho_e} = \sum_i \frac{w_{fi}}{\rho_i} \tag{13}$$

$$C_{pe} = \sum_i w_{fi} C_{pi} \tag{14}$$

$$\frac{1}{k_e} = \sum_i \frac{w_{fi}}{k_i} \tag{15}$$

where w_f is the weight fraction and i refers to the fiber mat and resin. The initial conditions, at time = 0, are as follows:

$$z = h \quad 0 \le x \le L \quad T = T_{\text{wall}}$$

$$t < z < h \quad 0 \le x \le L \quad T = T_{\text{resin}}$$

$$0 \le z \le t \quad 0 \le x \le L \quad T = T_0$$

$$0 \le z \le h \quad 0 \le x \le L \quad C^* = 0$$

where

$$C_{pr}\rho_r WUt(1 - V_f)(T_r - T_0) = C_{pm}\rho_m WUtV_f(T_0 - T_{\text{mat}})$$

W is the width of the die. The boundary conditions at time > 0 are as follows:

$$z = h \quad 0 \le x \le L \quad T = T_{\text{wall}}$$

$$t < z < h \quad x = 0 \quad T = T_{\text{resin}}$$

$$t < z < h \quad x = L \quad \left(\frac{dT}{dx}\right) = 0$$

$$z = t \quad 0 \le x \le L \quad k_r * \left(\frac{dT}{dz_r}\right) = k_e * \left(\frac{dT}{dz_e}\right)$$

$$0 < z < t \quad x = 0 \quad T = T_0$$

$$0 < z < t \quad x = L \quad \left(\frac{dT}{dx_e}\right) = 0$$

$$z = 0 \quad 0 \le x \le L \quad \left(\frac{dT}{dz_e}\right) = 0$$

$$0 \le z \le h \quad x = 0 \quad C^* = 0$$

The integration terms in the velocity and pressure equation are solved with the trapezoidal rule. The equation of energy and the equation of the chemical reaction are solved with the explicit finite difference method. Before the experimental verification of the mathematical model, testing for simplified cases for which an analytical solution could be derived was performed to confirm the mathematical model. The details can be found in ref. 3.

EXPERIMENTAL

An experimental setup was built to prototype the process and to verify the nonisothermal mathematical

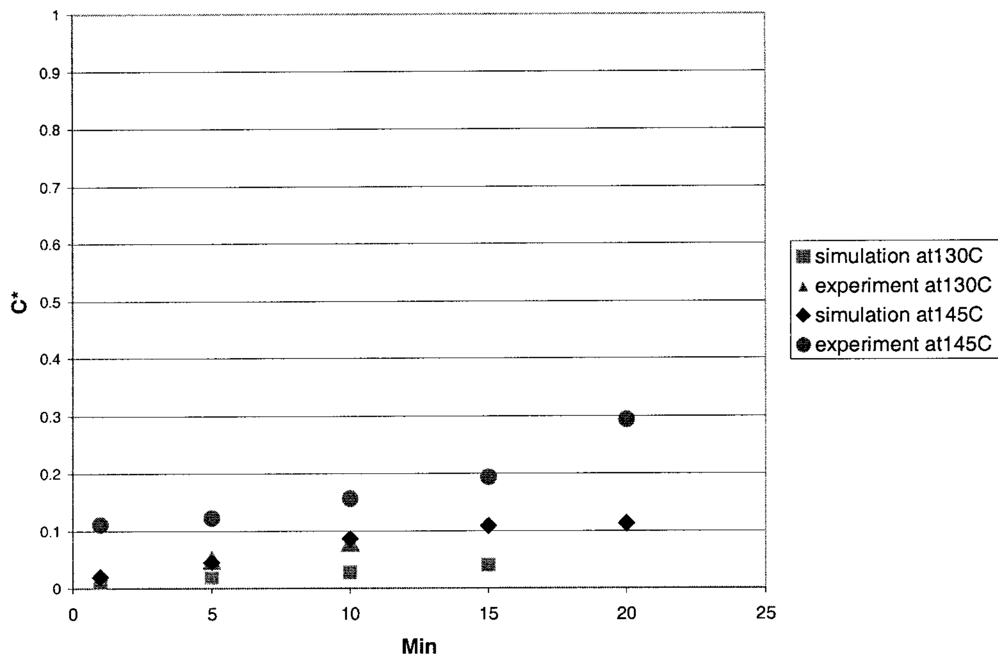

Figure 7 Experimental data versus the simulation results for a pulling speed of 0.01 m/s.

