Preliminary Study on the Utilization of Lignin as Filler in Ultra-Violet (UV) Curable System

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ABSTRACT: In this study, Alcell lignin was used as filler in aliphatic urethane acrylate ultra violet (UV) curable resin system. The coating system was UV cured in the presence of free radical photoinitiator and cationic photoinitiator. The results showed that those with free radical photoinitiator produced coating film with higher degree of curing than those with cationic photoinitiator. The result of iodine number determination also showed that the unsaturated groups present in the UV curable system had reduced. This indicated that radical polymerization had taken place in the cur-

ing process of UV curable resin incorporated with lignin. In addition, the lignin content did not influence the curing process of the coating film. As for the coating film, it showed that the mechanical properties of the film were significantly influenced by the lignin content. This phenomenon was contributed by inherent stiffness of the lignin. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2527–2533, 2011

Key words: lignin; UV curing; Taber abrasion; free radical photoinitiator

INTRODUCTION

Lignin is a natural polymeric material which serves as natural binder for cellulose fiber.[1] Lignin is the second abundant renewable material after cellulose which can be obtained from pulping process as a by-product.[2] There are various types of lignin available in the market, such as kraft lignin, lignosulfonates, organosolv lignin, etc. It is a highly branched polymer with wide variety of functional groups which can provide active sites for chemical interactions. However, the potential of lignin application are not comprehensively realized and almost all are burned for energy generation purposes.[3–4]

Lignin has been commonly used in various types of polymer preparation. For instance, Sun et al.[5] prepared epoxy resin from lignin, and Bonini et al.[6] reported that lignin from straw could be used as a raw material for polyurethane preparation which is suitable for wood adhesive and coatings formulation. Thielemans and Wool[7] used kraft lignin to treat flax fibre for composite preparation. The results showed that the fiber wettability was improved which enhanced the mechanical properties of the composite. According to Park et al.,[8] lignin was commonly used as a raw material in making coatings due to their

small particle size, hydrophobic behavior, and the ability to form a stable mixture with other components. In addition, lignin is nontoxic and extremely versatile in performance and qualities. This makes it popular in many industrial applications.[9]

Recently, antioxidant properties of lignin have been the focus in the lignin utilization research.[10] The scavenging action of lignin phenolic structure on oxygen containing reactive free radicals is considered (Dizhbite et al. 2004).[11] In ultra-violet (UV) curing system, quenching phenomenon is one of the undesired reactions where the free radicals generated by photoinitiator are being terminated by oxygen free radical. Commonly, this phenomenon can be prevented using several methods, such as nitrogen blanketing, producing more initiating species and using amine type of photoinitiator. Due to the antioxidant character of lignin, it is believed that lignin can be utilized as filler in UV curable system to prevent quenching phenomenon.

This study was embarked to investigate the effect of lignin incorporation into UV curable system on various aspects. By incorporating lignin in the UV-curable resin, the rigidity of the coating film could be improved which can be reflected in the physical and mechanical properties of the coatings produced. It is also believed that with antioxidant properties of lignin, the quenching phenomenon can be avoided.

EXPERIMENTAL

Materials

Aliphatic urethane acrylate was used as oligomer supplied by Cytec Industries Malaysia and surfactant (Ranex 709) was obtained from ICI Surfactant

(Cleveland, United Kingdom) whereas radical photo-initiators and cationic photoinitiators were obtained from Ciba, Singapore, and Dow Chemical Company, Midland, respectively.

Alcell lignin is a product obtained from organosolv pulping black liquor. Organosolv pulping is a pulping method where organic solvent or mixture of solvent and water is used for delignification process. This method has received considerable attention due to due to several advantages such as; (1) sulphur free process and sulphur-free by products for further processing, (2) the process of liquor regeneration is simple, (3) no additional cooking chemicals besides ethanol, and (4) readily bleachable pulp for paper making.[12] In this study, Alcell lignin in powder form (20–40 μm) was obtained from Repap Technologies (New Brunswick, Canada).

