Transverse Flow during Impregnation of Fabrics with Thermoplastic Matrices

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Introduction

Permeability of fabrics is a key characteristic for composite manufacturing. The permeability of a porous medium, such as a reinforcement fabric, can be defined according to Darcy law [1] strictly valid for Newtonian fluids [2]

\[ \nu = \frac{k \Delta P}{\eta L} \] (1)

In which \( k \) is a permeability, \( \eta \) is the viscosity, \( \Delta P \) is the pressure gradient, \( L \) is the thickness of reinforcement. Permeability measurements in composite manufacturing are mainly studied in relation with resin transfer moulding [3]. However, through-thickness flow occurring during processing of thermoplastic matrix composites requires the study of permeability of fabrics to high viscous fluids.

Prediction of the permeability of porous media has been the subject of intense research for at least last three decades [4]. In these studies the tests were performed using low viscosity Newtonian fluids (0.1Pa*s). In conventional processing of composite materials, two distinct types of impregnation are encountered: macro and micro-impregnation. Macro-impregnation is the result of matrix flow between bundles or yams, and involves elimination of large-scale dry spots. Micro-impregnation is the result of matrix flow inside each bundles, around individual fibres, and affects micro-porosity and the quality of the fibre bundle-matrix interface.

In this paper a continuous method for the measurement of transversal permeability during the impregnation of fibrous reinforcement impregnation with a high viscosity thermoplastic matrix has been studied. The model system used is composed of a unidirectional flax woven fabric and a thermoplastic blend of low Ethylene Vynil Acetate (EVA). Rheological analysis performed on the matrix at different temperatures showed that the matrix is characterized by a Newtonian behaviour.

The permeability of the reinforcement was measured by a plot of the measured pressure as a function of the set velocity during experiments performed with a properly modified capillary rheometer. The resulting structure of the composite was studied by means of optical microscopy analysis. This allowed for the measurement of the volume fraction of fibers. The volume fraction of fibers was used for the prediction of reinforcement permeability by using proper mathematical models.

2 Materials and Methods

The thermoplastic matrix used is thermoplastic blend of low Ethylene Vynil Acetate (EVA) and Wax, with a density 1040 kg/m³, provided by Axel (Italy). The matrix is characterized by a low melting point (in the range 50°C-80°C), evaluated by DSC METTLER TOLEDO 877. The fibrous reinforcement used is a unidirectional flax woven fabric 300 HS 45, provided by Fidia (Italy).

Matrix viscosity was measured in stationary mode using a cone and plate rheometer ARES II from TA Instrument, at four different temperature (85°C-90°C-95°C-100°C) in a range of shear rate between 0.1 and 10 s⁻¹.

Scanning Electron Microscopy (EVO 60 ZEISS) was performed on sample consolidated at different temperatures in order to measure the fiber-matrix distribution. A Nikon Model Epiphott 200 was used for optical microscopy analysis in order to evaluate the inter-bundle and intra-bundle volume fraction. Specimens cut from the centre part of composite were polished with SiC papers disks and then with diamond particles solutions before optical analysis.
Energy dispersive X-ray analysis, EDS (Bruker 127 ev), was used to identify the elemental composition of composite, in order to evaluate the degree of impregnation.

**Capillary rheometer experiments**

The experimental measurements of impregnation were carried out on samples made of two layers of flax at different temperatures, using a REOTESTER 1000 GOTTFERT capillary rheometer equipped with a 20 bar pressure transducer. This instrument was modified by substituting the capillary with a tool, capable of sustaining the reinforcement during impregnation. A sketch of equipment used for the impregnation of woven glass fiber is reported in Fig. 1.

![Sketch of equipment](image)

**Fig.1. Sketch of the equipment developed for the impregnation of woven flax fibre.**

It consists of a capillary rheometer (g), equipped with pressure transducer (f). The rheometer is modified by substituting the capillary with tool (e), capable of sustaining the reinforcement (c) during impregnation. During the tests, performed at four different temperatures (85°C-90°C-95°C-100°C), a piston (a) moves at a constant speed downward forcing the molten polymer (b) through the fabric (c).

The average velocity of matrix through the reinforcement was obtained as:

\[ v_p * S_p = v_M * S_M \]  

where:

- \( v_p \) is the velocity of piston;
- \( S_p \) is the cross section of the piston or the cylinder;
- \( v_M \) is the velocity of matrix through the thickness of woven fabric;
- \( S_M \) is the cross section of the woven fabric impregnated.

