Effect of the water absorptive capacity of reinforcing fibers on the process ability, morphology, and performance characteristics of composites produced from polyfurfuryl alcohol

Katharina Resch-Fauster, Jovana Džalto, Andrea Anusic and Peter Mitschang

*Materials Science and Testing of Polymers, Montanuniversität Leoben, Leoben, Austria; †Institute for Composite Materials, Manufacturing Science, Kaiserslautern, Germany

ABSTRACT

Some matrix polymers, such as polyfurfuryl alcohol (PFA) generate water during the processing of fiber-reinforced polymer composites which slows down the process speed and may adversely affect the overall material properties. In this paper, the effect of the water absorbance characteristics of reinforcing fibers on the process ability of PFA composites at short cycle times (industrial processing) is investigated and evaluated. Natural and synthetic fiber types which exhibit a high, medium, and low water absorbance capacity as well as different textile architectures are compared. The processing-induced composite morphology is assessed and correlated with the material’s mechanical properties. The results reveal a high potential of hydrophilic natural fibers for significantly reducing the processing time while maintaining the overall performance characteristics of PFA composites.

Introduction and scope

In recent years, composites based on renewable resources are becoming increasingly interesting/important as economic and ecological alternative to conventional composites produced from synthetic fibers and petrochemical-based matrix materials. In the employment of natural fibers, much effort has been directed toward the development of matrix thermosets based on renewable resources for high-performance composites. In this regard, polyfurfuryl alcohol (PFA), also referred to as furan resin, represents a promising, highly ecological (carbon neutral) and fully non-toxic material. Furfuryl alcohol is produced by digesting hemicellulose-rich agricultural waste into furfural, followed by catalytic hydrogenation. Elevated temperatures along with acidic conditions induce further polymerization/cross-linking of furfuryl alcohol into PFA by cationic condensation reactions. In terms of mechanical characteristics, PFA is competitive to conventional epoxy or phenolic resins. However, to reduce the viscosity and thus to enhance the process ability, water is applied as a solvent. The high amounts of (initial (solvent) and reaction (polycondensation)) water require a distinct process and curing control in order to avoid foaming, other defect formation or incomplete cure of PFA and thus adverse effects on its overall performance properties. Consequently, in academic composites processing, the cross-linking of PFA is done either by gradually and slowly increasing the processing temperature from 20 to 80 °C or isothermal/stepwise at temperatures between 90 and 160 °C so far. In both cases, the processing times range between 2 and 8 h. However, in many sectors of industry (e.g. automotive suppliers) merely materials which are capable for efficient serial production (i.e. short cycle times of several minutes maximum) are applied. Hence, in order to increase the market share of PFA composites, the fast producibility of a high performance material is crucial. Besides optimizing the process control, the manufacturing of PFA composites at short cycle times may be enhanced by adding components which absorb and release water during the processing. In this regard, the application of natural fibers, which are inherently hydrophilic, represents an interesting option. Thus, this study aims at evaluating the effect of the water absorptive capacity of reinforcing fibers on the process ability at short cycle times, the resulting morphology and hence the performance characteristics of PFA composites. Fibers exhibiting no/a little, a medium, and a high water absorptive capacity as well as different textile architectures are compared. For reference purposes, the obtained material characteristics are compared to properties of composites, which were produced by using the same fibers and textiles but a resin, which does not generate or release water during curing (epoxy resin...
Comprehensive processing–structure–property relationships are established and routes for optimizing the PFA composites formulation and an efficient process control are derived.

**Experimental**

**Materials**

The PFA BioRez 080101 was supplied by TransFurans Chemicals bvba (Geel, BE). It is a self-crosslinking resin formulation, which is diluted in water (20–22 wt.%) and exhibits a weight ratio of 78–80% furfuryl alcohol prepolymer. The viscosity at 20 °C ranges between 100 and 200 Pa s. The reference EP (resin Epikote RIMR 135; hardener Epikure RIMH 134, mixing ratio 10:3) was supplied by Hexion Specialty Chemicals GmbH (Duisburg, DE). The viscosity at 20 °C ranges between 0.5 and 1 Pa s.

