UV Curing and Cure Grafting of Novel Water Compatible Oligomers with Nanoparticle Fillers on Cellulosics Particularly Banana Ply Paper.

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Abstract

UV curing and cure grafting reactions have been performed with a range of novel water compatible oligomers on three papers: Whatman 41; label stock which is an acrylic coated paper used in the label industry; and a new product, banana ply paper. Fusion F300 (D-bulb) and LED (385 nm) lamps were used to cure films onto the substrates. The effects on cure and cure grafting by inclusion of two nanoparticle dispersions were investigated. The advantages of using water compatible oligomers in these UV processes are discussed. The great potential for the use of coated banana ply paper is reviewed.

Introduction

Current UV formulations are based on the traditional epoxy, urethane, polyester and polyether acrylates which are cut in multifunctional monomers to improve ease of application and fast cure via crosslinking processes. For certain specific applications involving these oligomers, such as spraying, the viscosity of these formulations may be reduced by the addition of solvents which must be flashed off prior to exposure to UV. Solvents are also needed for cleaning up in the plant at the conclusion of the processing. Some of many problems inherent in using solvents (cost, health and safety, flammability) can be effectively overcome by the use of water-based formulations. However, currently the solids contents of the commercially available water compatible resins (usually dispersions) are approximately 35%, again necessitating the use of flash-off ovens to the remove the excess water before curing.

In this paper, a range of novel water compatible oligomers will be described possessing solid contents up to 95% for use in UV curing and cure grafting formulations. Some of these unique oligomers could be synthesised with 100% solids whilst maintaining water compatibility. All of these formulations may be diluted with water for application purposes, if required. In addition the polarity of these oligomers renders them compatible with many fillers, particularly nanoparticle fillers. Formulations involving these water compatible oligomers were used to coat three typical papers: Whatman 41; label stock cellulose which is an acrylic coated paper used in the label industry; and a new commercial product, banana ply paper. Both UV curing and cure grafting[1] were performed on these cellulosics with two lamps: Fusion F300 (D-bulb) and LED (385 nm cut-off which is relatively safe for body exposure). In addition, the effects of nanoparticle fillers in these formulations were also investigated.

Experimental

Chemicals used to synthesise the oligomers were supplied by Aldrich, Monocure Pty Ltd, and Ballina Pty Ltd. The oligomers are propriety products but the classes are: acrylamide derivative, AM; extended pentaerythritol acrylate, PETA; pentaerythritol modified epoxy acrylate, PEPA; epoxy acrylate, EPA1; epoxy acrylate with higher proportion of epoxy resin, EPA2; and aromatic urethane acrylate, UA. BASF donated alumina nanoparticles suspended in water (Nanobyk 3600) or TPGDA (Nanobyk 3601). Photoinitiators (Irgacure 369 and ITX 2959) were donated by Ciba Geigy. All the resins were used as received with no diluents added to adjust the formulations to a constant viscosity.

For the curing experiments, two UV lamp systems were used, namely a Fusion F300 with a D bulb operating at a line speed of 15 m min^{-1} with an intensity of 1.4 W cm^{-2}, and a Con-Trol-Cure LED lamp operating under static conditions with a cut-off at 385 nm with an intensity of $1.2\text{x } 10^{-2}$ W cm^{-2}. The curing and cure grafting procedures have previously been reported[2].

Samples of each of the papers were equilibrated at 65% relative humidity (RH), and weighed (w_0). Formulations were applied to the substrates using a drawdown bar, UV cured, re-equilibrated at 65% RH and reweighed (w_c) to determine the cure % (= $100 \text{ x } (w_c - w_0)/w_0$). The cured samples were extracted using soxhlet extractors with chloroform as the solvent for 12 hours, equilibrated at 65% RH and reweighed (w_e) to determine the cure graft % (= $100 \text{ x } (w_e - w_0)/w_0$).

