MANUFACTURING OF BICOMPONENT FIBERS FOR THERMOPLASTIC COMPOSITES: A FEASIBILITY STUDY

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Abstract

We propose an alternative concept for hybrid intermediate materials used in high volume production of thermoplastic composites by coating individual glass filaments with a polymer sheath. Such bicomponent fibers provide a full wet-out while retaining the handling possibilities of fiber rovings. Dip-coating in-line with the glass fiber spinning process is suggested as a potential fabrication route and the feasibility of this method is assessed through theoretical considerations. Finally, a proof of concept for dip coating single filaments in dilute polymer solutions is given.

1. Introduction

Thermoplastic composites are attractive for high volume production schemes partly because they do not require time-consuming curing steps. In addition, they exhibit higher fracture toughness compared to thermoset composites and allow for multistep manufacturing methods where forming, re-forming and a variety of joining techniques – particularly welding – may be employed. The ability of the matrix to melt and re-solidify provides a high potential for recyclability and may therefore lead to more sustainable composites. Thermoplastic composites however require different processing approaches than thermoset composites due to the higher melt viscosities of thermoplastics, which makes impregnation-based methods difficult to use. This issue is usually overcome through the use of hybrid intermediate materials to reduce flow lengths needed for consolidation.

The state of the art in high volume production of continuous fiber-reinforced thermoplastic composites – especially for the manufacture of semi-structural components in the automotive industry – is stamp forming of preconsolidated materials [1]. However, preconsolidated materials, such as organosheets exhibit poor draping properties and their use is thus limited to simple part geometries. Organosheets or unidirectional tapes are also expensive in comparison to their constituents and as such struggle to position themselves in the low to medium budget markets. To be economically viable, preconsolidated materials must be produced in high volume and as such are only available in standard qualities; economical tailoring for specific applications is currently not feasible [1]. Flexible and more affordable hybrid intermediate materials are available in an unconsolidated form, such as commingled yarns, powder-coated and sheathed yarns or hybrid weaves. Previous investigations by Thomann et al. [2, 3] have shown that the use of commingled yarns for stamp forming has high potential, but due to the poor mingling quality of state of the art commingled yarns the time needed for full impregnation is not short enough to be viable

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for high volume production. As a rule of thumb, automotive manufacturers ask for cycle times of less than one minute when manufacturing composites to be competitive with metal forming techniques [1]. Low viscosity nonreactive and very low viscosity reactive thermoplastic polymer resins for use in thermoplastic resin transfer molding (T-RTM) are in development, but not yet ready for commercialization [4–6].

We propose an alternative concept to fill the gap between expensive preconsolidated materials and unconsolidated hybrids of low mingling quality by coating individual glass filaments with a thermoplastic sheath. The advantages of this morphology (Fig. 1) are firstly a full wet-out by definition and secondly reduced flow lengths. With regards to the latter point, flow lengths would be reduced to less than the diameter of a single fiber. Using these bicomponent fibers for the manufacture of textiles or nonwovens would create intermediate materials that can be consolidated in rapid stamp forming processes similar to those of organosheets, while retaining the drapeability of a textile.

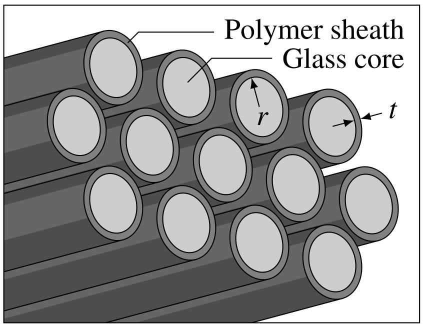

Figure 1. Schematic of an intermediate material made from bicomponent fibers, where r denotes the glass core radius and t is the polymer sheath thickness.

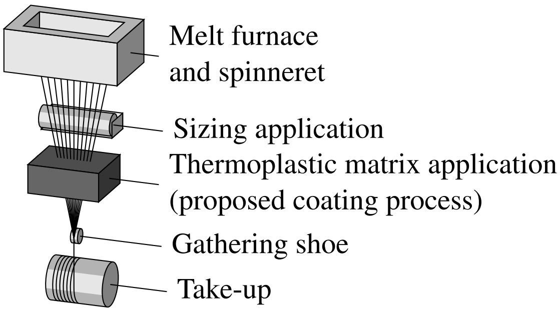

Figure 2. Schematic of a glass fiber spinning process with in-line coating for the manufacture of bicomponent fibers.

