Role of Additives on UV Curable Coatings on Wood

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SYNOPSIS

An epoxy resin-coating formulation was prepared from diacrylated epoxy bisphenol-A-epichlorohydrin and a reactive monomer, tripropyleneglycol diacrylate. The additives, silane and fluorochemicals, were included in the formulation to evaluate their effects on the UV curing of the epoxy resin onto timber. Thin films coated on wood substrates were cured under UV radiation in the presence of the photoinitiator, benzoin ethyl ether. Adhesion of the cured films onto wood substrates was evaluated using the cross-cut and the pull-off tests. Film hardness was evaluated using the pencil hardness and the pendulum hardness tests. Water repellency of the films were measured from contact angles using a telegoniometer. Scanning electron microscopy (SEM) was used to investigate the interface between the films and the wood substrates. These studies showed that silane only enhanced the adhesion of the film onto the wood substrates but had no effect on the hardness of the films. The additives improved the water repellency of the films with the fluorochemicals, exhibiting dramatic improvement. SEM revealed that only the fluorochemical aided the penetration of the resin into the wood. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The function of additives in accelerating radiation polymerization, in particular, the radiation grafting of monomers onto cellulose, has been extensively studied.[1,2] Additives, including mineral acids, cationic salts, and organic compounds such as urea and multifunctional monomers, enhance grafting initiated by UV.[1] An increase in grafting during curing should improve adhesion of the cured film to the substrate with improved properties in the finished product. The present work deals with the study of the effects of the additives, a silane coupling agent and two fluorochemicals, on the UV curing of epoxy acrylate/multifunctional monomer onto wood for which one of the major components is cellulose.

Alkoxy silanes were included as additives in epoxy-acrylic resin by Priola and co-workers[3] for the UV curing of epoxy-acrylate resin on glass. These additives were found to give rise to strong

adhesion bonds between the cured coatings and glass due to the condensation of the silanol groups present in the resin with the same groups present on the substrate surfaces. In our previous study on wood-polymer composites, vinyltriacetoxysilane (VAS) increased the adhesion between the polymer incorporated into the wood matrix and the cell wall of the timber in the analogous wood-polymer composites formation.[4] In this instance, VAS, a vinyl silane, functioned as an adhesion promoter because it possessed functional groups that may either react with the functional group of the surface of the cellulose of wood to form a silane bridge or the vinyl group may itself be included in the growing crosslinking matrix. Thus, VAS is used in this work for the first time in the UV process to promote the adhesion between the wood surface and the polymer coating. The fluorochemical FC-430 (3M product) is a nonionic surfactant and is therefore expected to be compatible with most polymers. It is an effective wetting, leveling, and flow controlling agent for water or solvent-based polymer coating systems. It should therefore aid the penetration of the oligomer/monomer mixture into the wood, resulting in a

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greater adhesion between the cured polymer film and the wood substrate. Hence, the surface adhesion between the polymer films and the wood substrates may be modified by the use of these additives, minimizing the possible problem of delamination. FC-251 (3M product) is a fluorochemical emulsion that confers oil and water repellency to nearly all types of fabrics made from either natural or synthetic fibers. It is a cationic surfactant and is included in this work for water repellency studies.

Epoxy acrylates are found to offer good all around properties that include cure rate, low skin irritancy, and glossy appearance when cured. They have been extensively used in UV curing in varnishes, roller coating varnishes for paper and board, and wood and plastic coatings.[5] The present study uses diacrylated epoxy bisphenol-A-epichlorohydrin (BAEA) as the prepolymer and tripropyleneglycol diacrylate (TPGDA) as the reactive monomer. The wood substrate is a popular Australian commercial plantation timber, the radiata pine.

EXPERIMENTAL

BAEA and TPGDA were supplied by Monocure Pty Ltd. The fluorochemicals FC-430 and FC-251 were obtained from 3M and VAS from Dow Corning. The photoinitiator, benzoin ethyl ether (BEE), was from Aldrich. These chemicals were used as received without further purification.