Results

The results and discussion for the banana ply paper have been separated from those of the other two papers, namely Whatman 41 and label stock, since banana paper has not been pulped and it is structurally different. Whatman 41 was chosen because it is relatively pure cellulose however this paper is quite porous and whilst suitable for some applications, it is unsatisfactory for others especially in the graphic arts area covering printing, coating and labels. For this latter application, the well known acrylic coated label stock has been used, the results of any curing and cure grafting using this substrate will thus be important commercially. The oligomers used in this work are proprietary products, but their unique properties mean that they are all water compatible and are at least 95% solids thus no water flash off ovens are needed prior to UV curing.

Whatman 41 and Label Stock Papers

All six water compatible oligomers UV cure well onto Whatman 41 paper in one pass at line speeds of 15 m min^{-1} under the Fusion 300 lamp with a D-bulb (Table 1). The cured films are strongly grafted to the substrate. The viscosities of the epoxy acrylate oligomers were lower than the other oligomers thus l affecting the amount of coating being applied to the other formulations. Despite this limitation, reasonable coating weights could be applied with all oligomers. This viscosity effect was particularly relevant to the film weight applied on the label stock paper, this pre-coated material being more difficult to wet than the Whatman paper (Table 2). With the two epoxy acrylates, cure grafting yields were also significantly reduced.

Table 1: UV Curing and Cure Grafting of Novel Oligomers Containing Nanoparticles on Whatman 41 Cellulose Using the Fusion Lamp.

Run number	Oligomer	Filler	Cure %	Cure Graft %	Cure/Cure Graft (%)
1	AM		150	140	93
2	AM	N-3600	140	140	100
3	AM	N-3601	265	260	98
4	PETA		215	215	100
5	PETA	N-3600	120	120	100
6	PETA	N-3601	155	155	100
7	PEPA		120	120	100
8	PEPA	N-3600	93	93	100
9	PEPA	N-3601	120	120	100
10	EPA 1		155	125	81
11	EPA 1	N-3600	120	85	71
12	EPA 1	N-3601	135	97	72
13	EPA 2		100	83	83
14	EPA 2	N-3600	83	68	82
15	EPA 2	N-3601	96	83	87
16	UA		125	125	100
17	UA	N-3600	225	225	100
18	UA	N-3601	83	73	88

Table 2: UV Curing and Cure Grafting of Novel Oligomers Containing Nanoparticles on Label Stock Cellulose Using the Fusion Lamp.

Run number	Oligomer	Filler	Cure %	Cure Graft %	Cure/Cure Graft (%)
1	AM		96	96	100
2	AM	N-3600	200	200	100
3	AM	N-3601	185	180	97
4	PETA		58	55	95
5	PETA	N-3600	32	12	38
6	PETA	N-3601	40	35	88
7	PEPA		55	55	100
8	PEPA	N-3600	65	65	100
9	PEPA	N-3601	115	115	100
10	EPA 1		32	19	59
11	EPA 1	N-3600	18	11	61
12	EPA 1	N-3601	32	18	56
13	EPA 2		23	13	59
14	EPA 2	N-3600	29	23	79
15	EPA 2	N-3601	32	21	66
16	UA		110	110	100
17	UA	N-3600	83	81	98
18	UA	N-3601	87	84	97

When the LED lamp was used to cure the oligomers onto the Whatman paper (Table 3), the observed reactivity was consistent with the results using the Fusion lamp. Curing using the lower powered LED lamp could be achieved after exposure of 5 seconds to 1 minute, depending on the PI used. The larger exposure times are ideal for car refinishing and coating of boards whereas the shorter exposure is required for graphic arts applications.

Table 3: UV Curing and Cure Grafting of Novel Oligomers (Some Containing Nanoparticles) on Whatman 41 Cellulose Using the LED Lamp.

Run number	Oligomer	Filler	Cure %	Cure Graft %	Cure/Cure Graft (%)
1	AM		164	157	96
2	AM	N-3600	161	154	96
3	AM	N-3601	126	120	95
4	PETA		119	97	82
5	PEPA		105	102	97
6	EPA 1		83	48	58
7	EPA 2		89	65	73
8	UA		147	123	84

With the label stock as the substrate, the UV curing and cure grafting data with the LED lamp (Table 4) are significantly different to those in Table 2. Only the acrylamide derivatives gave reasonable cure and cure grafting results. The data are particularly low for the extended pentaerythritol acrylate while the epoxy acrylate runs were only marginally better.

