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ANALYSIS OF GLASS FIBER MAT STRUCTURES AND THEIR IMPACT ON THE RESIN ABSORPTION PROCESS AND ON THE CHARACTERISTICS OF COMPOSITES

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1. Introduction

Composite materials are employed today in a rapidly growing array of applications. Glass fiber reinforced composites have been manufactured in Hungary throughout the last 40 years and this industry has grown particularly quickly in the last 15 years. Composites are built up from a high strength reinforcement and a surrounding tough matrix. It is necessary to establish strong adhesion between the reinforcement and the matrix. The quality of reinforcement largely depends on the impregnability of the reinforcement, because it must be completely impregnated by the matrix. The impregnatibility of the reinforcement is mainly determined by its structure and pore size distribution. The impregnability is quantified by permeability. The determination and modeling of permeability during the filling of the mold with resin (mainly in resin transfer molding) is a subject of many researches today. The knowledge of the structure, geometry and mechanical properties of fibrous reinforcements is crucial for the design and sizing of composite structures. The investigation of these properties is hampered by the fact that the geometry and mechanical properties of fibers and fibrous structures is statistical, and composites may be weakened by different types of structural flaws and defects. Composite properties are also strongly influenced by the quality of adhesion between the reinforcement and the matrix, which depends on the impregnation i.e. the permeation. In case of fiber reinforced structures the collective behavior of individual fibers must be also taken into account because according to experiences, the fiber bunches affect the mechanical behavior of fibrous structures as a mediate component. Composite reinforcements are always fibrous, because this enables the formation of intentionally anisotropic structures. The most common reinforcing material is the glass fiber due to its low price and good properties. Aramid, carbon and basalt fibers are also frequently used. Degradable matrix materials have been put on the market in the last few years, together with natural plant fibers for reinforcement. The other main recent innovation is the application of nano reinforcements. However, the effective utilization of the potentials in nano reinforcements has not been realized yet. I have chosen the glass fiber for my research because this is the mostly prevalent reinforcing material. Glass fibers are used as roving, fabric and mat. Glass fiber mats are used for making laminated composite sheets, often combined with glass fiber fabric. The most common matrix materials are unsaturated polyester, epoxy and vinyl ester. I chose polyester for my work. The aim of my work was the investigation of the structure, pore size distribution, permeability and resin absorbency of glass fiber mats. The other goal was the examination of resin absorbing process and its determinative factors concerning the manufacturing of glass fiber mat reinforced sheets.

2. Analysis of literature

One of the most important properties of fibrous reinforcing materials is the pore size distribution. Many methods have been worked out for measuring it. Direct methods are the different filtering and permeability tests, indirect methods are the image analysis and touch-free tests. It is hard to define pore size, both direct and indirect methods have their own inaccuracies. Some authors tried to describe the structure of fibrous reinforcements by numerous different statistical models, but the applicability of these models is not always confirmed by measurements. Many authors examine the permeability of fibrous structures, most of them on the basis of the Darcy equation. Permeability is important in composite industry because better permeability enables faster impregnation. It can be determined by models considering geometry and flowing parameters. The interaction between the fibers and the fluids has been described by Kaptay and Lukáš. The fluid absorption of fibrous structures can be described by the Lucas-Washburn equation. In case of composites, mostly only the resin filling process is analyzed and the differences between different glass fiber mats (powder and emulsion) are not described. The mechanical properties of unidirectional fibrous structures were described by Vas, and his model has been generalized for systems with oblique fibers, but this model needs further refinement. In my dissertation I intend to analyze the differences between the structure, geometry, impregnability, permeability and mechanical properties of glass fiber mats made with different binders but with the same specific weight. I also intend to analyze the effect of these differences on the vacuum infusion and composite properties. The aims of my work are summarized in the following sections:

1. Analysis of structure of glass fiber mats with different binders (powder and emulsion) and with the same specific weight, and the determination of differences.
2. Development of a method for measuring pore sizes optically, description of pore size distribution.

3. Evaluation of connection between pore size distribution and air permeability in case of glass fiber mats, determination of the effect of number of layers.
4. Evaluation of the surface interaction between the matrix and the applied glass fiber mats and analysis of resin impregnation in parallel and perpendicularly to the plane of the mat.
5. Manufacturing of a vacuum infusion tool for making laminated composite samples. Evaluation of resin intrusion process with optical and image analysis system.
6. Geometrical and mechanical analysis of glass fiber mat reinforced composite sheets. Evaluation of effect of powder and emulsion binder on composite properties.

3. Summary of the research

In my dissertation the structural differences of the same surface weight of powder and emulsion bonded glass fiber mats were studied by the pore size distribution, resin absorption and mechanical properties of glass fiber reinforced unsaturated polyester composite sheets.