The applied reinforcement fibers include E-glass (little/no water absorption) as well as rayon and hemp fibers (hydrophilic natural and bio-based fibers, respectively). The natural fibers were selected according to preliminary water sorption tests involving hemp, flax, jute, kenaf, sisal, and rayon fibers, whereas hemp and rayon fibers showed the highest and lowest water uptake, respectively. The basic chemical and physical fiber characteristics along with details as to fiber grade, textile type, and supplier are summarized in Table 1. The initial moisture content was determined by thermo-gravimetric analysis (TGA). Thermograms were recorded on a Mettler Toledo TGA/DSC (Schwerzenbach, CH) in the temperature range between 25 and 200 °C (nitrogen atmosphere). The heating/cooling rate was 10 K/min. Seventy microliter alumina (aluminum oxide) crucibles were used. The sample mass was 8 ± 1 mg. The number of replicate measurements was two to three. The surface morphology and apparent fiber diameters (micrographs of fiber cross section) were analyzed by Scanning Electron Microscopy (Vega 3, Tescan Brno s.r.o, Brno, CZ). Different to hemp fibers, which are grown naturally and hence may differ in the chemical component concentration and fiber geometry with the growing condition, rayon is a synthetic product which is produced from bio-based components (wood–cellulose).

**Processing**

In order to assure a consistent textile impregnation, the viscosity of PFA was reduced by adding 20 wt.% ethanol. The textiles were impregnated in an impregnation bath, whereas an absolute furfuryl alcohol prepolymer ratio of 50 wt.% (resulting theoretical fiber weight ratio of 50 wt.%; no consideration of the weight loss due to curing) was ascertained. Therefore, if x g furfuryl alcohol prepolymer was required (i.e. the natural fiber weight is x g), x/0.8 g furfuryl alcohol prepolymer and 0.2x/0.8 g ethanol were added to the solution. The pre-impregnated textiles were stored at a temperature ranging between 16 and 20 °C for 24 h. Weight measurements revealed a storage-induced weight loss, which was attributed to an evaporation of ethanol and water. However, the prepreg weight still exceeded the desired furfuryl alcohol prepolymer ratio of 50 wt.%. Since ethanol is highly volatile, the excess weight was attributed to residual water. The water concentration within the prepreg prior to processing ranged between 10 and 18 wt.% (according to weight balance before and after storage).

The PFA prepregs were processed to composite panels (dimension of 340 × 480 × 1–2 mm) by isothermal compression molding in a lab-scale hydraulic press at a temperature of 155 °C, a pressure of 10 bar and a processing time of 300 s (standard process; number of textile layers given in Table 1). Since natural fibers are thermally stable up to temperatures of 180 °C, the selected processing...
temperature is assumed not to affect either their water absorption characteristic or their mechanical properties. The male and female dies were not hermetically sealed, so that water vapor could evaporate slowly when the mold was closed. Two distance bars enhanced the isochoric compression of the prepregs and predefined the thickness and density of the resulting composites. The detailed process parameters are outlined in Fig. 1. In the beginning, the mold was opened (lid lifted) for four times (after 15 s each; Fig. 1 left) in order to release any residual initial water and/or reaction water of the PFA polycondensation.

To investigate the effect of the mold-opening and hence the water evaporation quantity on the resulting composite characteristics, additional PFA hemp fabric panels were produced by opening the mold only twice (after 15 and 30 s processing time; Fig. 1 right). Moreover, for reference purposes PFA rayon fabric panels were produced in a prolonged process according to the state of the art.8,9 Thus, isothermal curing at different temperatures and a pressure of 10 bar was done for 7.5 h in total. The applied processing time-temperature profile is presented in Fig. 2. The mold was not opened during processing.

For the production of reference panels based on EP, the fibers were impregnated with resin manually and afterwards processed by autoclave technology. Also in this case, the desired fiber weight ratio was 50 wt.%. The curing was done at a pressure of 25 bar (-1 bar in vacuum bag + 24 bar pressure) for 16 h at ambient temperature and subsequently for 5 h at 50 °C.

**Characterization**

**Water absorbance of natural fibers**

Prior to the water-sorption studies, the natural fibers were separated from the different textiles, dried at 80 °C for 24 h and afterwards exposed to standardized thermal environment (DIN EN ISO 291; 23 °C, rel. humidity 50%) for 24 h. The initial moisture content of the fibers is given in Table 1. The water absorbance was investigated by immersing the fibers in distilled water (ambient temperature) for up to 3000 min (fiber length: 50–70 mm; fiber weight: rayon separated from textile 100–200 mg, rayon separated from nonwoven 25–30 mg, hemp separated from textile 200 mg, hemp separated from nonwoven 150–200 mg). The sampling was done after 0.25, 0.5, 0.75, 1, 5, 10, 60, 120, 1000, and 3000 min. The fiber weight was analyzed immediately after the sampling, whereas water drops on the fiber surface were removed by absorbent paper in a quick procedure and water that was trapped between the fibers was thoroughly wiped away with print-out paper (paper which is minimal absorbent) prior to the measurements. Nevertheless, it was unavoidable that some water remained trapped between the single fibers. However, these little amounts of residual water do not falsify the principal water absorption ranges of the different fiber types as well as the observed trends.

