

THE DEVELOPMENT AND PROCESSING OF A SUSTAINABLE FULLY BIO DERIVED POLYFURFURYL ALCOHOL MATRIX FLAX FIBRE PREPREG

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Abstract

Recently, the rising cost and declining supply security of petrochemical constituents coupled with increasing environmental concerns have increased the attractiveness of polyfurfuryl alcohol resin as a carbon neutral renewable alternative to traditional thermoset resins. When combined with flax fibres, this resin offers an opportunity to produce an entirely sustainable bio-derived composite with relatively high mechanical performance and potential for fire resistance. Compression moulding of beta-staged flax-furan prepreg showed greatly improved performance over vacuum moulding. A review of furan and phenolic cure chemistry has found that these resins share similar chemistry, fire performance, and manufacturing difficulties associated with the solvent and cure process. The difficulties associated with a rapid exothermic reaction and water solvents are highlighted and are believed to be responsible for the poor performance of vacuum moulded laminates.

1 Introduction

Furfural is produced by the acid-catalysed digestion of hemi-cellulose rich agricultural by-products such as corn cobs, rice hulls and sugar cane bagasse [1]. Furfuryl alcohol is then produced by the catalytic hydrogenation of furfural [2]. Furfuryl alcohol is capable of self-polymerisation under elevated temperature and acidic conditions yielding polyfurfuryl alcohol, a dark viscous thermoset colloquially termed ‘furan resin’ containing water as a solvent. The addition of catalyst and elevated temperature restarts the polymerisation process until a fully cross-linked solid network structure is formed. Two polymerisation and three crosslinking mechanisms have been suggested to contribute towards the final structure (Fig. 1) [3-5]. The regularity of each type is thought to be dependent on conditions at the time of cure [6]. The majority of linkages appear to be the result of methylene bridges between end groups. However, linking of the furan ring is also believed to occur by a Diels-Alder type reaction also believed to be responsible for the resins dark colour [5].

Due to its excellent resistance to thermal and chemical attack, the most common historical usage of furan resin has been in the foundry industry as semi-rigid chemical binder for sand casting [7]. More recently, the rising cost and declining supply security of petrochemical constituents, coupled with increasing environmental concerns, have increased the attractiveness of furan as a carbon neutral renewable alternative to traditional thermoset resins [8, 9]. Furan resins also offer excellent fire resistance and comparable mechanical strength

when combined with glass fibres [10, 11]. When combined with a natural fibre, furan resins offer the opportunity to produce a fully bio-derived composite. Flax fibres have been typically chosen for their superior mechanical performance, cost and availability [12]. Initial studies on the application of flax-furan composites as exterior automotive body panels have proved reasonably successful [13]. However, a reduction in the fire resistant properties of furan resin and the mechanical properties were observed [10, 11]. Both were attributed to a high void content and it was suspected that the high acidity of furan resin could contribute to a reduction in mechanical properties by chemical degradation of fibres [11].

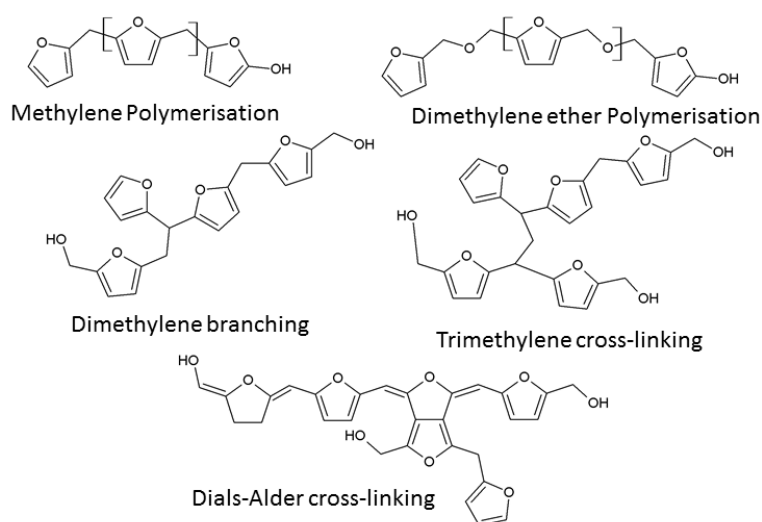


Figure 1. Mechanisms of polymerisation and cross-linking believed to occur in furan resin systems.

