EVALUATING THE CARBON STORAGE POTENTIAL OF FURAN RESIN-BASED GREEN COMPOSITES

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1 Introduction

Awareness and understanding of the significant impact to climate changes of anthropogenically driven processes primarily run by fossil fuel combustion has grown over the last few years. This, in turn, has fuelled various research investigations on options to mitigate likely impacts. Approaches involving the capture of carbon dioxide and its storage in geological formations, or in marine waters, paved the way to various proposed man-made solutions. Ecological concerns and global warming have initiated a considerable interest in using natural or renewable materials to produce "green" products and reduce anthropogenic carbon dioxide emissions. Among the identified mitigating schemes, natural fibers have excellent potential in not only lowering CO_2 emission levels but also in conserving non-renewable resources- by replacing glass fibers in fiber reinforced plastics (FRP's) [1].

At present, there is already a great abundance of research on natural fiber reinforced polymeric (NFRP) composites- mostly on the evaluation and improvement of mechanical performance when using non-biodegradable composite matrices such as thermosetting resins. However, limited data is available to gauge the environmental advantages of these materials- in particular, the carbon storage potential with the use of renewable bio-based materials. Several reports on life cycle analysis (LCA) applied to natural fiber-reinforced composites have been published- mostly aimed to compare the environmental impact of natural fibers with that of glass fibers in the form of carbon dioxide emission and total energy consumption [1-3]. Since carbon dioxide fixation capacity is the key environmental parameter evaluated in this study, certain LCA principles are applied on the material to serve as a guide and tool for the evaluation of carbon storage potential. However, analyses of this kind are mainly concerned on the overall CO_2 emission and not on the bio-based carbon content of the material. In this study, it is attempted to develop a systematic approach to evaluating the carbon storage potential of green composites, using thermoset-based NFRP composites as subjects.

Furan resin (polyfurfuryl alcohol) is a biosynthetic thermoset derived from vegetable byproducts such as corn cobs. Compared to other common resins, this highly stable polymer offers a very significant improvement in the carbon storage potential of green composites when used as a matrix. In this paper, the mechanical and environmental aspects of furan-based natural fiber-reinforced plastic composites (NFRP) are measured quantitatively and evaluated in comparison to those of an equivalent thermoset-based NFRP, using orthophthalic-type unsaturated polyester (ortho-UP) as representative petroleum-derived synthetic thermoset. The carbon storage potential comparison is performed to quantitatively determine the possibility of the more eco-friendly furan as a feasible replacement to the more conventionally used ortho-UP in various long-term applications.

2 Carbon Balance

Aside from the use of renewable materials, one advantage of using furan resin as NFRP matrix is the additional CO_2 fixation by the polymer itself. As a biosynthetic thermoset, it is strongly believed that furan resin has the capacity to store carbon from biomass produced by the utilization of atmospheric CO_2 by plants during photosynthesis. However, as with any industrial process, the manufacture of this

material entails the use of energy, which translates to CO_2 emission that could easily offset the effectiveness of furan to sequester CO_2 as stored bio-based carbon. Therefore, it is also crucial to identify the different pertinent flow streams of carbon and the energy consumption throughout the entire production process of furan resin.

In the evaluation of carbon storage potential of green composites, the primary objective is to quantify the extent of carbon fixation by the material in bio-based form (e.g., as laminated natural fibers) by also considering the amount of CO_2 released during the material's production stage- mainly from the consumption of fossil fuels for energy supply. In terms of equivalent carbon content, there are essentially two direct methods of evaluating carbon storage potential that can be adopted:

1. The first method for defining carbon storage potential is by calculating for the net bio-based carbon content or $E(NB)$ of the material [4]. By definition, the net bio-based carbon content refers to the difference between the renewable, bio-based carbon content and the non-renewable, fossil-based carbon content of the material, including the carbon-intensive energy consumption.
2. Because this energy is produced by fuel combustion, its generation has an equivalent amount of CO_2 emission. This energy-equivalent CO_2 may be classified as either fossil-based or bio-based, depending on the nature of the fuel burned. This energy-CO_2 equivalence allows for the quantification of carbon storage potential.