Table 4: UV Curing and Cure Grafting of Novel Oligomers (Some Containing Nanoparticles) on Label Stock Cellulose Using the LED Lamp.

Run number	Oligomer	Filler	Cure %	Cure Graft %	Cure/Cure Graft (%)
1	AM		66	56	85
2	AM	N-3600	107	102	95
3	AM	N-3601	34	28	82
4	PETA		3	0	0
5	PEPA		12	4	36
6	EPA 1		20	8	39
7	EPA 2		12	3	27
8	UA		45	19	42

Banana Ply Paper

Generally the results in Table 5 for the banana paper under the Fusion lamp differ significantly from the other two papers (Tables 1 and 2). Only the acrylamide derivative and the pentaerythritol modified epoxy acrylate give yields which compare favourably with the other two papers.

Table 5: UV Curing and Cure Grafting of Novel Oligomers Containing Nanoparticles on Banana Ply Cellulose Using the Fusion Lamp.

Run number	Oligomer	Filler	Cure %	Cure Graft %	Cure/Cure Graft (%)
1	AM		53	52	98
2	AM	N-3600	105	97	92
3	AM	N-3601	115	110	96
4	PETA		32	9	28
5	PETA	N-3600	42	8	20
6	PETA	N-3601	36	8	21
7	PEPA		105	105	100
8	PEPA	N-3600	65	65	100
9	PEPA	N-3601	84	84	100
10	EPA 1		75	61	81
11	EPA 1	N-3600	32	22	69
12	EPA 1	N-3601	55	26	47
13	EPA 2		44	32	73
14	EPA 2	N-3600	29	14	48
15	EPA 2	N-3601	54	23	43
16	UA		33	29	88
17	UA	N-3600	73	73	100
18	UA	N-3601	56	41	73

When the LED lamp was used (Table 6), very good yields were observed with the oligomer based on the acrylamide derivative, with reasonable yields obtained with the remaining oligomers except for the extended pentaerythritol acrylate resin.

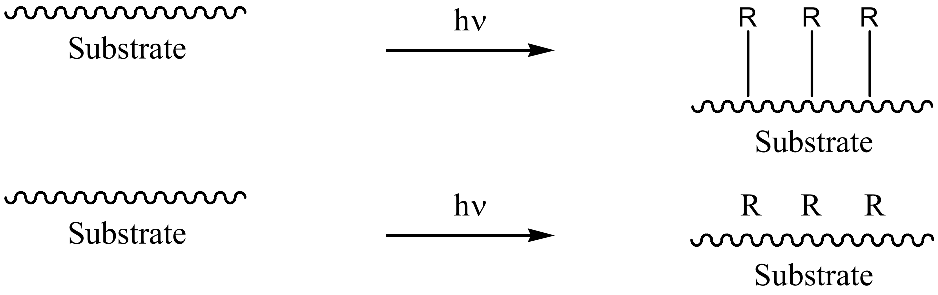
Table 6: UV Curing and Cure Grafting of Novel Oligomers (Some Containing Nanoparticles) on Banana Ply Cellulose Using the LED Lamp.

Run number	Oligomer	Filler	Cure %	Cure Graft %	Cure/Cure Graft (%)
1	AM		72	72	100
2	AM	N-3600	75	70	93
3	AM	N-3601	73	73	100
4	PETA		0	0	0
5	PEPA		49	46	94
6	EPA 1		33	17	52
7	EPA 2		61	42	69
8	UA		63	39	60

Discussion

Whatman 41 and Label Stock Papers Under the Fusion Lamp

The importance of water compatible resins, such as those used in this work, is demonstrated by the results of UV curing and cure grafting on Whatman 41 and label stock papers. The presence of a small amount of water (even 5%) is an advantage. The water may wet and swell the cellulose leading to efficient adsorption of these formulations resulting in excellent adhesion with no delamination of the cured film. The grafting data confirm this and show that interfacial bonding between the polymer and cellulose must essentially involve chemisorption (reaction 1) rather than the much weaker physisorption (reaction2). The grafting proceeds via reactions (3)-(7) where SH represents the substrate and RH the oligomer[1,3]. Reaction can be accelerated if required by the inclusion of appropriate photoinitiator (PI).