model. It consisted of a transfer pot, a die, and a pulling system. The transfer pot was used to store the resin injected into the die. Because the resin needed to stay above 105°C to remain a liquid and below 110°C to avoid any chemical reaction,[5] a hot plate and heating tape were used to heat the transfer pot. During the process, air was used to apply pressure to the transfer pot from the top so that the resin flowed to the die.

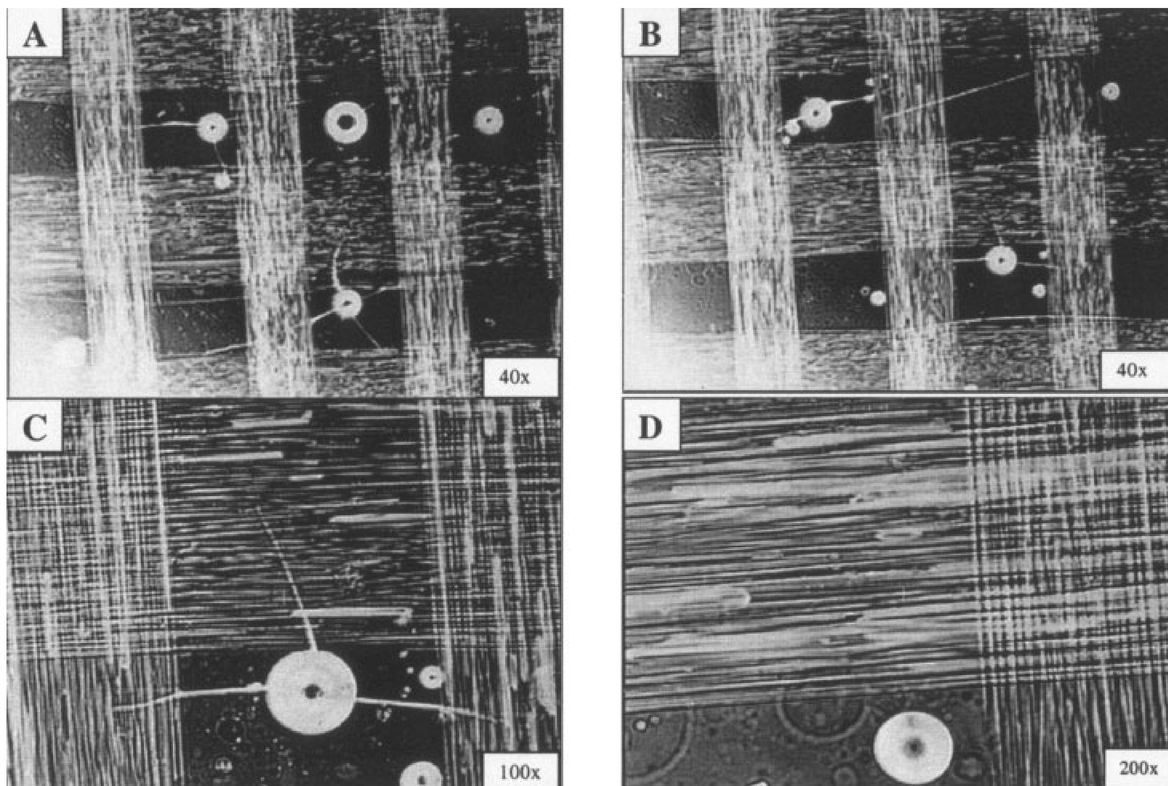

Figure 8 Standard FR-4 prepreg.

