Novel UV/EB Curable Flame Retardant Coatings Using Unique Water Compatible Oligomers; Applications of the Coatings Particularly for Recycling Waste Products Such as Banana Tree Trunks.

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Abstract

The use of novel water compatible epoxy acrylate oligomers in UV curing of unique coatings onto cellulosic materials particularly of waste origin is described. The application of the process in treating a novel veneer/paper product obtained from the peeling of waste banana tree trunks is discussed. This product which is not pulped is shown to possess exceptional flame retardancy properties, the potential of which is discussed in the fields of packaging, timber veneers and general paper applications. Mechanically pulped paper from the waste banana tree has also been prepared, coated and UV cured and its flame retardancy compared with the peeled product, and also commercial chemically pulped papers. The mechanism of the flame retardancy is examined, especially the environmental advantages of not using halogens for this purpose. The commercial potential of the flame retardant product from the peeling process is discussed and is supported by a carbon trading/ecological footprint analysis.

Introduction

Currently the world energy crisis, compounded by global warming, has accelerated the demand for products from recycled materials, particularly of waste origin. UV/EB curing is a valuable tool for converting such waste materials into value added products, especially cellulosics[1,2]. Timber and related products are particularly relevant in this respect since virgin materials are becoming expensive and more difficult to resource as are other cellulosics such as high quality paper and poorer quality materials such as cardboard which is essential for the packaging industry especially for foodstuffs.

A potentially huge untapped source of cellulosics which has been dormant and is currently being strongly investigated are the trunks of waste banana trees after the fruit has been cropped. There are 330 billion banana trees grown annually in the world and their waste trunks are either mulched at the site to ultimately become poor fertiliser, or are burnt leading to massive aerial pollution since these trunks contain up to 75% water and smoulder for weeks after being ignited.

These trunks are predominantly cellulosic but contain up to 15% lignin. They can be peeled in a manner similar to timber logs to give a sheet product capable of being used as a special type of paper, cardboard or as a veneer. There are potentially a wide variety of end-users where these products could be marketed. An important but unusual application for these products is for low priced emergency housing for disaster areas where tens of thousands of people may require urgent help to survive. After a disaster, it is envisaged that pre-packaged housing made from these recycled products could be air-dropped to the disaster site then immediately opened up to provide an emergency two room house. For this purpose and related applications, the recycled product would need to possess additional physical properties such as water proofing and the like. On-line UV curing of current coatings on the wet product as it is being dried is an appropriate process for achieving these value added properties. For many applications, the product needs to be flame retardant. Fortunately, the banana ply products are naturally flame retarded, but additional work is required to determine the flame retardancy of coatings on this substrate.

In the present paper, the use of UV curing of novel water compatible oligomers to improve the properties of the waste banana trunk products will be evaluated. Flame retardancy (FR) will be the key property investigated with unique oligomers prepared for this purpose. Two banana type papers will be studied in this work, the first obtained by direct peeling of the paper followed by drying and the second is a product obtained from mechanical pulping of the trunk of the banana tree. The possibility that the FR work will be applicable to other fields will also be examined. For this purpose, the FR of the banana paper will be compared with the same property exhibited by two other commercial papers, namely a Fasson label stock material and a brown Kraft product supplied by Daltons Pty Ltd. Finally a carbon trading and ecological footprint analysis of these UV cured recycled processes will be performed to demonstrate the environmental advantages applicable to these systems.