$$RH \xrightarrow{h\nu} R^{\bullet} + H^{\bullet} \quad (3)$$

$$SH \xrightarrow{h\nu} S^{\bullet} + H^{\bullet} \quad (4)$$

$$PI \xrightarrow{h\nu} P^{\bullet} + I^{\bullet} \quad (5)$$

$$P^{\bullet} + SH \longrightarrow PH + S^{\bullet} \quad (6)$$

$$R^{\bullet} + S^{\bullet} \longrightarrow \text{Graft} \quad (7)$$

The significant feature with the utilization of current oligomers is that for most end uses, no additional monomer(s) are required for application of these formulations and the cured films will have the properties of the cured oligomer rather than those of the oligomer plus the diluent monomer(s). However this does not preclude the incorporation of other monomers into these novel formulations for optimization of specific properties of the cured film.

The results in Table 2 also demonstrate that cure grafting to the label stock paper is satisfactory, but as expected, it is not as efficient as with the more porous Whatman 41 paper. In this respect, the epoxy acrylate oligomers are less reactive with the label stock than with the Whatman paper reflecting the effect of the lower polarity of the epoxy acrylate resins compared to the other more polar oligomers in the group. The more polar the resin, the more facile the swelling of the acrylate coated label stock when in contact and thus the higher the graft.

Whatman 41 and Label Stock Papers under the LED Lamp

One of the important reasons for the development of the LED lamp was to cure coatings in a region of the spectrum which was safe for body exposure. To the present time, these lamps do no cure as efficiently as their equivalents at 365 nm wavelength, however the LED lamps currently are designed for a variety of systems including those where cure times up to minutes can be satisfactory.

The data in Table 3 demonstrate that the LED lamps can cure the current range of water compatible oligomers efficiently after exposures of up to one minute. Cure grafting yields are relatively high for all oligomers cured under these conditions on Whatman 41 paper. The mechanistic aspects of photopolymerization previously discussed are also applicable to the LED results.

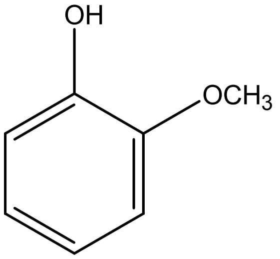
The effect of the power of the LED lamp when compared to the Fusion system is demonstrated by comparing the results in Table 4 with those in Table 2. The pre-coating on the label stock paper greatly reduced the UV curing yields for all systems, particularly with the epoxy acrylates. The low yields for cure grafting reflect the difficulty of creating grafting sites on the surface of the acrylic coated label stock paper by the traditional radical abstraction process with the initiator (reaction 6).

Banana ply Paper

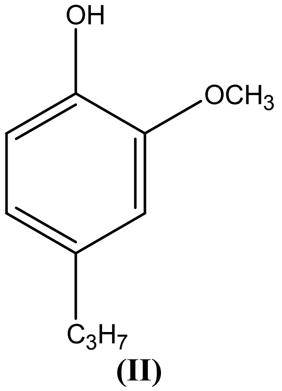
The data in Table 5 contain the first reports of UV curing and cure grafting on banana ply paper. The results are important because this paper is a novel product which has just been introduced into the market. It has great potential because of the economics of its production, being a fraction of the cost of the conventional papermaking process because there are no pulping operations required during its manufacture. The banana paper is made by a process which is similar to that used for the production of wood veneers. It is made from the stump of banana plants which are banana plantation residues. After the veneer is produced in the primary process, it is laid up into multi-ply paper which is fed through a mangle to remove excess water, and then dried using microwaves. Current veneering machines are capable of producing product at 0.8 m s^{-1}. The manufacturing technique is relatively simple, environmentally friendly and inexpensive.

