HIGH PERFORMANCE COMPOSITES PRODUCED FROM POLYFURFURYL ALCOHOL: ENHANCING THE PROCESS ABILITY AT SHORT CYCLE TIMES BY APPLYING HYDROPHILIC REINFORCEMENT

Katharina Resch-Fauster[1], Jovana Džalto[2], Andrea Anusic[1] and Peter Mitschang[2]

[1]Materials Science and Testing of Polymers, Polymer Engineering and Science, Montanuniversitaet Leoben, Franz Josef Strasse 18, 8700 Leoben, Austria
Email: katharina.resch-fauster@unileoben.ac.at, web page: http://www.kunststofftechnik.at

[2]Institut für Verbundwerkstoffe GmbH, Manufacturing Science, Erwin-Schrödinger-Straße 58, 67663 Kaiserslautern, Germany
Email: peter.mitschang@ivw.uni-kl.de, web page: http://www.ivw.uni-kl.de

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Abstract

Polyfurfuryl alcohol (PFA) represents a promising, highly ecological (carbon neutral) and fully non-toxic resin material, which - in terms of mechanical characteristics - is competitive to conventional epoxy or phenolic resins. However, PFA generates and releases water during the processing of fiber reinforced polymer composites which slows down the process speed and adversely affects the overall material properties. This study outlines an approach for decreasing the processing times of PFA composites by applying hydrophilic bio-based fibers.

1. 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 [e.g. 1-3]. In this regard polyfurfuryl alcohol (PFA), also referred to as furan resin, represents a promising, highly ecological (carbon neutral) and fully non-toxic matrix material, which exhibits similar mechanical properties to conventional epoxy or phenolic resins [4-8]. PFA is generated from furfuryl alcohol by cationic condensation reactions [9-12]. To reduce the viscosity and thus to enhance the process ability, typically water is added as a solvent. These 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 [13]. Consequently, in academic composites processing, the cross-linking of PFA is done either by gradually and slowly increasing the processing temperature from 20 °C to 80 °C or isothermal/stepwise at temperatures between 90 °C and 160 °C so far. In both cases, the processing times range between 2 and 8 h [5-6]. However, for many sectors of the industry a process ability at short cycle times is required. Thus, the present study aims at investigating the effect of the water absorbance characteristics of the reinforcing fibers on the process ability of PFA composites at short cycle times. The main focus is on generally evaluating if the hydrophilicity of bio-based fibers can be utilized explicitly for enhancing the manufacturing of high-performance PFA composites.

2. Water Absorbance Capacity of Biobased Fibers

The water sorption studies were done on flax, hemp, jute, kenaf, rayon and sisal fibers. The basic chemical and physical characteristics of the selected and investigated fiber types are summarized in Table 1. The fiber surface and diameters were analyzed by Scanning Electron Microscopy (Vega 3, Tescan Brno s.r.o, Brno, CZ).

For the water sorption studies, the fibers were dried at 80 °C for 24 h followed by exposure to standardized thermal environment (DIN EN ISO 291; 23°C, rel. humidity 50%) for 24 h. Afterwards the fibers were exposed to distilled water (ambient temperature) for up to 3,000 min (fiber length: 50-70 mm; fiber weight: sisal 40-60 mg, jute 150-250 mg, kenaf 80-150 mg, flax 300-500 mg, rayon 100-200 mg, hemp 200 mg). The sampling was done after 0.25, 0.5, 0.75, 1, 5, 10, 60, 120, 1,000 and 3,000 min. The molar percentage uptake Q_t for water per 100 g fiber was determined according to Equation 1

$$Q_t = \frac{m_e(w)/m_r(w)}{m_i(s)} \times 100 \qquad (1)$$

with $m_e(w)$ as the fiber weight after water immersion, $m_r(w)$ as the relative molecular mass of water (18g/mol), and $m_i(s)$ as the initial fiber weight. The presented data were averaged over three measurements.