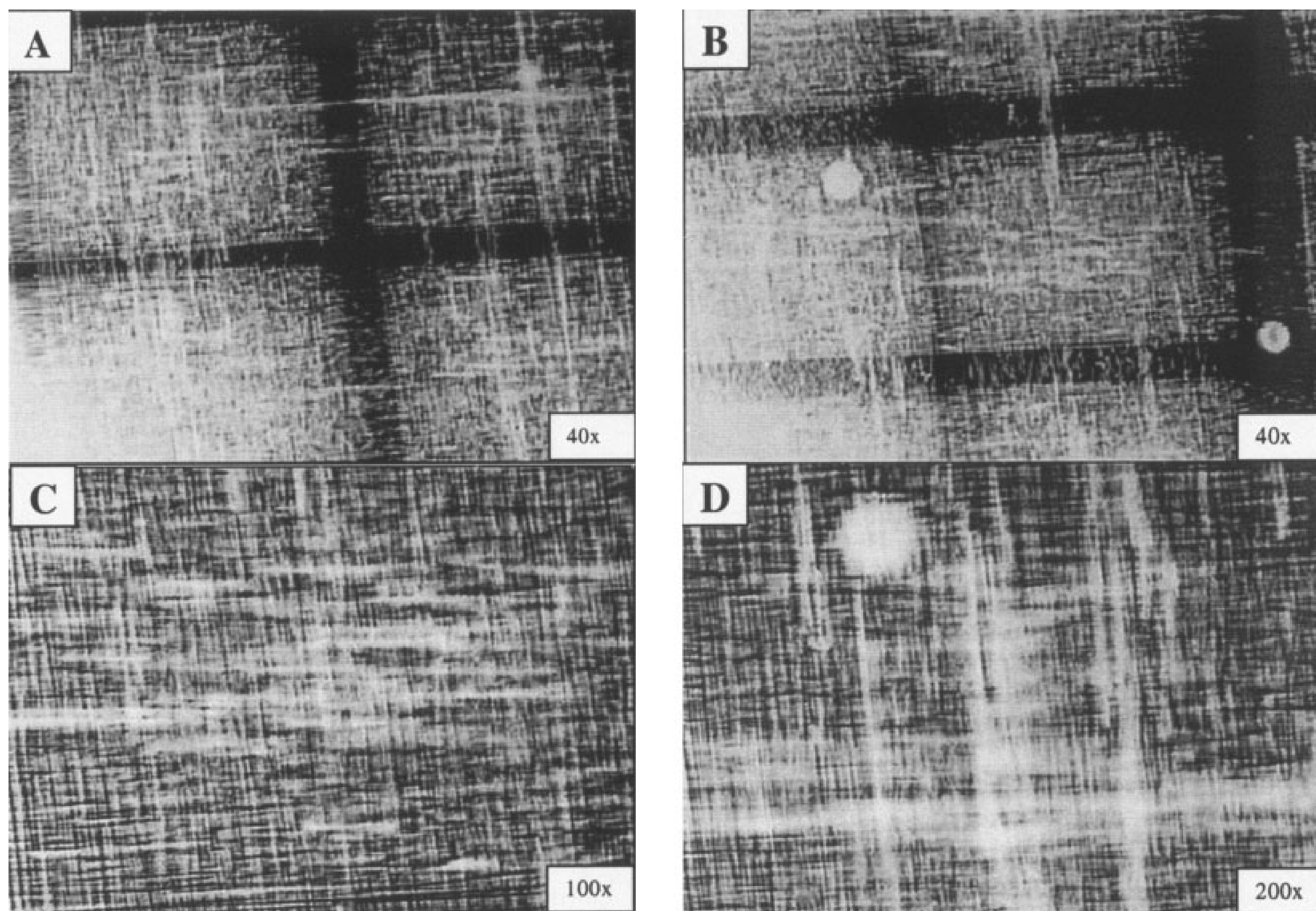

Figure 9 Solventless prepreg at 110°C.

The die, made from aluminum, consisted of top and bottom parts that fit together and two injection gates, one for the top and one for the bottom. The top and bottom halves were separated by precision shims to control the gap. The injection gate had a manifold to spread the resin. To heat up the die, heating tape was used. A National Instrument data acquisition system was used to obtain the temperature along the die. Bolts were to used secure the top and bottom halves. To connect the transfer pot to the die, a copper tube was used. The copper tube was also heated with heating tape. A motor did the pulling. Figure 4 shows the experimental setup. The fiberglass was 028TC from BGF.