2,2-Diphenyl-1-picrylhydrazyl (DPPH) radical-scavenging activity determination

The scavenging activity of lignin was conducted using DPPH as radical source. Various concentrations of lignin were mixed with 5.0 mL of methanolic solution containing DPPH radicals (0.004% w/v). The mixture was shaken vigorously and left to stand for 30 min in the dark. The reduction of the DPPH radical was determined by reading the absorbance at 517 nm using Perkin Elmer UV/Vis spectrophotometer. The radical-scavenging activity (RSA) was calculated as a percentage of DPPH discoloration, using the equation: % RSA = [(ADPPH − AS)/ADPPH] × 100, where AS is the absorbance of the solution when the sample extract is added at a particular level, and ADPPH is the absorbance of the DPPH solution.[13]

Film preparation

Lignin was mixed with oligomer at different percentages together with 1% photoinitiator (radical photoinitiator or cationic photoinitiator). After it was well mixed, the mixture was coated on a glass plate before being subjected to curing by IST Strahlentechnik UV machine with lamp M-200-U2C type. It is a medium pressure mercury vapour lamp (1–2 atm) generating UV-radiation in the range of 180–450 nm. The conveyer belt speed was set at 5 m/min. The cured film was then removed from the glass plate for measurements. As for adhesion test (Cross hatch), the mixture (lignin, oligomer, and photoinitiator) was coated on rubber wood (*Hevea brasiliensis*) panel to investigate the compatibility between them.

Iodine number determination (Hanus method)

The iodine number test is a procedure devised for the determination of unsaturation in hydrocarbon.

Iodine number is numerically equal to the weight in gram of iodine absorbed by 100 g of the sample or the percentage by weight of iodine absorbed by the sample. First, $\sim$ 0.2 g of film was added into a conical flask before 10 mL of $CHCl_3$ was added into the conical flask. Hanus solution was prepared by dissolving iodine and bromine in acetic acid. Then, 40 mL of Hanus solution was pipetted into the conical flask, and the mixture was shaken. The conical flask was left to react in the dark for 1 h. After 1 h, 25 mL of 10% potassium iodide KI and 100 mL of distilled water was added into the conical flask. The sample was then titrated immediately with a standardized 0.1 N $Na_2S_2O_3$ with constant agitation until the yellow color of iodine became faint. Starch indicator (1 mL) was added, and the titration was continued until the pH of the solution was 1.8. The content of the flask was shaken vigorously towards the end of the titration to ensure that all the iodine had been removed from the $CHCl_3$ layer. A blank test was also conducted using the same reagents and procedure (without the film). The iodine number was calculated using the following formula:

$$\text{Iodine number} = \frac{(B - A)N \times 12.69}{\text{gram of sample}}$$

where A = Volume of $Na_2S_2O_3$ of normality N required for the sample and B = Volume of $Na_2S_2O_3$ of nor.

Gel content determination

The gel content or degree of curing was calculated as follows (ASTMD2765-95, 1998). After UV irradiation, the film was conditioned for 24 h in a desiccator. Then, the prepared film was placed in a cellulose extraction thimble for soxhlet extraction with methyl ethyl ketone as solvent for 2 h. The film was taken out and dried in an oven and conditioned it for 24 h before the weight was determined using equation shown below.

Gel content (%) =

$$\frac{\text{Weight of the film after extraction}}{\text{Weight of the film before extraction}} \times 100$$

Fourier transform infrared spectroscopy

The mixture of lignin, oligomer, and photoinitiator was applied on a KBR pellet and scanned using a Nicolet Avatar 360 FTIR in the range 4000–400 cm^{-1}, with 64 scans carried out for each sample. The sample was immediately scanned after the sample passed through the UV machine with a speed of 5

m/min (1 pass is $\sim$ 10 s). This was to determine the time required by the mixture to be cured or to form a film.