The potential of bicomponent fibers is however not limited to stamp forming of thermoplastic composites; since the combination of the constituent materials happens at the level of single filaments, the use of the resulting fibers in continuous processes – such as filament winding, tape laying, pultrusion or even fused deposition modeling – stands to reason.

2. State of the Art

Bi- and even multi-component fibers already exist in different sizes and material combinations [7]. Most applications have however been limited to pairings of similar materials which can be co-extruded due to similar processing temperatures – e.g. self-reinforced composites or optical glass fibers. The combination of a ceramic fiber core with a polymeric sheath for use in structural composites has so far only been proposed by Reifenhäuser GmbH & Co. via a 2013 patent application [8]; however the patent only describes the product itself and lacks a proposal for a method of production. Experiences were made by Owens Corning, who filed a patent in 1997 describing the production of glass fibers with a thermoplastic sheath through co-spinning in a rotary process [9]. This process however causes high degrees of warp, thus being useful for the production of insulating glass wool but not for directionally reinforced, thin composite laminates.

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3. Objective

The goal of this project is to design and demonstrate an economical process for fabricating bicomponent fibers. We believe this is most easily achieved by implementing the chosen coating method *in-line* with the glass fiber spinning process (Fig. 2). The advantage of incorporating the coating into the glass spinning process is that the glass filaments can be delivered to the coating stage in a separated arrangement, rendering any fiber spreading or separation steps unnecessary. As a result, necessary fiber handling equipment – such as spreaders, winders, spools and guides – can be minimized, thus also reducing the risk of fiber breakage due to processing.

In order to enable production in high volumes, a continuous coating technology such as dip coating is beneficial. In this feasibility study we examine the processing windows of industrial glass spinning processes and investigate the implications they have for a compatible in-line dip coating process. We study a glass fiber and low melt viscosity poly(ester-amide) (PEA) system as a first example.

4. Materials and Methods

E-glass fiber rovings with a mean diameter of 13 µm were used for this study. Poly(ester-amide) (PEA), an aliphatic segmented block co-polymer with low molecular weight, was provided by Dow Europe GmbH. Dilute solutions of PEA in chloroform were prepared for measurements and dip-coating trials.

Densities ρ of the solutions were calculated assuming no change in volume:

$$\rho\left[\mathrm{g\,cm^{-3}}\right] = \frac{1.63}{1.1 + 0.38 w_{\mathrm{PEA}}} \tag{1}$$

where w_{PEA} denotes the mass fraction of PEA in the solution. Dynamic viscosities of PEA-chloroform solutions of varying concentration were measured on a Mettler Toledo Rheomat RM180 using rotational cylinders. Surface tensions of different solutions were measured on a Krüss DSA100 using the pendant drop method.

Results of the dynamic viscosity and surface tension measurements are plotted in Fig. 3 and 4, respectively.

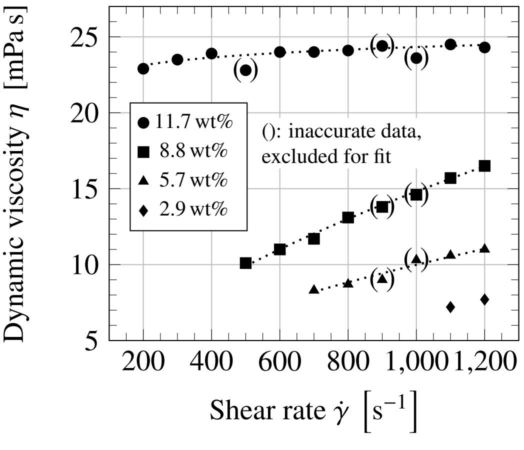

Figure 3. Dynamic viscosity of the PEA-CHCl$_3$ solutions. Dotted lines represent power law fits.

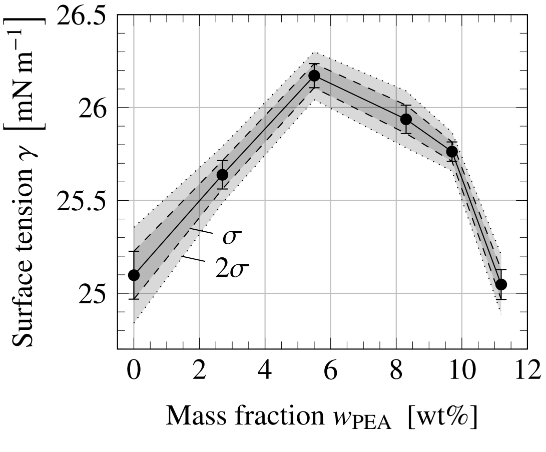

Figure 4. Surface tension of PEA-CHCl$_3$ solutions. σ denotes the standard deviation.