The experimental study had two purposes. The first was to verify that there was no reaction at 110°C. The second one was running the setup at different pulling speeds and die temperatures. The two pulling speeds were 0.0025 and 0.01 m/s. The temperatures were 130 and 145°C. The samples were taken from the prepregs as they existed in the die at 1, 5, 10, 15, and 20 min. The amount of the reaction in the samples was measured with differential scanning calorimetry (DSC) by a comparison of the heat evolved from the samples with respect to the fresh resins. The reaction, calculated by DSC, was compared against the average reaction at the die exit, calculated with the nonisothermal mathematical model. The resin in the transfer pot was also measured with DSC to confirm that no reaction had occurred. The details of the experiments can be found in ref. 3.

RESULTS

Figure 5 gives a summary of the extent of reaction for all the experimental runs. It confirms that there was no reaction at 110°C. The 145°C run with a pulling speed of 0.0025 m/s had the highest reaction, whereas the 130°C run with a pulling speed of 0.01 m/s had the lowest reaction (except for the run at 110°C), as expected. Figures 6 and 7 show a comparison of the experimental data against the average reaction from the simulation for the 0.0025 and 0.01 m/s pulling speeds, respectively. The higher pulling speed experiments agree with the simulation data very well. At the lower pulling speed, the simulation slightly underpredicted the experimental results.