Preparation of Wood Samples

Radiata pine without visible defects was selected as experimental samples. The surfaces of the wood substrates (20 × 10 × 50 mm) were sanded before coating.

Coating Preparation

The composition of BAEA : TPGDA : BEE that gave the optimum curing condition was 65% : 30% : 5%. The UV curable formulation was prepared first by dissolving BEE in TPGDA, followed by the addition of BAEA and the additive (0.5%). A formulation without any additive was also prepared and used as the control. After thorough mixing, the resulting mixture had a viscosity that allowed it to be easily applied onto the surfaces of the wood substrates. Thin films of this mixture were coated onto the substrates with the aid of a drawdown bar, and the resulting materials were then passed under a

UV lamp system consisting of a mercury lamp with an intensity of 200 W/inch and at the belt speed of 10 cm/s for curing.

Coating Characterization

Adhesion of the cured films onto wood substrates were evaluated using the cross-cut test, according to Australian Standard Method 408.4, and the pull-off test. The cross-cut test is designed for assessing the adhesion of thin coatings to substrates by applying and removing pressure-sensitive adhesion tape over cuts made in the coating.[6] Test results scaled from 0 to 5 provide information on the degree of adhesion, with the lowest value indicating the maximum adhesion. The pull-off test measures the pull-off force of an aluminium bar glued to the coating surface by a cyano-acrylate adhesive, using an Instron 4300 Series Universal Testing Machine.

Hardness of the cured films was evaluated using the pencil hardness test and pendulum hardness test according to Australian Method 405.1[7] and ASTM D 4366-87,[8] respectively. The results obtained from the pendulum hardness test were calculated as a percentage measured on the standard glass plate.

Contact angles that served as measurements for water repellency were determined using a telegoniometer, Model 102 by RAME-Hart Inc.

Scanning electron microscopy (SEM) was used to investigate the interface between the polymeric coating and the wood substrate. Micrographs of the interfaces of the samples from the pull-off test were obtained. This technique provided information of the extent to which the epoxy resin had penetrated into the wood.

RESULTS AND DISCUSSION

Adhesion

Two sets of results from the cross-cut test were obtained. Samples in Batch 1 were obtained by immediate application of the coating formulations containing either FC-430 or VAS, followed by UV curing. The test result was scaled to a value of 3 for these samples, indicating rather weak adhesion between the films and the wood substrates. However, excellent adhesion was exhibited for the control and Batch 2 samples that were obtained by allowing the formulations containing additives to stand for at least an hour before coating, and test result scaled to a value of 0 for these samples indicated maximum adhesion.

Batch 1 samples showed easier delamination, probably due to the fact that FC-430 is a surfactant that foams when agitated. Therefore, if the coating formulation were to be used for coating the wood substrate immediately after mixing, air bubbles (microbubbles) would be present in the formulation, even at the wood–film interface. This would result in the reduction in the area of contact between the film and the wood substrate. Moreover, the curing process was very rapid, and the coating was cured within seconds; hence, the air bubbles had no opportunity to migrate out of the formulation. Hence, a decrease in the adhesion between the polymeric coating and the wood could be attributed to these factors. Another explanation for the ease in delamination could be due to the partitioning of the surfactant at the air–coating formulation and wood–coating formulation interfaces. The surfactant may migrate away from the wood–mixture interface. However, this transport phenomenon would be dependent on the quantity of the additive present.

Batch 2 samples exhibited greater adhesion between the coatings and the wood, probably for the following reason. When the coating formulation was allowed to stand for an hour, the air bubbles that formed as previously mentioned would have a chance to escape. At the same time, the surfactant molecules had greater opportunity to migrate more evenly throughout the coating formulation, thereby preventing any possibilities of pockets of higher concentration in the formulation. This would then enable FC-430 to function effectively as a surfactant in lowering the surface tension of the formulation, resulting in its greater ability to penetrate more deeply into the wood substrate. Coatings containing VAS showed similar results due to its ability to function as a coupling agent in enhancing the adhesion.