Table 1: Chemical composition and structural parameters of the investigated bio-based fibers (lignin, cellulose, hemi-cellulose, pectin, and wax content according to [14])

fiber type	lignin content [wt.%]	cellulose content [wt.%]	hemi-cellulose content [wt.%]	pectin content [wt.%]	wax content [wt.%]	textile type	diameter [µm]
flax	2.2	71	18.6-20.6	2.3	1.7	fabric	16.9 6.0
hemp	3.7-5.7	70.2-74.4	17.9-22.4	0.9	0.8	fabric	15.0 ± 7.9
						non woven	15.0 ± 7.9
jute	12-13	61-71.5	13.6-20.4	0.2	0.5	fabric	10.6 3.3
kenaf	15-19	31-39	21.5	-	-	fabric	6.8 1.7
rayon	-	82.7	5.7	-	0.6	fabric	12.5 ± 2.6
						non woven	15.3 ± 7.7
sisal	8.0-11.0	67-78	10.0-14.2	10.0	2.0	fabric	14.6 4.7

In Figure 1 the molar percentage uptake Q_t for water per 100 g fiber is plotted as a function of the exposure time in water. In general the main components of the investigated bio-based fibers, namely cellulose and hemicellulose, cause a considerable water uptake due to their strongly polarized hydroxyl groups. The differences between the various fiber types are attributable to slight differences in their chemical composition. The highest and lowest water uptake was ascertained for hemp fibers and rayon fibers, respectively. Different to the natural fibers flax, hemp, jute, kenaf and sisal, which are grown naturally and exhibit lumen, rayon is a synthetic product which is produced from bio-based components (wood-cellulose) and does not exhibit lumen. Lumen allows for the incorporation of additional liquid “free” water into the fibers once the cell wall is saturated. Consequently, the water uptake of rayon fibers is lower compared to the natural fiber types. The data scatter - especially after long exposure times - is primarily ascribable to the felting of fibers immediately after sampling, which complicated the removal of water which was trapped between the individual fibers.

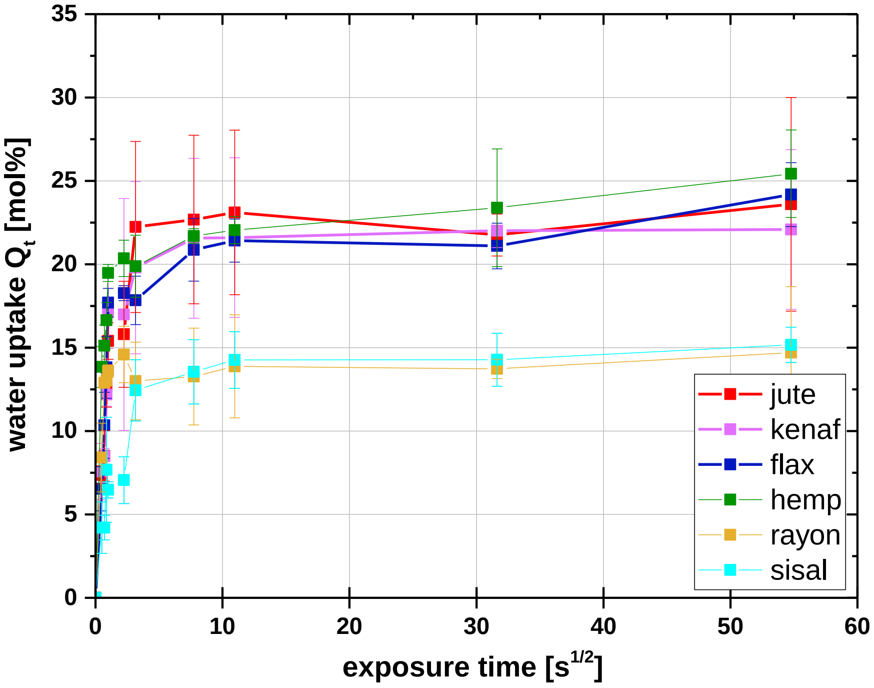

Figure 1. Sorption curves of bio-based fibers for exposure to distilled water at ambient temperature.