For composite laminate production, prepreg typically offers guaranteed fibre matrix compatibility, optimum volume fractions, ease of handling and improved placement accuracy [14]. Prepreg also offers the opportunity for solvent removal and additional polymerisation after fibre impregnation. Therefore, the development of a semi-structural flax-furan prepreg is now underway. Several production methods such as autoclave, vacuum bagging, and press moulding and their parameters have been considered in an effort to reduce void content. Furan resin has been reformulated for prepreg production with reduced acidity in order to reduce the potential for fibre degradation.

2 Materials and method

2.1 Resin casting

Studies were carried out by casting 'Biorez 080101' furan prepreg resin supplied by Transfuran Chemicals (TFC) into reusable silicone muffin cases. Ambient pressure casting was conducted in a SNOL PLC controlled calibrated oven. Internal resin temperature was monitored using a K-Type thermocouple, accuracy $\pm 0.5^\circ\text{C}$, centrally mounted inside the silicone mould case. Mould tare and resin masses were measured to an accuracy of $\pm 0.0001\text{g}$. *para*-toluenesulfonic acid (PTSA) based catalyst, 'S Type + D', supplied by TFC was also used whenever additional catalyst was required. RTM closed mould casting was carried out in a steel mould with a cylindrical cavity of $\varnothing 50 \times 150$ mm with an approximate injection pressure of >0.1 bar.

2.2 Viscosity measurements

Viscosity measurements were carried out using a Bohlin CVOR 200 rheometer using $\varnothing 25$ mm parallel plates with a $500 \mu\text{m}$ gap. An average was taken from steady state rheology

measurements at six logarithmic intervals between an increasing and decreasing strain rate of 1-200 s⁻¹ which did not appear to show any strain rate sensitivity for any of the solvent content levels.

2.3 Fibre impregnation

A unidirectional 275 g/m² and 2x2 twill weave 420 g/m² flax fibre fabric supplied by Composites Evolution were used for prepreg production. Initial studies were carried out on hand roller impregnated fabric with no further treatment before moulding. Prepreg studied later was subjected to a controlled proprietary impregnation and pre-treatment process by NetComposites Ltd which includes additional polymerisation and solvent removal. In this instance the prepreg is referred to as beta-staged.

2.4 Prepreg moulding

Prepreg moulding was carried out by vacuum and compression moulding. Vacuum moulding was carried out using a single sided polished stainless steel plate coated with Chemlease® PMR 90 release agent. The prepreg was covered with non-perforated release film to reduce resin bleed out which was found to be excessive during previous trials. The vacuum panel was then subjected to a temperature cycle of 20 mins at 150 °C with a 5 °C/min ramp rate and ambient cooling cycle.

Press moulding was conducted using a Macky Bowley 100 Tonne upstroke press with platen heating and cooling capability. Prepreg was placed between polished stainless steel plates which had been coated with release agent. In the case of the unidirectional fabric a steel frame was used to prevent spreading of the fabric during pressing, not necessary with woven fabric prepreg. The press was closed with an applied load equivalent to 20 bar pressure. The press was then heated at 5 °C/min to a platen temperature of 140 °C. It was held at this temperature for 20 minutes before being cooled rapidly to 50 °C at which point the pressure was removed followed by de-moulding.