Experimental

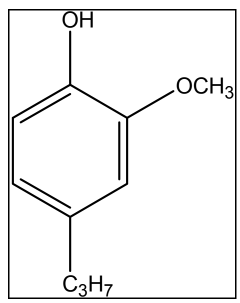
The waste banana tree trunks were from Cavendish banana plants grown in Queensland, Australia and supplied by Papyrus Australia Pty Ltd. Two proprietary oligomers were used in this work and were synthesised from chemicals supplied by Aldrich, Monocure Pty Ltd, Wattyl Pty Ltd, and Nucleation International Pty Ltd. Both oligomers were epoxy acrylates, the first being a conventional type of product synthesised from a standard epoxy resin and acrylated with acrylic acid. The second oligomer was a water compatible epoxy acrylate made from the same basic components as the first material however specific additives were added during the synthesis to incorporate into the finished product the physical properties such as water solubility and flame retardancy. The coatings based on the first epoxy acrylate were reduced 30% with tripropylene glycol diacrylate for application purposes and incorporated Darocur 1173 as the photoinitiator whereas the formulation utilising the water compatible oligomer used water as the diluent if required (usually up to 5%). For the curing experiments[3,4], the paper samples were coated with formulations applied to the substrate using a drawdown bar (approximately 10-15 gsm), then exposed to a Fusion F300 lamp fitted with a D bulb operating at a line speed of 15 m min^{-1} with an intensity of 1.4 W cm^{-2}.

The flame retardancy experiments were carried out using a modification of Australian Standard 1530 where the coated substrate is held vertically and a standard flame is applied at the front of the substrate. To pass this test, the material had to possess a self extinguishment time of less than 12 s. The Test was used as a comparative guide in assessment of the relative flammability.

Results and Discussion

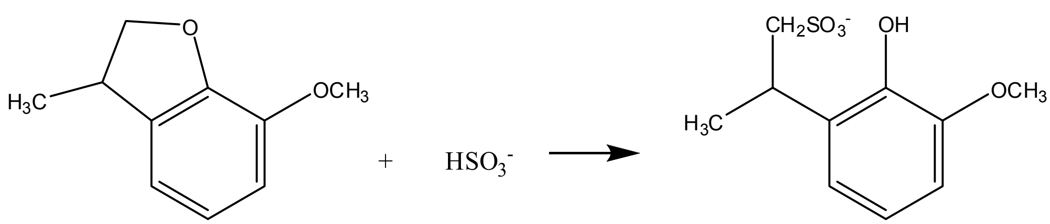
Banana Ply Papers (BPP)

BPP is a product made from the stems of banana trees after fruit harvesting. In addition to being treated as a type of paper, the product can be considered to be a veneer, however the term BPP will be used in this discussion to cover other types of product, the essential difference between the two being the thickness of the BPP. In the first series of experiments, the BPP 1 has been made by a peeling process similar to that used for the production of timber veneers. After peeling, the BPP 1 can be laid up (if needed) to give a multiply paper which is fed through a mangle, then pressure rollers and finally an oven to remove the incorporated water (75%). Since no pulping is involved in this process, the BPP 1 contains residual lignin (approximately 15%) which is a polymeric mixture, this has, as yet, only been partially characterised but is known to contain aromatic structures such as guaiacol, 4-n-propyl guaiacol (I) and vanillin.



(I)

Similar compounds have been isolated from waste liquors obtained from pulping of wood by the acid sulfite process. In this process the lignin has reacted with the cooking liquor to yield lignosulfites (reaction 1)



(1)

The presence of lignin in BPP 1 can be useful in UV curing since it is aromatic leading to increased rates of polymerisation due to enhanced UV absorption i.e. it acts as a photoinitiator. The presence of the aromatic ring may also reduce the adhesive strength of the coating because of the difficulty of breaking bonds in the aromatic ring to create free radical sites where cure grafting may occur to form strong chemical, as distinct from physical, bonds between the coating and the substrate. Overall, the BPP 1 manufacturing process is relatively simple, environmentally friendly and inexpensive when compared to chemical pulping.

The second series of experiments were performed with a banana ply paper which has been pulped mechanically (BPP 2). The degree to which the process removed lignin remains controversial, however, it is accepted that the level of lignin in BPP 2 is lower than BPP 1. The mechanical pulping process disperses the BPP 2 fibres extremely thoroughly after which they are collected and dried on a screen. The BPP 2 product is softer and more water adsorbent than BPP 1 reflecting the loss of lignin during pulping. Since no toxic chemicals are used in mechanical pulping, the process is environmentally friendly.