The results of the investigations of glass fiber mats are presented, mainly focusing on the pore size distribution and air permeability. Pore size distribution was determined by assessing the area of through-going pores using the Vas statistical fiber mat model. These results showed good correlation with the test results obtained with image analysis of optical micrographs. Air permeability was determined perpendicularly to the plane of the mat and also in parallel direction. The emulsion bonded glass fiber mats show better air permeability than powder bonded ones. It can be explained by the fact that the emulsion binder completely covers the fibers, thus larger pores can come into existence, while the powder binder can be found on the fibers only locally, leading to loose fiber bundles and smaller pores.

The resin absorption process was investigated with a polyester resin in parallel and also perpendicularly to the plane of the glass fiber mat. The process was approximated with the Lucas-Washburn equation in both cases. Resin impregnation was evaluated by observing the filling of a resin transfer molding tool. 4 layers of glass fiber mats were laid in the tool, the resin was mixed with 1.5% catalyst and pushed into the tool with 0.5 bar pressure. The process was approximated also with the Lucas-Washburn equation.

The tensile process of the elementary glass fibers and glass fiber bundles is explained, together with the modeling of the tensile process. The results obtained by FiberSpace software showed that fiber bundles are better integrated in case of emulsion bonded mats, resulting in a better utilization of the strength of the fibers.

The tensile testing of the glass fiber mat reinforced composite sheets is described. The tensile process was approximated with the FiberSpace software. The results show that the tensile process of emulsion and powder bonded glass fiber mat reinforced composite sheets can be well determined using the mathematic model.

4. Theses

The following theses are written according to the results [1-16]:

1st thesis

I have proven that the diameter distribution defined for the circles inscribed into pore areas in the Vas statistic fiber mat model can be adapted to the area equivalent diameter distribution of through-pores measured in an optical way in multilayer laminated fiber mats. During its generation the minimal pore radius detected with image analysis can also be taken into consideration. Pore size distribution ($r \geq r_{min}$) applicable for the radii of pore area equivalent circles and also for the circles inscribed into pores and takes both the number of layers ($n \geq 1$, integer) and the detectable minimal pore radius (r_{min}) into consideration:

$$F_\rho(r) = 1 - e^{-n\kappa\left[2(r-r_{min})\left(1+\frac{\bar{b}\pi}{2\bar{l}}+\frac{r_{min}\pi}{\bar{l}}\right)\bar{l}+(r-r_{min})^2\pi\right]} \qquad \text{(T1)}$$

where κ [1/mm^2] is the average area density of pore centers, $\bar{l}$ and $\bar{b}$ are the average length and width of glass fibers, respectively. The application of area equivalent pore diameters when approximating the measured distributions results in 3.0…7.8 times lower average square relative deviation compared to the inscribed circular approximation, in case of the examined one-layer powder and emulsion bonded glass fiber mat samples altogether.

2nd thesis

Concerning the pore sizes of the examined emulsion and powder bonded glass fiber mats that had the same surface weight (nominally 450 g/m^2) but were produced by different companies, I have revealed with optical microscopic and image processing methods that although there is only 1…5% relative difference between their pore sizes, the average pore sizes in emulsion bonded samples are 60…210 μm, and their maximums are 37…212 μm higher than in case of powder bonded ones. The latter result was also confirmed with bubble investigations. According to the electron microscopic investigations, the fundamental reason for this phenomenon is that the emulsion bonding material covers almost the whole fibers within the bundle evenly, hence the fiber bundle structure is denser, and this way larger pores can be formed. On the other hand, the powder bonding material is only present locally on the fibers, which only connect to each other volumetrically in a loose way, hence the pores among them are smaller.

3rd thesis

I have worked out a theoretical relation that handles through-pores as reducing lips that can be detected with image processing and the pore chains composed of capillaries that cannot be detected this way separately in order to determine the air permeability factor perpendicular to the plane of one- and multi-layered glass fibers mats that can be approximated well with a third power polynom that can be used as a good estimation for the measurement results of variable $1/\sqrt{\Delta p}$ (dependent from Δp pressure difference). The following statements can be made based on fitting of the shape of the third power polynom of this relation to the measurement data and also using the analysis of the coefficients:

(a) I have proven based on measurements that the ratio of pores including capillaries and the total flow cross section decreases hyperbolically both in case of emulsion and powder type fiber mats as the number of layers increases.