Pendulum hardness

The hardness of UV cured sample was determined according to the ASTM D4366-95 (1999) Standard Test Methods for Hardness of Organic Coatings by Pendulum Damping Test, Test Method A-König Pendulum Hardness Test. The test was performed with ERICHSEN-make Pendulum Damping Tester Model 299/300. In this test, a pendulum made contact with a coated panel through two steel balls. As the pendulum swang back and forth through a small angle, movement of the balls caused some deformation on the coating near the surface. The instrument was equipped with an automatic counter and acoustic signal. The digital value on the counter indicated the number of oscillations executed by the pendulum in changing the angle from 6 to 3°.

Adhesion to wood

Adhesion of UV cured film on wood was carried out according to ASTM D3359-97 (1999) (Measuring Adhesion by Tape Test) Method B-Cross Cut Tape Test, adhesion test methods). Rubber wood panel was sanded and coated with the UV curable coating formulation. After curing, the surface was cut into 100 squares of 1 mm × 1 mm using the Cross Hatch Cut Model 295 tester (ERICHSEN-make). An adhesive tape was applied on the crosscut area and was later removed to check adhesion. The number of squares intact without showing signs of peeling gives a measure of the adhesion (%) as calculated below:

$$\text{Adhesion } (\%) = \frac{N_{\text{intact}}}{N_{\text{total}}} \times 100$$

where N_{intact} = number of squares remaining intact after the test and N_{total} = number of total squares in the tape application area.

Impact test

Impact test was carried out using Tubular impact tester model Sheen Ref 804 with a standard weight of 1 kg. The film prepared was coated on the aluminum plate with a dimension of 9 cm (length) × 8 cm (width) × 0.3 cm (thickness), and the impact strength of the film was determined by observing the height of the standard weight required to fail the film coated on the aluminum plate.

Increment of lignin content
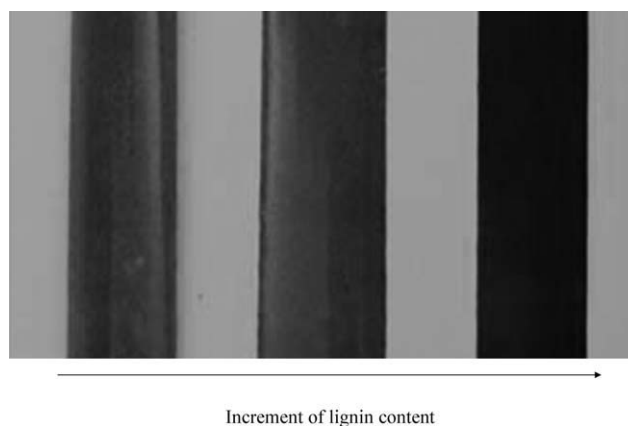
Figure 1 The film appearance prepared from different lignin content.

Tensile test

The film produced was cut into tensile test samples. Tensile test was carried out using LLOYD Instrument model TG420 according to ASTM D822-97 at a cross head speed of 100 mm/min on samples with dimension of 150 mm × 15 mm × 0.035 mm (Length × width × thickness).

Taber abrasion test

Taber abrasion test was carried out according to ASTM D 4060-01. The mixture (lignin, oligomer, and photoinitiator) was applied to a rigid panel and cured. The surface was then abraded by rotating the panel under weighted abrasive wheels. Abrasion resistance was calculated as loss in weight at 2000 of cycles required to remove a unit amount of coating thickness. The weight loss of the film was calculated as follows:

$$\text{Weight loss } (\%) = \frac{(A - B)}{A} \times 100$$

where A = weight loss of the coating film without lignin and B = weight loss of the coating film with lignin.

RESULTS AND DISCUSSION

Figure 1 shows the appearance of the film prepared from various lignin contents. It is obvious to see that the more lignin was used, the darker colour film would be produced due to the colour of lignin. However, the lignin content did not affect the photocuring process which is attributed to the antioxidant activity of the lignin which will be discussed later.