Flame Retardancy of Conventional Industrial Papers

The FR tests with the first of the standard industrial papers studied, namely Fasson label stock chosen because it is frequently used in packaging, are reported in Table 1. Because it was difficult to find a standard test for determining the FR of treated papers, a modified textile standard test method (Australian Standard 1530) was used. This Standard covers testing of cellulosic textiles, so the results are a reasonable guide for determining the various efficiencies of the different FR formulations used to coat the sample papers. Two results are reported for each sample, the first is the self extinguishing time after the ignition source is removed once combustion has been initiated. This should be less than 12 s for most applications. The second FR property, burn time, is the time taken for 10 cm of the sample to combust when the standard flame is applied to the bottom front surface of the sample. Although these are arbitrary measures of the FR of the papers, a comparative analysis of the results indicated the relative FR properties of each of the systems.

The reference oligomer used in this work was a proprietary water based epoxy acrylate (EPA) described in the Experimental. In addition, four other epoxy acrylates (EPA 1-4) were synthesised with different proprietary FR. The results in Table 1 show that when the formulation containing EPA was coated onto one side of the paper only, there was a marginal increase in the burn time. The formulations containing EPA 1-4 demonstrated significant improvement in the burn time, EPA 3 and 4 being the most efficient. More importantly, incorporation of aluminium trihydrate as a synergistic FR into EPA 3 and 4 led to even better burn times. With respect to self extinguishing times, EPA 2-4 were greater than 12 s but EPA 1 was marginal. The results show that if a relevant FR chemical can be chemically bound to a UV curable EPA during synthesis and aluminium trihydrate added to the formulation, an oligomeric system with extremely high FR properties is obtained. In this instance, the mechanism of action of aluminium trihydrate is attributed to the release of bound water.

Table 1: Flame Retardancy of Coatings on Fasson Label Stock.

Run	Coating System	Burn Time (s)[a]	Self Extinguishing[b]
1	None	5	N
2	EPA	7	N
3	EPA 1	10	N
4	EPA 2	12	Y
5	EPA 3	20	Y
6	EPA 3 + Trihydrate	22	Y
7	EPA 4	22	Y
8	EPA 4 + Trihydrate	26	Y

Superscripts: a) time for 10 cm of the sample to burn and b) Y means that the ignited sample self extinguished in less than 12 seconds

The degree to which the paper is coated (i.e. number of coats) is also important in determining the FR properties of the product (Table 2). The results in the Table for Fasson label stock are consistent with those in Table 1. It is also observed that even coating one side of the paper with an appropriate formulation can be sufficient to enhance significantly the FR properties of the whole substrate. This is important since, in this instance, the flame during heating does not rapidly migrate up the exposed uncoated side of the paper. This observation is consistent with the suggestion that vapours generated from heating the FR coating on the other side possess sufficient activity to restrict migration of the flame up the uncoated side.

Table 2: Flame Retardancy of Coatings on Fasson Label Stock- Effects of Numbers of Coats.

Run	Coating System	Sides	Coats	Burn Time (s)[a]	Self Extinguishing[b]
1	None			5	N
2	EPA 1	1	1	9	N
3	EPA 1	2	1	10	N
4	EPA 2	1	1	11	Y
5	EPA 2	1	2	12	Y
6	EPA 2	2	1	14	Y

Superscripts a, b: Terms defined in Table 1

Flame Retardancy of Brown Kraft Paper

The FR results with the industrial brown Kraft paper were significant in that most of the polymeric systems used could enhance the burn time and self extinguishing properties of the samples almost to satisfactory levels (Table 3). EPA 4 with two coats on both sides was the best of the systems exhibiting marginal FR behaviour, however, from the trends in Table 1, addition of aluminium trihydrate as a synergist to the last EPA 4 sample should lead to satisfactory FR properties in the material. The marked difference in FR reactivity in these experiments between the Fasson label stock (white paper) and the brown Kraft paper reflects the difference in manufacture of these two products. The Fasson label stock contains significant percentages of traditional paint fillers used as matting agents and also titanium dioxide pigment which would enhance the FR properties. These fillers and pigments also increase the weight of the relevant paper compared to brown Kraft paper which is relatively thin, although physically strong reflecting the binding efficiency of the starch which is one of the paper's main components.