The water absorption (WA) was determined according to Equation (1).

\[
WA_t = \frac{m_t - m_0}{m_0} \cdot 100 [%]
\]

where \(m_t\) is the fiber weight after the water immersion and \(m_0\) is the initial fiber weight (before the water immersion). The presented data are average of three measurements.

**Morphology and performance properties of composites**

The composite morphology was analyzed by light microscopy. Micrographs were recorded on an Olympus BX51 (Wien, AT) operating in reflectance mode. Appropriate cross sections were prepared by cutting the compression molded plates (saw Isomet 11-1180, Buehler USA, Lake Bluff, IL, US) followed by grinding and polishing on a grinding machine Phoenix Beta (Buehler USA, Lake Bluff, IL, US; grain sizes between 800 and 4000).

---

**Figure 1.** Processing parameters for the manufacturing of fiber-reinforced PFA composites; left: standard process; right: process with reduced mold opening quantity.
The densities of the composites were determined by analyzing the volume and the weight of the specimens. The fiber weight fraction of the specimens $\psi_{\text{Fiber}}$ was calculated according to Equation (2)

$$\psi_{\text{Fiber}} = \frac{AW_{\text{Textile}}}{AW_{\text{Composite}}}$$  \hspace{1cm} (2)

whereas $AW_{\text{Composite}}$ is the area weight of the composites and $AW_{\text{Textile}}$ is the initial textile area weight.\(^\text{20}\)

The resin weight fraction $\psi_{\text{Resin}}$ was calculated according to Equation (3).

$$\psi_{\text{Resin}} = 1 - \psi_{\text{Fiber}}$$ \hspace{1cm} (3)

The volume fractions of the fibers $\varphi_{\text{Fiber}}$ and the resin $\varphi_{\text{Resin}}$ were calculated according to Equations (4) and (5).

$$\varphi_{\text{Fiber}} = \frac{\rho_{\text{Composite}}}{\rho_{\text{Fiber}}} \cdot \psi_{\text{Fiber}}$$ \hspace{1cm} (4)

$$\varphi_{\text{Resin}} = \frac{\rho_{\text{Composite}}}{\rho_{\text{Resin}}} \cdot \psi_{\text{Resin}}$$ \hspace{1cm} (5)

The porosity content $\varphi_{\text{Porosity}}$ was determined according to Equation (6).

$$\varphi_{\text{Porosity}} = 1 - (\varphi_{\text{Fiber}} + \varphi_{\text{Resin}})$$ \hspace{1cm} (6)

The thermo-mechanical properties and glass transition temperatures ($T_g$) were characterized by dynamic mechanical analysis (DMA) on a DMA861e (Mettler Toledo GmbH, Schwerzenbach, CH). Rectangular specimens with dimensions of $30 \times 4 \times 1$–$2$ mm (thickness varied between plates) were cut to size using a Mutronic Diadisc 5200 (Mutronic Präzisionsgerätebau GmbH & Co. KG, Rieden, DE). The measurements were done in preferred direction. The DMA was carried out in tensile mode by applying a constant sinusoidal strain amplitude (the path length was determined for each composite type individually and ranged between 0.5 and 3 μm) at a frequency of 1 Hz. The gauge length was 19.5 mm (small tension clamp). Scans were run in a temperature range from $-10$ to $250$ °C at a heating rate of 2 K/min. The storage modulus ($E'$) was recorded as a function of temperature and curves were evaluated as to the glass transition temperature $T_g$ (onset temperature).

The tensile testing was performed according to DIN EN ISO 527-4/2/5 on a standard tensile testing machine (Zwick Z010, Zwick/Roell GmbH & Co. KG, DE) using pneumatic grips. Prismatic specimens with dimensions of $200$ mm $\times$ $25$ mm $\times$ $1$–$2$ mm were used. Prior to testing, the area weight and density of the specimens were evaluated. Stress–strain curves were recorded at standardized thermal environment (DIN EN ISO 291; 23 °C, 50% r.h.) by applying a crosshead speed of 5 mm/min. The strain was measured by classic displacement transducers with a displacement of 50 mm (free clamping length 150 mm). The Young’s modulus was evaluated as secant modulus in the elongation range between 0.05 and 0.25%. The presented data are average of five measurements.