A typical plot of \( v_M \) and pressure build up as a function of time is reported in Fig. 2. In correspondence of each velocity step increase, the pressure increases in a continuous way, reaching a plateau value after about 50-100 s. The time necessary for pressure to reach the plateau is the time of transient behavior of the fluid, necessary to reach again steady state condition but at a higher flow rate. During the transient period, Darcy equation, which is derived in steady state conditions, neglecting all acceleration and/or convection terms in the momentum continuity equation, cannot be applied. After the transient interval, the plateau value of pressure corresponds to a steady state behavior and Darcy equation can again be applied. Therefore, each value of the set velocity and the plateau value of pressure were used, according to eq. 1, for calculation of the permeability. The permeability of the fabric was therefore calculated from the slope of the pressure-velocity plot, \( B \), as:

\[ K = \frac{\eta L}{B} \]  

**Fig.2. Velocity of the matrix and experimental pressure vs time.**
Results and discussions
The results of rheological measurements, reported in Fig. 3, show the evolution of viscosity as a function of shear rate for the matrix at four different temperatures. At each temperature, the matrix shows a weakly shear thinning behavior, which can be reasonably approximated by a Newtonian behavior, with the characteristic values of viscosities reported in Table I.

![Fig. 3. viscosity vs shear rate at four different temperatures.](image)

The experimental pressure as a function of matrix velocity for the flax woven fabric is reported in Fig. 4. The slope of the curves decreases with increasing temperature, which is due to the decrease of the matrix viscosity. On the other hand, according to Darcy law, the plot should yield a linear behaviour in the whole range of pressures. As it can be observed in Fig. 4, the plot at each temperature is characterized by two distinct linear behavior zones. The low pressure zone is characterized by a higher slope, whereas the zone at high pressures is characterized by a lower slopes. According to eq. 3), this indicates an increase of the permeability.

Two different approaches can explain the existence of the two zones:

a) The behavior of the matrix is not completely Newtonian. Therefore, an increase of the average velocity yields an increase of the shear rate during impregnation, and a decrease of the matrix viscosity. A decrease of the matrix viscosity, for a fixed value of permeability, yields a decrease of the slope of the pressure-velocity plot. In this case, the pressure rise during impregnation should be related to the velocity by eq. 4) [2-5]:

\[ v_{avg} = K \left( \frac{\Delta P}{\eta_0 L} \right)^{\frac{1}{n}} \]  

(4)

where \( n \) is the viscosity index of the matrix. The non linear curve fitting according to eq. 4) of the data at 90°C is reported in Fig. 5, and where obtained with a coefficient \( n = 0.64 \), which is significantly different from the value obtained by fitting of viscosity data according to the power law model, which was evaluated to be \( n = 0.98 \).

b) The impregnation of the fabric by the molten matrix is actually governed by two different mechanisms, the first one occurring at the lower pressures, and the second one occurring, alone or simultaneously to the first, at the higher pressures. Each of the two mechanisms is characterized by a permeability values.

![Fig. 4. measured pressure as a function of the average matrix velocity at four different temperatures.](image)

In order to prove hypothesis b), a tests was performed in the capillary rheometer at 90°C up to 0.47MPa pressure, which is a value below the slope variation observed in Fig. 5. A SEM image of the fabric after impregnation at low pressures is reported in Fig. 6. It is evident that the matrix has flown around bundles, therefore leading to what has been defined as “macro-impregnation”. There is no evidence of flow of the matrix inside bundles.
Fig. 5. Non linear curve fitting of the pressure-velocity data at 90°C according to equation 4.

A SEM image of the fully impregnated fabric up to 1 MPa pressure is reported in Fig.7, showing that matrix flow inside the bundles has occurred, indicating that impregnation into bundles (or micro-impregnation) is achieved.

According to the results of Figure 6- Figure 9, the macro-impregnation takes place at the lower pressures, whereas once a threshold value of pressure is achieved, both the macro-impregnation and micro-impregnation processes become active. Therefore, the low pressure slope observed in Figure 6 reflects the macro-impregnation permeability, whereas the high pressures slope reflects the global permeability, which takes into account the two mechanisms of impregnation.

The EDS analysis was performed on the sample of the fabric impregnated at low pressure. The microanalysis revealed that the carbon amount on the fiber was about 68%, whereas the carbon amount on the matrix was 95%. The carbon amount in the intra-bundle voids reveals the same amount of carbon equal to 68% on the flax fiber and on the intra-bundle porosity.

