FLOW OF THERMOPLASTICS THROUGH FIBER ASSEMBLIES

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ABSTRACT

The permeation of thermosetting resins through fiber assemblies has been characterized in depth. Can this knowledge be applied in processing thermoplastic composites? In order to address this question the permeation of a variety of thermoplastics through aligned and random fiber assemblies is being studied. For the permeation of random glass mats by polypropylene a Kozeny constant near 8 was obtained, which is consistent with similar studies using low viscosity resins. It was necessary to use a power law model for the polypropylenes investigated.

Additional studies are in progress using polypropylene and nylon and aligned carbon and glass fiber beds. Both "dry" and "wet" aligned fibers are being studied in order to assess the importance of surface tension. In addition, the consolidation of partially impregnated fiber tows produced by powder coating is being evaluated for comparison with the model flow studies. The ultimate goal is to develop a model for permeation and consolidation in thermoplastic composites which has broad utility.

INTRODUCTION

Permeation is a major concern in processing thermoplastic composites. In many cases in processing thermoplastic composites complete wetting of the reinforcing fibers is deferred until the composite is finally consolidated as a structure. This wetting is delayed to retain flexibility in the tows and preforms. Powder coated tows and commingled tows are examples with little or no wetting before consolidation of the structure. Since thermoplastics typically have viscosities more than a thousand times greater than many thermosetting prepolymers permeation through the reinforcing tows and preforms is often the rate limiting step in processing thermoplastic composites. Therefore it is important to have a quantitative understanding of thermoplastic permeation through fiber assemblies.

In this paper the primary focus is on evaluating the permeation of two grades of polypropylene through a random glass mat. The use of a non-Newtonian "power law" model is emphasized and compared with its Newtonian counterpart. This model can be applied to the production of "GMT" (glass mat reinforced thermoplastic) by double belt laminating. Then current work on other fibers, preforms and matrices will be discussed.

THEORY

For thermoplastic composites the primary concern is the permeation of "dry" fiber assemblies by a thermoplastic. Due to the complex geometry of the mixtures found in commingled tows and powder coated tows, it is instructive to consider a simplified geometry for measuring permeability. The diagram in Figure 1 represents one dimensional flow into a packed bed of dry fibers. The rate of penetration of a Newtonian fluid into the packed bed based on Darcy's Law is:

$$\frac{dZ}{dt} = \frac{S}{\eta}\frac{dP}{dZ} \tag{1}$$

where Z = the penetration depth, t = time, S = the permeability of the bed, η = the Newtonian viscosity and dP/dZ is the pressure gradient from the surface of the bed to the flow front. The permeability can be related to the porosity of the bed through the Kozeny-Carmen relation:

$$S = \frac{{r_p}^2 \varepsilon^3}{4K(1-\varepsilon)^2} \tag{2}$$

where r_p is the average radius of the particles, K is the Kozeny constant, and ε is the porosity of the bed. For beds based on fibers r_p is replaced by r_f, the radius of the fiber, and ε is replaced by $(1- V_f)$ where V_f is the volume fraction of fibers in the bed. To obtain the penetration distance as a function of time equation 1 is integrated assuming, constant pressure and constant permeability, to obtain:

$$Z^2 = \frac{r_f^2}{2K}\frac{(1-V_f)^3}{V_f^2}\frac{\Delta P t}{\eta} \tag{3}$$

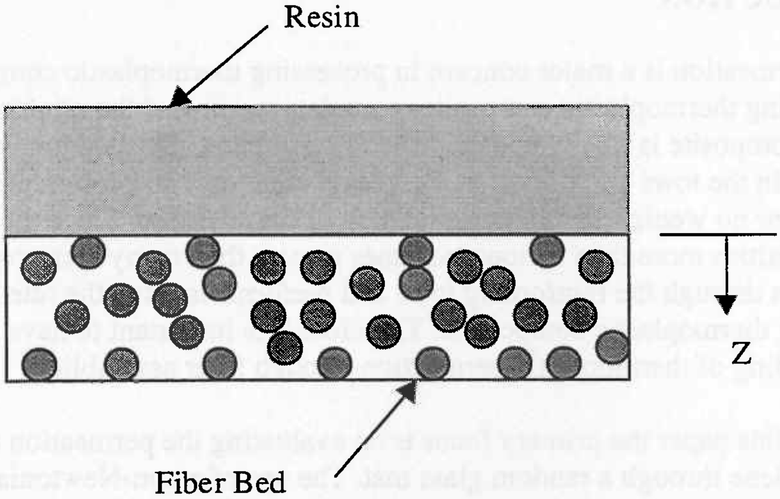

Figure 1. One dimensional model for resin penetration into a fiber bed.