**Results and discussion**

**Water absorbance of natural fibers**

In Fig. 3, the water absorbance of the fibers is plotted as a function of the exposure time in water. Cellulose and hemicellulose – the main components of both, rayon and hemp fibers – exhibit strongly polarized hydroxyl groups and are thus inherently hydrophilic and hygroscopic, respectively. Although the chemical composition of the investigated fiber types is similar (Table 1; the maximum difference in the total cellulose and hemicellulose fraction is 7%), the absorption of water is significantly higher for hemp fibers (separated from fabric: weight increase after 3000 min by 560%; separated from nonwoven: weight increase after 3000 min by 640%) than for rayon fibers (separated from fabric: weight increase after 3000 min by ~360%; separated from nonwoven: weight increase after 3000 min by ~300%). This is attributable to the existence of lumen in hemp fibers, which allows for the incorporation of additional liquid “free” water into the fibers once the cell wall is saturated. However, the initial slope of the curves and hence the water uptake rate is identical for both fiber types. The data scatter is primarily ascribable to the felting of fibers immediately after sampling, which complicated the removal of water which was trapped between the individual fibers. In general, no correlations between the initial moisture content (given in Table 1) and the water absorption capacity of the fibers are observable.

**Processing-induced structure and morphology**

Figure 4 displays the weight loss of pre-dried PFA (no solvent water) as a function of the exposure time in a vacuum oven at a temperature of 155 °C. The weight
whereas \( m_{\text{Prepreg}} \) is the weight of the wet prepreg prior to processing and \( m_{\text{Textile}} \) is the weight of the dry textile prior to impregnation. The parameter \( k \) was set to 2, since the weight of the consolidated composite panel should be twice the initial textile weight (i.e. theoretical fiber weight fraction of 50 wt.%).

In general, the weight loss of the composites decreases with an increasing water absorbance capacity of the reinforcing fiber (from glass to hemp) and ranges between 7.2 and 37.3%. Irrespective of the processing procedure, the overall weight loss of PFA rayon and PFA glass panels exceeds the theoretical weight loss (Table 2 and Fig. 4). For these composites, an extensive vaporization of water along with a significant spilling of resin (i.e. resin leaking from the mold) during opening the mold was observed. Thus, the differences between the detected and the theoretical weight loss are attributable to resin spill. The resin spill increased with a decreasing water absorbance capacity of the reinforcing fiber. Thus, it is assumed to be triggered by the flow of free water in the resin during molding on the one hand. On the other hand, the vaporization of water during opening the mold might sweep resin away. Generally, the weight loss is higher for composites produced from fabrics than for composites produced from nonwovens. Although the amount of reaction water is higher if the curing time is increased (Fig. 4), the weight loss is lowest for PFA rayon composites, which were produced in the prolonged process. A spilling of the resin was also ascertained in this process (although the mold was not opened), but the quantity was rather low. Thus, the detected weight loss is closer to the expected/theoretical weight loss due to the evaporation of fiber moisture and initial and reaction water in PFA.

The weight loss is lowest for PFA hemp composites whereas no significant difference between the applied textile types is ascertainable. However, the detected values are still higher than the assumed theoretical weight reduction induced by the evaporation of fiber moisture and initial and reaction water in PFA (Table 2 and Fig. 4). A decrease in the mold opening quantity further
Table 2: Processing-induced weight loss (polycondensation plus resin spill) of PFA composite panels compared to theoretical weight loss (polycondensation reaction); *no resin spill (i.e. resin leaking from the mold), but gathering of excess resin at the edges of the mold.

| Fiber          | Fabric       | Weight loss (%) | Nonwoven       | Weight loss (%) |
|----------------|--------------|-----------------|----------------|----------------|
|                | Theoretical  | Detected        | Theoretical    | Detected        |
| E-glass        | 2.2          | 37.3            | 35.4           | 2.2            |
| Rayon (standard process) | 5.1          | 27.7            | 22.6           | 6.7            |
| Rayon (prolonged process) | 5.1          | 16.3            | 11.2           | –              |
| Hemp (standard process) | 3.8          | 8.9             | 5.1*           | 4.8            |
| Hemp (reduced mold opening quantity) | 3.8          | 7.2             | 3.4*           | –              |

Figure 5. Fiber weight fraction of EP composites and PFA composites produced from different reinforcing fibers and textile architectures.