Table I summarizes the adhesion measurements between the epoxy acrylate coating and the wood substrates using the pull-off test. It is evident from the data that samples with coatings containing either the fluorochemical or silane adhered more strongly to the timber. The results also indicate that FC-430 is more effective in enhancing adhesion than VAS. It is interesting to note that the Batch 1 samples with coatings containing either FC-430 or VAS exhibit similar low adhesion toward the wood substrate, and both coatings had the tendency to delaminate.

The adhesive strength produced by the two additives when used concurrently was extraordinary. Results showed a dramatic enhancement in the

Table I Measurements of Pull-off Test for Epoxy Acrylate Coating on Wood

Additive	Pull-off Test (N/mm^2)
No additive	237
FC-430 (Batch 1)	62
FC-430 (Batch 2)	397
VAS (Batch 1)	63
VAS (Batch 2)	361
FC-430 (Batch 2) + VAS (Batch 2)	2421

Concentration of additive = 0.5%.

adhesion. The force required to pull the coating off the substrate was threefold that of the combined force required to pull off coatings containing the additives individually. It thus appeared that the concurrent use of both the additives would synergistically increase the adhesion of the coating onto the timber.

Hardness

Preliminary tests on the hardness of the films were carried out using the pencil hardness test. The Hardness Test Scale for this test on coatings with and without the additives gave very similar results. As expected, there was a correlation between the hardness of the coatings and the number of passes through the UV curing system as the crosslink density increases with increasing intensity of radiation. Pencil hardness was 4H (8H being the hardest) for the first three passes but increased to 5H for four and five passes. However, the pendulum hardness test performed on coatings that cured after four passes through the UV curing system revealed that silane had no effect on the hardness of the film; FC-430 increased the hardness by 19% and the concurrent use of both silane and FC-430 improved the hardness by 12%. This test thus indicated that VAS only enhanced the adhesion of the epoxy acrylate coatings onto the wood and had no effect on hardness. However, FC-430 appeared to have improved both the hardness and adhesion of the epoxy acrylate coatings onto wood substrates. The positive effect of FC-430 had on the hardness was probably due to the formation of hydrogen bonding brought about by the fluorine atoms present in the FC-430 and the hydrogen atoms in the epoxy resin.

Contact Angles

Contact angles control a variety of important surface properties, such as wettability and waterproofing. The contact angle θ is defined as the angle formed between the surface of a solid and that of a liquid; it relates the surface tensions at the solid, liquid, and liquid–solid interfaces. When a drop of liquid is brought into contact with a flat solid surface, the final shape taken up by the drop depends on the relative magnitudes of the molecular forces that exist within the liquid (cohesion) and between the solid and liquid (adhesion).

The surface energies of the cured epoxy acrylate coatings may be characterized by measurement of the contact angle θ of water with the surfaces of the coatings. For practical purposes, when $\theta = 0°$, the liquid is said to wet the surface. On the other hand, wetting is considered not to occur when $\theta < 90°$. The spreading coefficient $S_{l/s}$ of liquid on solid may be calculated when the contact angle is determined. $S_{l/s}$, which is defined as the difference between the adhesion work between solid and liquid and the cohesive work exists within the liquid, can be calculated using the following equation[9]:

$$S_{l/s} = \gamma_{l/v}(\cos \theta - 1)$$

where $\gamma_{l/v} = 72.9$ mN/m for water.[9] If $S > 0$, spreading is accompanied by a decrease in free energy, that is, the process of spreading will take place spontaneously.

Table II gives a summary of the spreading coefficient values of water on the surfaces of plain wood and coatings with and without additives. The negative spreading coefficient values indicate the cohesion of water is greater than the adhesion between water and the films; hence, the process of spreading would not occur spontaneously. Therefore, as the spreading coefficient value decreases, the water repellency of the film increases. From the results, it is evident that the fluorochemicals and VAS decrease the spreading coefficients of water on the coatings, with the fluorochemicals exhibiting dramatic decreases. There is no significant difference in the spreading coefficient values between the two fluorochemicals. The concurrent use of both the fluorochemicals did not appear to produce any positive effect.