For a power law fluid the viscosity, η, depends on shear rate,γ:

$$\eta = m\dot{\gamma}^{n-1} \tag{4}$$

where m and n are the power law parameters. Since the average shear rate for flow through a fiber bed will change with time, it is preferable to derive an expression for the penetration depth using the power law model. The resulting expression is:

$$Z^{\frac{1}{n}+1} = \frac{2+2n}{1+3n}\frac{(1-V_f)^2}{V_f}\frac{r_f}{K_0K_1}\left(\frac{r_f}{2mK_1}\frac{1-V_f}{V_f}\Delta P\right)^{\frac{1}{n}} t \tag{5}$$

where K_o and K_1 are the shape factor and tortuousity respectively. The Kozeny constant is K = K_o K_1^2. Although the shear rate does not appear in equation 5 it is still necessary to determine if the power law parameters are appropriate for the experimental conditions studied.

EXPERIMENTAL

The primary fiber bed investigated is a glass mat obtained from PPG Industries. It is sized for polyester resin and has a basis weight of 450 g/m^2. The fibers are grouped into bundles with a rectangular cross section. An equivalent radius for these bundles was estimated to be 70 μm based on the average area of the bundles. The bundles were well compacted, having a fiber volume fraction close to 0.90. The glass mat had an available void fraction of 0.37, excluding the voids within the bundles.

Two polypropylenes were investigated. PP1 is based on waste fibers which were hot pressed into sheets for the permeation experiments. PP2 was purchased from Allied Resinous Products, Inc. as a 1.5 mm thick sheet. Viscosity versus shear rate was obtained for the polymers at a series of temperatures using a parallel plate rheometer from Bohlin Instruments.

The permeation experiments were performed in a matched die mold as illustrated in Figure 2. The mold was equipped with heating cartridges and compressed air cooling channels as well as a temperature controller to permit isothermal operation at elevated temperatures.The mold area was 100 x 100 mm. Glass mats were placed above and below the resin layer to minimize resin loss between the top piston and the walls of the mold. Multiple layers of glass mat were used to insure that the resin did not reach the mold surfaces quickly. Equations 3 and 5 are based on a semi-infinite bed with no boundary wall effects. The penetration depth was calculated from the separation distance between the top and bottom molds.