3 Results

3.1 Resin casting

Initial casting of prepreg resin at the recommended temperature of 150 °C for 20 min produced a foamed specimen approximately four times its original volume (Fig. 2a). The resin had a specified water content of 20.9%. Therefore, it was believed that the boiling of the water occurring at the time of gelation was responsible. A strategy of moulding at a lower temperature and a higher pressure, where water boiling temperature is increased, was therefore adopted. A cure cycle of 140 °C for 40 min was utilised. At this temperature the boiling point of water is approximately 3.6 bar. An RTM resin cast was therefore performed in a sealed mould which had been previously pressure tested to 8 bar. The mould tool was found to leak a small amount of resin resulting in a casting with reduced foaming but unacceptable void content (Fig. 2b). To ensure that significant pressure was maintained the experiment was repeated in an autoclave with a vessel pressure of 6 bar. The result was a further reduction in foaming, however, the foaming remained unacceptable (Fig. 2c)

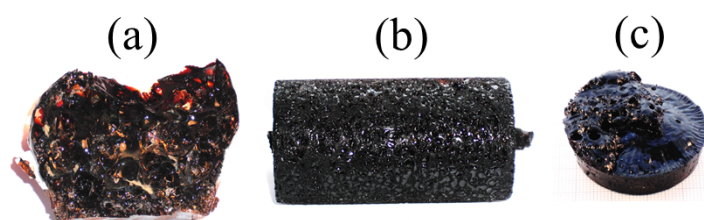


Figure 2. Foaming during cure of furan resin samples at (a) 150°C ambient pressure, (b) 140°C RTM closed mould pressure tested to 8 bar and (c) 140°C 6 bar autoclave.

It was therefore suspected that the exothermic reaction of the resin cure may be causing internal resin temperatures to exceed the vapour point. A traditional differential scanning calorimetric (DSC) analysis of this resin was prevented by the resin foaming and losing mass from sealed pans. Open pans did not yield useful results due to the unquantifiable energy loss in water evaporation. Therefore, experiments proceeded with embedded thermocouples within resin samples. Additional catalyst was added to the resin specimen to enable cure at a lower temperature. A cure at 70 °C with a 2 °C/min ramp produced an exothermic peak of 106 °C, above the vapour point resulting in a foamed specimen (Fig. 3a). A cure at 60 °C with 1 °C/min ramp rate resulted in an exothermic peak of 94 °C, below the vapour point, without foaming (Fig. 3b).

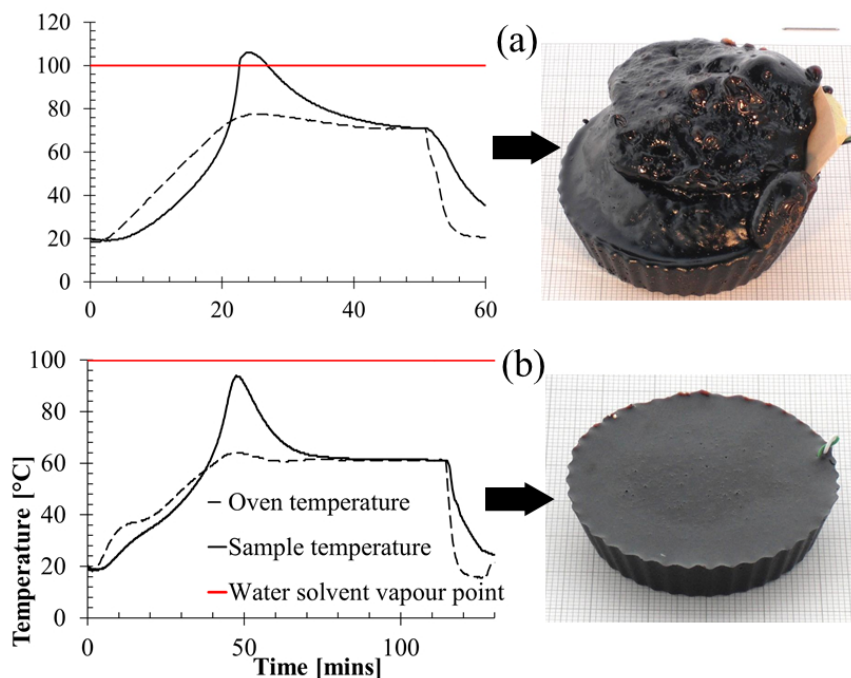


Figure 3. Furan resin cure with an exothermic peak cure temperature of (a) 106 °C and (b) 94 °C

Removal of the water content was also attempted by vacuum degassing of the resin at near ambient temperatures. A minimum of 3.8% water content was achieved in a 24 hour period at 30 °C an exponential increase in steady state viscosity was also observed (Fig. 4).