3. Processing of PFA composites

According to the results from the water sorption studies, rayon and hemp fibers (low and high water absorption) were selected for further investigations regarding the producibility of PFA composites at short cycle times. In addition and for reference purposes E-glass fibers, which absorb no water were used. In order to investigate an effect of the textile architecture on the proceassability, plain weave fabrics and non wovens were tested. The PFA BioRez 080101 was obtained from TransFurans Chemicals bvba (Geel, BE). This self-crosslinking resin formulation is diluted in water (20-22 wt. %) and exhibits a weight ratio of 78-80 % furfuryl alcohol prepolymer. For enhancing the textile impregnation, the viscosity of PFA was further reduced by adding 20 wt. % ethanol. Ethanol and partly also water were evaporated by storing the pre-impregnated textiles at a temperature ranging between 16 °C and 20 °C for 24 h. PFA prepregs with a fiber weight ratio of 50 wt.% were prepared and processed to composite panels 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. The mold was lifted after 15, 30, 45 and 60 s in order to evaporate the water (initial water and reaction water). Since the male and female dies were not hermetically sealed, water vapor could evaporate slowly when the mold was closed. Two distance bars predefined the thickness and density of the resulting composites. For reference purposes PFA rayon fabric panels were produced in a prolonged process according to the state of the art [5-6]. Thus, isothermal curing at different temperatures and a pressure of 10 bar was done for 7.5 h in total. The mold was not opened during processing.

In Figure 2 the detected processing-induced weight loss (balance prior and after processing) and the theoretical weight loss (evaporation of initial and reaction water in PFA) of the PFA composite panels produced from different reinforcing fibers and textile architectures are compared. The detected weight loss ranges between 7.2 % und 37.3 % and increases with a decreasing water absorbance capacity of the reinforcing fiber (from hemp to glass). Especially for PFA rayon and PFA glass panels the detected weight loss exceeds the theoretical weight loss by far, whereas the weight loss is higher for the composites produced from fabrics than for composites produced from nonwovens. 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. Consequently, the differences between the detected and the theoretical weight loss for these composites are attributable to this resin spill. Since the resin spill increased with a decreasing water absorbance capacity of the reinforcing fiber, it is assumed to be triggered by the flow of free water in the resin during molding on the one hand. Additionally, the vaporization of water during opening the mold might sweep resin away. By applying the state of the art manufacturing process, the weight loss is remarkably reduced (PFA rayon composites). A spilling of the resin was also ascertained in this process (although the mold was not opened), but the quantity was rather low. 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. No distinct resin spill (resin leaking from the mold) was observed for PFA hemp composites. However, resin gathering at the edges of the female die was unavoidable (due to sealing gaps compression tools are not hermetical). Condensed, the weight loss data indicate, that the resin spill decreases with an increasing water absorption capacity of the reinforcing fiber.