Figure 6 displays the volume fractions of the fiber, the resin and the pores in the EP and PFA composites. Irrespective of the fiber and textile type, the fiber volume fractions in PFA composites, which are manufactured by the standard process, range between 30.5 and 37.5 vol.%. The values correspond to the fiber volume fractions detected for the EP composites produced from non-woven, which vary between 33 and 40 vol.%. However, the fiber volume fractions in the EP composites produced from fabrics are higher and range between 44 and 51.5 vol.%. In contrast to the EP composites, all PFA composites which were manufactured by the standard process feature a high porosity (31–41 vol.%). A correlation between the processing-induced weight loss/resin spill and the degree of the panel porosity (and consequently the resin volume fraction) is observable: the porosity is lowest for PFA hemp and highest for PFA glass composites. Most likely, the porosity develops from
which is higher for nonwoven (lower packing density). The high porosity in the EP composites produced from hemp nonwoven is attributable to the low packing ability of the applied hemp nonwoven, which hindered a consistent impregnation of the textile with the EP resin. However, with PFA, the initial textile impregnation was excellent.

The observations as to the porosity correspond to the micrographs of the composites given in Fig. 7, which show numerous pores for PFA composites. Since the porous morphology of PFA composites produced from fabrics and nonwovens is similar, merely micrographs of PFA composites based on fabrics are displayed exemplarily. In the EP composites, the pores are merely discernible in the panels produced from hemp nonwoven (Fig. 8). The PFA composites produced from glass fabrics also exhibit numerous pores within the fiber bundles. In close proximity to the pores, the fibers are packed denser. For the PFA composites produced from rayon fabrics, a splitting of the fiber bundles (damage of the inherent bonding between the elementary fibers) is ascertainable.

The flow of significant amounts of free water during molding and/or from the fast vaporization of residual initial and reaction water during opening the mold, which generates voids. Since no effect of the mold opening quantity on the porosity and on the fiber and resin content is ascertainable (PFA hemp composites produced from fabrics), the highest vaporization-induced portion of voids might arise at the very beginning of the molding process. The porosity is lowest (22.3 vol.%) for PFA rayon samples produced from fabric which were cured by a slow and gradual polycondensation in the prolonged process. The associated increased overall resin volume fraction corresponds to the reduced processing-induced resin spill detected for this composite (Table 2). By trend – irrespective of the reinforcing fiber type – the composite porosity increases with an increasing packing density of the textile (i.e. higher porosity for fabric than for nonwoven). This indicates that the porosity is not only affected by the fiber's water absorbance capacity, but also by the efficient transfer of water from the resin to the fiber and thus by the single-fiber wetting, which is higher for nonwoven (lower packing density).

Figure 6. Volume fractions of fiber, resin, and pores in EP composites and PFA composites produced from different reinforcing fibers and textile architectures

Figure 7. Micrographs of PFA composites produced from fabrics
Compared to the samples which were produced in the standard process, the splitting of the fiber bundles is pronounced rather weakly for the samples which were produced in the prolonged process. Thus, most likely, the changes in the fiber bundle morphology are caused by the fast vaporization (initial and reaction) water during opening the mold. Since the effects are not observable for PFA composites produced from hemp fabric (moreover no effect of mold-opening quantity) it might be affected mainly by the fiber’s water absorption (additional absorbance of liquid free water in lumen of hemp fibers) and transfer (lumen yielding additional paths for water transport) characteristics. Deductive, the water sorption characteristics of the reinforcing fibers significantly affect the morphology of PFA composites.