Net bio-based carbon content is a more direct representation since it expresses stored carbon in terms of carbon weight fraction within the material, while the energy-equivalent carbon in terms of CO_2 is viewed in the same manner depending on whether fossil fuels or bio-fuels are consumed during production. On the other hand, expressing carbon storage potential in terms of amount and reduction of fossil-based CO_2 emission allows for a more convenient assessment of carbon fixation through comparison with emission data from pre-existing LCA studies. For this paper, both methods for expressing carbons storage potential are used- the first is used in the carbon audit around the manufacturing process, while the second one is for the comparative evaluation of NFRPs using different types of resins. The evaluation is necessary for thermoset-based NFRPs since most investigations on green composite aim to promote biodegradation- i.e., carbon storage potential analysis is rarely done, and these very few and fairly recent investigations primarily focus on the production stage and with little consideration for the material's lifetime.

3 Experimental

Furan resin was supplied by Hitachi Chemicals Co., Ltd. and cured using 1 wt% alkylbenzenesulfonic acid solution. For the basis of comparison, ortho-UP (Rigolac U1557) was cured using methyl ethyl ketone peroxide from NOF Corporation as hardener and cobalt naphthenate from Wako Pure Chemicals Industries as accelerator at a mixing ratio of 100:1:0.5 by weight, respectively.

For the reinforcement, long, continuous fibers of abaca or Manila hemp (*Musa textilis*) were used. Raw abaca fiber bundles were obtained from a local handicrafts vendor in Manila, Philippines. The fibers were cut into 20 cm lengths, washed and chemically treated prior to lamination. The curing procedure for the furan was adopted from a previous report [5], while ortho-UP was cured in a hot press at 50°C and 10 MPa for 2 hours. The unidirectional (UD) fiber sheets were laminated by hand layup method at different fiber weight fractions. The resulting NFRP specimens were cut and subjected to mechanical strength test according to ASTM methods.

For the evaluation of CO_2 fixation, some assumptions were made to facilitate the audit of pertinent carbon flow streams and energy consumption rates. Finally, thermogravimetry were performed on both furan and ortho-UP using Shimadzu Simultaneous TGA/DTA Analyzer DTG-60H to evaluate long-term carbon storage potential.

4 Results and Discussion

4.1 Net bio-based carbon content

A schematic diagram of the major steps involved in furan resin production is presented in Figure 1. For the production of furfural, the steam consumption is based on the patented Skogh-Savo process [6]. The basis of the mass and energy balance calculations for

each step is always at 1 ton of raw material for convenience. The total carbon dioxide emission associated with the manufacture of furan resin is therefore equal to the sum of the emissions from the three synthesis steps. In this scenario, it is assumed that the energy requirement for steam production, electricity generation and temperature elevation is met by burning crude oil, which is a common practice in any industrial plant. Based on the stoichiometry shown in Figure 1, the approximate value for total CO_2 emission of furan resin is equal to 4.70 kg per kilogram of resin produced. This stoichiometric equation can also be used to solve for the total energy consumption. Because all the released CO_2 come from the combustion of fossil fuels for steam and electricity generation, all of the energy-equivalent CO_2 are considered fossil-based; on the other hand, the primary raw material of furan resin is biomass (wood, corn cobs, etc.), therefore all of its material carbon content shall be treated as bio-based. These carbon content values are then used to evaluate net biobased carbon, as shown in Table 1.

For the manufacture of furan-based NFRP, the amount of $E(NB)$ is increased due to the addition of natural fibers, which have 100% bio-based content. The weight of C in abaca is estimated based on the average fraction of cellulose in the fiber and the weight percent of C in cellulose. On the other hand, aside from the reduced fossil-based carbon content, the addition of the fibers also reduces the bio-based carbon contribution of the furan resin, which is expected to be larger compared to that of the fibers. In Table 2, the value of $E(NB)$ is slightly higher compared to that of the pure furan resin. However, this difference can still be further increased by increasing the amount of fibers incorporated in the NFRP composite, which effectively increases the amount of bio-based carbon content of the material without significantly increasing the amount of CO_2 emission. This is especially true for abaca fibers obtained from the Philippines, since their processing is essentially done manually without the need to consume a relatively high amount of energy.

