An Overview of Impregnation Methods for Carbon Fibre Reinforced Thermoplastics

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Abstract. Carbon fibre reinforced plastics (CFRPs) can be classified according to whether the matrix is a thermoset or a thermoplastic. Thermoset-matrix composites are by tradition far more common, but thermoplastic-matrix composites are gaining in importance. There are several techniques for combining carbon fibres with a thermoplastic-matrix system. The composite's characteristics as well as its manufacturing costs are dependent on the impregnation technique of the carbon fibre and the textile structure respectively. Carbon fibre reinforced thermoplastics (CFRTPs) are suitable for fast and economic production of high-performance components. Despite the higher material costs thermoplastic-matrix systems show cost benefits in comparison to thermoset-matrix due to substantial time savings in the production process. Moreover CFRTPs can be manufactured in large production runs. The commingling of reinforcement fibres with matrix fibres is a well-established process. Another approach is the coating of the carbon fibre with a thermoplastic subsequent to the carbon fibre production (carbonization, activation and deposition of sizing). The latter point is currently subject of research and is a promising method for further increasing the production speed.

This paper presents the different possibilities of impregnating carbon fibres with a thermoplastic matrix. Diverse technologies along the process chain of the CFRTP production will be discussed.

Introduction

Today, carbon fibre reinforced composites are beginning to make inroads into mass application markets, e.g. automobile construction and wind turbines [1]. The need for lightweight structural materials in the automotive market is driven by the demand for improved fuel efficiency and reduced CO₂ emissions [2, 3]. At the same time, increasing demands with respect to comfort, safety and driving performance led to an increase in weight of the car. Thus, strict EU emission regulations, rising fuel costs and the emerging electromobility are prompting manufacturers to more than double the share of lightweight components in their vehicles [4]. Due to its unique properties CFRPs can be used where other materials have reached their limits and therefore are suitable to overcome prevailing weight issues.

CFRPs consist of two distinct components. The reinforcement is carbon fibre which provides the strength and stiffness, whereas the matrix binds and holds the reinforcements together into a solid. Moreover it offers protection to the reinforcements from environmental impacts and serves to transfer load. The long-standing dominance of thermoset-matrices is based on the resin's low viscosity enabling an easy impregnation, the good fibre-matrix-adhesion and outstanding mechanical properties [5]. Nevertheless, immense interest in thermoplastic-matrix systems was aroused due to the time-consuming cross-linking reactions, energy-intensive curing processes and the low degree of automation of thermoset composites. In comparison to conventional carbon fibre reinforced composites CFRTPs have much lower cycle times and are recyclable [6]. The possibility

of thermoforming and back injection moulding further improves the production rates. Even though material costs for thermoplastic resins are higher substantial time savings and the manufacturing in a continuous process lead to cost benefits. Further advantages of thermoplastic composites are high impact strength, good damping properties, unlimited transport and storage time at room temperature [7]. However, thermoplastics have a high viscosity complicating the impregnation of the fibre reinforcement and exhibit high creep tendency [9].

CFRTPs are generally produced on the basis of prepregs [8]. These semi-finished products are used in order to separate the technically difficult impregnation step from the shaping step. Thus, the degree of automation and the production rate can be increased [8]. There are two main approaches to manufacture semi-finished products (cf. Fig. 1).

Fig. 1: Impregnation of fibre reinforced thermoplastics [5]

Fully impregnated semi-finished products already are consolidated composites. Ideally, all fibres are completely wetted by the matrix. Hence, in subsequent production steps, only the material's surface needs to be melted and consolidated with other layers. On the contrary the fibre reinforcement and the matrix of semi-impregnated semi-finished products are not consolidated but in close proximity to each other [10, 11].

As thermoplastic matrices exhibit a considerably higher viscosity ($\eta_{TP} = 200\text{-}5,000 \text{ Pa s}$) than thermoset matrices ($\eta_{TS} = 0.2\text{-}10 \text{ Pa s}$) impregnation with a molten thermoplastic is a challenging procedure [5]. Only if all individual filaments of the fibre bundle are fully covered with matrix coating the composite will show high-performance characteristics. Thus, a uniform wetting of the single fibres is the main issue. Different methods, such as film stacking, powder impregnation, solution impregnation, hot melt coating and hybrid structures have been developed to resolve the problem of high viscosity. The impregnation techniques differ by the infiltration length of the matrix system (cf. Fig. 2).