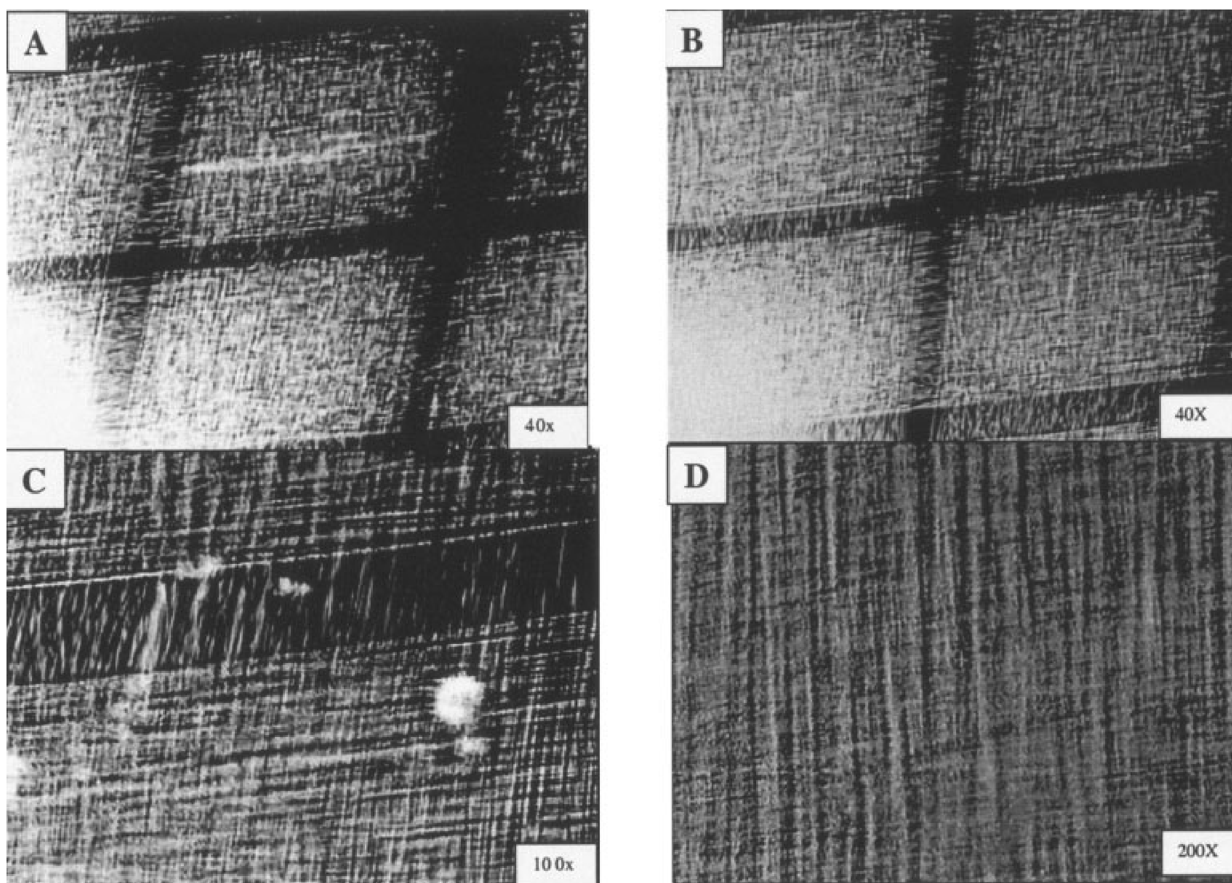

Figure 10 Solventless prepreg at 130°C.

Properties

Dielectric constant (DK) and dielectric loss (DF)

DK or the permittivity measures the capacity of a material to store an electric charge. It is given as the ratio of the ability of a material to store a charge to the ability to store a charge of that material *in vacuo*. With a lower DK, the signal can be transferred more quickly. This property is very important for analog electronic products, such as computers. DF measures the ability of a material to support an electrostatic field while dissipating minimal energy in the form of heat. It is given by the tangent loss, which is the ratio of loss current to charging current. A low DF value means that the material can transfer a signal with low loss; this is necessary in digital electronic components, such as telecommunication products. For example, a digital cellular phone will have a clearer signal, a longer talk time, and a longer battery life if a low-DF material is used.

It was important to establish if the solventless prepregs met the Institute for Printed Circuits (IPC) FR-4 standard. If the value obtained was lower than the IPC FR-4 standard, the resin system did not need to be changed. When the testing was performed, the die had not been built. Therefore, to produce samples similar to the ones made by the proposed process, we used a hydraulic press to prototype the process in a batch mode. First, all the components of the resin system and the catalyst were mixed at 110°C. The resin was then poured onto a glass mat. The mat, impregnated with the resin, was pressed and left in the press for 14 min at 150°C to fully cure the prepreg. All the samples were tested with a 1-MHz dielectric cell under the D23/24 condition (24-h exposure to 23°C at 50% relative humidity); this is a standard test by IPC (a permittivity and tangent loss standard). The measurements were performed at GE Electronic Laminates (Koschocton, OH). The DK and DF values obtained for the solventless prepreg were 4.30 and 0.021, respectively. According to the IPC standard, the DK and DF values have to be less than 5.4 and 0.035 to be considered acceptable. According to these measurement, our resin system was acceptable.

Void content

As discussed earlier, voids can cause internal registration problems in the board shop. There are two types of voids: cigar voids and spherical voids. Cigar voids are caused by incomplete impregnation, and spherical