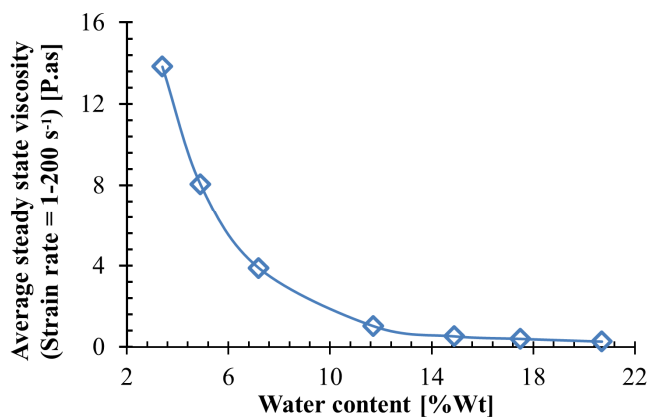


Figure 4. Steady state viscosity as a function of water content for furan resin at 22 °C

The mass loss of the resin was also recorded during an extended cure cycle. The Biorez furan resin was found not to cure during an initial cycle of 3 hrs at 60 °C. However, 4.75% in mass was lost, believed to be due to water evaporation (Fig. 5). Complete cure appeared to occur after temperatures reached 150 °C where a 30% reduction in mass was observed and the rate of mass loss appeared relatively stable. Biorez with added catalyst appeared to cure after 3 hrs at 60 °C, however, continued to lose mass at a rate which did not reduce significantly throughout the cure cycle.

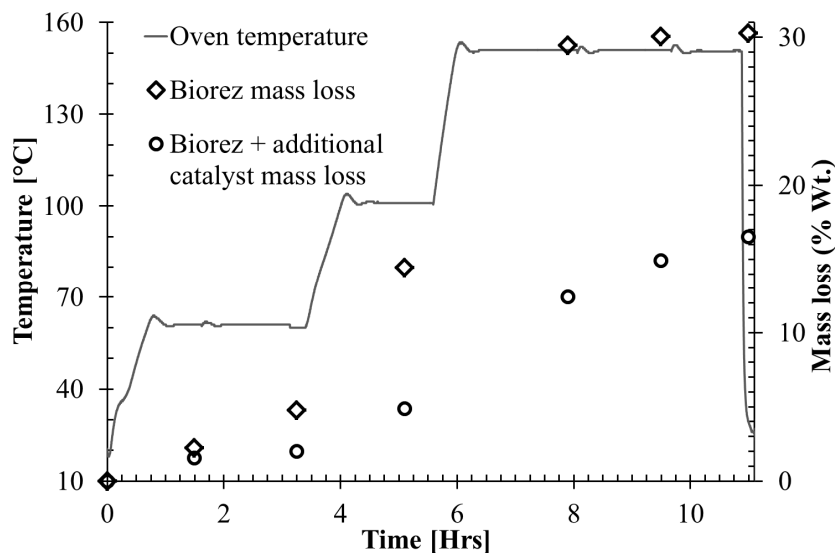


Figure 5. Furan volatile mass loss at intervals throughout an extended cure at ambient pressure

3.2 Prepreg moulding

Vacuum moulding of prepreg at 140 °C showed a high resin bleed out with a 20% drop in vacuum pressure as the resin appeared to boil under the bag. A porous poor surface finish and high void content was observed (Fig. 6a). Resin bleed out could be reduced by beta staging of the prepreg. However, minimal beta staging results in resin bleed out due to apparent boil. Increasing the amount of beta-staging eventually leads to dry prepreg which does not flow under moulding. Compression moulding of prepreg at 140 °C showed improved surface finish and reduced void content (Fig. 6b).