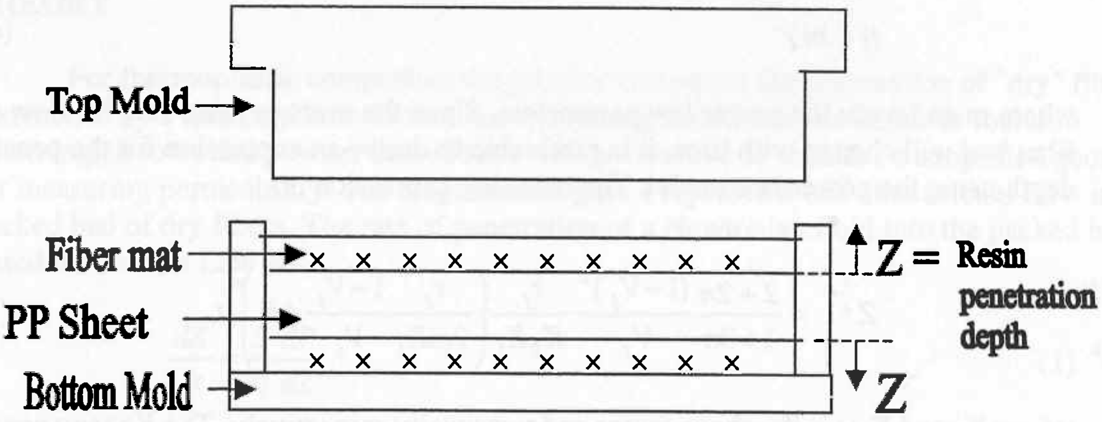

Figure 2. Schematic diagram of matched die molding

The matched die mold was used as a test fixture in a mechanical testing machine, illustrated in the Figure 3. The two halves of the stainless mold with a preform between them were inserted between the crosshead of the hydraulic testing machine (MTS 810) equipped with a 222 Kn load cell. The crosshead movement served as an indicator of the thickness of the preform and resin inside the mold cavity, and was measured as a function of time at constant pressure and temperature. The change in thickness is directly proportional to the depth of molten resin permeation into the glass mats. Therefore, the experimental data of permeation depth vs. time can be recorded and compared with theoretically predicted curves.

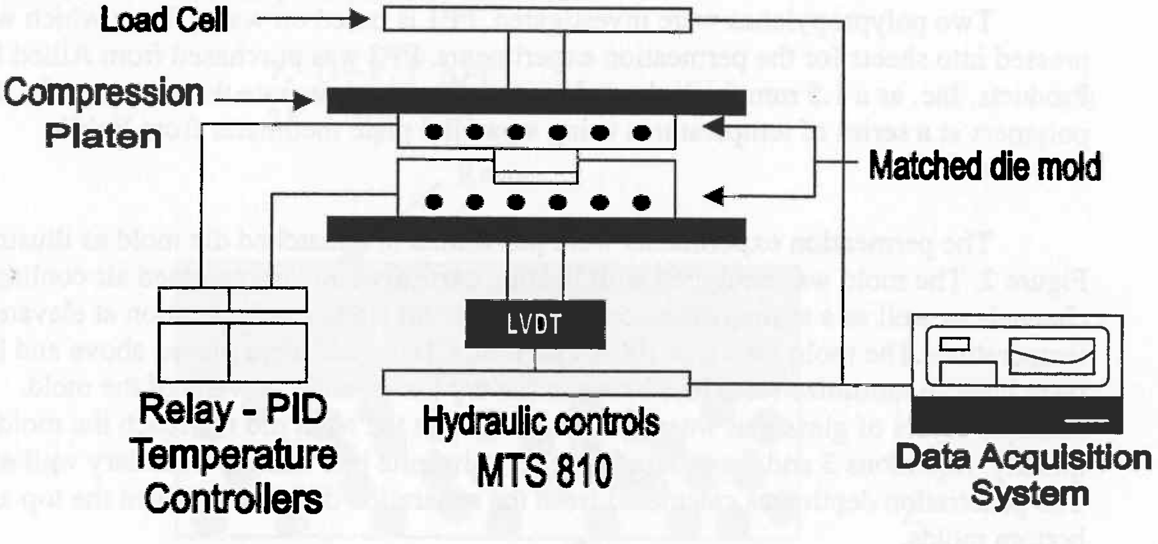

Figure 3 Schematic of the machine setup for permeation experiments

RESULTS AND DISCUSSION

The viscosities of the two polypropylenes were represented well by power law models. Table 1 summarizes the model parameters. The shear rate range is 0.1 to 10 s^{-1}. Based on the permeation experiments the average shear rate during the experiments was close to 3 s^{-1}. The temperature range for PP1 was 165 to 210 °C and for PP2 the range was 190 to 240 °C. The flow index, n, was found to be independent of temperature. The temperature dependence was expressed as:

$$m = a \exp\left(\frac{-\Delta E}{RT} \right) \tag{6}$$

where ΔE is the activation energy and R is the gas constant.

The viscosity for PP1 is much lower than PP2. For example, at a shear rate of 3 s^{-1} and a temperature of 210 °C the viscosity of PP1 was 560 Pa s whereas the viscosity of PP2 was 3,820 Pa s. PP2 is considerably more non-Newtonian based on its lower flow index.

Table 1

Power law parameters

Material	a Pa $s^{1/n}$	ΔE KJ/mole	n
PP1	0.0014	5.18	0.85
PP2	5.2	2.97	0.61

The experimental design for the permeation experiments is shown in Table 2. Lower temperatures and lower time were used for PP1 due to its lower viscosity.

