The influence of bath temperature on the properties of pultruded glass fiber reinforced rods

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Abstract
Pultrusion is one of the several manufacturing processes for polymer composites. It involves resin-impregnated fibers that passed through a heated die, while the resin cures to produce a solid profile in the desired shape. Many processing variables such as die temperature, pull speed, fiber impregnation, resin viscosity, among others, affect the composite quality and the process efficiency. In fact, a good understanding and careful control of all these variables are needed to avoid defective profiles as well as to achieve better processing conditions. In this paper, the relationship between the resin bath temperature and the mechanical properties of pultruded rods such as tensile strength, elastic modulus, and hardness was established. The effect of resin viscosity on the fibers wet-out, cure position inside the die and the void formation was also investigated. The results showed that the rods made at higher bath temperatures presented higher tensile strength, elongation at break and hardness, but lower modulus of elasticity. This behaviour was correlated with the void content yielded during the profile formation.

Keywords
Pultrusion process, thermoset resin, composites, void content, mechanical properties

Introduction
Pultrusion is a continuous process of manufacturing composites of several shapes with constant cross-sections composed of a polymeric matrix and reinforcement fibers. In this process, a number of continuous strands (rovings), mats and surface veils are oriented through guide plates and pulled by a specific pulling system (caterpillar or reciprocating pullers), first to a resin bath and then through a heated die. Inside the resin bath, the reinforcing fibers are impregnated with a polymeric matrix (epoxy, vinyl ester, unsaturated polyester and phenolic) and then pulled to the interior of a closed die at a constant speed. As the pre-moulded profile pass through the heated die, the thermosetting resin reacts chemically, initiating an exothermic reaction and causing the profile to solidify gradually in the selected shape. Finally, a saw machine cuts the composite in several lengths. Nowadays, pultruded composites are being largely used throughout the world in several applications such as civil construction, aerospatial, aeronautical and transportation, among others. Although the process may seem quite simple, there are a great number of variables involved such as resin formulation, die temperature, pull speed, resin viscosity, bath temperature, fibers impregnation, fiber content, gel and cure time, among others. All these variables have a direct influence in the pultrusion process and may also affect the mechanical properties of the composites.
as mentioned by several researchers. Paciornik et al.,\textsuperscript{14} for example, described the influence of the fiber and filler fraction as well as the size and spatial distribution of the fibers on the mechanical properties of I-shaped pultruded profiles. Chen and Chen\textsuperscript{15} optimized the pultrusion process achieving the best mechanical properties of unidirectional glass fiber reinforced composites evaluating different die temperatures, pulling speeds and fillers. Therefore, to fully understand the pultrusion process, it is necessary to consider these variables and evaluate their effects on the properties of pultruded composites.

Most of the pultrusion process variables are set depending on the type of the polymeric matrix and its combination with several additives such as inhibitors, accelerators, diluents, retardants and crosslinking promoters also known as curing agents, initiators and hardeners. Once the polymeric system is selected and the formulation is prepared, the operational conditions of the process can be properly set, adjusting the pull speed and the die temperature.\textsuperscript{16} However, the determination of these conditions only is not enough to ensure the manufacture of a composite with the best mechanical properties. There is a crucial step in this process which begins in the resin bath with the impregnation of the reinforcement fibers. During this step, which is totally dependent on time and the final viscosity of the resin, a suitable reinforcement fibers impregnation is essential to ensure, along with the pull speed and the die temperature that the composite will acquire the best mechanical properties. If the viscosity is not properly set, the composite may have a series of defects and imperfections causing a significant loss in its properties. For this reason, the viscosity control is essential in this process.