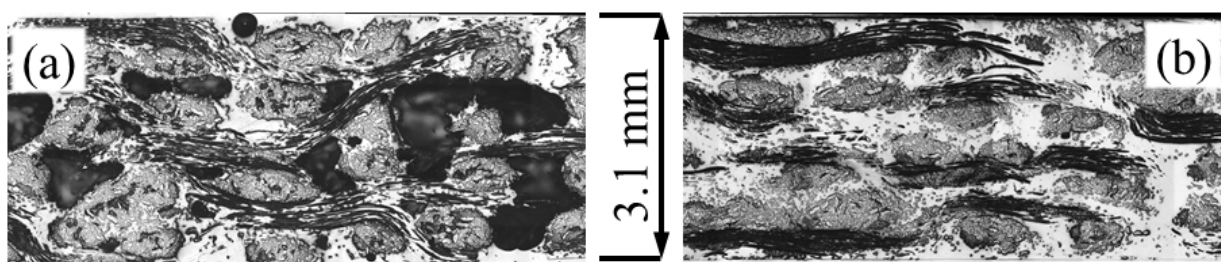


Figure 6. Cross sectional micrographs showing voids in (a) Vacuum bag and (b) compression moulded beta-staged prepreg flax-furan laminates.

3.3 Tensile test results

Mechanical test results reveal that flax-furan prepreg performance is greatly sensitive to the processing method. A three and a half fold increase in UD and two fold increases in 2x2 twill laminates can be observed when switching from vacuum to compression moulding (Table 1).

Mould method	Material	Tensile properties	
		Strength (MPa)	Modulus (GPa)
Vacuum	UD flax, roller infused	59.5±4.3	10.2±0.8
	2x2 Twill flax, beta-staged prepreg	34.9±1.84	6±0.47
Compression	UD Flax, beta-staged prepreg	211±24	25.6±1.9
	2x2 twill flax, beta-staged prepreg	69±3	10.4±0.4

Table 1. BS EN ISO 527-5 and 527-4 mechanical test results for flax-furan laminates produced by vacuum and compression moulding.

4 Discussion

The chemistry, water content, and fire resistant properties of furan resin bear similarities to phenolic resins. The simplest, bisphenol F, novolak is prepared by conducting a reaction of phenol and formaldehyde under acidic conditions (Fig. 7a) [15]. Although the cure mechanism is not completely understood; it is believed to occur by condensation of hydroxymethyl groups to form methyl linkages (Fig. 7b) [16]. In furan resin the furan ring appears synonymous with the benzene ring. The addition of formaldehyde is no longer required as the hydroxymethyl group is present in the starting product (Fig. 7c). Cross-linking is again then believed to occur by condensation of hydroxymethyl groups to form methylene linkages Fig (7d) [4].

The curing mechanisms of furan resin remain to be fully understood. There is potential for three identified mechanisms to occur simultaneously. This appears to be supported by observations of the furan resin where the onset of cure appears quite rapid when considering the exothermic response (Fig. 3). A proposed mechanism includes the condensation of hydroxymethylene groups which would result in the formation of water. This appears to be supported in observations of resin mass loss where volatile mass loss exceeds solvent content by up-to 8%. Although water is the most probable volatile, there is also potential for formaldehyde evolution during the decomposition of dimethylene ether linkages [6].

In order to produce a prepreg resin the catalyst level in 'Biorez' has been significantly reduced with the intention of reducing acidity, for compatibility with flax fibres, and increasing shelf life. However, an elevated curing temperature of above 120 °C is then required for cure in a reasonable cycle time. At this elevated temperature furan resin appears susceptible to foaming believed to be caused by water solvent vaporisation and volatile production. Therefore, closed cavity and vacuum methods of production are increasingly problematic and result in a laminate or casting with a high void content. However, removal of solvents and some advancement of polymerisation in a beta-stage combined with a high pressure compression moulding technique allow the production of laminates with reduced void content and improved mechanical performance. This is attributed to a combination of solvent reduction and internal laminate pressure exceeding the vapour point during cure.