(b) I have revealed with measurements that the ratio of the area of pores decreases if the number of layers increases, and meanwhile the cross section area of capillaries increase. The pressure drops on the pores increase slightly if the number of layers increases, and that corresponds to narrowing pores, while pressure drops on capillaries decrease and that refers to the an increasing number of not visible through-pores, and this way refers to the increase of average capillary sizes.

4th thesis

I have developed a device that can be connected to a universal tensile testing machine. With the help of this device the liquid absorption ability perpendicular to the plane of the glass fiber mat can be studied. I have prepared a measurement and evaluation method for this device based on periodic immersion with the help of which the resin absorption process of fibrous structures can be determined well, and similar samples can be compared this way. The principle of the measurement method can be used well for different porous materials in also other application fields.

5th thesis

I have proven that the approximate explicit solution of the Lucas-Washburn equation can be used well to describe the differently defined resin absorption processes of the examined same surface weight (nominally 450 g/m^2) powder and emulsion bonded glass fiber mats. The relative average square deviations between the measured and approximated resin absorption processes perpendicular to the plane of the glass fiber mat, and along the sheet in the measuring device, and in the vacuum injection mold were always less than 4.9%, and the curve fitting parameter of p=1.5 was applicable in all cases.

(a) I have revealed that the intensity of spontaneous resin filling both in the plane of the glass fiber mat and perpendicular to that decreases as the pore sizes increase, since in this case the reason for the absorption into the device, namely the capillary effect also decreases. The resin adsorption intensity values show a similar decreasing tendency in case of powder bonded materials both in the plane of the samples and perpendicular to that, while in case of emulsion bonded materials significantly lower values were experienced than in case of absorption perpendicular to the plane as the pore sizes increased.

(b) I have proven with measurements that the intensity values of filling due to pressure in vacuum injection molds increase with the average pore diameters (R^2=0.88), average maximal pore diameters (R^2=0.99) and their maximum (R^2=0.95) linearly, and the values measured in case of powder and emulsion bonded mats fall on the same line. This can be explained by the phenomenon that during filling caused by pressure difference the resistance of structures with larger pores is smaller.

6th thesis

I have revealed that the following statements and relations are valid for the measured tensile processes of glass fiber mat bundles taken out from glass fiber mats and E type elementary glass fibers that build up these bundles, as well as glass fiber mat reinforced composite plates produced in vacuum injection molds based on the fiber bundle cell models containing E (ideally positioned and ideally clamped fibers), EH (wavy fibers), ES (pulling out fibers) and ET (skew fibers) type bundles and prepared with software FiberSpace:

(a) Based on the tensile tests carried out it can be concluded that emulsion bonding provides a better adhesion than powder (the tensile strength for one fiber of the emulsion bonded fiber bundles is 16% higher in average than in case of a powder bonded one). However, the co-working within one emulsion bonded fiber bundle reaches such a high extent that their fiber tensile strength utilization is 8.9% higher than that of an ideally clamped fiber bundle made up of statistically independent single fibers, while this ratio for powder is 6.7% smaller.

(b) I have revealed based on the fiber bundle cell models that the measured tensile processes of glass fibers as fiber bundles can be modeled with the parallel connection of the following bundles at the given ratio: in case of emulsion bonded samples: 10% E, 29% EH, 24% ES and 37% ET type bundles, and in case of powder bonded samples 50% E, 5% EH, 25% ES and 20% ET type bundles. The relative square deviation is around 1% in both cases. Based on all this it can be concluded that the order of the emulsion bonded fiber bundles (40% more ideal fibers, 24% less wavy and 17% less skew fibers) is significantly higher than that of powder bonded mats, and that improves fiber strength utilization besides the better bonding agent.

(c) I have revealed with tensile tests that the tensile strain of fiber bundles taken out of the fiber mat and composite sheets have similar values, i.e. the tensile strain of composite sheets is determined by the tensile strain of the fiber bundles as intermediate elements. Based on the analysis of the average tensile strength processes of composite sheets it could be concluded that sheets reinforced with emulsion fiber mats failed at larger elongation (2.0…2.5%) than those reinforced with powder bonded fiber mats (1.6…2.1%), and similarly the emulsion bonded fiber bundles failed at 2.1%…3.1% elongation, while fiber bonded ones at 1.7%…2.7% tensile strain values. Based on the analysis of the fiber bundle cell models of the average tensile processes of composite sheets it could be stated that sheets reinforced with emulsion (1.9% E, 3.2% EH, 31.6% ES, 63.3% ET) and powder (1.2% E, 6.1% EH, 33.9% ES, 58.8% ET) bonded glass fiber mats have nearly the same ratio of E, EH, ES and ET bundles, and in both cases the ratio of skew fiber ET bundles is dominant according to the structure of the mat.

5. List of publications

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