The viscosity control is often performed using a viscosimeter, right after the mixture of all selected components into the resin at room temperature. If it is necessary, adjustments can be made by simply adding diluents or fillers in the mixture.\textsuperscript{1} However, this is not the only way to control the resin viscosity in a polymeric system. It is possible to carry out this action also by heating the resin bath. This procedure is not usual in pultrusion process but it may work in special circumstances where increasing the resin temperature until a certain level does not interfere drastically in its pot life. This is the case, for example, of the unsaturated polyester resins. This type of polymeric system uses initiators like organic peroxides as promoters for the crosslinking reaction. In conventional pultrusion processes usually three initiators are used, each one being activated at different temperatures (low, medium and high). If only one initiator is used instead of three, which is activated at a medium or high temperature,\textsuperscript{17} then the viscosity control by increasing the bath temperature can be done. This procedure allows a better impregnation of the reinforcing fibers since the resin viscosity decreases as the temperature increases in the system. Also, there is no need of extra addition of diluents or fillers to compensate the viscosity. Finally, the difference in the resin temperature between the bath and the die also decreases, allowing thus, to generate a gradual amount of heat on the pre-moulded profile as it passes through all the process steps until it is fully cured.\textsuperscript{18}

Even if the pultrusion process variables are well controlled, the composite will always have some kind of defect or imperfection in its structure. These defects (described in detail in ASTM D3918 and ASTM D4385) usually act negatively on the mechanical properties and performance of these materials. According to Huang and Talreja,\textsuperscript{19} they are a result of the manufacturing process and can be found in the fiber architecture (misalignment, irregular fiber distribution and broken fibers), in the matrix phase (voids), and in the interfacial regions (debonding, delaminations). The composite geometry also will contribute to form defects in the profiles. Many researches have been devoted to study these defects in an attempt to understand their formation mechanisms, its influence on the composite properties and to find ways to minimize them through the process control. Hagstrand et al.\textsuperscript{20} and Hong-yan et al.,\textsuperscript{21} for example, described the influence of void content on mechanical properties of composites. Huang and Talreja,\textsuperscript{19} explained that the void geometry interfere on elastic properties of unidirectional fiber reinforced composites. Therefore, the key to have a global view of the influence of these defects in pultruded composites is the evaluation not only of the amount of defects, but also the type, its distribution and its micro structural aspect. Furthermore, it is also important to correlate these defects and imperfections
with the process variables and the operational conditions during the composite manufacture. In this way, it will be possible to increase productivity, achieve better operational conditions and produce pultruded profiles with better properties and performance for different applications.

The aim of this paper is to evaluate the influence of bath temperature on the mechanical properties such as the tensile strength, elastic modulus, elongation at break and hardness of pultruded solid rods made with an unsaturated polyester resin and one initiator, the benzoyl peroxide. The effect of the bath temperature on the resin viscosity, fibers wet-out, peak exothermic within the die and the void formation was also investigated.

Materials and methods

Pultrusion apparatus and manufacturing of solid rods

The pultrusion equipment used in this study was a Pultrutee machine capable of withstanding three tons of pulling force. The selected profile was a solid rod of 13 mm diameter, which was obtained using an enclosed die made of P-20 steel with dimensions 100 mm × 100 mm × 960 mm (height × width × length). The internal surfaces of the die were treated by chrome plating. The heating temperature profile of the die was controlled by four heating plates of chrome plating. The heating temperature profile of the die was found for this system on tests carried out previously by this laboratory using a differential scanning calorimeter. The pulling speed was set considering the resin reactivity and the position, within the die, of the exothermic peak. These parameters were found previously in our laboratory through a series of measurements of the internal exothermic temperature of the solid rods. For practical purpose, the pulling speed was fixed as 0.46 m/min and was kept constant throughout the process. At this speed, the exothermic peak temperature and the position where this temperature was found are located exactly at the end of the die. Therefore, any changes in this position (shifting towards the die entrance) caused by the increase of the bath temperature can be clearly detected and measured.