The fluorochemicals showed much more pronounced nonwetting characteristics than the corresponding hydrocarbon surfaces, probably due to the large size of the $-CF_2-$ groups. Because fewer

Table II   Spreading Coefficient Values of Water on Surfaces of Plain Wood and Wood Coated with Epoxy Acrylate Formulations

Additive	Spreading Coefficient
Plain wood[a]	−20.5
No additive	−20.4
FC-430	−51.6
VAS	−29.0
FC-251	−59.0
FC-430 + VAS	−50.4
FC-430 + FC-251	−52.8

Additive concentration = 0.5%.

[a] Contact angle reading was taken immediately as the value of θ diminished with time.

$-CF_2-$ groups can be packed into a given area of the surface, work of adhesion W_a is less.[10] W_a can be defined using the following equation:

$$W_a = \gamma_{l/v}(1 + \cos \theta)$$

Therefore, θ is greater for the fluorocarbon surface.

Due to the presence of the vinyl group in VAS, the addition of this additive may raise the level of the formation of three-dimensional networks (crosslinking) in the coating upon radiation curing. This could possibly result in the formation of a film with less porous structures that may then give rise to a decrease in the adhesion between water and the coating and consequently an increase in the contact angle.

SEM

For the pull-off test, there were three possible sites where failure may occur: at the aluminium bar–coating interface, within the wood itself, and at the wood–coating interface. To have some indication of the extent to which the epoxy resin had penetrated the wood, micrographs at the interfaces of the samples from the pull-off tests were obtained.

It was expected that a correlation would exist between the results of the pull-off test and that of the SEM analysis. The greater the penetration of the resin into the wood would result in an increase in adhesion, and, consequently, a greater force was required to pull the coating off the wood substrate. Hence, the micrographs of the interfaces would reveal a greater amount of the polymer being adhered to the cellulose fibre of the wood.

Figure 1(a)–(d) give representations of the SEM analysis. As shown distinctly in Figure 1(a), which
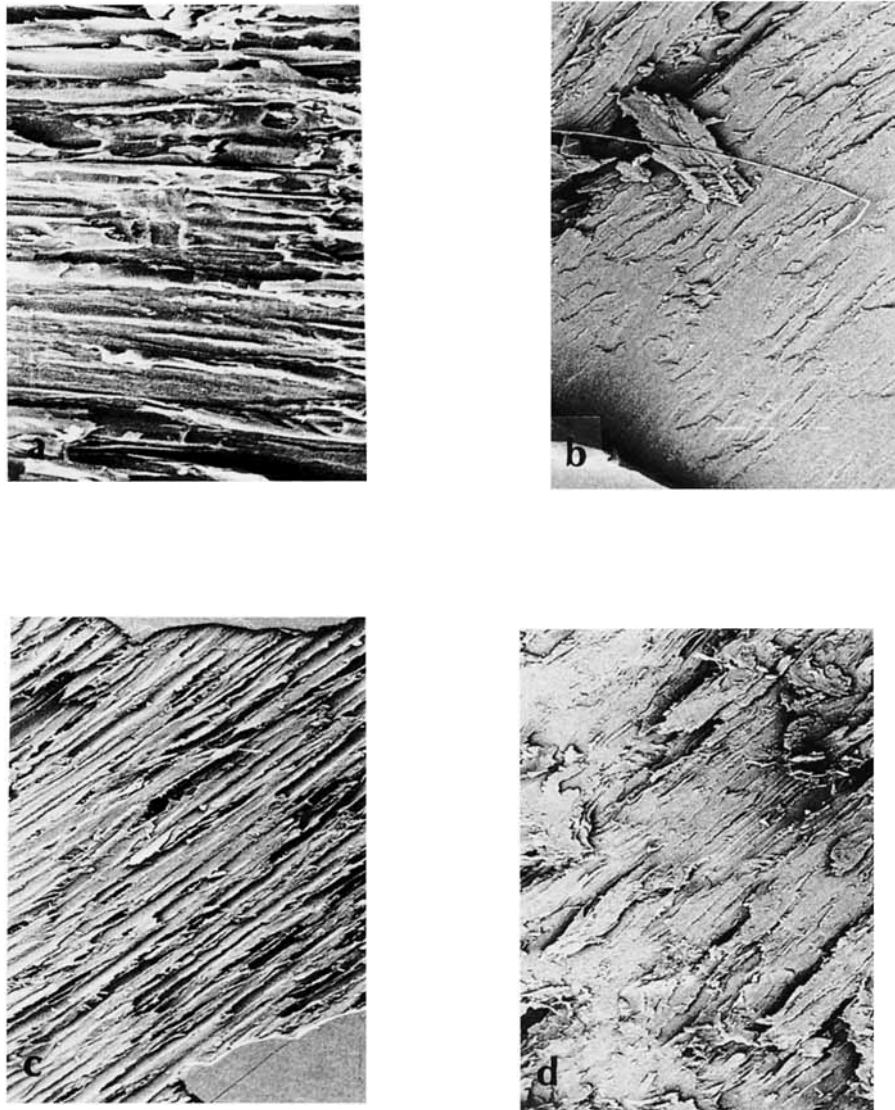
Figure 1 Electron micrograph of the wood surface with interface of (a) the control sample in which the polymer coating contained no additive (×90 magnification), (b) the polymer coating contained 0.5% FC-430 (×75 magnification), (c) the polymer coating contained 0.5% VAS (×75 magnification), and (d) the polymer coating contained 0.5% FC-430 and 0.5% VAS (×40 magnification).