For the estimation of carbon content in ortho-UP, certain assumptions are imposed to simplify the calculations; for instance, the mass and molar ratios of the primary reactants are based on a published ^{13}C-NMR study on the crosslinking of UP with styrene [7], while the emission data is based from a previously reported list of gross energy requirements for different intermediates and plastics [8]. Table 3 shows a sample calculation of the net bio-based carbon content for abaca/ortho-UP composites.

Figure 2 shows the carbon storage potential of furan and ortho-UP as NFRP matrices. Because of its plant-based origin, the $E(NB)$ value for furan resin is significantly higher. Therefore, the manufacture and use of furan resin may be considered as an excellent vehicle for advancing CO_2 sequestration. However, it must be noted that the production of furan resin itself is not CO_2 neutral- this is primarily due to energy requirements, which directly translates to fuel consumption. For the production of NFRPs, CO_2 neutrality may be achieved at high fiber fractions; this can be lowered by the use of biosynthetic thermosets. From Figure 2, it is shown that the use of furan over ortho-UP reduces this fiber fraction requirement by ~20%.

4.2 Thermogravimetric analysis

For long-term CO_2 fixation, the bio-based carbon content of a material is just one of the parameters that must be determined in order to evaluate overall carbon storage potential. Another parameter that must be considered is its lifetime. In order to assess environmental impact in comparison with other thermoset systems, the lifetime of the matrix must be estimated since it can provide information on the total energy consumption and CO_2, including within the waste disposal stage. Due to the long lifetime of highly stable resins (>10^2 years), it is not feasible to directly measure the longevity of carbon fixation of thermosets and their composites. One popular method of lifetime prediction for polymers is by thermogravimetric analysis (TGA). The resins are subjected to TGA at different constant heating rates, q (°C/min). For lifetime predictions, the simplest and most popularly used method is the Flynn-Wall-Ozawa method [9]. This technique converts typical TGA plots (Figure 3) into isoconversion curves at different conversions, α (Figure 4), which are represented linearly by Doyle approximation:

$$\log q = \log\left[\frac{AE}{Rg(\alpha)}\right] - 2.315 - 0.457\left(\frac{E}{RT}\right) \quad (1)$$

The integral function $g(\alpha)$ is dependent on the nature of the degradation mechanism for the material. The kinetic parameters can be evaluated from the average slope (m) and y-intercept (b) from fitting Equation 1 into the isoconversion lines:

$$E = -\frac{mR}{0.457} \tag{2}$$

$$A = \frac{Rg(\alpha)}{E} 10^{b+2.315} \tag{3}$$

The predicted lifetime (t_F) of a polymeric material is considered when 5% weigh loss is reached from the dynamic thermogravimetric analysis. Using the obtained kinetic parameters, the lifetime prediction model equation can be derived as follows:

$$t_F = \frac{0.05}{A} \exp\left(\frac{E}{RT}\right) \tag{4}$$

The activation energies of furan and ortho-UP at normal room temperature are about 85kJ/mol and 144kJ/mol, respectively, which indicates that furan resin have a shorter lifetime than ortho-UP resin.

It must be pointed out that for NFRP laminates, the bio-based fibers are completely embedded within the stable thermosetting resin, which prevents them from degrading; therefore the lifetime of the NFRP will be completely dependent on the lifetime of the polymer matrix.

4.3 Net CO_2 emission

The carbon storage potential is evaluated using the information obtained from carbon balance and the lifetime prediction. It must be noted that while the predicted lifetime of the thermosets goes well beyond 1,000 years, the actual expected long-term application is only up to 50-100 years. Therefore, the length of carbon storage for both resins may be assumed to be 100 years, and may be considered as a minor factor in the comparative analysis.