Fig. 2: Infiltration length of thermoplastic semi-finished products [12]

Film-Stacking

The most common impregnation technique for continuous fibre reinforced thermoplastics is the so called film-stacking. It is the standard technology for producing organic sheets in a hot press [5]. In this process, a fibre reinforcement layer or a two dimensional textile structure (woven fabrics, knitted fabrics, non-crimp fabrics) lies between two thermoplastic matrix layers. Both components are stacked atop each other to get the desired thickness of the composite. The alternating arrangement of textile and polymer layers reduces the infiltration length during impregnation and consolidation.

When heat and pressure are applied, the thermoplastic component melts and impregnates the fibre reinforcement. This procedure can be realized either in a continuous or discontinuous way. The desired fibre-matrix-ratio is determined by the number of used layers. Stacking of both components leads to inhomogeneous polymer distribution. Therefore, relatively high consolidation pressures and times are needed [13]. In Fig. 3 the schematic set up of the film-stacking technique as well as the impregnation of the reinforcement material is illustrated. This method can only achieve medium impregnation qualities [14].

Fig. 3: Film-stacking [14]

Powder Impregnation and solution impregnation

In this impregnation technique the polymer is in powder form (wet or dry powder). In order to get a uniform coating the particle size should match the fibre diameter [5]. Both, fibres as well as two dimensional semi-finished products such as woven fabrics or mats can be impregnated. After the application of the thermoplastic powder the semi-finished products are subjected to a heating device

(e.g. furnace, radiant heating device, double belt press) which melts the thermoplastic powder. Depending on the operating process pressure the polymer will partially or completely enter the reinforcement structure. In Fig. 4 a partial wetting of the reinforcement structure by powder impregnation is shown.

The application of the thermoplastic polymer powder can take place in either an impregnation bath (whirling bath or a polymer solved in a liquid) by direct applying or electrostatic bonding [14]. The powder is dispersed in an air stream which simultaneously spreads the fibre bundle [15]. Hence the powder is distributed evenly on the single fibres. However, preparing the fine thermoplastic powder is expensive and the spherical shape ability, also known as drapability, is lost [14, 16].

Another approach to impregnate fibre reinforcements with highly viscous thermoplastic matrix is the solution impregnation. Lowering the viscosity of the polymer solution enables wetting of fibres and textile fabrics [17]. Fibres or textile semi-finished products in form of woven fabrics can be pulled through the polymer solution. This technique is primarily suitable for amorphous thermoplastics such as PEI because many semi-crystalline thermoplastics are difficult to solve [5].

However, remaining solvent residues in the semi-finished product impairing the composite's quality are unfavourable. In addition, vaporizing of the solvent may lead to air pockets and a rough surface (cf. Fig. 4) [18]. A subsequent high pressure and high temperature consolidation is therefore needed to improve the composite's quality. Moreover preventing the release of hazardous materials into the environment requires substantial technical effort [19].

Fig. 4: Powder impregnation and solvent impregnation [14]

Hot melt impregnation

Prepregs are often manufactured by hot melt impregnation which is similar to the solution impregnation technique. A fibre tow is unwound from a feed spool, guided through a resin bath and wound up on a take-up roll [20]. A key factor for a uniform impregnation of the filaments is a constant bath temperature [21]. The fibre tow is usually wrapped around stationary bars placed in the resin bath to increase the dwell time and squeeze the resin into the bundle [20, 21]. Finally, the fibres pass through a die that consolidates the wetted fibres [21].

In another method the fibre bundle is guided over a porous roll [5]. A flow channel supplies the fibres with a constant flow of liquid matrix. The matrix then solidifies resulting in high quality prepregs. In Fig. 5 the hot melt impregnation technique with the porous roll is illustrated. However, producing prepregs via hot melt impregnation is time consuming [22].

