NATURAL RESINS BASED VACUUM INFUSION TECHNOLOGY AS ALTERNATIVE TOOL FOR TRANSPORT INDUSTRY

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Abstract

Furfuryl alcohol derived resins are thermosetting resinous systems coming from renewable resources like agricultural by-products (bagasse, rice hulls…) that, although relegated mainly to foundry sand binders, could mean a technical and environmentally efficient alternative to conventional oil derived resins within plastic composites industry. This work describes the first approach to furan based vacuum infusion technology using a new low viscosity furfuryl alcohol derived resin that, even though it shows different current difficulties and limitations derived from the lack of optimisation of resinous system for acceptable industrial process conditions, demonstrates the immediate potential of these resins for infusion technology. Evaluation of resin cure, achieved mechanical properties with different reinforcements and excellent fire reaction performance allows forecasting soon suitable features for applications in transport sector, among others.

Keywords: Furan resins, Vacuum infusion, Renewable resources.

Introduction

The interest in producing polymeric resins and composites from renewable resources is increasing considerably due to not only the increase of oil price but also the promotion and encouragement of efficient use of natural resources towards 'sustainable development' [1]. Therefore, agricultural by-products constitute a potential source for products. In particular, furfural is an strategic renewable chemical, derived from the acid hydrolysis of pentose sugar-rich agricultural biomass such as corncobs, bagasse, cotton husks or rice hulls, as feedstock for different solvents, including furfuryl alcohol [2, 3].

Like phenol, furfuryl alcohol polymerises in controlled acid conditions through condensation reactions to produce low molecular oligomers with methylene linkages between furan rings. These oligomers or 'pre-polymers', thus, may continue reacting to lead to thermosetting furan resins [4, 5].

Conventionally, although well known their good thermal, fire and chemical resistances, furan resins have been mainly restricted to foundry sand binders and some special chemical resistant concretes and adhesives. However, new developed resins are attracting much more attention thanks to not only the mentioned properties, in particular fire resistance, but also coming from renewable resources. Then, these resinous systems could turn into an alternative to conventional oil derived resins in composites technology, specially an alternative to phenolic thermosets, which are the more similar systems attending to chemical structure, crosslinking and performance. In particular, facing to current fire safety related normative for building sector and the immediate new normative for transport sector [6, 7, 8, 9, 10], the furan resins could provide a renewable resources derived suitable alternative for the use of polymers materials against fire hazard.

On the other hand, among the different types of technologies for thermoset resin based composites, the resin film infusion moulding is becoming increasingly popular for making large structures [11]. It shares different characteristics of resin transfer moulding (RTM), hand lay-up and vacuum bag moulding but overcoming some of the problems of these techniques, like advantages related to health and safety in comparison to hand lay-up [12] and reduction of the higher costs of closed mould methods [11, 12, 13].

The vacuum infusion process is based on drawing the resin into a dry reinforcement under a vacuum film, using only the partial vacuum to drive the resin and compressing the composite.

Experimental

Materials and Methods

The furan resin employed is a low viscosity new prototype resin developed by Transfurans Chemicals bvba. The used cure agents are acid catalysts (Transfurans) coded as A-type and B-

type catalyst, respectively. A coupling agent (Transfurans) was used to improve the resin/fibre compatibility. All the reagents were utilized as provided without further purification. Varieties of mats and wovens were used as fibre reinforcements (see table I).

Table I- Reinforcements used.

Reference	Description
- Pentacore mat 450/250/450 (Glasscom)	- Two glass chopped strand mat external layers of 450 g/m^2 with a 250 g/m^2 polypropylene core.
- CFM 200 (Saint-Gobain)	- 200 g/m^2 continuous filament mat of random orientation.
- Mat/fabric complex 350/1200-0º/90º (Owens Corning)	- Combination of 350 g/m^2 chopped strand mat and 1200 g/m^2 bidirectional woven fabric (0º/90º).
- Flax mat 500 (Ekotex)	- 500 g/m^2 flax chopped strand mat.
- Chopped strand mat 400	- 400 g/m^2 glass-fibre chopped strand mat.
- CFM/chopped 450	- 450g/m^2 glass-fibre mat (combining continuous filament mats and chopped strand mats)

Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA) and Gel Time

Differential Scanning Calorimetry (DSC) was used to evaluate the resin cure by measurement of the heat of reaction (area under the exothermic curve) and the peak reaction temperatures. The DSC measurements were conducted on a Mettler DSC 30 using sealed capsules. For the first scan, the temperature range was from 25 to 200ºC at a heating rate of 10ºC min^{-1}, whereas the second scan was performed from 25 to 300ºC at 10ºC min^{-1} to check the total crosslinking degree.