Table 4 shows a comparison of the estimated net CO_2 emission for the manufacture of furan resin and ortho-UP. It can be seen from that furan resin production results to a higher net CO_2 emission in comparison to ortho-UP. Furthermore, the estimated yearly CO_2 emission is further reduced with the inclusion of natural fibers, especially at higher fiber fractions, as shown in Figure 5. This is in agreement with the previously discussed concept of net bio-based carbon content. For the production of abaca fiber-reinforced furan composites, a zero net CO_2 emission is also found to be attainable at about 65wt% of abaca fiber content. Therefore, the eco-friendliness of the thermoset-based NFRP strongly depends on the natural fiber reinforcement used in its fabrication.

4.4 Mechanical strength

For the abaca/furan NFRP, it has been found that acid treatments for the abaca fibers are due to the ineffectiveness of alkali treatment (~60 MPa, lower than that of neat furan's). The mildly acidic nature of the fiber surface treatment promotes the curing of furan near the fiber surface. Figure 6 shows a comparison of the effect of fiber weight fraction on the strength of furan and ortho-UP-based NFRP. For long NFRP's, a high fiber content (>50wt%) is desired to reach strength levels well above 200 MPa. This high fiber fraction can be achieved for NFRP laminates by pressing the long fibers into UD fiber sheets prior to incorporation to the matrix resin. Figure 6 also shows that the performance of furan resin is comparable to that of ortho-UP resin.

5 Conclusions

For thermoset-based NFRPs, evaluation of carbon storage potential is vital in establishing their environmental impacts. Their ability to sequester carbon in the form of laminated natural fibers for a very long period of time compensates for the fact that they are not biodegradable, thus making them both environment-friendly and suitable for long-term applications. The use of biosynthetic resin such as furan shows a substantial improvement to the NFRP's carbon storage potential with the increased utilization of bio-based carbon over fossil-based carbon. Finally, CO_2 neutrality may be achieved by thermoset NFRPs by increasing their fiber content.

6 Acknowledgement

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Fig. 1. Schematic process and stoichiometric ratios of furfuryl alcohol to furfural and furan

Table 1. Carbon balance from furan resin production

Items	Value	Unit
CO_2 production/kg furan resin	4.698	kg
Fossil-based carbon equivalent, F	1.281	kg
MW of furfuryl alcohol, $C_5H_6O_6$	98	g/mol
Wt. furfuryl alcohol used/kg furan resin	1.145	kg
Weight C/kg furan resin	0.701	kg
Bio-based content in furan resin, W(b)	100	%
Bio-based carbon equivalent, B	0.701	kg
Total carbon content equivalent, E(T) = F + B	1.983	kg
Bio-based carbon content equivalent, E(B) = B/(F + B)	0.354	kg/kg
Net bio-based carbon content equivalent, E(NB) = B – F	-0.580	kg

Table 2. Carbon balance from abaca/furan NFRP production at 10wt% abaca fibers

Items	Value	Unit
Wt. percent abaca fibers in NFRP	10	%
Wt. abaca fibers/kg NFRP	0.100	kg
Wt. fraction cellulose in abaca fiber	0.600	kg/kg
Wt.percent C in cellulose	52	%
Wt.furan resin matrix/kg NFRP	0.900	kg
Wt.C from furan resin matrix	0.631	kg
Fossil-based carbon equivalent	1.153	kg
Bio-based content in NFRP	100	%
Bio-based carbon equivalent	0.662	kg
Total carbon content equivalent	1.816	kg
Bio-based carbon content equivalent	0.365	kg/kg
Net bio-based carbon content equivalent	-0.491	kg

Table 3. Carbon balance from abaca/ortho-UP NFRP production at 10wt% abaca fibers