Figures 2 and 3 depict the gel content of film cured by different types of photoinitiator. It can be seen that radical photoinitiator could produce film with higher gel content than those cured by cationic
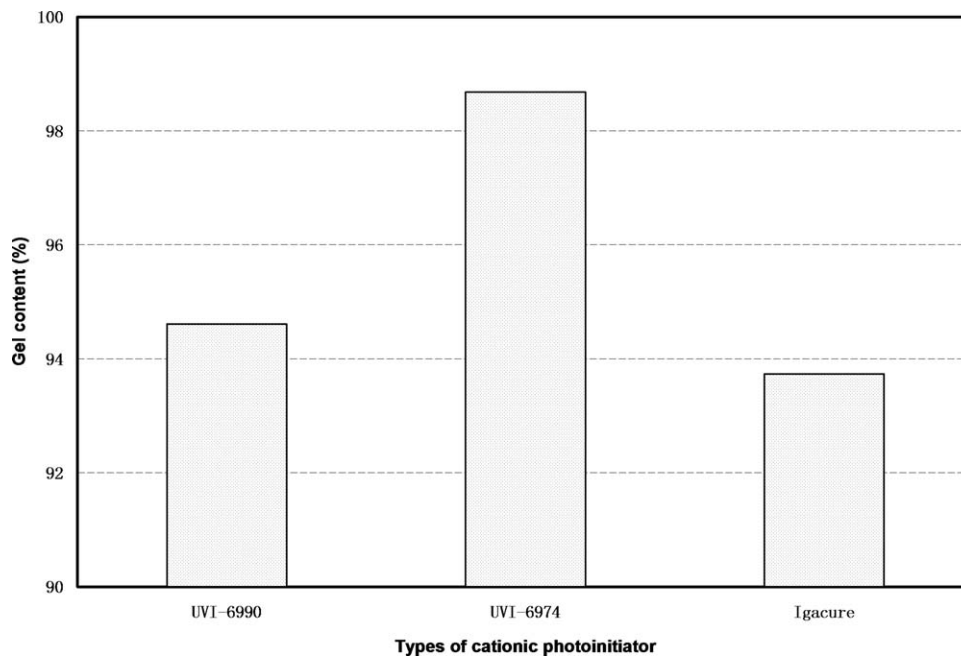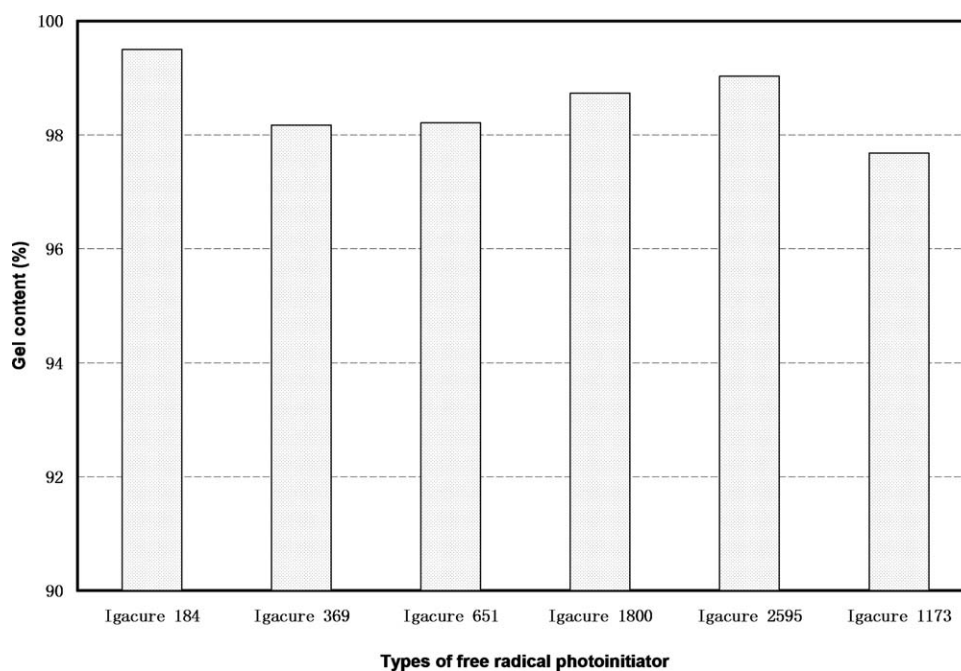
Figure 2   Gel content of film prepared from different types of cationic photoinitiator.