The overall degree of cure of the PFA composites was not determinable by Differential Scanning Calorimetry (DSC) since the thermograms did not exhibit any post-curing reaction. However, the conversion of PFA in the natural fiber composites is deducible from the storage modulus-temperature curves which are displayed in Fig. 9 (representative curves). Due to the high porosity along with an irregular resin distribution, the PFA glass composites were not properly analyzable by DMA. Hence, the curves are not displayed. For all samples, the storage modulus decreases continuously with increasing temperature up to the glass transition region (ranging between 80 and 135 °C). A distinct drop (peak) in the storage modulus subsequent to the glass transition temperature, which is followed by an increase in the stiffness with further increasing temperature, indicates a post-curing of the PFA. Due to an increased mobility of the reactants after reaching the actual glass transition temperature of the partially cured material, a further cross-linking is initiated. The incomplete reaction is also reflected in a shift of the glass transition ($T_g$ of fully cured resin $\approx 160$ °C) to lower temperatures (80 °C). The post-curing is not ascertainable for PFA rayon samples which were produced in the prolonged process. For thermodynamic reasons (reaction), water must be removed in order to prevent an inhibition of the polycondensation reaction (principle of Le Chatelier). Consequently, the post-curing features in the DMA curves indicate an incomplete removal (absorbance or evaporation) of fiber moisture and initial and reaction water during the processing. This is also emphasized by the fact, that the post-curing is specifically pronounced for PFA samples produced from hemp fabric, which were manufactured by opening the mold merely twice. The findings correspond excellent to the reduced weight loss of PFA hemp panels as discussed above. Interestingly, both natural fiber types are able to absorb (and hence remove) the amounts of initial and reaction water (Fig. 3) in PFA in principle. Moreover, a distinct post-curing is discernible especially for the composites produced from fabrics. Hence, the reaction kinetics may be controlled to a large extent by an efficient transfer of water from the resin to the fiber and thus by single-fiber wetting, which is higher for nonwoven (lower packing density). A comparison...
characteristics between EP and PFA composites can be evaluated: the stiffness of the composites differs by 28 and 52% for hemp and rayon fiber reinforcement, respectively. Irrespective of the reinforcing fiber type, the tensile strength differs by ~47%. The results correspond to the processing-induced morphology as discussed above. Most likely, the differences between the hemp and the rayon fiber reinforcement are ascribable to the higher porosity of the composites based on rayon. Moreover, the splitting of the fiber bundles in the PFA rayon composite may adversely affect the load transmission characteristics and hence the mechanical performance. Interestingly, the differences in the composites morphology are merely reflected in the Young’s modulus and not in the tensile strength.

A prolonged processing enhances the mechanical performance of the PFA rayon composites: the Young’s modulus and the tensile strength differ from the EP rayon samples merely by 21 and 35%, respectively. On the one hand, this is attributable to an increase in the fiber volume fraction by 13% and a decrease in the overall porosity by 16% due to the reduced processing induced resin spill. On the other hand, the splitting of fiber bundles and hence, the number of voids is minimized by the prolonged processing, which might enhance the load transmission characteristics.

The degree of cure of PFA resin (i.e. mold opening quantity, compare DMA results presented in Fig. 9) does not affect the Young’s modulus and tensile strength of PFA hemp composites based on fabrics. This also accords with the overall composite morphology, porosity and fiber volume fraction, which is not altered by reducing the mold-opening quantity.

Regarding the fabrics, the Young’s modulus and tensile strength are higher for EP than for PFA composites, which can be attributed to the higher fiber volume fraction of the composites based on epoxy resin (Fig. 6). Since the fiber volume fractions are equal for both EP composite types and both PFA composite types, which were produced in the standard process, respectively, the relative differences in the mechanical performance characteristics between EP and PFA composites can be evaluated: the stiffness of the composites differs by 28 and 52% for hemp and rayon fiber reinforcement, respectively. Irrespective of the reinforcing fiber type, the tensile strength differs by ~47%. The results correspond to the processing-induced morphology as discussed above. Most likely, the differences between the hemp and the rayon fiber reinforcement are ascribable to the higher porosity of the composites based on rayon. Moreover, the splitting of the fiber bundles in the PFA rayon composite may adversely affect the load transmission characteristics and hence the mechanical performance. Interestingly, the differences in the composites morphology are merely reflected in the Young’s modulus and not in the tensile strength.

A prolonged processing enhances the mechanical performance of the PFA rayon composites: the Young’s modulus and the tensile strength differ from the EP rayon samples merely by 21 and 35%, respectively. On the one hand, this is attributable to an increase in the fiber volume fraction by 13% and a decrease in the overall porosity by 16% due to the reduced processing induced resin spill. On the other hand, the splitting of fiber bundles and hence, the number of voids is minimized by the prolonged processing, which might enhance the load transmission characteristics.

The degree of cure of PFA resin (i.e. mold opening quantity, compare DMA results presented in Fig. 9) does not affect the Young’s modulus and tensile strength of PFA hemp composites based on fabrics. This also accords with the overall composite morphology, porosity and fiber volume fraction, which is not altered by reducing the mold-opening quantity.