is the micrograph showing the interface of the control sample, only a small amount of polymer can be seen to adhere to the cellulose fiber, implying that only a small quantity of the resin had penetrated into the wood.

Figure 1(b) depicts the micrograph of the interface of the wood and the coating containing 0.5% FC-430, and Figure 1(c) is that of the system with coating containing 0.5% VAS. Figure 1(b) shows a significant amount of polymer embedded in the wood, indicating a greater penetration of the expoxy acrylate into the wood substrate. Figure 1(c) shows very little evidence of polymer in the area of failure. It thus implies that VAS does not have the wetting and leveling properties of FC-430 in aiding the penetration of the prepolymer into the wood. However, VAS in this case may act as the adhesion promoter by bonding to the wood cellulose fiber via a silanol

bond and is at the same time incorporated into the polymeric coating through the vinyl substituent. Figure 1(d) portrays the micrograph of the system with the coating containing both the additives. A large quantity of polymer is evident, indicating a greater penetration of the prepolymer due to the synergistic effect brought about by the presence of the two additives.

CONCLUSION

Adhesion tests show an enhancement in the adhesion of epoxy acrylate resin onto wood by both FC-430 and VAS, with the former additive exhibiting a greater efficiency. The pull-off test revealed a significant increase in the force required to pull off the coating that involved the concurrent use of both the additives. This force was three times the combined force required to pull off each coating containing the individual additive, thus suggesting a synergistic effect of one additive on another. This finding could be useful in commercial UV processing. One example is the coating of the Australian bank notes that was UV cured; there have been adhesion problems between the UV-cured coating and the actual note. Studies such as the present one may throw some light onto the problems and overcome these difficulties.

Pendulum hardness test revealed that only FC-430 enhanced the hardness of the cured film. Contact angles studies reveal that all the three additives, in particular the fluorochemicals, decrease the spreading coefficient values that correspond to an increase in water repellency. FC-430 when used concurrently with either FC-251 or VAS did not exhibit any positive effect. The present study also shows that of the two fluorochemicals, FC-430 is the one that has the dual function of aiding the penetration the epoxy resin into the wood substrate and enhancing the water repellency of the film after curing. This finding may be valuable for commercial applications in the radiation curable coatings for timber products.

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