photoinitiator. Overall, those with Irgacure 184 show the highest gel content. According to Vinardell et al.,[14] lignin is a free radical scavenger which can stabilize the reaction induced by oxygen and its radical species. This indicates that radicals produced by photoinitiator in this study may not be scavenged by lignin since it is not an oxygen free radicals. From the result of DPPH radical scavenging activity, it shows about 26% of antioxidant activity. In other words, the presence of lignin could reduce quench-

ing effect due to the presence of oxygen free radical. From the result of DPPH radical scavenging activity, it shows about 26% of antioxidant activity. Hence, it can be said that lignin did not affect the curing process of the film.

Iodine number determination on the lignin and film was also carried out to monitor the radical polymerization of the coating film. From the results presented in Table I, the iodine value decreases after the film is cured. The iodine value for the cured film

Figure 3   Gel content of film prepared from different types of free radical photoinitiator.

TABLE I
Iodine Values of Coating Film
(Iodine Value for Lignin = 55.02)

Lignin content	Before UV curing	After UV curing
0%	82.96 ($\pm$2.92)	19.03 ($\pm$4.46)
5%	71.36 ($\pm$3.23)	11.42 ($\pm$5.16)
20%	107.9 ($\pm$5.34)	20.38 ($\pm$5.23)

TABLE II
The Effect of Lignin Content on Gel Content

Lignin content	Gel content (%)
0%	98.40 ($\pm$1.21)
5%	98.38 ($\pm$1.03)
10%	98.34 ($\pm$0.87)
15%	97.52 ($\pm$0.94)
20%	97.86 ($\pm$0.73)

is lower than the iodine value for Alcell lignin, which is 55.02. This also indicates that C=C polymerization has taken place involving those in oligomers as well as those from Alcell lignin.

Figure 4 shows the effect of different types of free radical photoinitiator on the pendulum hardness of the cured film. This study is necessary because different types of photoinitiator have different behavior in UV energy absorption to produce free radicals. Those with Irgacure 184 show the highest hardness as compared to those with the other photoinitiators. This is in agreement with the highest gel content shown in Figure 3.

The effect of lignin content on gel content of the film is shown in Table II. It can be seen that no significant trend is observed. This phenomenon shows that the presence of lignin has no influence on the curing process of the coatings film. This result is supported by the analysis of FTIR as depicted in Figure 5. Peak at 1630 cm^{-1} indicates the presence of unsaturated groups in the oligomer and it disappears after the resin is exposed to UV light for about 10 s. This observation proves the reaction of C=C groups. In addition, peaks observed around 1420 cm^{-1} and 820 cm^{-1} which are attributed to the pres-

ence of benzyol groups, disappear after being exposed to UV for 10 s. This phenomenon indicates that benzoyl radical has been formed and consumed by polymerization. Hence, the results show that lignin can be used as filler in the UV curable system.

Table III illustrates the effect of lignin content on Pendulum hardness of the coating film. It can be seen that the hardness of the film increases as the lignin content is increased until reaching a threshold point, after which it decreases. This observation may due to the insufficient resin or oligomer to act as a matrix to hold the lignin as filler in the system. This may lead to a weak interaction between these two materials and result in lower performance of the prepared film. The effect of lignin content on cross hatch adhesion test of the coating film is shown in Table III. The result shows a similar trend with pendulum hardness, thus, the same explanation applies.