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5. Theory

Several theoretical models have been developed to describe both glass fiber spinning and the coating of fibers by liquid baths. Here, we limit our investigations to glass fibers with diameters that are most interesting for application in structural composites, i.e. 10 µm to 20 µm [10]. The following provides a theoretical study on the processing windows needed for both glass fiber spinning and dip coating to determine if any overlap exists that would facilitate the design of an in-line coating system into the glass spinning process.

5.1. Theoretical Process Conditions for Glass Fiber Spinning

The flow rate of glass at the spinneret is determined by the Hagen-Poisseuille law for laminar stationary flow through a tube with boundary conditions caused by atmospheric and hydrostatic pressure [11, 12]:

$$Q_v = \frac{p_i - p_o}{R} \underset{\substack{p_i=\rho g h + p_{atm} \\ p_o=p_{atm}}}{=} \frac{\rho_g g h}{R} \tag{2}$$

where Q_v denotes the volumetric flow rate, p_i and p_o are the pressure at the in- and outlet respectively, g is the gravitational acceleration, ρ_g is the glass melt density, h is the height of the glass melt above the spinneret and R is the tube's flow resistance. Assuming a purely cylindrical nozzle without a tapered entrance or counterbore, the flow resistance is [11]:

$$R = \frac{32}{\pi} \eta_g \frac{L}{d^4} \tag{3}$$

where η_g is the glass melt viscosity, L is the inner length of the nozzle and d its inner diameter. The mass flow rate Q_m at the winder is simply the product of the fiber fineness Tt and the take-up velocity v [12]. Inserting the definition for fiber fineness and comparing with Eq. 2 for mass conservation gives:

$$Q_m = Tt\, v = \rho_g \pi r^2 v \overset{!}{=} \frac{\rho_g^2 g h}{R} \tag{4}$$

Solving Eq. 4 for the take-up velocity and assuming the limits for η_g, d and L mentioned in section 3 as well as $\rho_g = 2500\,\mathrm{kg\,m^{-3}}$ and $h = 90\,\mathrm{mm}$ [12] results in a processing window from $1.15\,\mathrm{m\,s^{-1}}$ to $1078\,\mathrm{m\,s^{-1}}$ for fiber diameters in the range of 10 µm to 20 µm. Note that further extension of these limits is possible by varying h or by accounting for more complex nozzle geometries [11].

Table 1 gives an overview of typical process conditions in industrial glass spinning.

5.2. Theory of Dip Coating

The coating of a glass fiber can be approximated as the steady-state dip-coating of a cylindrical substrate (for intermediate withdrawal speeds), which has been modeled by Landau and Levich [16] and by Derjaguin [17] as:

$$h = 1.34 r Ca^{\frac{2}{3}} \quad \text{with } Ca = \frac{\eta v}{\gamma} \tag{5}$$

where h denotes the final coating thickness, r is the core fiber radius, Ca is the (dimensionless) capillary number, η is the fluid viscosity, v is the steady-state withdrawal velocity and γ is the surface tension of the liquid.

An extension of this model is necessary when dealing with: (i) higher withdrawal speeds – where intertial effects have a higher influence; (ii) non-Newtonian fluid behavior – which is the case for various thermoplastic melts and solutions [18]; or (iii) when the assumptions of an infinite bath and axial symmetry are

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Table 1. Typical process windows in industrial glass melt-spinning.

Filament diameter [13]	3 µm to 25 µm
Filament diameter for use in textiles [14]	< 13 µm
Spinning temperature [10, 13]	1200 °C to 1500 °C
Nozzle diameter [11, 13, 14]	1 mm to 2.5 mm
Nozzle length [11, 13, 14]	2 mm to 6 mm
Take-up speed (possible range) [11, 13]	$8\,\mathrm{m\,s^{-1}}$ to $83\,\mathrm{m\,s^{-1}}$
Take-up speed (frequently used) [10, 11, 14]	$40\,\mathrm{m\,s^{-1}}$ to $60\,\mathrm{m\,s^{-1}}$
Glass melt viscosity for successful melt-spinning* [11]	50 Pa s to 100 Pa s
*Corresponding temperature for E-glass [15]	1240 °C