Table 2

Permeation test Conditions

Material	Time s	Low Press. kPa	High Pres. kPa	Low Temp. °C	High Temp. °C
PP1	30	172	345	165	185
PP2	60	172	345	210	240

For each of these test conditions the best individual Kozeny constant was determined by nonlinear least squares fitting. It was necessary to assume a value of 2 for the shape factor, K_o. Then the best fit for K_1 was determined and then K was calculated. The results of these estimates are shown in Figures 4, 5 and 6. The high and low values shown are based on one standard deviation. The difference in K for the two pressures studied is statistically significant. The higher K for the higher pressure implies that permeation of the mat is more difficult at the higher pressure. It is likely that the void volume of the mat at the higher pressure is lower, leading to the increase in K.

The difference in K shown in Figure 5 for the two grades of polypropylene is not statistically significant. Also, the differences in K shown in Figure 6 for the four test temperatures is not statistically significant.

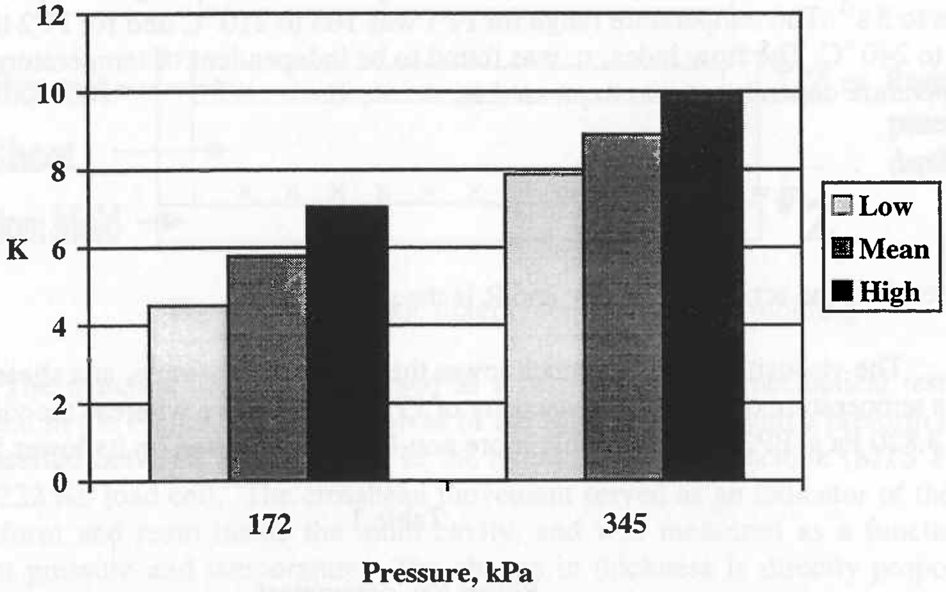

Figure 4. Effect of pressure on Kozeny constant.