The internal temperature of the solid rods was measured using the methodology proposed by Sumerak and Martin and the ASTM D2471. In this method, a thin thermocouple was introduced at the center of the pre-moulded profile, specifically between the wet fibers, at the die entrance as shown in Figure 2. As the material travels through the heated die, the thermocouple records the internal temperature of theprofile and stores the data for further analysis. The data recorder used in this experiment was a FieldLogger, supplied by Novus Electronic Products. A computer was used to

Table 1. Unsaturated polyester resin formulation for pultrusion.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Parts/ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsaturated polyester resin</td>
<td>100/67.34</td>
</tr>
<tr>
<td>Filler</td>
<td>30/20.20</td>
</tr>
<tr>
<td>Pigment</td>
<td>2/1.35</td>
</tr>
<tr>
<td>Initiator</td>
<td>3.5/2.36</td>
</tr>
<tr>
<td>Diluent</td>
<td>10/6.73</td>
</tr>
<tr>
<td>Mould release</td>
<td>3/2.02</td>
</tr>
</tbody>
</table>

*Parts by weight of resin (pbw).
analyze the data and build the exothermic curves after the experiments. The software used for data analysis was the Field Chart 8C, version 1.57. The thermocouple was a type J, whose measuring range is from $-50^\circ C$ to $760^\circ C$. The experiment was performed at four different bath temperatures: 30, 40, 50 and 60$^\circ C$. The die temperature and the pulling speed remained constant throughout the tests.

The exothermic peak temperature was set as highest temperature recorded by the thermopar throughout the tests and the position within the die where this temperature was found was set as the exothermic peak position.

Density, void, fiber and matrix content measurements

Samples of 1 cm$^3$ were cut perpendicularly to the fiber direction in which the solid rods were made. The specimens were measured with a micrometer and weighted in a Multitec AX200 balance at room temperature. Five samples from the rods made at 30, 40, 50 and 60$^\circ C$ were used in this investigation. The average values were used to calculate the sample volume and density according to ASTM D792. The void, fiber and matrix content were calculated following the orientation of ASTM D3171. The mass fractions of the components were measured following the guidelines of ASTM D5630. The value of the glass fiber density used was 2.54 g/cm$^3$. The remaining densities were calculated experimentally as described above.

Microstructure analysis

The void morphology (size and shape) was investigated by optical assessment following the same procedures used in metallographic analysis. The specimens for the image analysis were cut perpendicularly to the fiber direction in which the solid rods were made. The samples were carefully polished using a polish machine with 200, 400, 600, 1200 and 1500 grit size silicon carbide abrasive paper. Then, the samples were finished with 1 $\mu m$ diamond paste and fixed into a glass surface of $2.0 \times 0.3 \times 10.0 \text{ cm}^3$ (length $\times$ height $\times$ width) with an epoxy resin. The samples were observed using an optical microscope, Axio Scope A1 Brightfield model. The images were analyzed through the image analysis software, Axio Vision release 4.7.2.

Mechanical behaviour and hardness measurements

Tensile testing of pultruded glass-fiber-reinforced rods was performed using a KRATOS universal testing machine with capacity of 200 kN. Each specimen was tested to failure following the procedure described in ASTM D3916. The nominal cross-head speed was determined as 5 mm/min. Five specimens of each rod made at bath temperatures of 30, 40, 50 and 60$^\circ C$ were used in this test. The length of the samples was 1 m. Indentation hardness measurements were performed using a Woltest Barcol Impessor, model 934-1, following the procedure in accordance with ASTM D2583-95 standard. The number of readings used in this test was at least 16.

Results and discussion

Influence of viscosity on the wet-out of fibers

Figure 3 shows the variation of the system (resin) viscosity and the ability to wet-out the fibers as the temperature of the resin bath increases according to equation (1) described elsewhere. As expected, the system viscosity decreased as the bath temperature increased, reaching values below 400 mPa.s at 70$^\circ C$. At this temperature, the ability to wet-out the reinforced fibers also reached its highest value which was around 0.185. This condition should be very welcome to the pultrusion process since the reinforced fibers
would be well impregnated with the resin. Nevertheless, this is not the case. According to Sumerak and Martin, resin systems with very low viscosity, i.e., less than 400 mPa.s, may create a problem for this process. The resin cannot wet the reinforcing fibers properly before entering the die in order to develop an adequate pressure head at the die entrance, which is essential to produce profiles with low internal and surface porosity. The main reason for this low capacity of impregnation is because there is not enough adhesion strength to keep the resin upon the fibers. As a result, most of the resin will flow through these reinforcing fibers, leaving the pre-moulded profile with low content of matrix phase. To correct this problem, usually fillers are added to the formulation in order to increase the system viscosity or additional glass is introduced in the process to fully pack out the volume which is not filled by the resin. In this study, no additional glass or fillers were introduced into the resin, and the system viscosity was adjusted by controlling the bath temperature. Similar problem of impregnation can be found in high-viscosity systems (above 5000 mPa.s) but in these cases, the excess resin must be stripped off to some extent from the fibers prior to entering the die. Therefore, according to the data shown in Figure 3, bath temperatures above 65°C are not suitable for the pultrusion process since the system viscosity is too low.