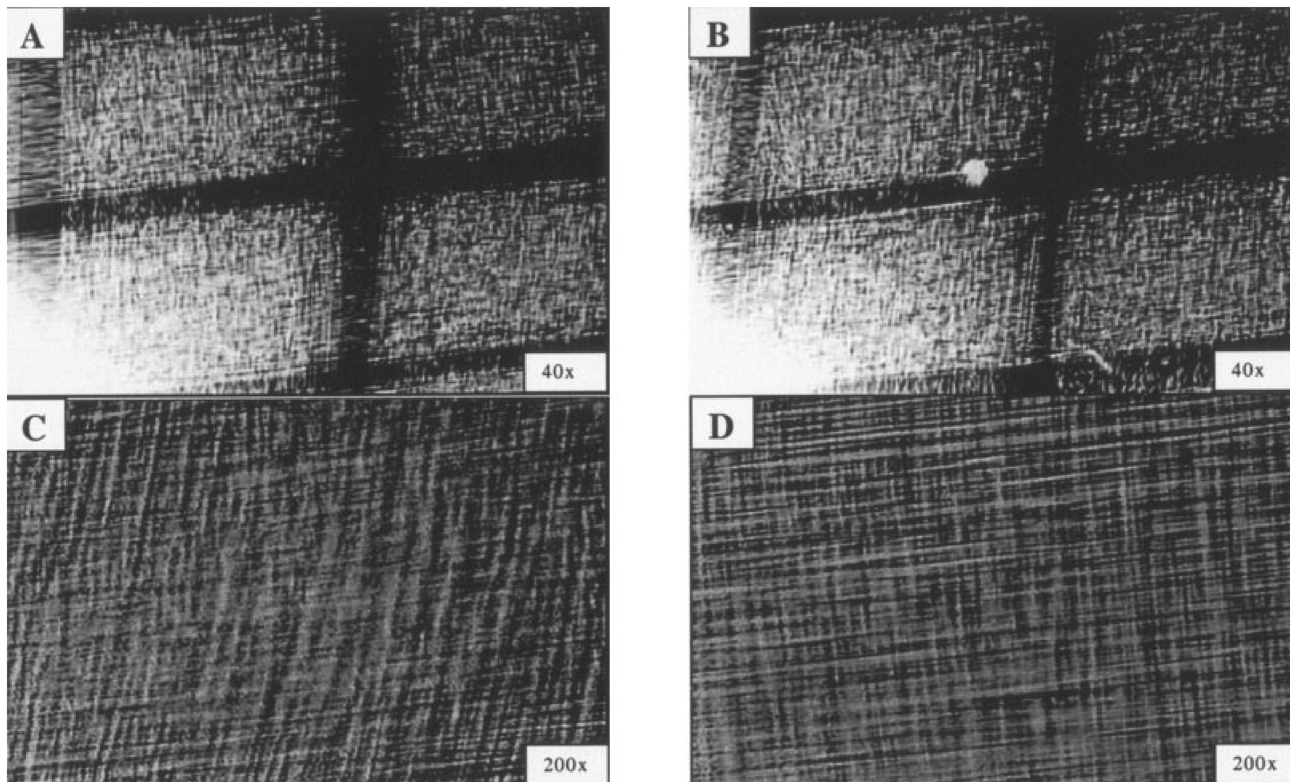

Figure 11 Solventless prepreg at 150°C.

voids are caused by solvent boiling when the prepreg is dried too quickly in the treater. Microscopic analysis shows that the new solventless process has better impregnation than this process. In addition, increasing the die temperature improves the impregnation.

We used three different die temperatures (110, 130, and 150°C) to make the samples. The fiberglass type was BGF 028 TC. The pulling speed was 0.0025 m/s. These runs were performed without a catalyst. We used microscope magnifications of 40×, 100×, and 200×. As a reference, we used samples of standard FR-4. There was one main difference between the standard prepreg and the solventless sample: the type of fiberglass. The standard FR4 used Clark-Schwebel 1080 fiberglass. This type of fiberglass is thinner than BGF 028TC.

Figures 8 shows pictures of standard FR-4 under a microscope. In all these pictures, there are many cylindrical (cigar) and spherical (solvent boiling) voids shown.

Figures 9–11 show pictures of the solventless prepreg obtained under different die temperatures. For a sample produced at 110°C, some spherical voids can be observed, most likely due to air trapped during mixing. We can also notice fairly poor impregnation by looking at the thick white lines in Figure 9, especially in the center of each bundle. These lines show that there may still be some cigar voids in the prepregs. In Figure 10, there are almost no thick white lines. This figure shows that there is great improvement in impregnation at 130°C. In addition, there are fewer spherical bubbles observed. For a sample at 150°C, the impregnation is very uniform, and air trapping is minimal. In conclusion, the impregnation can be improved by an increase in the die temperature.

Even though the fiberglass type is different from that of the FR4 prepreg, we can conclude that the quality of the solventless prepregs is better overall. The solventless prepreg has no solvent voids. Degassing the resin before injection can eliminate the spherical voids due to air trapping. There were also very few cigar voids in the 130°C sample and none in the 150°C sample. To improve the impregnation at 110°C, the injection region of the die needs to be redesigned, and a higher pressure should be used.

Process alternatives

Two potential manufacturing alternatives are discussed for the solventless B-staging process based on the mathematical model.