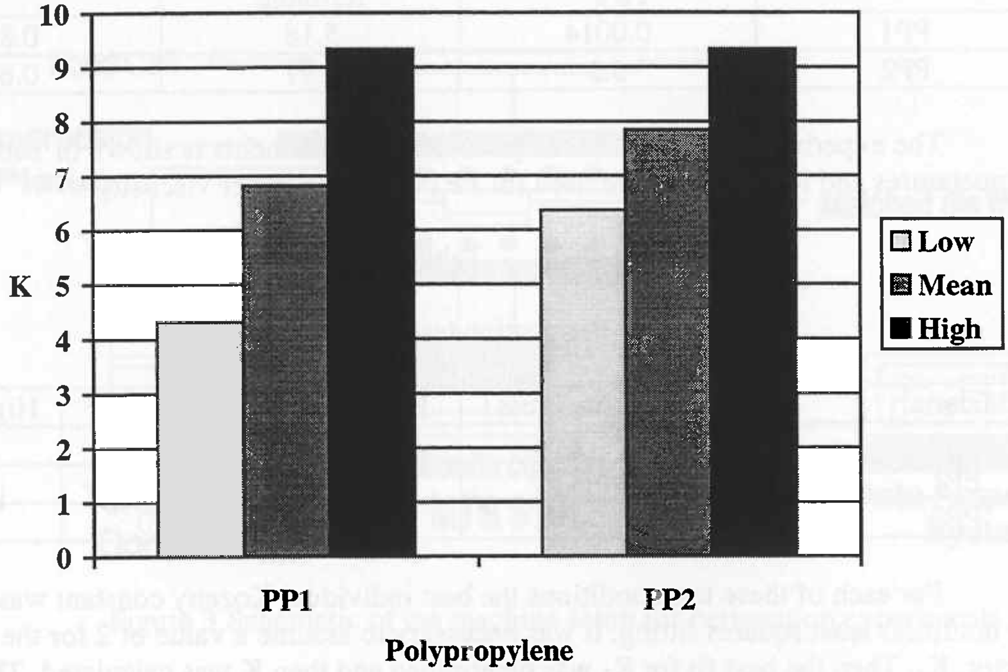

Figure 5. Effect of polypropylene grade on Kozeny constant.

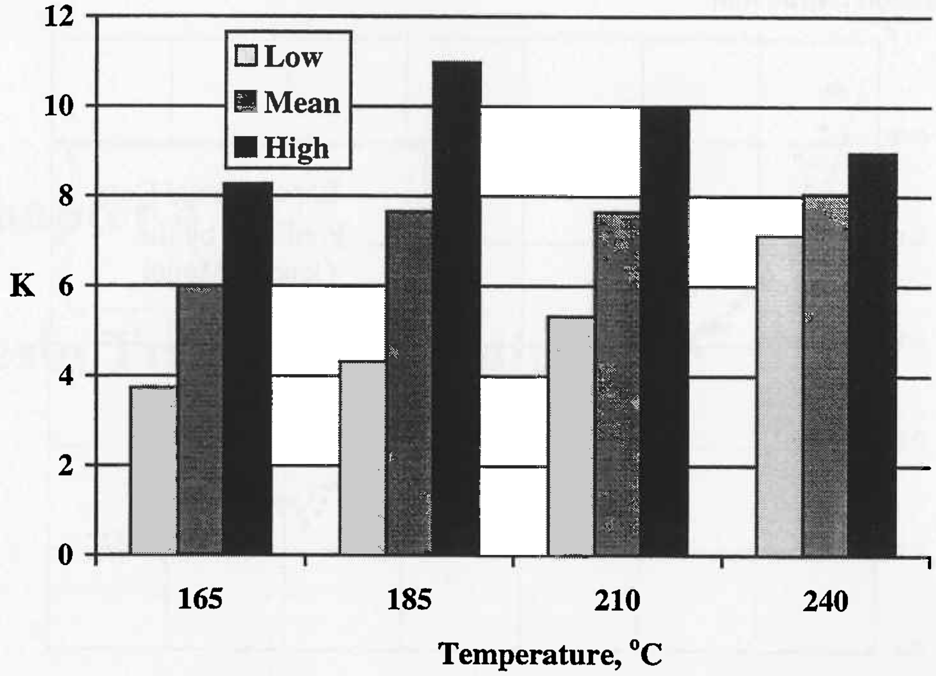

Figure 6. Effect of temperature on the Kozeny constant.

Since the variation in K is not great, a best fit value for K was obtained using all the conditions in Table 2. The value obtained was $K = 7.6$. An illustration of the fit achieved is shown in Figure 7. The break in the data and line near 15 seconds is due to the initial ramp up to the maximum pressure. This initial section was modeled incrementally using an average pressure for one second intervals.

Skartsis, *et al* (1) have reported a Kozeny constant of 10 for the flow of a Newtonian fluid through a random fiber bed. For oil flowing through an aligned carbon fiber bed Gutowski, *et al* (2) obtained a Kozeny constant of 18. Thus, the non-Newtonian flow of a thermoplastic through a random mat is not substantially different than results obtained with low viscosity Newtonian fluids.