Increasing the bath temperature to improve the wet-out of the reinforcing fibers will also affect the system pot life. The pot life can be understood as the time in minutes (hours, days or weeks), at a particular temperature and initiator addition condition, that a catalyzed thermoset resin (in this case, the unsaturated polyester) can be processed. As the bath temperature increases, the system viscosity decreases as discussed above but its pot life becomes shorter to the extent that the resin temperature approaches the temperature of dissociation of the benzoyl peroxide at 60°C approximately. By this reason, the bath temperature cannot also reach temperatures close to 60°C. Therefore, considering these statements we assume that the maximum temperature of the resin bath to be used in the pultrusion process in this case cannot be over 50°C. At this temperature, the system pot life is almost stable, the resin viscosity is about 700 mPa.s and the ability to wet-out the reinforcing fibers (T/η) is 0.071. Thus, it is assumed that the range of bath temperatures that can be used to pultruded the solid rods in this research is from 30°C to 50°C. These results shows, as expected, that it is possible to improve the wet-out of the reinforcing fibers in the pultrusion process, controlling the bath temperature with no addition of extra diluents or fillers.

**Figure 3.** Variation of viscosity and fibers wet-out as a function of bath temperature. (▲) Viscosity (mPa.s), (●) Fibers wet-out (T/η).

**Influence of bath temperature in the exothermic peak**

Introducing a thermocouple into the center of the pre-moulded profile at the die entrance and recording the temperature of the material as it is heated and pulled at a constant speed, yields a set of exothermic curves as shown in Figure 4. As can be seen, by increasing the bath temperature, both the exothermic peak temperature as well as the position within the die, where the crosslinking reaction takes place at its higher rate to...
consolidate the solid rods, were changed. According to Figure 4, at bath temperature of 30°C, the exothermic peak position is exactly at the exit of the die (96 cm) and the internal temperature of the rod was about 169°C. At this bath temperature, the composite was not yet fully cured since there was not enough time for the crosslinking reaction to take place completely. According to ASTM D3918, pultruded profiles with incomplete cure usually show a dull surface appearance, dimensional loss, low Barcol hardness and low physical properties. Situations like this are not desirable in the pultrusion process. To avoid this problem, it is necessary to have enough time for the heat transfer between the die walls and the profile surface occurs gradually, so that the composite can be completely cured before leaving the die. This can be solved optimizing the operational conditions of the pultrusion process. The solutions usually employed are: lower the pull speed keeping the die temperature constant or increase the die temperature keeping the pull speed constant. However, there is another way to solve this problem for this particular system, which is increasing the bath temperature keeping both the die temperature and the pull speed constant. This operation will shift the exothermic peak towards the die entrance and away from the die exit, allowing the cure reaction to have enough time to be completed. This shifting can be clearly seen as the bath temperature increases from 30°C to 50°C. At bath temperature of 40°C, the exothermic peak is located at 90 cm from the die entrance. The shifting was about 6 cm in comparison to the previous condition. On the other hand, the exothermic peak temperature increased, reaching 175°C. This increase in the internal temperature of the composite can be explained by the fact that there is a little more thermal energy given to the rod during the process. This energy source came from the bath temperature and from the exothermic cured reaction of the unsaturated polyester resin. The extra heat generated during this process helped to improve the extent of reaction as well as the composite properties. When the bath temperature reached 50°C, the internal temperature of the solid rod reached 181°C and the shifting of the exothermic peak was even higher. It is now located at 75 cm from the die entrance and 21 cm from the die exit. This is a significant shifting because the sooner the composite starts its crosslinking reaction, higher is the assurance that it will complete its cure before exiting the die. The exothermic curve obtained at bath temperature of 50°C is usually the shape desired to be found in the pultrusion process in order to avoid problems in the composite properties and appearance. This shape shows that a gradual thermal transfer from the outside surfaces of the rod in contact with the die walls to the center of the profile was properly done assuring the complete cure of the profile before it exits the die.