Dynamical-mechanical testing provides information about stiffness and elasticity of viscoelastic materials by means of evaluating the mechanical loss and storage moduli [14]. The storage modulus (E'), the loss modulus (E'') and the tan δ were evaluated for analysing post-curing process (the frequency employed was 10 Hz, the heating rate was 2ºC/min, and a strain of 256 micrometers). The DMTA equipment used in this work (Polymer Laboratories, Mark II DMTA) has a bending head and a universal temperature programmer. Test samples for flexural test were prepared by manufacturing a hand-lay sample with the 400 g/m^2 chopped strand mat.

The gel-time of the catalysed resinous systems was measured using a Gelnorm Gel-Timer from Gel Instrument AG. The measurements were performed at 25 and 45ºC with the different catalysts/resin ratios.

Infusion moulding

Composite panels were manufactured using vacuum infusion process. The obtained specimens had the dimensions 30 x 30 cm. The preform was vacuum bagged on a flat mould and the resin was dragged into the reinforcement by vacuum negative pressure at room temperature. The curing conditions were defined by the analysis performed (see results and discussion section).

Physical and mechanical performance

The viscosity data of the resin at different temperatures were supplied by TransFurans Chemicals. After the infusion process, the physical and mechanical properties of the obtained specimens were characterised. Fibre content was conducted under UNE 53 269-80 standard. Flexural properties were measured at room temperature under UNE EN ISO 14125 standard, whereas tensile tests were performed under UNE EN ISO 527-4 standard at room temperature and Charpy impact tests were conducted at room temperature under UNE EN ISO 179 standard.

Fire resistance

The reaction to fire of 40x40 cm sample with a 41.2% w/w of inorganic content, manufactured by spray-lay up, was evaluated. In particular, the tests carried out were the following ones:

- Reaction to fire test according to UNE 23721:1990. Epirradeateur test.
- F classification according to NF F 16101:1988 by means of optical smoke density determination according to NF X 10702 and gas toxicity determination according to NF X 70100.
- Determination of burning behaviour of interior materials according to ISO 3795:1989 (road vehicles, tractors, machinery for agriculture and forestry).

Results and Discussion

Resin/Catalyst Ratio

Different resin/catalyst ratio were analysed by DSC. The figure 1 shows the first scan of different resin/catalyst ratio. The heat of cure, peak curing temperature and inflection temperature are listed in table II. The subsequent DSC scan showed that the samples were totally cured.

Table II- DSC significant results.

Reference	[A-cat]-[B-cat] (%w/w)*	Heat of cure ($J\ g^{-1}$)	Peak curing temperature (ºC)	Inflection temperature (ºC)
10A	10 - 0	285	96.24	67.01
8A-1B	8 - 1	317	92.40	65.00
5A-3B	5 - 3	321	88.66	63.31
6B	0 - 6	377	82.65	60.46

* % w/w of A-type catalyst and B-type catalyst, respectively.

As it can be seen in table II and figure 1, considering the exothermic peak of DSC, which controls the curing reaction of the system, differences between used catalysts can be observed. The B-type catalyst shows a higher reactivity than the catalyst A, as the lower peak curing temperature and higher curing enthalpy demonstrate. These data also were confirmed by the evaluation of gel-time. The table III shows the gel-times at 25ºC and 45ºC of the reactive systems.