Table IV shows the effect of lignin content on impact strength. It can be noticed that the impact strength increases until 10% lignin content. A decreasing trend is observed as the lignin content is increased to 15 and 20%. The decreasing
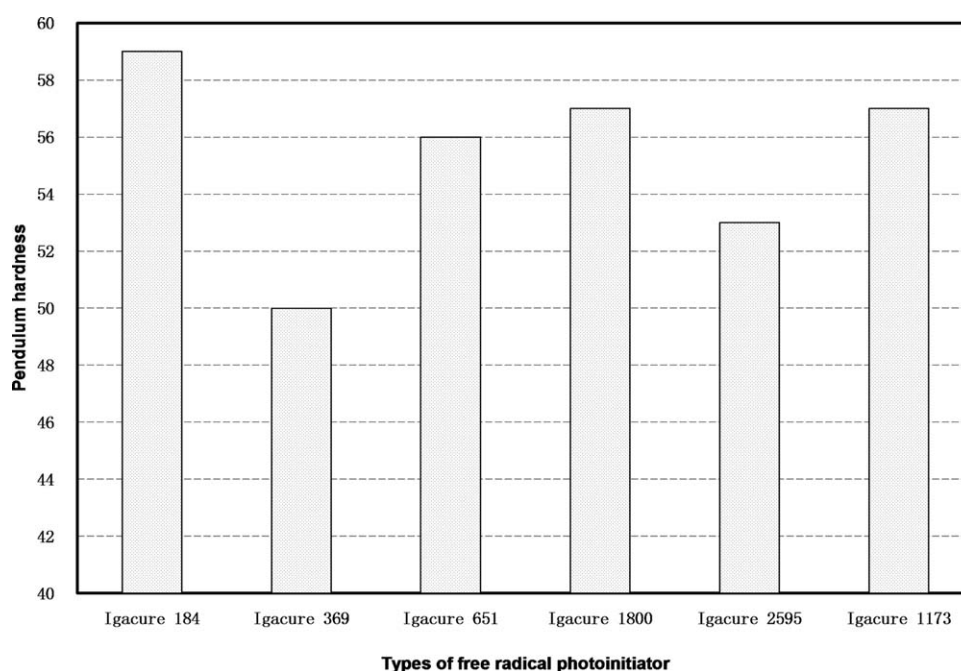
Figure 4 Pendulum hardness of film prepared from different types of free radical photoinitiator.
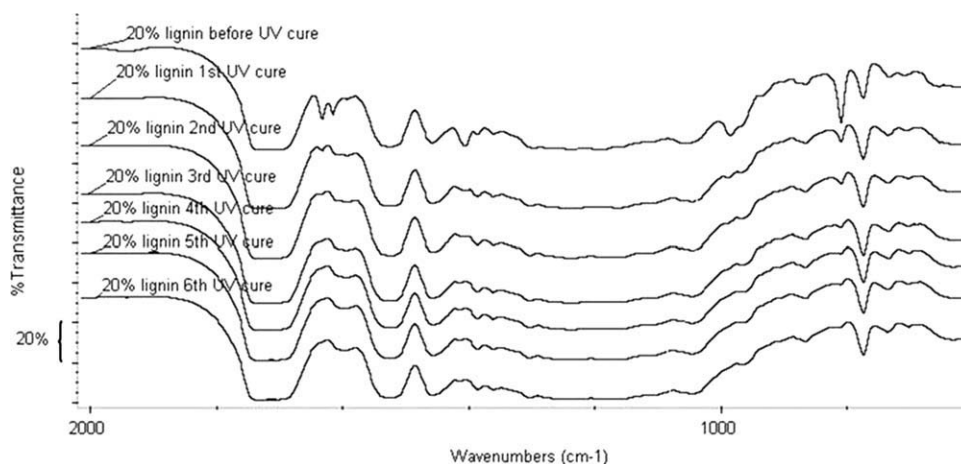
Figure 5 FTIR spectra of UV curable resin incorporated with lignin at different curing time.

phenomenon may be attributed to: (i) insufficient matrix component to effectively hold lignin particles and (ii) the inherent stiffness of the lignin. According to Strong,[15] impact strength is strongly depending on the ability of the material to move or deform to accommodate the impact. Generally, polymer with high stiffness would result in low impact strength due to the low ability of the material to move in order to absorb the impact energy. Hence, it is believed that phenylpropanoid monomers in lignin contribute to the stiffness of the coating film produced which limits the movement of the molecule against the impact energy.