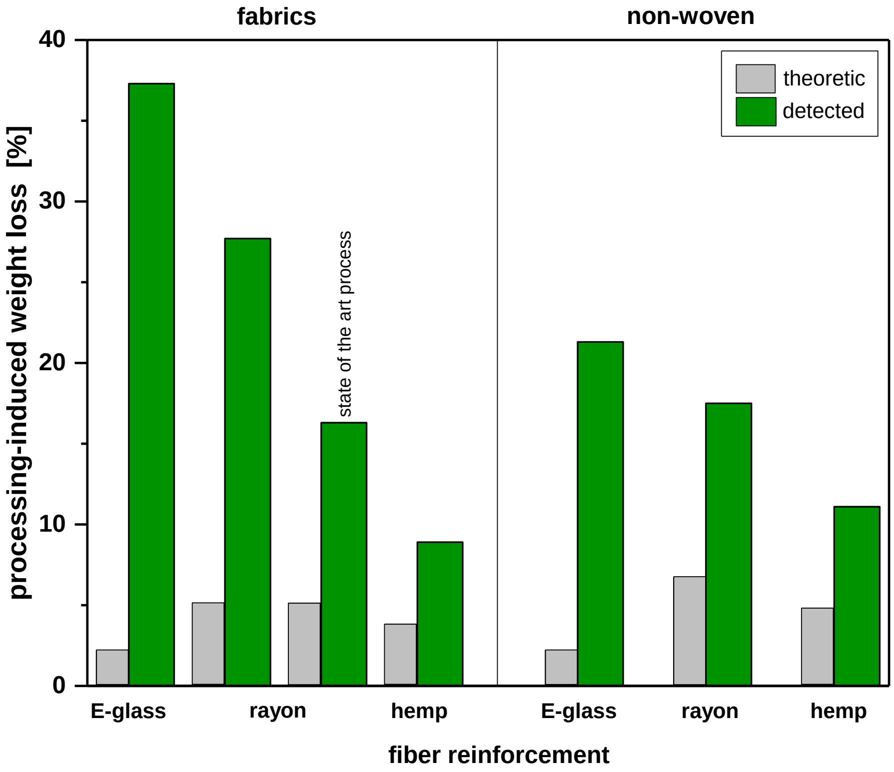

Figure 2. Processing-induced weight loss (resin spill) of PFA composite panels composites produced from different reinforcing fibers and textile architectures compared to theoretical weight loss (polycondensation reaction).

In Table 2 the volume fractions of the fiber, the resin and the pores in the PFA composites produced from different reinforcing fibers and textile architectures are summarized. Details as to the evaluation procedure are given in [15]. Irrespective of the fiber and textile type, the fiber volume fractions in PFA composites range between 30.5 vol. % and 37.5 vol. %. The porosity is lowest for PFA rayon samples which were cured according to the state of the art (22.3 vol. %). The associated increased overall resin volume fraction corresponds to the reduced processing-induced resin spill for this composite (Figure 2). All other PFA composites feature a high porosity which ranges between 30.6 and 40.9 vol. %. A correlation between the processing-induced weight loss/resin spill (and hence by the water absorbance capacity of the reinforcing fiber) and the degree of the panel porosity is observable: the porosity is lowest for PFA hemp and highest for PFA glass composites. Most likely, the porosity and consequently numerous voids develop from the flow of significant amounts of free water during molding and/or from the fast vaporization of residual initial and reaction water. By trend - irrespective of the reinforcing fiber type - the composite porosity is higher for fabrics than for non wovens. The results indicate that the porosity is not only affected by the fiber’s water absorbance capacity (porosity decreases with increasing water absorbance capacity) but also by the efficient transfer of water from the resin to the fiber and thus by the single fiber wetting (higher for nonwoven due to lower packing density).

Table 2. Volume fractions of fiber, resin, and pores in PFA composites produced from different reinforcing fibers and textile architectures

textile type	fiber type	volume fraction [vol. %]		
		fiber	pores	resin
fabric	E-glass	32.1	40.9	27.0
	rayon	37.5	38.7	23.8
	rayon (state of the art)	42.9	22.3	34.8
	hemp	35.7	30.7	33.6
non woven	E-glass	30.6	32.7	36.7
	rayon	36.6	34.5	28.9
	hemp	37.0	30.8	32.2

4. Conclusions

In general, the porosity of the produced PFA composites was high. However, the porosity decreased with an increasing water absorbance capacity of the reinforcing fiber. Moreover an efficient transfer of water from the resin to the fiber and consequently a high single fiber wetting capability were found to reduce the overall degree of porosity. Thus, the hydrophilicity of bio-based fibers enhances the processing and manufacturing of high-performance PFA composites at short cycle times. Moreover the morphological characteristics of PFA composites are stronger affected by the material composition than by the processing time and process control.

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