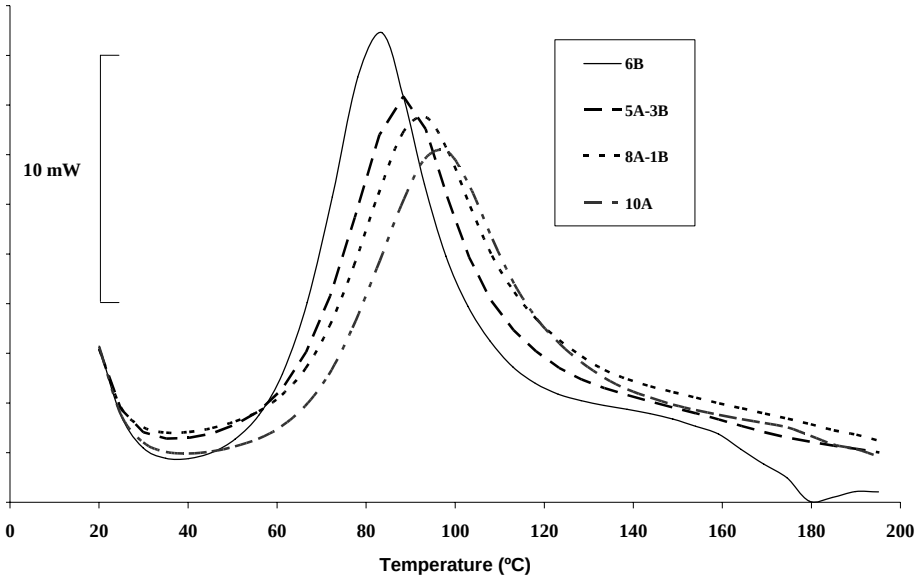

Fig. 1- DSC scanning curves of different resin/catalysts ratio.

Table III- Gel-time of analysed systems.

Reference	Gel-time at 25ºC (min)	Gel-time at 45ºC (min)
10A	> 360	210 ± 10
8A-1B	> 300	170 ± 8.5
6B	> 180	10 ± 0.5

Obviously, the gel-time strongly depends on the resin volume, more in case of highly exothermic systems, as it was confirmed by the system coded as 6B, which showed a very short gel-time at room temperature when 1 Kg of resinous system was used.

Thus, attending to obtained results and looking for a balance between suitable curing cycles for industry and good mechanical performance coming from a low void content, the formulation coded as 8A-1B was selected for the subsequent manufacturing of infusion samples. In particular, the void content is a key aspect in this kind of furan resins due to the co-solvents and water content, which comes not only initially but also from the water formed during the polycondensation crosslinking reaction. The boiling of the solvents, then, must be minimised during the infusion moulding so too high process temperatures and pressures (although suitable for reducing void content with conventional resins) were not suitable under vacuum conditions.

Infusion Process

Once selected the catalysed system, the processing conditions were evaluated. The viscosity of the resin at different temperatures is collected in the figure 2.

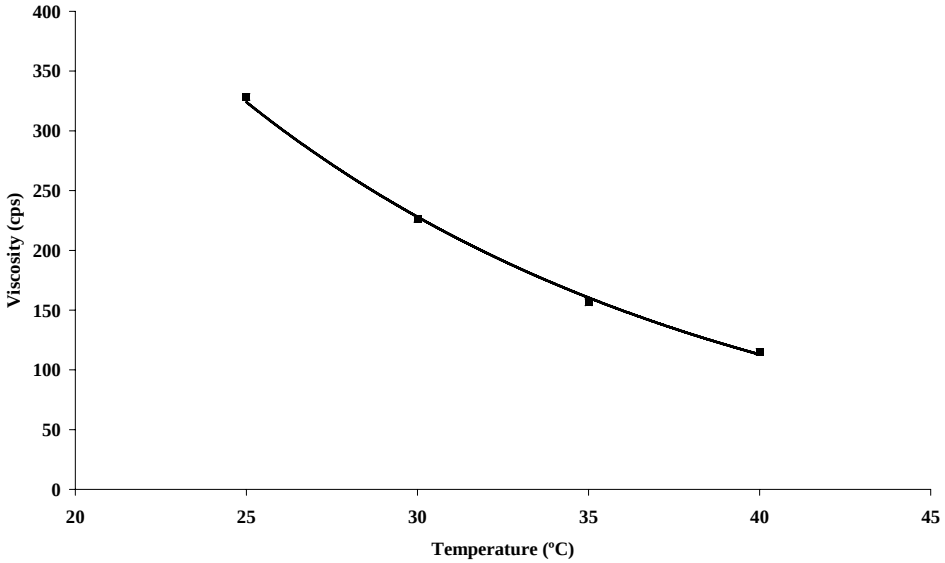

Fig. 2- Viscosity vs. temperature.