Items	Value	Unit
Wt. percent abaca fibers in NFRP	10.0	%
Wt. abaca fibers/kg NFRP	0.100	kg
Wt. fraction cellulose in abaca fiber	0.600	kg/kg
Wt. percent C in cellulose	52.0	%
Wt. C from abaca fibers	0.0310	kg
Wt.UP resin matrix/kg NFRP	0.900	kg
Wt.C from ortho-UP	0.604	kg
Fossil based carbon equivalent	1.19	kg
Bio-based content in NFRP	10.0	%
Bio-based carbon equivalent	0.0310	kg
Total carbon content equivalent	1.22	kg
Biobased carbon content equivalent	0.0260	kg/kg
Net biobased carbon content equivalent	-1.16	kg

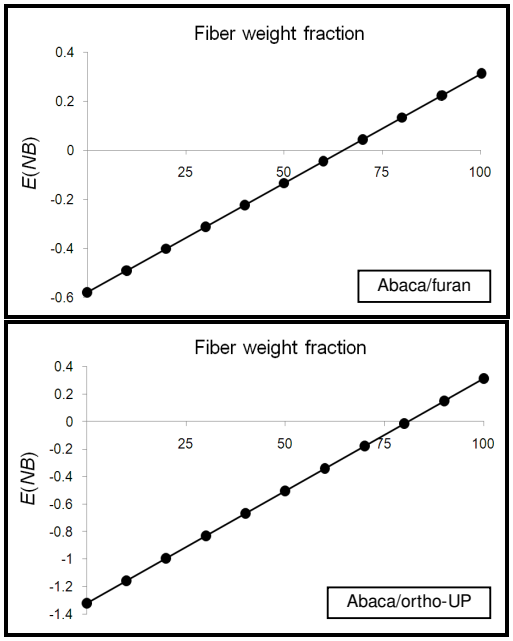

Fig. 2. Correlation between fiber content and *E*(*NB*) for abaca/furan and abaca/ortho-UP NFRP

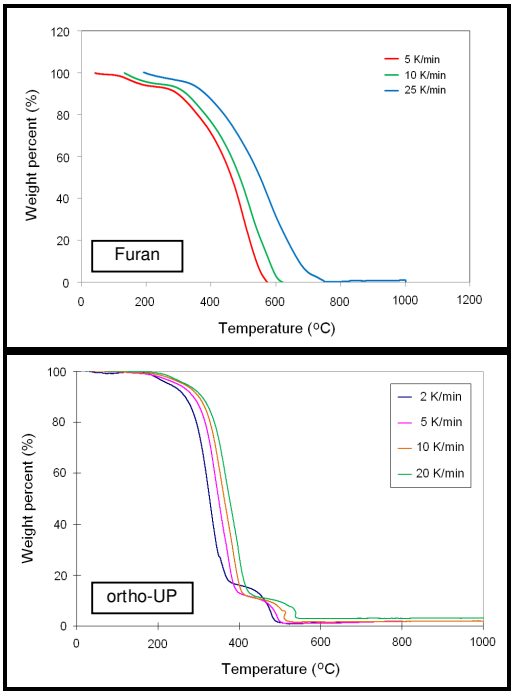

Fig. 3. TGA data for furan and ortho-UP resin at various constant heating rate

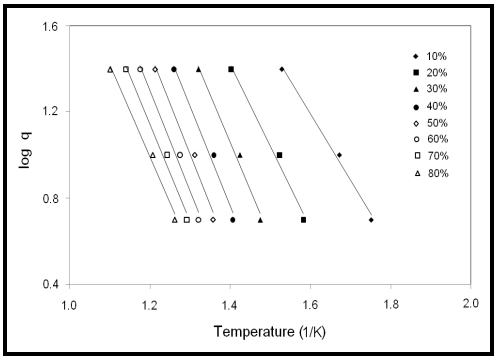

Fig. 4. Plots of log *q* vs. 1000/T for furan resin at different percent conversions according to Flynn-Wall-Ozawa method