Fig. 5: Hot melt impregnation with porous roll

Hybrid fabrics and hybrid yarns

In addition to the techniques mentioned above, there are other methods to combine fibre reinforcement and matrix. One approach is to produce a hybrid fabric at which both components are fibres. In a hybrid fabric the fibre reinforcement and the matrix act as warp and weft thread respectively (Co-weaving). A schematic drawing of a hybrid fabric can be seen in Fig. 6. However, the benefits of good drapability, being free of solvents and the possibility to use economic, textile manufacturing processes are countered by complex matrix fibre production [14]. Moreover, the infiltration length is not reduced resulting in long cycle times in the composite production [23, 14].

Fig. 6: Hybrid fabric

Another way to combine reinforcement and matrix fibres are hybrid yarns. Two established processes are direct spinning and commingling. In the direct spinning process the reinforcing fibre and the matrix fibre are produced at the same time. Then both fibres are merged. Unfortunately this process is not suitable for carbon fibres. In the commingling process the reinforcement and matrix components are guided into a mixing box through two separate delivery godets (cf. Fig. 7). Additionally, the reinforcement fibres are opened via two spreading bars in order to break its sizing and to ease the mixing process. The air jet nozzle in the mixing box creates a turbulent flow profile so that entanglements in and along the filaments are generated [24]. Finally, the resulting hybrid yarn is taken off and wound up.

Fig. 7: Production of hybrid yarns - the commingling process

With the commingling process any desired material combinations with any required fibre volume content can be produced [24]. Like hybrid fabrics commingled yarns show a good drapability [25]. Both components are well mixed and the short infiltration length results in short cycle times [26]. Finally, consolidation of hybrid yarns requires lower processing pressures than other semi-finished products. The operating pressure is reduced from 20 to 8 bar. Though, the commingling process causes fibre fracture and the alignment of the hybrid yarn's components is not parallel which impairs the composite's properties.

Future Scope

In recent years a promising technology to overcome the high viscosity of thermoplastic matrices was developed. Most CFRTPs are produced from fully polymerized matrices. By introducing the fibres into the matrix prior to polymerization the high viscosity of the thermoplastic does not impede the full impregnation of the reinforcement fibres. Anionic polymerization of ϵ -caprolactam into polyamide-6 is the oldest and up to now the most developed way for reactive processing of thermoplastics through ring-opening polymerization [27]. The reaction is performed at 130-170 °C whereas the conversion can be obtained in a few minutes, depending on the amount and type of activator and initiator added to the ϵ -caprolactam [28, 27]. Since processing takes place below the polymer melting and crystallization point, polymerization and crystallization take place simultaneously [29, 30].

Until now, the focus of the industry was to apply the in-situ polymerization technology for large-scale production [31, 32]. The Institute for Textile Technology of the RWTH Aachen University applied together with an industry company partner for a public funded project with the aim of developing a small scale system which uses the in-situ polymerization technology to impregnate a carbon fibre based non-crimp fabric. The impregnated fabrics are wound up a spool, cut and consolidated into a semi-finished product (cf. Fig. 8). The system is characterized by its flexibility

and rapid adjustability. In particular, small and medium sized enterprises (SMEs) as well as research facilities will be able to try new material combinations easily.

Fig. 8: Production of semi-finished products via in-situ polymerization

Conclusion

Until today, thermoset matrices are the predominant resin systems used for fibre reinforced composites. Thermoplastics represent 80 % of the entire plastics market, but thermoplastic composites only represent 20 % of material used in current composites market [33]. However, since CFRTPs can be manufactured in short cycle times they offer great potential concerning automation and mass production. The low industrial distribution is partially related to the technically demanding impregnation process which increases the costs of the thermoplastic semi-finished products.

The in-situ polymerization is a promising approach to finally introduce CFRTPs to mass market applications. By using unpolymerized matrix the required pressure and temperature in the manufacturing process of thermoplastic semi-finished products is lowered. The small scale system for SMEs and research facilities will contribute to further expansion of market share.

Potential application areas are the aircraft industry respectively the transportation industry, industrial and medical applications as well as building industry applications. Examples of thermoplastic composite applications in the aircraft industry are: access panels and doors, engine cowlings, movable wing surfaces such as elevators, rudders, flaps and ailerons and spoilers [34, 35]. Furthermore, short and long carbon fibre reinforced thermoplastics can be used for secondary parts like diffusors or car seats and for load bearing parts in cars [36, 37]. Further possible applications are helmets, turbo machinery components, bicycle frames and wind turbine blades [34, 27].

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