Figure 3 shows the mechanical-dynamical behaviour for different cure conditions. As can be seen in the evolution of flexural modulus E' and tan δ for the samples with and without postcuring at 150ºC, the composites require a post-curing treatment to ensure a 100% conversion and, hence, optimised mechanical performance.

The specimens of 30x30cm with the different reinforcements, thus, were infused at room temperature and low vacuum pressure. Then, the samples were cured at 45ºC, 60ºC and 80ºC for 2 hours, 30 minutes and 1 hour under vacuum, respectively and, once cured the samples, they were subjected to post-curing treatment at 150ºC for 1 hour.

Composites Properties

The key properties of the obtained prototypes were characterised. The reaction to fire of spray lay-up samples were characterised (see table IV) and the physical and mechanical properties of infused moulded samples are summarised in table V.

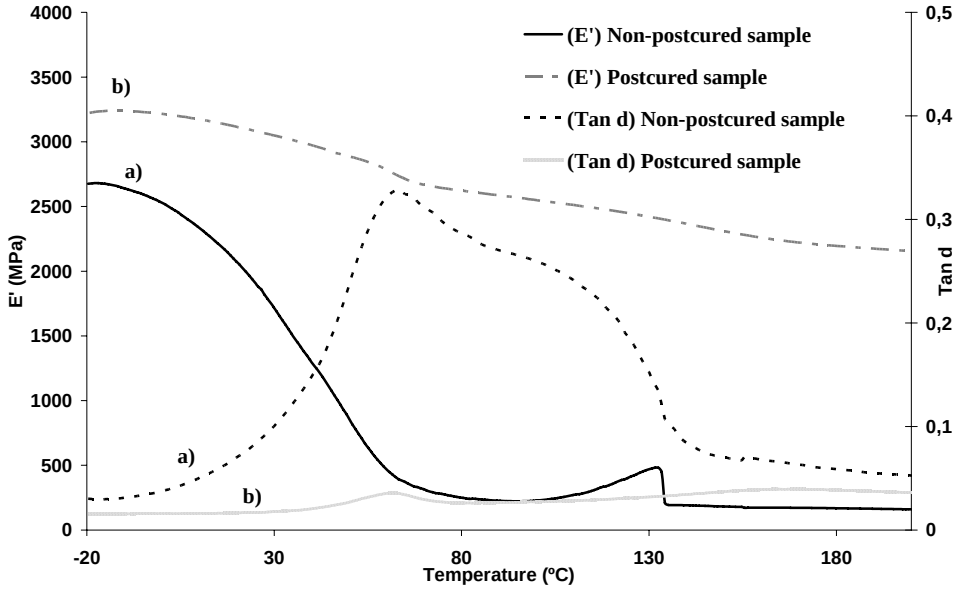

Fig. 3- Evolution of E' modulus and tan δ with temperature for a) sample without post-curing and b) sample post-cured at 150ºC for 1 hour. (Frequency: 10Hz, heating rate: 2ºC min-1).

Table IV- Results of reaction to fire.

Test/Index	
Reaction to fire test A/T UNE 23721:1990	
- *Flammability index (i)* [a)]	0.00
- *Flame development index (s)* [a)]	0.00
- *Maximum flame height index (h)* [a)]	0.00
- *Combustibility index* © [a)]	< 1.00
CLASSIFICATION [a)]	**M1**
Optical Smoke density a/t NFX 10 702	
- *V0F4*	17.00
- *Dmax*	92.00
Gas toxicity a/t NFX X 70 100	
- *ITC/2*	8.38
- *Fumes index (IF)*	9.87
CLASSIFICATION	**F1**
Burning behaviour of interior materials A/T ISO 3795:1989	
- Combustion velocity (mm/min) [b)]	0.00

a) Test carried out only on one specimen instead of the four required in the Standard. These individual results could lead to a M1 classification according to UNE 23727:1990.
b) The material does not ignite. The test piece does not show any flame after the 15 seconds ignition period.