As Figure 4 shows, it is also possible to find valuable information about gel and cure time of the solid rods within the die. The gel time can be understood as the time period following the entrance of the wetted fibers into the die until the point where the solid rod will assume its soft-gel condition. In exothermic experiments such as these, the gel time can be detected by an abrupt change in the internal temperature of the composite which occurs at a specific position within the die. On the other hand, the cure time can be
described as the time period from the entrance of the wetted fibers into the die until the solid rod reaches its exothermic peak to fully cure the composite. As can be seen in Figure 4, by increasing the bath temperature both the gel time and cure time were changed. At bath temperature of 30°C, for example, the gel time of the solid rod needed about 90 s to start and it occurred at 70 cm from the die entrance. The cure time, on the other hand needed about 125 s to reach its higher rate of the crosslinking reaction to fully cure the composite and the position within the die where it was located was exactly at the die exit as mentioned before. As the bath temperature increases, the difference in temperature between the resin bath and the first die zone decreases. Therefore, more thermal energy is given to the material before it enters the die, causing a decrease in time for the rods to be cured. These changes in time (gel and cure) can be seen when the bath temperature reaches 50°C. At this temperature, the gel time needed about 65 s to start, 15 s less than the previous condition and it was detected at 50 cm from the die entrance. The cure time on the other hand, needed about 98 s and it was found at 21 cm from the die exit. This behaviour clearly shows that the bath temperature influence in a positive way the exothermic peak (temperature and position) as well as the gel and cure time of the solid rods within the die. By this reason, this technique can be very well used to both establish the best operating conditions in the pultrusion process and to maintain production at the desired level.

Influence of bath temperature in the void content

Table 2 shows the measurements of the void, fiber and matrix content as well as the densities for the pultruded rods made at different bath temperatures. As can be seen, the composite density decreases from 1.90 g/cm³ to 1.83 g/cm³ and the void content increases from 4.85% to 6.95% when the bath temperature is changed from 30°C to 50°C. This behaviour was expected and can be understood by analyzing the mechanism of formation of voids which is controlled by some parameters in the pultrusion process, such as cure temperature, pressure head at the die entrance and resin viscosity. As explained earlier, when the bath temperature is increased, the ability to wetting out the fibers is improved and the amount of matrix which adheres to the fibers becomes higher, due to a decrease in the resin viscosity. When the wetted fibers reach the die, which is at a temperature much higher than the resin bath, the resin viscosity decreases even more. At this point, part of the resin will flow through the reinforced fibers, reducing the pressure head at the die entrance and the amount of matrix in the composite. This loss of material can be clearly seen in Table 2, where the matrix content of the pultruded rods is reduced from 49.95% to 47.76% when the bath temperature is changed from 30°C to 50°C. Since there is no addition of glass or the rupture of fibers during the process, the composite fiber content is not changed, but remains constant around 45% as shown in Table 2. Therefore, more space in volume is available in the die cavity that will be filled by the matrix that remained adhered to the fibers soon after its entry in the die. As the process continues at a constant speed and the crosslinking reaction is carried out within the die, a significant amount of volatile by-products are generated and transformed into vapour. As a result, the internal pressure of the die is increased causing the vapour to diffuse along the fibers’ direction due to its least resistance and allowing the thermal expansion of the composite as well as the void formation. When the crosslinking reaction is completed, the composite shrinkage entraps the air left from the evaporation of all volatiles into a series of little pockets distributed throughout the solid rod. Since only the resin is replaced by voids, the lower the amount of matrix adhered to the fibers, the higher will be the void content of the composite. Consequently, the density of the pultruded rods decreases and the fiber content remains unchanged.