Alternative one

In this alternative, the die is heated to a temperature greater than 110°C, and the resin is injected at 110°C (Fig. 12). Then, the mat is pulled at speed U. In this

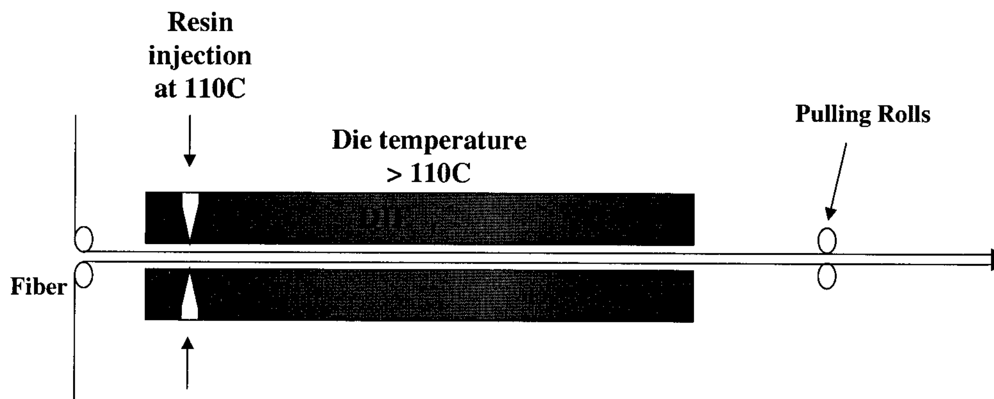

Figure 12 Schematic representation of alternative one.

case, the resin at the wall starts to cure. The objective is to see how fast the resin will build up inside the die. Figure 13 shows the results of heating the die at 150°C. According to the simulation results, the resin that is near the die surface will solidify. However, the resin layer that is close to the mat will remain a liquid.

The liquid resin layer is able to reach a quasi-steady state, so this alternative will have a very long running time without the prepreg being caught up inside the die. This is due to the very high velocity underneath the cured resin. The thicker the cured resin layer is, the higher the velocity is, as shown in Figure 14. However, according to Figure 13, the conversion of the prepregs coming out of the die is not uniform; these prepregs cannot be used for high-quality MLB prepregs. A uniform-conversion prepreg is required for better flow control during the MLB laminating process. However, the prepreg from this alternative still has good potential for rigid boards. A rigid board is a type of thicker PCB used as a single layer. In this case, the prepreg out of the die can be fed directly to a continuous lamination clamp, as shown schematically in Figure 1.

Alternative two

Because the resin does not react at temperatures below 110°C, we can avoid a reaction at the wall if the die wall temperature is kept at 110°C or lower. Thus, the die will be used only to impregnate the mat with the resin. An oven immediately after the die exit will be then used to partially cure the resin. Therefore, for this alternative, an oven is needed to partially cure the