The fibres in the banana paper are relatively long, thus the paper is quite strong and possesses other desirable properties such as flame retardancy. Since there is no pulping step, the residual lignin can contribute useful properties to the paper. It is interesting that many attempts have been made to pulp banana tree stems for production of paper by the conventional processes i.e. either by the sulfite or alkali technologies, but these have all failed. Low cellulose recoveries were obtained because of the relatively high lignin contents of the material, and also strong bonding of the lignin to the cellulose which makes it difficult to break the cellulose-lignin bond in pulping to yield pure cellulose.

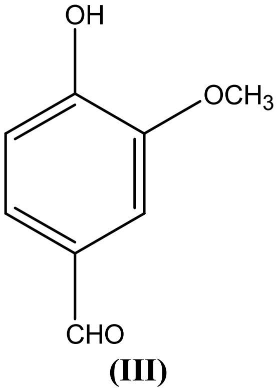
The performance of the banana paper in UV curing was expected to be influenced by the residual lignin as well as the cellulose in this paper. Lignin is chemically complicated in its structure, being non-carbohydrate and aromatic. Amongst the basic units isolated from lignin are guaiacol (I), 4-n-propyl guaiacol (II) and vanillin (III). Degradation studies have shown that the basic subunit of lignin is similar to structure (IV). These structures show why banana paper should have excellent adhesion to the novel UV cured coatings. The only grafting sites on conventional papers will be the hydroxyl radicals produced on the cellulose fibres, and these radicals are aliphatic. Banana paper contains both cellulose and lignin, and thus possesses both aliphatic and aromatic sites for grafting during UV cure. The grafting yield could be selectively enhanced by choice of oligomer systems that favour formation of donor acceptor intermediates between the aromatic rings of the banana paper and the unsaturated moiety of the adsorbed oligomer.



(I)



(II)



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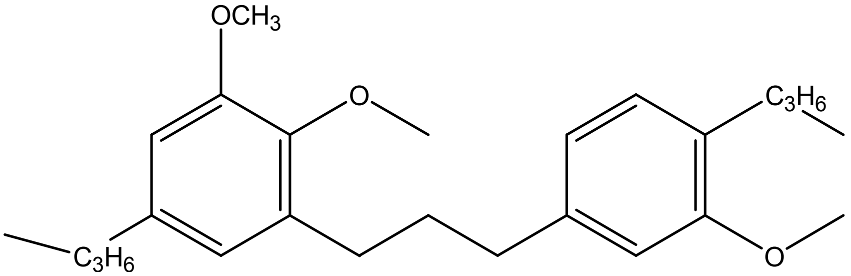

(IV)

The data in Table 5 show that the current water compatible oligomers are potentially ideal for UV curing of coatings on banana paper using the Fusion lamp. The LED lamp can also accomplish UV cure and cure grafting of oligomers onto banana paper (Table 6). As expected, the cure grafting efficiency of the LED process is lower than with the Fusion lamp because of the lower yield of the abstraction reactions required to produce the surface radicals required for grafting. However, significant concurrent cure grafting is still observed using the LED lamp. Preliminary studies showed that matt, semi-gloss and gloss finishes with good adhesion can be achieved on the banana paper with this technique and related studies also confirmed that UV inks can be cured onto this paper[4].

Nanoparticle Additives

Nanoparticle additives are becoming increasingly important for improving the properties of films, especially scratch resistance and gas permeability[5-7]. The present results show that the recently developed Nanobyk nanoseries of additives are compatible with these novel oligomers, and they do not significantly affect UV curing or cure graft yields when incorporated into these formulations (Tables 1-6). The results show that there is little difference in reactivity of the two Nanobyk additives indicating that the solvent used in these products (either TPGDA or water) is not relevant in the curing of these formulations. Preliminary results show that cured films containing the Nanobyk additives possess greater abrasion resistance and hardness.