From these results, it is obvious that the brown Kraft paper can be satisfactorily flame retarded however the process would be significantly more expensive than with the Fasson label stock.

Flame Retardancy of BPP

The results of the flame retardancy studies using BPP 1 and BPP 2 are shown in Table 4. The extraordinarily high FR exhibited by neat BPP 1 has necessitated a completely different approach to FR work with this material. Even after 50 seconds exposure to the standard flame, this material is not fully combusted. This exceptional FR property enables a new, more economical approach to be made in formulating FR coatings for BPP 1 products. The problem is that for many potential industrial applications of BPP 1 such as veneers and building products, a protective coating must be applied to improve properties such as abrasion resistance and the like. Normally, as was observed for the Fasson label stock and the brown Kraft paper, appropriate coatings containing FR chemicals need to be synthesised to give adequate FR properties for these coated papers. However, because of the very high intrinsic FR properties of the BPP 1, it is conceivable that conventional non FR coatings could be applied to BPP1 and the coated product could possess sufficient FR to meet industrial specifications. Such a process, if successful, would simplify the design of FR coatings for BPP 1, and would be economically valuable since any general purpose matt, satin or gloss UV coating could be used to achieve a satisfactory level of FR in the coated product.

Table 3: Flame Retardancy of Coatings on Brown Kraft Paper.

Run	Coating System	Sides	Coats	Burn Time (s)[a]	Self Extinguishing[b]
1	None			2	N
2	EPA 1	1	1	2	N
3	EPA 2	1	1	4	N
4	EPA 3	1	1	5	N
5	EPA 4	1	1	5	N
6	EPA 4	1	2	7	N
7	EPA 4	2	1	8	N
8	EPA 4	2	2	10	N

Superscripts a, b: Terms defined in Table 1

Table 4: Flame Retardancy of EPA Coating on Banana Ply Paper.

Run	Pulped[a]	System	Sides	Coats	Burn Time (s)[a]	Self Extinguishing[b]
1	N	One ply BPP 1			50+	Y
2	N	One ply BPP 1	1	1	6	N
3	N	One ply BPP 1	2	1	4	N
4	N	Two ply BPP 1			50+	Y
5	N	Two ply BPP 1	1	1	11	Y
6	N	Two ply BPP 1	2	1	12	Y
7	Y	Light weight BPP 2			6	N
8	Y	Light weight BPP 2	1	2	10	N
9	Y	Light weight BPP 2	2	2;1	9	N
10	Y	Medium weight BPP 2			10	N
11	Y	Medium weight BPP 2	1	2	10	N
12	Y	Medium weight BPP 2	2	2;1	9	N
13	Y	Heavy weight BPP 2			16	Y
14	Y	Heavy weight BPP 2	1	2	18	Y
15	Y	Heavy weight BPP 2	2	2;1	18	Y

Superscripts a, b: Terms defined in Table 1

The data in Table 4, runs 1-6, indicate that under the appropriate experimental conditions, the non-FR EPA can be used to coat the BPP 1 and yield a product that would be commercially viable in terms of FR. This conclusion applies to the two ply BPP 1 whereas the treated one ply is not satisfactory. The data however indicate that the one ply BPP 1 could be treated satisfactorily if the coating applied were slightly flame retardant. In this respect, the difference in the FR results between runs 1-3 and 4-6 reflects again the effects of the thickness of the substrate in these experiments, the thicker material exhibiting higher natural FR. This observation is important in practice because for many potential applications of BPP 1, thicker materials than one ply would be required even four ply.