The voids found in the solid rods are seen as micro and macro voids with spherical or elliptical shape in a perpendicular section to the fiber direction and are located in the polymer rich regions as shown in Figure 5. The morphology of these voids is a result of the chosen processing procedure and may be different for each manufacturing process. In Figure 5(a) a polished cross-section of a pultruded rod made at bath temperature of 30°C is shown. As can be seen, the fibers are well wetted and are distributed uniformly throughout the composite. There are no indications of specific regions where the fibers form bundles. This is because the fibers are well oriented before entering the die and also due to the cylindrical shape of the composite which has no angles to force the fibers to be allocated in certain regions more than others. In Figure 5(b), a solid rod made at bath temperature of

<table>
<thead>
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<th>Parameters</th>
<th>Bath temperature (°C)</th>
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<tbody>
<tr>
<td>Void content (Vol %)</td>
<td>30</td>
</tr>
<tr>
<td>Fiber content (Vol %)</td>
<td>30</td>
</tr>
<tr>
<td>Matrix content (Vol %)</td>
<td>30</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Measurement of density, void, fiber and matrix content as function of bath temperature.
50°C is shown. The fibers’ impregnation and their distribution in the composite are shown in Figure 5(a), with an exception that the porosity increases in 30% approximately. The voids are seen as black spots located at the polymer reach areas and the size of these voids are larger than those seen in Figure 5(a). When the voids are formed they push aside surrounding fibers as expand. All fibers remain in the composite and are still continuous, only more packed together around the void. Due to the circular shape and the thickness of the composite, most of the macro voids are located at the center of the rod, where the cure cycle will be completed last as the heat moves from the surface to the center of the profile. From a mechanical point of view this particular pattern may exhibit some advantage. The load transfer to the fibers can be relatively good and uniform in spite of the increase of void content.

**Influence of bath temperature in the mechanical properties**

The results of tensile strength, modulus of elasticity, elongation at break and hardness measurements of the pultruded rods made at different bath temperatures are shown in Table 3. As can be seen, the tensile strength increases by 34.03% and the modulus of elasticity decreases by 9.83% when the bath temperature is changed from 30°C to 50°C. This increase in tensile strength along with the increase of the void content is not usual and is not expected in fiber reinforced composites since it is known that the porosity has a negative effect in most of its mechanical properties as mentioned by Huang and Talreja, Hagstrand et al., and Hong-yan et al. Voids usually reduce the composite density (see Table 2) and the degree of the applied load which is transmitted to the fibers by the matrix phase. Also, the voids act as stress concentrators, which means that the applied stress is amplified or concentrated at the tip of these flaws reducing the composite capacity to bear the imposed load. The magnitude of this amplification and the degree of the applied load transmitted to the fibers depend not only on the void content but also on its shape, size and location in the composite. Therefore, it was expected that the tensile strength and the modulus of elasticity would be negatively affected with the increase of the void content. However, the behaviour observed in this case, especially by the tensile strength, may be understood considering the fracture process in which the solid rods were submitted under a certain load and the improvement of the cure reaction of the composite caused by the increase of the bath temperature.
When the pultruded rods are submitted to stress-strain tests, some modifications occur in their structure. The result of these changes is the composite fracture in a fragile form. The fracture process initiates with the stretching of the chemical bonds which were created during the crosslinking reaction of the matrix phase and the interfacial bonds between the fibers and the matrix when a force is applied onto the composite. The stretching of the interatomic bonds and the small changes in the interatomic spacing cause an elastic deformation in the solid rods which is favoured by the increase of the void content. During this stage, no chemical bond is broken and the material stiffness can be measured. As seen in Table 2, the pultruded rods become less dense and more porous as the bath temperature changes from 30°C to 50°C. Also, the matrix content decreases and less material is incorporated in the composite. The fiber content remains unchanged since there is neither extra addition of glass nor the rupture of fibers during the process. As a result, the composite resistance to prevent the elastic deformation will be lower and the ratio between the fibers and the matrix will increase as the void content increases, allowing the composite to elongate more until break. According to Table 3, the modulus of elasticity of the pultruded rods decreases from 34.57 GPa to 31.17 GPa and the elongation at break increases in 39% when the bath temperature increases.