Advantages of Current Water Compatible Oligomers in UV Curing

Studies with this current series of water compatible oligomers illustrated the following advantages of their use in UV curing systems:

1) Low water contents (<5%) eliminate the need for flash-off ovens on line before UV exposure. Most current water compatible systems are dispersions where the solid content is relatively low (<35%) necessitating the use of ovens.
2) The relative low viscosities of these oligomers obviate the need to use reactive diluents. Monomers can be added to the water compatible oligomer to maximise desired properties rather than be mandatory simply to reduce viscosity.
3) The novel oligomers are compatible with a wide range of conventional UV active monomers and oligomers which should widen the scope of their use.
4) The addition of low percentages of water (<5%) leads to better wetting and swelling of polar substrates such as cellulose with enhanced adhesion of the UV cured films.
5) Many of the oligomers can be produced without any water, but they can be diluted with any proportion of water for the specific application.
6) If the degree of cure graft is high and renders recycling of the UV cured product difficult, additives can be included in the coating formulation to reduce the level of cure graft and permit recycling.
7) Clean-up procedures in the plant after processing can be achieved with water.
8) If, for any reason organic solvents are required including processing or clean-up of the plant, these oligomers are compatible with most solvents.
9) The oligomers are safer to transport and store than conventional acrylates.
10) The manufacturing process is fast compared to conventional acrylates.
11) The oligomers are relatively inexpensive due to the low cost of the raw materials used during manufacture.
12) The oligomers are flame retardant and thus safer.
13) The oligomers have low odour and are environmentally friendly.
14) These oligomers are water soluble which means that solutions should be more stable than other products which are stabilized dispersions
15) Many of the new nanoparticle additives have hydrophilic surfaces and these oligomers are ideal because they readily wet the surface which greatly simplifies homogeneous dispersion.

Overall, the final advantage of the use of these oligomers is their specific application for products based on the banana ply paper. The raw product after primary manufacture is stronger than conventional paper, is naturally flame retardant, and the process used to produce it is environmentally friendly. The last point is particularly important since there are no pulping costs associated with the production of banana paper whereas to produce one metric ton of pulped paper requires the use of up to 40,000 litres of water i.e. a tremendous drain on environmental resources. At this early stage in banana paper production, there is a great potential to develop new products by incorporating value added processes to this raw feedstock. The present work has shown that UV technology is ideal for this purpose, being the first report of such successful treatments. The process is important since the finished product possesses a very large commercial potential in packaging (liner board, corrugated board, packaging boxes), building (panels), office supplies (filled and coated papers), and bags. Obviously this range is not meant to be comprehensive but is an illustration of the wide spectrum of potential applications of banana ply paper with UV coating processes utilizing the novel water compatible oligomers.

Conclusions

A range of novel water compatible oligomers based on acrylamide, epoxy acrylate and urethane technologies have been prepared and UV cured under Fusion F-300 and Con-Trol-Cure LED 385 nm lamps. With all oligomers, the Fusion lamp gave efficient UV cure and cure grafting yields on all three papers. As expected, the LED lamp gave lower curing and cure grafting efficiencies. The data demonstrate the range of excellent coatings which may be obtained with all of the advantages inherent in the use of water compatible oligomers. The UV cured coatings on banana paper should have great commercial applications because this paper has unique properties, is relative inexpensive and is environmentally friendly compared to traditional papers prepared by pulping technologies.

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References

1. J. L. Garnett, G. R. Dennis and G. V. McKean, Proc RadTech Asia 2005, Shanghai, China, 2005, p. 614.
2. G. R. Dennis, J. L. Garnett and E. F. Zilic, Proc. RadTech North America, e|5 2004, Charlotte, North Carolina, 2004
3. P. A. Dworjanyn and J. L. Garnett, in: Radiation Curing in Polymer Science and Technology, Volume 1: Fundamentals and Methods. JU. P. Fouassier and F. J. Rabek (Eds).Elsevier. London, p.63.
4. G. R. Dennis, J. L. Garnett and K. J. Jarrett, unpublished work.
5. A. Tauber, E. Hartman, H.-J. Glösel, F. Bauer, R. Mehnert, J. Monkiewicz and R. Edelman, Proc. RadTech North America 2002, Indianapolis, Indiana, p. 300.
6. C. Roscher, J. Adam, C. Eger, M. Pyrlik, Proc. RadTech North America, 2002, Indianapolis, Indiana, p. 322.
7. C. Decker, L. Kellar, S. Benfarki, K. Zahrnik, C. Blanche, Polymer Preprints, 45(2), 18 (2004).