Attending to M and F classification and combustion velocity test (table IV), the materials could be considered for nearly all the 'classification grilles' collected in NF F 16101:1988 standard (rolling stock, fire behaviour, materials choosing). This fact, for example, means that they are suitable for

materials placed inside and outside the railway vehicles (mainline, regional, urban and suburban vehicles). And attending the 95/28/CE directive, the materials should be suitable for applications such as inner ceiling and floor coverings, inner rear and lateral panels, division panels, etc.

However, regarding to mechanical performance, moderated properties have been achieved. The, measurements of density and water absorption were conducted under UNE EN ISO 1183-2 and UNE EN ISO 62 standards to analyse the void content of the samples. The evaluated low density and the high water absorption (above 1.5 % w/w) data demonstrated a no desired high void content in the samples that restrict the achievable mechanical properties. Analysing the resin, this problem results mainly from the poor adhesion between furan resin and glass fibres (partially solved by a specific coupling agent and no identified for cellulosic fibres) and from the boiling of co-solvents during the infusion moulding at selected temperatures.

Table V- Physical and mechanical properties.

Test	Pentacore	CFM 200	Complex	Complex + Coupling agent	Flax
Physical properties					
- Fibre content (%)	38.1	45.7	70.5	73.4	-
Mechanical properties					
- Tensile strength (MPa)	114	63.1	124	208	18.4
- Tensile modulus (MPa)	4700	5713	14040	13490	5903
- Flexural strength (MPa)	65.0	118.0	88.1	131.5	27.5
- Flexural modulus (MPa)	4426	4540	9107	8745	4240
- Charpy impact strength (KJ/m^2)	71.4	41.6	72.2	95.6	3.2

By the optimisation of resinous systems, catalysts and process conditions, as performed with other furan resins for compression moulding techniques and previously with phenolic resins, the achieved mechanical properties are expected to improve up to a 50%, so they would be totally suitable for most of the applications in transport and building industry.

Conclusions

On one hand, the application of vacuum infusion moulding is increasing considerably for the last years, especially in the manufacture of large and complex parts. This growing comes from certain advantages in comparison to traditional thermosets moulding processes. These advantages are mainly related to the optimisation of the reinforcement content and arrangement, together with the reduction of costs and chemicals emissions compared to closed-mould and open-mould technologies, respectively.

On the other hand, the development of composites based on new renewable resources based resins is turning into a key priority towards sustainable development. The furfuryl alcohol derived thermosets, thus, become a real alternative to conventional resins thanks to optimal features.

Taking into account the novelty of these resins into plastic composites technology, further into infusion moulding, this first approach to furan based infusion moulding has shown the current limitations and difficulties of the process. However, this work, at the same time, also demonstrates the potentiality of this kind of resins as an immediate alternative to conventional materials for transport sector, among others.

It has been observed that the moderate mechanical performance of the different manufactured composites results from the poor adhesion of the resin to the glass fibre and, mainly, from the high void content. The former, as demonstrated, can be solved by using developed coupling agents, although could be also overcame by new furan sizing. Nevertheless, this problem is minimised in case of natural fibres due to the compatible chemical nature of the resins and the cellulosic fibres surface. The later, the high void content, is the key detected problem for these polycondensation resins (like for very starting phenolic ones) in industrially acceptable process conditions (times, temperatures…). It is obvious the need of improvements of these first furan resin grades, particularly solvents, and a better optimisation of catalyst system and process parameters (higher vacuum pressure, lower boiling, lower trapped bubbles, lower curing cycles and temperatures…..). However, it is outstanding the good flow behaviour of these resins during the infusion through all the used reinforcement beds (not published results) and the excellent reaction to fire performance, allowing to be used for most of the ‘classification grilles’ collected in NF F 16101:1988 standard.

Summarising, these resins are starting into plastic composites, in particular in infusion moulding, but show excellent features which lead to think that, thanks to immediate expected improvements of about a 30-50% on mechanical properties (improvements already observed for compression moulding processes), will become a new environmentally friendlier alternative, further if combined with natural fibres.

Acknowledgements

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