heavily violated. Tallmadge proposed more advanced models for dip-coating from non-Newtonian fluids, including the axisymmetric case of fiber withdrawal [19, 20]. The equation for withdrawal velocity in the case of a power law fluid reads [21]:

$$v = \left[1.09\left(\frac{3}{2n+1}\right)(DC_m)^{\frac{n+2}{2n}} + \left(G\sqrt{2Y}\right)^{\frac{n+1}{n}}\right]\gamma\left[\frac{1}{K}(\rho g\gamma)^{\frac{1-n}{2}}\right]^{\frac{1}{n}} \tag{6a}$$

with

$$C_m = \frac{3.36\,(SG)}{1+3.36\,(SG)} + \frac{1}{2\,(SG)} \tag{6b}$$

$$D = h\left(\frac{\rho g}{\gamma}\right)^{\frac{1}{2}} \tag{6c}$$

$$S = 1 + \frac{h}{r} \tag{6d}$$

$$Y = S^2 \ln S - 0.5\left(S^2 - 1\right) \tag{6e}$$

$$G = r\left(\frac{\rho g}{2\gamma}\right)^{\frac{1}{2}} \tag{6f}$$

where C_m denotes the meniscus curvature, D, S, Y and G represent dimensionless parameters, K is the power law consistency index and n is the power law exponent:

$$\eta = K\dot{\gamma}^{n-1} \tag{7}$$

Eq. 6 is written in the centimeter-gram-second system of units. Accounting for the withdrawal from a polymer solution, the relation between the immediate coating thickness h and the desired fiber volume fraction v_f reads:

$$\frac{\frac{1}{v_f} - 1}{\left(1+\frac{h}{r}\right)^2 - 1} = \frac{\rho}{\rho_p} w_p \tag{8}$$

where ρ_p and w_p denote the density and mass fraction of the dissolved polymer. Eq. 6–8 are employed for the presented feasibility study.

Fitting the η–$\dot{\gamma}$ curves in Fig. 3 with Eq. 7, interpolating the surface tension data in Fig. 4 for PEA mass fractions of 5.7 wt%, 8.8 wt% and 11.7 wt% and inserting this material data in Eq. 6 and 8 together with Eq. 1 yields the necessary withdrawal velocities for the fabrication of bicomponent fibers with respect to

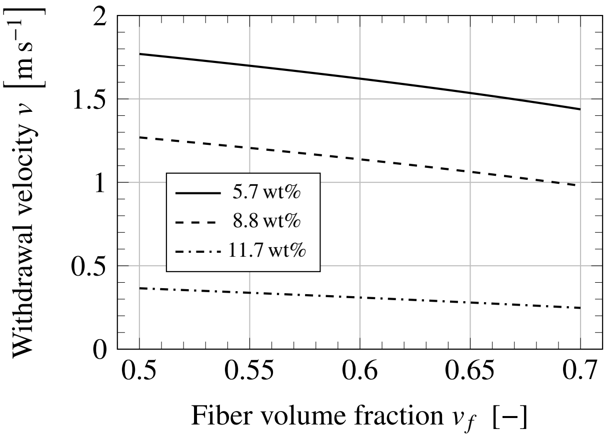

Figure 5. Necessary withdrawal velocities for the fabrication of bicomponent fibers using dip-coating from PEA-CHCl$_3$ solutions, calculated using Tallmadge's model for power law fluids [19, 20].

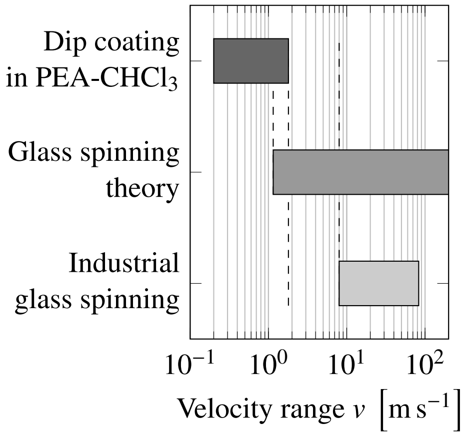

Figure 6. Comparison of processing windows of industrial glass spinning, glass spinning in theory and dip coating in PEA-CHCl$_3$ solutions.

a given fiber volume fraction (Fig. 5). In this case, calculations were carried out for glass fiber radii r ranging from 5 µm to 10 µm; the influence on the results is however negligible (< 0.017 %).