Regarding the nonwoven, the fiber volume fractions of the composites based on EP and PFA are similar, which allows for comparing their absolute mechanical characteristics. The Young’s modulus is significantly higher for PFA hemp composites than for EP hemp composites. This is attributable to the comparatively high porosity of EP hemp composites. Nevertheless, despite its porosity,
the tensile strength of the EP hemp composite exceeds the tensile strength of the PFA hemp composite. In terms of rayon fiber reinforcement, the Young’s modulus and the tensile strength are higher for EP than for PFA composites. The differences are prevalently ascribable to the lower porosity of the composites based on EP. Compared to the fabric reinforcement, the differences in the Young’s modulus between the PFA hemp and PFA rayon composites produced from nonwoven are pronounced weaker. The tensile strength of PFA composites produced from nonwoven is not at all affected by the applied fiber type. The observations correspond to the porosity data, which – in contrast to the porosity of the composites produced from fabrics – differ merely marginal between composites produced from hemp nonwoven and rayon nonwoven.

Conclusions and outlook
In this study, the effect of the water absorbance characteristics of the reinforcing fibers on the process ability of PFA composites at short cycle times was evaluated. The investigation revealed that the hydrophilicity of natural fibers enhances the processing and manufacturing of high-performance PFA composites.

In general, the produced PFA composites exhibited a significant porosity, which naturally adversely affected their mechanical performance characteristics. The porosity is attributable to the flow of free water in the resin during molding and to the vaporization of water during the mold opening (initial water in PFA as well as reaction water of PFA polycondensation), which generates voids. For composites produced from reinforcing fibers, which exhibit a low or no water absorbance capacity, the vaporization of water during the mold opening also caused a significant resin spill as well as – in the case of fabrics – changes in the fiber bundle morphology (splitting of the fiber bundles). To some extent, the porosity, resin spill, and splitting of the fiber bundles were reduced by significantly extending the processing time along with gradually increasing the molding temperature (uneconomic process control). However, the overall degree of porosity was found to be dependent on two main aspects:

- the water absorbance capacity of the reinforcing fiber (porosity increases with decreasing water absorbance capacity of the fiber)
- the efficient transfer of water from the resin to the fiber and thus the single-fiber wetting/textile architecture (resin spill and porosity are higher by applying fabrics than by applying nonwovens)

The outcomes indicate that the porosity/morphology of PFA composites is stronger affected by the material composition than by the processing time and process control. Consequently, the fast producibility of high-performance PFA composites is given in principle, provided that the fiber reinforcement is appropriate and tailored for PFA resin. Thus, the next step will be a systematic optimization of PFA composites in terms of natural fiber type, textile architecture, and fiber weight fraction. The aim is to simultaneously and considerably minimize the porosity (reduction in void formation) as well as the processing times compared to the prolonged process according to the state of the art. In this regard, also the addition of super absorbent polymers (i.e. polymers which are able to absorb and retain high amounts of water, such as polymeric hydrogels) to the composite represents an interesting option in order to reduce the spill of resin and consequently the formation of voids in PFA composites produced from fibers which exhibit a low water absorbance capacity.

Acknowledgments
The authors are grateful to Erhard Natter and Uwe Schmitt (both Institut für Verbundwerkstoffe GmbH, Kaiserslautern, DE) for composite processing, to Walter Rath (Materials Science and Testing of Polymers, Montanuniversitaet Leoben, Leoben, AT) for microscoping and to Hans Hoydonckx (TransFurans Chemicals bvba, Geel, BE) for supplying PFA resin.

Disclosure statement
No potential conflict of interest was reported by the authors.