CURRENT STUDIES

The same matched die mold has been used to study the consolidation of nylon/carbon fiber and polyetherimide (PEI)/carbon fiber composites made by powder coating carbon fiber tows. The Kozeny constant was very high, particularly with the PEI matrix. Also, difficulties with resin squeeze out from the preforms complicated analysis. Therefore, a 250 x 250 mm matched die mold has been constructed for use in a compression press. This design minimizes edge effects. Also, the first experiments used consolidated nylon/carbon fiber unidirectional composites containing 65 volume % resin. Bleeder plies were used on the top and bottom of the composite to accommodate the excess resin squeezed out of the composite. This experiment is equivalent to determining the Kozeny constant under "wet" conditions. At 230 °C and 2.8 MPa a Kozeny constant of 15 was obtained. This result is consistent with Gutowski, *et al* (2).

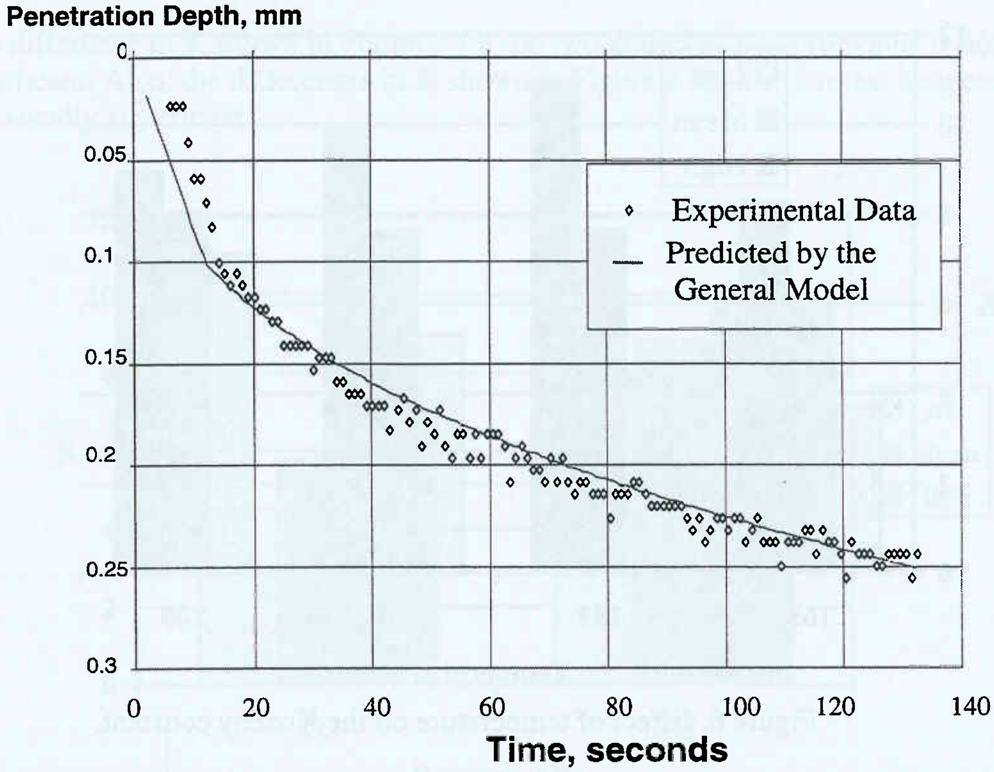

Figure 7. Penetration depth versus time for PP2 at 190 °C and 172 kPa using K = 7.6.

An attempt to duplicate the permeation of thermoplastic into an aligned fiber bed was not successful. The fibers compressed into a bed with a fiber volume fraction exceeding 80 %, preventing resin flow.

The next steps entail permeation measurements using nylon and polypropylene of random mats comprised of carbon and glass fibers. In this case the mats were made by a wet process which disrupts the fiber bundles. These mats are more difficult to permeate. Finally, the permeation and consolidation of powder coated tows and commingled tows will be studied.

CONCLUSIONS

The transient permeation of glass mat by two polypropylenes has been measured as a function of pressure and temperature and modeled using a power law penetration model. The Kozeny constant was found to be moderately dependent on pressure and independent of temperature and the type of polypropylene. An average Kozeny constant of 7.6 was obtained.

REFERENCES

1. L. Skartsis and J. Kardos, *Amer. Soc. For Comp. 5th Tech. Conf.*, 548 (1990).

2. T. Gutowski, Z. Cai, S. Bauer, D. Boucher, J. Kingery and S. Wineman, *J. Compos. Mater.*,**21**, 650 (1987).