The next step of the fracture process involves the propagation of micro cracks formed during the cure reaction in the matrix phase and the formation of new cracks while the axial force is applied in the composite. In both cases, chemical bonds are now broken and a plastic deformation is created. Since the matrix strain is lower than the fibers, it is expected that the matrix will fail before the fibers. And once the matrix has fractured, the majority of the load that was borne by the matrix is transferred to the fibers. Therefore, the ultimate strength of the pultruded rods will depend on the strength of the fiber–matrix interfacial bonds, the crosslinking bonds created during the cure reaction of the unsaturated polyester resin and the magnitude of the load transmitted to the fibers by the matrix phase. As mentioned before, when the bath temperature is changed from 30°C to 50°C, the fibers’ impregnation and the cure reaction of the pultruded rods were improved as discussed elsewhere and shown in Figures 3 and 4. These results suggest that the magnitude of the crosslinking bonds of the matrix phase as well as the adhesive forces between the fibers and matrix were also improved although the void content has increased and less material (matrix) has being incorporated into the composite. Because of these improvements, it is reasonable to think that the propagation of cracks in the pultruded rods during a tensile test becomes restricted by the matrix which will work as a barrier to prevent the plastic deformation and the composite failure. Even though some of the individual fibers may fail, total composite fracture will not occur until the matrix phase along with a large numbers of adjacent fibers have failed and formed a cluster of critical size. Furthermore, when the bath temperature increases, the void size also increases, but its location in the composite changes due to the internal pressure at the rods surface which increases during the composite expansion in the course of the curing reaction within the die. At bath temperature of 50°C, for example, due to the circular shape of the composite, the largest fraction of voids with large size is located at the center of the pultruded rods whereas a smaller fraction of smaller size is present at the external surface. Therefore, it is expected that the superficial hardness, which is the measure of a material’s resistance to a localized plastic deformation when a force is applied and the magnitude of the load transmitted to the fibers by the matrix at the external surface of the pultruded rods may increase in comparison with its center. The result is the increase of the tensile strength In fact, as can be seen in Table 3, when the bath temperature is changed from 30°C to 50°C, the composite tensile strength increases from 337.70 MPa to 452.63 MPa while the Barcol hardness increases from 54 to 67. These results show that increasing the bath temperature, the mechanical properties of the pultruded rods is affected. Although it was observed an increase in the composite void content which has resulted in a decrease in its modulus of elasticity and an increase in its elongation at break, the tensile strength and the surface hardness, in turn, had a significant increase which was caused by the improvement of the cure reaction of the solid rods within the die and by the migration of the voids in the composite which was favoured by the profile shape and by the internal pressure at the rods surface.

Conclusions

The results in this study clearly showed that the resin bath temperature influences the pultrusion process, by improving the fibers wet-out through the proper control of the system viscosity, changing the exothermic peak position and temperature within the die and improving the tensile strength, hardness and elongation at break of the solid rods. It was found that as the bath temperature increases from 30°C to 50°C, the exothermic peak temperature increases and the position within the die where the crosslinking reaction takes place at its higher rate to consolidate the solid rods also changes, allowing its complete cure in a shorter time and far from the die exit. This condition is essential in the pultrusion process in order to produce profiles with good...
properties. It was found that the solid rod produced at 50°C showed better visual appearance, improved brightness, absence of defects on the surface and greater resistance to indentation. At this temperature, the fibers were better wetted, the pre-molded profile had enough time and heat within the die to complete its cure reaction and the solid rods exhibited its higher tensile strength and hardness even with the increase of the void content. These results also show that the pultrusion process can be done with one initiator in its formulation when using an unsaturated polyester resin as a matrix. Finally, the operational conditions of this process can be controlled by the proper control of the bath temperature while the others process variables such as the die temperature and speed can be maintained unchanged.

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Conflict of interest

None declared.

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