Table 4. CO_2 emission for furan and UP production

Environmental Impact	Furan	Ortho-UP
Fossil-based CO_2 emission (kg/kg)	4.7	2.4
Bio-based carbon content (kg/kg)	0.70	0.00
Fixed CO_2 content (kg/kg)	2.6	0.00
Net CO_2 emission (kg/kg)	2.1	2.4

Table 5. Long-term carbon storage of furan and UP

Environmental Impact	Furan	Ortho-UP
Fossil-based CO_2 emission after resin production (kg/kg)	4.7	2.4
Bio-based carbon content (kg/kg)	0.70	0.00
Approximate lifetime at 25°C (years)	100	100
Fossil-based CO_2 emission after incineration (kg/kg)	0.00	2.5
Net CO_2 emission (kg/kg)	2.1	7.9
Estimated CO_2 emission (g/yr)	21	79

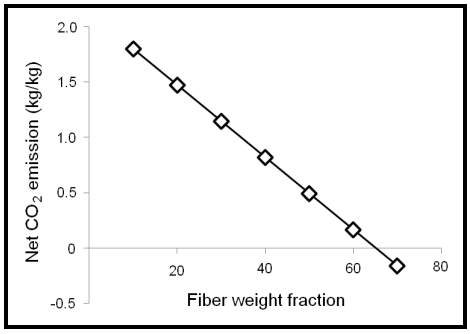

Fig. 5. Correlation between fiber content and net CO_2 emission for abaca/furan

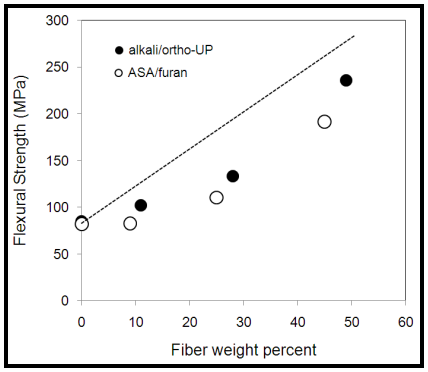

Fig. 6. Flexural properties of abaca/furan and abaca/ortho-UP at different fiber weight fractions

References

[1] M. Pervaiz and M. Sain "Carbon storage potential in natural fibre composites". *Resources, Conservation and Recycling*, Vol. 39, pp. 325-340, 2003

[2] S. V. Joshi, L. T. Drzal, A. K. Mohanty and S. Arora "Are natural fiber composites environmentally superior to glass fiber reinforced composites?". *Composites: Part A*, Vol. 35, pp. 371–376, 2004

[3] T. Corbiére-Nicollier, B. G. Laban, L. Lundquist, Y. Leterrier, J. Manson and O. Jolliet "Life cycle assessment of biofibres replacing glass fibres as reinforcement in plastics". *Resources, Conservation and Recycling*, Vol. 33, pp. 267–287, 2001

[4] ASTM D6852-02. "Standard guide for determination of biobased content, resources consumption, and environmental profile of materials and products". ASTM International, 2006

[5] A. Thygesen, B. Madsen, A. B. Thomsen and H. Lilholt "Effect of acidic conditions on interface and strength of cellulose fibers". *Proceedings of the 28th Riso International Symposium on Materials Science*. Roskilde, Denmark, pp 289-296, 2007

[6] C. Skogh and G. E. Savo "Method for continuous production of furfural from suitable raw materials". US Patent 2862008, filed October 5, 1953 and issued November 5, 1958

[7] M. Paci and F. Campana "^{13}C-NMR study of the crosslinking of unsaturated polyester-styrene cured resins". *European Polymer Journal*, Vol. 21, No. 8, pp. 717-721, 1985

[8] M. Patel "Closing carbon cycles" Doctoral dissertation, Utrecht University. Retrieved from http://www.uu.nl/university/library/nl/igitur/Pages/default.aspx, 1999

[9] J. H. Flynn "A critique of lifetime prediction of polymers by thermal analysis". *Journal of Thermal Analysis*, Vol. 44, pp. 499-512, 1995