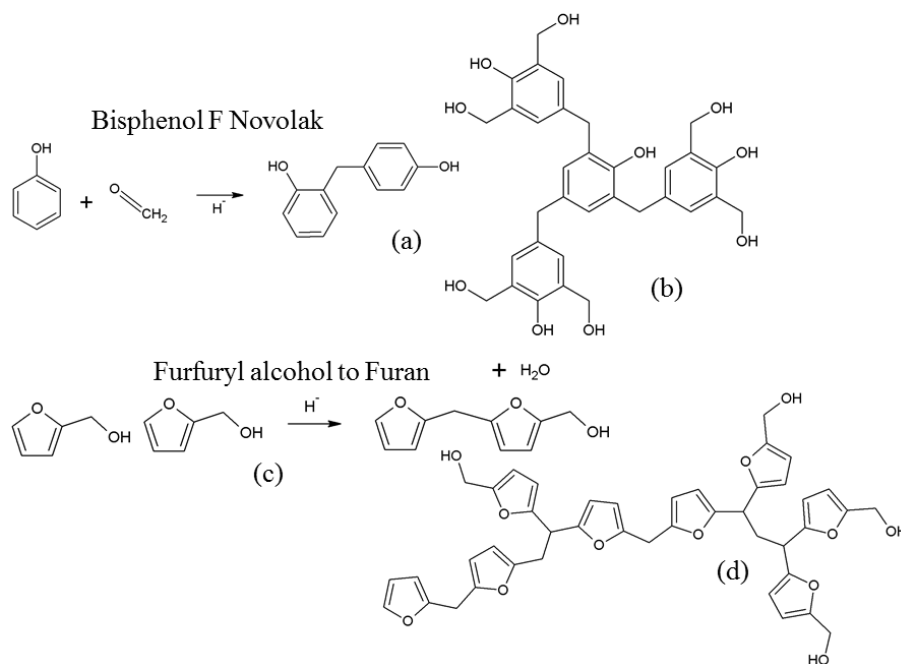


Figure 7. Similarities between novolac and furan resin polymerisation (a & c) and cross-linking (b & d)

Unfortunately, compression moulding greatly increases mould and production costs reducing the flexibility and attractiveness of the prepreg product. Phenolic resins share a similar problem which is alleviated by the use of a catalyst which allows cure at a temperature, typically 60-70°C, that is below the water vapour point [15]. Typically these phenolic resins are used in an RTM process which offers a potentially lower cost alternative. However, furan resin viscosity appears to increase exponentially with solvent removal (Fig. 4) indicating that infusion would become increasingly difficult. Therefore, a high resin water content is typically required for RTM increasing the problems associated with volatile production. Typically a partial vacuum is applied during the curing cycle to relieve symptoms. However, voids and poor surface finish are generally expected to occur. This then requires finishing operations for decorative parts or restricts use of the products to hidden parts.

Prepregging offers an excellent opportunity to remove a significant amount of volatiles during beta-staging. Unfortunately, prepreg becomes stiff and resin flow is reduced with progression of beta staging. Therefore, volatiles remain problematic as they cannot be completely removed and are also produced during cure. Placing the prepreg under vacuum lowers the vapour point of the water solvent to below room temperature again causing resin boil and associated voids (Fig. 6).

5 Conclusions

Furan resin combined with flax fibres offers excellent potential as a bio-derived sustainable thermoset composite. Mechanical and fire resistive properties are comparable to those of phenolic resin with which it shares a similar chemical structure. A relatively high tensile strength of 211 MPa for a UD flax fabric has been achieved by compression moulding of a beta-staged prepreg. Unfortunately, resin casting and vacuum moulding of furan resin has proved problematic, attributed to the boiling of the water solvent. Complete removal of the solvent does not appear possible due to exponentially increasing viscosity. It is also suspected that additional solvent is produced during the cure reaction. Curing below the vapour point is possible with increased catalyst, however, it appears that solvent is then trapped within the matrix.

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