Table V depicts the results of tensile properties of the film prepared from different lignin contents. For the tensile strength, similar trend as impact strength results is shown. This observation is expected as the lignin content increases, the amount of matrix decreases resulting in insufficient polymer matrix to hold the lignin. This means the lignin is not well embedded in the matrix. This affects the efficiency of stress transfer from the matrix to the lignin. Tensile modulus of the film increases as the lignin content is increased (Table V). It is expected because lignin in general has its inherent stiffness, which is higher than the matrix. This inherent stiffness adds up with the stiffness of the matrix, resulting in higher modulus. This is in agreement with the result shown on elonga-

tion at break (EB) of the film. The incorporation of lignin into polymer matrix drastically reduces the EB. Reduction in EB is due to the decreased deformability of a rigid interface between lignin and matrix. As the elongation is reciprocal to the stiffness of a material, thus, the results show that higher percentage lignin imparts a greater stiffening effect as compared to those produced from lower percentage of lignin content.

Table VI depicts the effect of lignin content on abrasion resistance. The resistance of the film to abrasion has obviously enhanced as the lignin content is increased to 20%. From previous studies carried out on rubber compounds, incorporation of lignin improved the abrasion resistance of the rubber product.[16,17] According to Setua et al.,[18] addition of phenolic resin provided superior resistance to abrasion of rubber compound. Hence, it is believed that this result is attributed to the presence of lignin which is rich in phenol groups and high inherent stiffness.

TABLE IV
The Effect of Lignin Content on Impact Strength

Lignin content	Impact strength (lb/in)
0%	52.00 (±2.70)
5%	55.00 (±0.00)
10%	59.00 (±2.45)
15%	40.00 (±4.08)
20%	35.00 (±4.08)

TABLE III
The Effect of Lignin Content on Pendulum Hardness and Adhesion

Lignin content	Pendulum hardness (counts)	Adhesion (%)
0%	18 (±2)	84.33 (±0.94)
5%	21 (±1)	90.33 (±3.09)
10%	32 (±1)	96.33 (±0.47)
15%	24 (±2)	87.67 (±1.89)
20%	23 (±2)	84.0 (±4.50)

TABLE V
The Effect of Lignin Content on Tensile Properties

Lignin content	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
0%	9.93 (±0.77)	154.70 (±22.93)	26.44 (±1.39)
5%	12.43 (±1.42)	299.85 (±31.75)	17.07 (±3.25)
10%	17.95 (±0.65)	320.80 (±28.40)	16.25 (±0.47)
15%	10.08 (±0.14)	420.87 (±14.45)	11.23 (±0.82)
20%	9.64 (±0.31)	543.02 (±37.74)	9.35 (±0.68)

TABLE VI
The Effect of Lignin Content on Abrasion Resistant

Lignin content	Abrasion resistant (%)
5%	11.53 (±0.09)
10%	14.44 (±2.81)
15%	17.96 (±1.46)
20%	32.22 (±7.91)

CONCLUSIONS

A UV curable resin incorporated with Alcell lignin was produced. The resin was prepared together with a free radical photoinitiator. The gel content of the coating film was not influenced by the amount of lignin present in the UV curable resin. Generally, the presence of lignin in UV curable resin has enhanced the properties of the coating film. The decrease in the strength of the film for those with more than 10% lignin content was due to the insufficient polymer matrix to effectively hold the lignin. However, the stiffness of the coating film was significantly improved as the lignin content was increased. In addition, the abrasion resistance of the film was also enhanced with the presence of lignin. This was probably due to the presence of phenol groups in lignin and the inherent stiffness of the lignin.

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