The theoretical study suggests that the use of continuous dip-coating allows for processing speeds on the order of $\sim 1\,\mathrm{m\,s^{-1}}$ (Fig. 6). This is one order of magnitude lower than the common take-up speed in commercial glass fiber spinning; however the calculations on mass balance in fiber formation suggest that spinning can be slowed down enough for the two processing windows to overlap. This overlap has considerable potential to become larger when considering (i) alternative nozzle geometries in the spinneret, which would affect the flow resistance R; (ii) additional tuneability through the height h of the glass melt, which would alter the hydrostatic pressure above the spinneret and thus the mass flow; (iii) the fact that the dilute PEA-CHCl$_3$ solutions considered herein exhibit a shear-thickening effect, whereas a polymer solution which shows shear-thinning [18] would allow for higher withdrawal velocities; and (iv) when specifically optimizing the coating procedure for higher speeds.

6. Proof of Concept

To prove the effectiveness of dip coating as a potential coating process, single glass filaments of finite length were isolated from a roving and drawn through a steel loop immersed in a reaction tube filled with PEA-CHCl$_3$ solutions of different concentrations at velocities ranging from $0.1\,\mathrm{m\,s^{-1}}$ to $0.7\,\mathrm{m\,s^{-1}}$. The resulting bicomponent fibers were observed using scanning electron microscopy (SEM) (Fig. 7 and 8). In Fig. 8, the electron beam was focused on a single spot for a few minutes in order to raise its temperature and burn off the polymer sheath, to reveal the underlying glass filament.

Fig. 7 and 8 prove that the coating of glass filaments with a dilute PEA-CHCl$_3$ solution is indeed possible. A variation of the polymer concentration does not only affect the flow regime but apparently also results in a different coating quality with respect to surface smoothness (Fig. 7). Trials using a solution with a mass fraction of 10.5 wt% have shown that coating thicknesses in the range of ~ 1.4 µm (on a glass fiber of 13 µm in diameter) can be achieved, resulting in fiber volume fractions of 52 % to 88 %. As the fiber volume content is very sensitive to changes in coating thickness, it is evident that accurate control of process parameters – i.e. the withdrawal velocity and homogeneity of the solution – is crucial.

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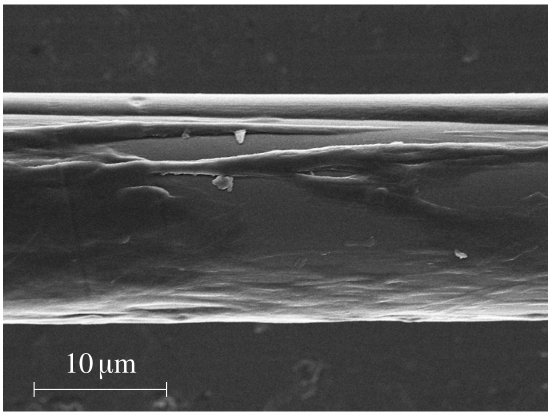

Figure 7. Morphology of a bicomponent fiber (w_{PEA} = 14.2 wt%).

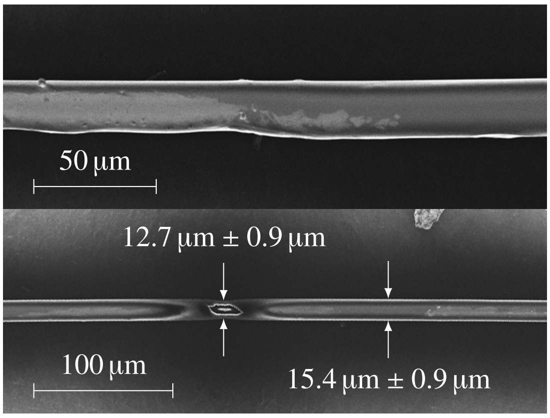

Figure 8. Morphology of a bicomponent fiber (w_{PEA} = 10.5 wt%) (top) and burnt polymer sheath revealing the glass core (bottom).

7. Conclusion

We have shown that the fabrication of bicomponent fibers is possible through dip-coating of glass filaments in a dilute polymer solution and that fiber volume fractions in a range suitable for the production of composites can be realized. Theoretical considerations suggest that continuous dip-coating – under the assumptions of Tallmadge's theory – can be implemented in-line with glass fiber spinning, thus rendering the need for fiber spreading techniques obsolete. Whether the presented processing regime is fast enough for a commercially viable production remains to be shown; corresponding measures for a potential increase in output volume have been outlined. Further investigations with regards to continuous processing for the manufacture of bicomponent fibers and the characterization of their behavior in stamp forming are essential for the advancement of this technology.

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