<table>
<thead>
<tr>
<th>Test’s Temp. (°C)</th>
<th>Visc. [Pa*s]</th>
<th>I slope [MPa*s/µm]</th>
<th>II slope [MPa*s/µm]</th>
<th>Kinter-bundle [m²]</th>
<th>Kglobal [m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>254</td>
<td>0.05169±2.88E-3</td>
<td>0.03975±7.35E-4</td>
<td>8.05E-12±4.48E-13</td>
<td>1.04E-11±1.93E-13</td>
</tr>
<tr>
<td>90</td>
<td>136</td>
<td>0.02792±4.45E-4</td>
<td>0.01951±8.50E-5</td>
<td>7.98E-12±1.27E-13</td>
<td>1.14E-11±4.98E-14</td>
</tr>
<tr>
<td>95</td>
<td>116</td>
<td>0.01694±6E-5</td>
<td>0.01306±1.7E-4</td>
<td>1.12E-11±3.98E-14</td>
<td>1.45E-11±1.89E-13</td>
</tr>
<tr>
<td>100</td>
<td>88</td>
<td>0.01205±1.16E-3</td>
<td>0.01086±1.48E-3</td>
<td>1.20E-11±1.16E-12</td>
<td>1.34E-11±1.85E-12</td>
</tr>
</tbody>
</table>

The values of inter-bundle permeability and global permeability determined for the data reported in Fig. 4 by linear fitting according to eq. 3), using the viscosity values of Table I, are also reported in Table I.

As expected, both, the inter bundle and global permeabilities are not dependent on the test temperature. This is in agreement with the fact that permeability is a characteristic of the fabric, and is independent on the rheological properties of the matrix.

The discrepancy on the values of global transversal permeability appeared to depend on the fabric. This was certainly related to the difficulties in cutting and handling the samples that would increase the bundle’s distance. At each temperature, the permeability obtained in the first zone, associated to the inter-bundle impregnation, is less than that obtained in...
the second zone, attributed to the sum of inter-bundle and intra-bundle impregnation process. Papathanasiou [6] numerically solved the Stokes equation in two dimensions using the Boundary Element Method in square arrays of permeable multifilament yarns, where each yarn was composed of circles representing the cross-sections of the constituent filaments. The effective permeability of the medium was reported as a function of the weave and yarn porosities. Similar studies were conducted for square and hexagonal arrangement of filaments in yarns, where the yarns had circular cross-section [7], and for yarns with elliptical cross-section [8]. Papathanasiou [9] reported a correlation for the effective permeability of two-dimensional hexagonal arrangements of filament bundles as a function of the weave and yarn permeabilities, as follows:

\[
K_{\text{global}} = K_{\text{inter}} \left[ 1 + \alpha \left( \frac{K_{\text{inter}}}{K_{\text{intra}}} \right)^{3/2} \right] \tag{5}
\]

where \(K_{\text{global}}\) is the effective permeability of fabric, \(K_{\text{inter}}\) is the inter-bundle permeability, \(K_{\text{intra}}\) is the intra-bundle permeability and \(\alpha\) and \(n\) are constants related to the geometric structure of the fabric.

The relationship is constructed based on dimensional arguments and from consideration of the behavior at high and low \(K_{\text{inter}}/K_{\text{intra}}\) ratio asymptotes. Papathanasiou [9] determined values for \(\alpha\) and \(n\) by fitting to the numerical simulation data, and obtained: \(\alpha = 2.3\) and \(n = 0.59\) when filaments are arranged in a square array; \(\alpha = 2.67\) and \(n = 0.89\) when filaments are arranged in a hexagonal array. In order to use eq. 5), the experimental values of \(K_{\text{inter}}\) reported in Table I can be used. Instead, the value of \(K_{\text{intra}}\) must be predicted by means of the Carman–Kozeny equation, which correlates the intra bundle permeability to the fiber bundle volume fraction \(V_{\text{intra}}\), the characteristic fiber diameter \(d_{\text{fiber}}\) and a lumped parameter called the Kozeny constant \(k\):

\[
K_{\text{Kozeny–Carman–int rabundle}} = \frac{d_{\text{fiber}}^2}{k_0} \times \left( \frac{1 - V_{\text{intra}}}{V_{\text{intra}}} \right)^3 \tag{6}
\]