When the FR results of the BPP 1 are compared with those of the mechanically pulped BPP 2, marked differences are observed. For BPP 2 runs, three types of materials were used each varying in weight. The first series were labelled light weight, the second (termed medium weight) were twice the weight of the first, and the third (termed heavy weight) were three times the weight of the first. The data in Table 4, runs 7-15, indicate that all three uncoated type BPP 2 samples were significantly inferior in FR properties to BPP 1, only the heavy weight paper (run 13) giving a satisfactory result for the burn test. When all samples 7-15 were coated with the non-FR EPA, the trend in flammability properties was similar to that of the uncoated materials i.e. runs 7, 10 and 13. Thus, in practical applications, the light and medium weight materials would need to be coated with an FR oligomer to achieve satisfactory burn test properties. In the mechanical pulping process, a significant proportion of the original lignin has been removed thus lowering the residual FR properties of the sample. The amount of lignin left after pulping is not accurately known, but other physical tests on the material have indicated that some lignin remains in the pulped material.

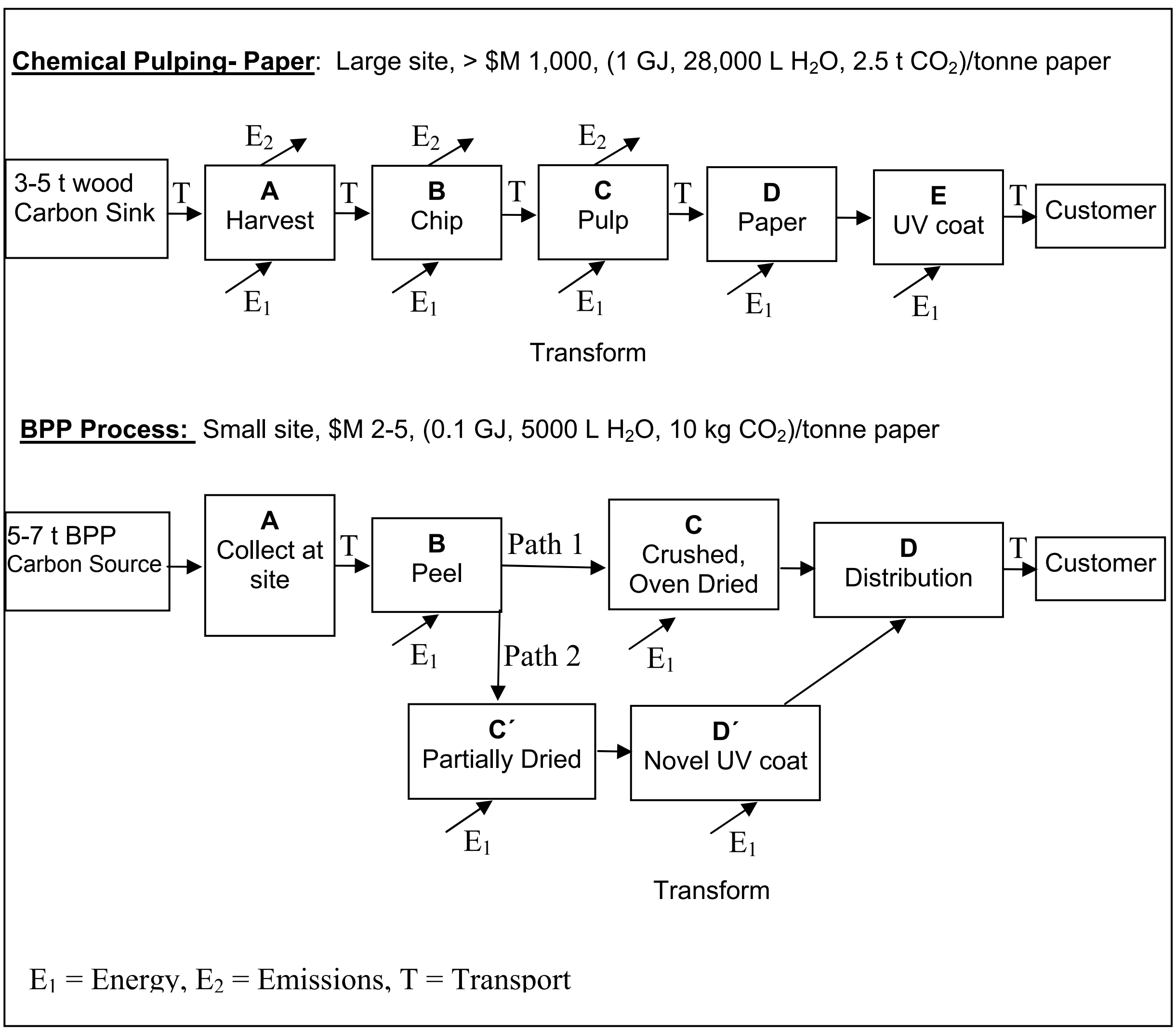
Evaluation of the Environmental Significance of the Current BPP Process