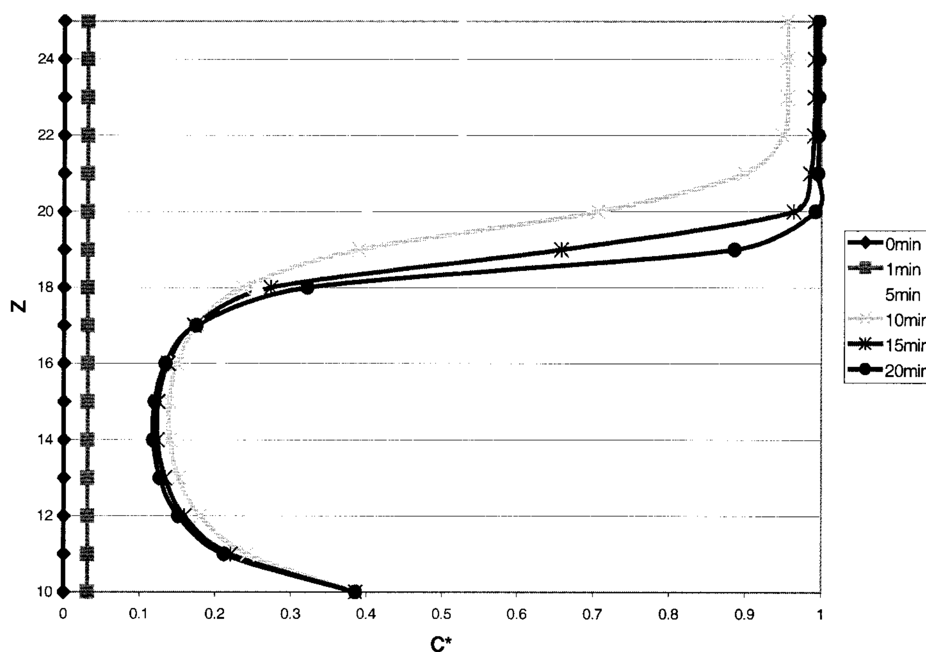

Figure 13 Extent-of-reaction profile at 150°C.

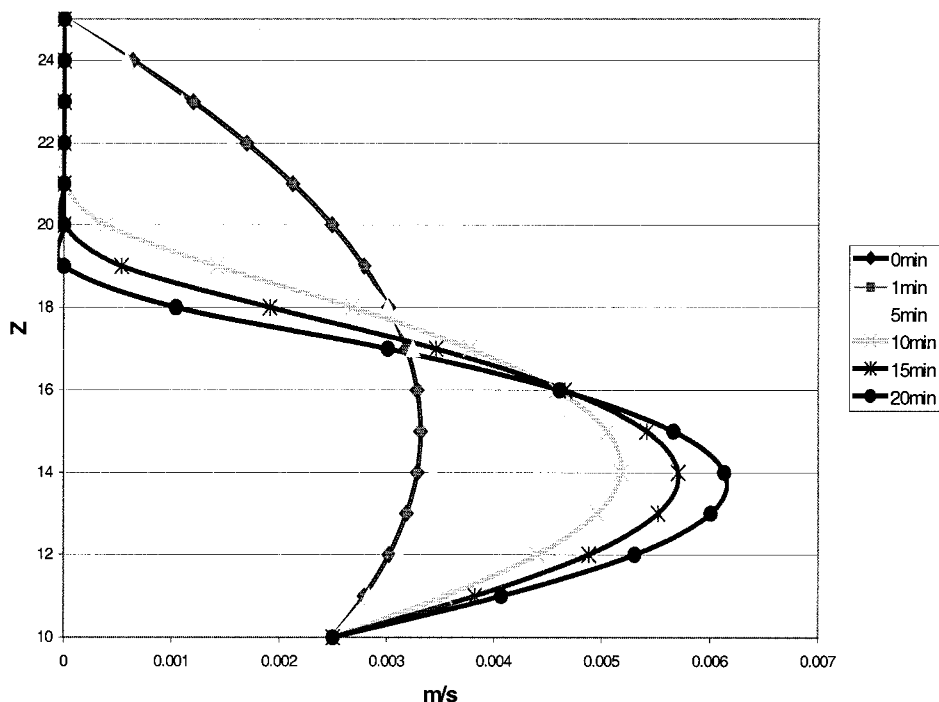

Figure 14 Velocity profile at 150°C.

prepreg after the die. This alternative can be used to manufacture prepregs for MLB boards or to feed them directly to a belt clamp (see Fig. 1) for the laminating stage.

CONCLUSIONS

In this research, a new solventless process for manufacturing prepregs for PCBs was prototyped. A die was designed and built to impregnate or partially cure resins. A mathematical model was also developed to predict the flow, heat transfer, and chemical reaction for this new prepregging process. A prototype die was used as the experimental setup to test the predictions of the model. There was no reaction observed at 110°C. In addition, the predictions of the mathematical model agreed very well for the slow pulling speeds. However, for the fast pulling speeds, the mathematical model slightly underpredicted the experimental results. The significant findings of this research include acceptable DK–DF values and less void content than found in a standard prepreg. Under a 1-GHz dielectric cell, DK–DF values of 4.3 and 0.021, respectively, were obtained.

Using the mathematical model, we developed two potential process alternatives for the B-staging step. The first alternative, in which the die is used to partially cure the prepreg, can be used to manufacture rigid boards. The second alternative, in which the die is only used as an impregnation device with an oven to partially cure the prepreg, can be used to manufacture higher quality MLB prepregs or laminates.

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