In order to obtain a correlation between experimental permeability data and model prediction, the intra-bundle volume fraction was defined as reported in eq. 7):

\[
V_{\text{intra}} = \frac{A_{\text{fibers}}}{\pi a b} = \frac{A_{\text{fibers}}}{A_{\text{TOT}}} \tag{7}
\]

Where \(A_{\text{fibers}}\) is the actual area occupied by the fibers, \(a\) and \(b\) are the two semi axes of the elliptic bundle, determined by optical microscopy. In order to evaluate the intra-bundle volume fraction, the total area occupied by fibers was calculated as follows. A bundle ok known length \(L\) was extracted from the fabric, and its weight \(M\) was determined. This allows to calculate the area of fibers, as:

\[
A_{\text{fibers}} = \frac{M}{\rho L} \tag{8}
\]

Where \(\rho\) is the material density. From optical microscopy and knowledge of the \(A_{\text{TOT}}\), the intra-bundle volume fraction was calculated according to eq. 7). The values of intra-bundle permeability calculated according Carman Kozeny model, using a value of constant \(k_0=50\), and parameters reported are reported in Table II. Substituting the values of experimental inter-bundle permeability (Table I) and predicted intra-bundle permeability (Table II) into Papathanasiou model a global permeability was obtained. The values of parameter \(\alpha\) and \(n\) are consistent with the values reported in previous work [10]. As expected Kozeny-carman model prediction for intra-bundle permeability is much lower than inter-bundle

<table>
<thead>
<tr>
<th>Test's Temp. (°C)</th>
<th>A_{\text{TOT}} [µm²]</th>
<th>V_{\text{intra}}</th>
<th>K_{\text{intra, Carman-Kozeny}} [m²]</th>
<th>K_{\text{Papathanasiou}} [m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>185207±9308</td>
<td>0.58</td>
<td>1.36E-13</td>
<td>1.06E-11</td>
</tr>
<tr>
<td>90</td>
<td>198946±25137</td>
<td>0.545</td>
<td>1.53E-13</td>
<td>1.01E-11</td>
</tr>
<tr>
<td>95</td>
<td>201456±31456</td>
<td>0.538</td>
<td>1.56E-13</td>
<td>1.39E-11</td>
</tr>
<tr>
<td>100</td>
<td>215995±40631</td>
<td>0.502</td>
<td>1.70E-13</td>
<td>1.54E-11</td>
</tr>
</tbody>
</table>
experimental permeability reported in Table II. The values of global permeability predicted by Papathanasiou are consistent with global experimental permeability reported in Table I.

Conclusion
In this work, a new methodology for the measurement of fibrous reinforcement transversal permeability has been described. The presented setup makes use of a properly modified capillary rheometer, and allows the determination of the reinforcement permeability by a direct approach, which does not require any hypothesis, but allows for the measurement of the physical parameters appearing in the Darcy equation. The results obtained in this work, derived for a Newtonian matrix, show that the pressure-velocity curves are characterized by different regimes. Initially, a higher slope of the pressure vs velocity curve is indicative of a lower permeability of the reinforcement. Reinforcement samples impregnated in the low pressure zone showed the presence of polymeric fluid in the spaces between the bundles, but no flow of the matrix inside each bundle. This phenomenon, which is referred to as “macro-impregnation” is characterized by a relatively high value of permeability, which allows for impregnation even at low values of the applied pressure. On the other hand, at higher pressures, the slope of the pressure vs velocity curve decreases, which indicates an increase of the overall permeability of the reinforcement. In facts, when impregnated in the high pressure zone, the reinforcement shows significant flow of the matrix inside each bundle. This phenomenon, which is referred to as micro-impregnation, is characterized by a lower value of permeability, requiring higher pressures. The overall permeability, in the high pressure zone, is given by a proper combination of macro-scale and micro-scale permeabilities.

In facts, the slope in the lower pressure zone was used for evaluating the macro-scale permeability. As expected, this property is independent on the temperature of the test, being only dependent on the reinforcement architecture. The micro-scale permeability was evaluated by means of the Carmen-Kozeny equation, by using the geometric properties of the reinforcement, measured by SEM and optical microscopy. The experimental macro-scale and predicted micro-scale permeabilities were combined by following the approach proposed by Papathanasiou, an the global permeability was therefore calculated. The estimated value of the global permeability is in very good agreement with the experimental value determined in the high pressure zone. Such results indicate the sensitivity of the developed measurement techniques. Future works will be directed towards flow analysis of non Newtonian matrices in dry reinforcements.

Reference