References
1. K. L. Pickering, M. G. Aruan Efendy and T. M. Le: ‘A review of recent developments in natural fibre composites and their mechanical performance’, Compos. Part A, 2016, 83, 98–112.
2. E. Zini and M. Scandola: ‘Green composites: an overview’, Polym. Compos., 2011, 32, (12), 1905–1915.
3. J. Summerscales, N. P. J. Dissanayake, A. Virk and W. Hall: ‘A review of best fibres and their composites. Part I’, Compos. Part A, 2010, 41, 1329–1335.
4. K. Resch-Fauster, A. Klein, S. Lloret Pertegasand R. Schledjewski: ‘Design and manufacturing of high performance green composites based on renewable materials’, in Handbook of composites from renewable materials, Vol. 2. Design and Manufacturing, 2017, Hoboken, NJ, Wiley, 1–24. ISBN: 978-1-119-22365-8.
5. H. E. Hoydonckx and W. M. Van Rijn: ‘Application of novel furan resins in composites’, JEC Compos. Mag., 2008, 38.
6. R. J. Crossley, P. J. Schubel, A. Stevenson and M. Moreira: ‘The development and processing of a sustainable fully bio derived polysaccharide composite’, Proc. ECCM15 – 15th Eur. Conf. on ‘Composite materials’, Venice, IT, Jun 24–28, 2012.
7. E. L. Arnold, B. M. Weager, H. Hoydonckx and B. Madsen: ‘Next generation sustainable composites: development and processing of furan-flax biocomposites’, Proc. ECCM17 – 17th Int. Conf. ‘Composite Materials’, Edinburgh, UK, July 27–31, 2009.
8. N. Guigo, A. Mija, L. Vincent and N. Birrazzouli: ‘Eco-friendly composite resins based on renewable biomass resources: Polysaccharide alcohol (lignin) thermosets’, Eur. Polym. J., 2010, 46, 1016–1023.
9. G. Marsh: ‘Composites that grow in fields,’ Reinf. Plast., 2008, 52, 16–22.
10. T. Pohl, M. Bierer, E. Natter, B. Madsen, H. Hoydonckx and R. Schledjewski: ‘Properties of compression moulded new fully biobased thermoset composites with aligned flax fibre textiles,’ Plast. Rubber Compos., 2011, 40, 294–299.
11. R. Crossley, P. Schubel and A. Stevenson: ‘Furan matrix and flax fibre as a sustainable renewable composite: mechanical and fire-resistant properties in comparison to phenol, epoxy and polyester,’ J. Reinf. Plast. Compos., 2013, 33, 58–68.
12. S. Goodman and H. Dodiuk: ‘Handbook of thermostet plastics,’ 2013, Amsterdam, Elsevier.
13. H. E. Hoydonckx, W. M. Van Rhijn, W. Van Rhijn, D. E. De Vos and P. A. Jacobs ‘Furfural and derivatives. Ullmann’s Encyclopedia of Industrial Chemistry,’ 2007, Weinheim, Wiley-VCH.
14. N. Guigo, A. Mija, L. Vincent and N. Sbirrazzuoli: ‘Chemorheological analysis and model-free kinetics of acid catalysed furfuryl alcohol polymerization,’ Phys. Chem. Chem. Phys., 2007, 9, 5359–5366.
15. H. Dekaa, M. Misraa and A. Mohantya: ‘Renewable resource based “all green composites” from kenaf biofiber and poly(furfuryl alcohol) bioresin,’ Ind. Crops Prod., 2013, 41, 94–101.
16. G. Riveroa, V. Pettarina, A. Vázquez and L. B. Manfredia: ‘Curing kinetics of a furan resin and its nanocomposites,’ Thermochim. Acta, 2011, 516, 79–87.
17. U. L. De Vergara, M. Sarrionandia, K. Gondra and J. Aurrekoetxea: ‘Impact behaviour of basalt fibre reinforced furan composites cured under microwave and thermal conditions,’ Compos. Part B: Eng., 2014, 66, 156–161.
18. M. Neitzel, P. Mitschang and U. Breuer: ‘Handbuch Verbundwerkstoffe – Werkstoffe, Verarbeitung, Anwendung,’ 2014, München, Carl Hanser Verlag.
19. A. K. Mohanty, M. Misra and G. Hinrichsen: ‘Biofibres, biodegradable polymers and biocomposites: An overview,’ Macromol. Mater. Eng., 2000, 276, 1–24.
20. J. Dzalto, L. Medina and P. Mitschang: ‘Volumetric interaction and material characterization of flax/furan bio-composites,’ Int. J. Appl. Sci. Technol., 2014, 7, (1), 11–21.
21. B. T. Åström, R. B. Pipes and S. G. Advani: ‘On flow through aligned fiber beds and its application to composites processing,’ J. Compos. Mater., 1991, 26, (9), 1351–1373.
22. R. C. Lam and J. L. Kardos: ‘The permeability and compressibility of aligned and cross-plied carbon fiber beds during processing of composites,’ Polym. Eng. Sci, 1991, 31, (14), 1064–1070.