The FR results reported here demonstrate one of the outstanding natural properties of BPP 1. The fact that BPP 1 is a naturally occurring waste product is of great importance environmentally since it is not pulped and can potentially replace many commercial end-uses of conventional paper which has been produced from chemically pulped wood. It is therefore of interest to attempt to quantify this environmental aspect of BPP 1 using carbon trading/ecological footprint concepts. For this purpose, it is appropriate to compare the current proposed BPP 1 process with the conventional and widely used chemical method of pulping. This comparison is shown in Figure 1.

In the chemical process, the trees are harvested (A), then chipped (B), followed by pulping (C) at the mill site (D), then final post treatment applied which may be UV curing (E). In this process, it is economical to use one large pulping site (500 -1000 M$) to service a wide area of trees necessitating the use of extensive transport. The process per tonne of wood uses large amounts of water (28,000 L) and uses significant quantities of a variety of chemicals, emits 2.5 tonne of CO_2 and from 3-5 tonnes of wood yields 1 tonne of paper.

In contrast, the BPP process utilises no water or chemicals and, and is a relatively simple process (path 1), since the paper is peeled from the banana tree trunk, then crushed to reduce the incorporated water level from 75% to 20-25%, then dried under mild oven conditions. Alternatively, using path 2, after the peeling step, the paper is crushed to 20-25% water, then before the final drying step, exposed to a UV curing process with the water compatible resins reported in this current work. As the oligomer UV polymerised, the polymer formed in situ will be highly hydrophobic and will repel water from the paper. The UV process thus assists the drying step. UV curing could also be performed at an earlier stage where higher water contents remain in the paper. Again UV curing should assist in drying of the paper. This final drying step is delicate and must occur simulating an equilibrium process otherwise the paper may shrink. From 5-10 tonne of banana trunks, 1 tonne of banana ply paper is obtained with little energy needed (0.1 GJ), no chemicals, 5000 L of water, and little CO_2 emissions (<10 kg). The magnitude of the environmental advantages of the BPP system can be clearly demonstrated if the process outlined in Figure 1 is interpreted in terms of carbon trading/ecological footprint concepts. The chemical pulping utilising cut down trees is a carbon sink where each of the successive steps A, B, and C requires energy inputs and large gas emissions. In the pulping operation, the site is large and expected to service a wide area with logs being transported a large distance. The sites are expensive utilising large quantities of energy with big gas emissions.

Figure 1: Environmental Analysis of Chemical Pulping versus BPP Peeling Process- Carbon Trading/Ecological Footprint



Conclusions

Novel water compatible epoxy acrylate resins can be formulated into coatings which may be UV cured onto a paper/veneer type product peeled from the trunk of the waste banana tree. This UV process assists with the drying of the paper/veneer during manufacture and also acts as a protective surface coating on the finished dried material. By virtue of its method of preparation, the product is not pulped and exhibits exceptional intrinsic flame retardancy especially when compared with a corresponding mechanically pulped paper from the same source, and also conventional papers made by chemical pulping of timber, typically commercial materials such as Fasson label stock and brown Kraft paper. The process for the synthesis of the non-pulped paper veneer is environmentally friendly since no toxic chemicals are used and no halogenated derivatives are need to achieve flame retardancy. This conclusion is confirmed by the positive carbon trading and ecological footprint analysis which is reported. The exceptional flame retardancy property of this paper/veneer can be utilised in a wide range of industries, namely packaging, timber veneers and building products especially where paper is required for surface treating boards in both interior and exterior applications.

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