Songklanakarin J. Sci. Technol.
31 (1), 49-55, Jan. - Feb. 2009

Songklanakarin Journal
of Science and Technology

http://rdo.psu.ac.th/sjst

Original Article

Ultraviolet curing of acrylated liquid natural rubber for surface coating application

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Received 10 July 2008; Accepted 11 December 2008

Abstract

Ultraviolet curable acrylated liquid natural rubber was prepared by grafting of photosensitive molecule onto liquid natural rubber for surface coating application. The liquid natural rubber (LNR) was firstly obtained by degradation of natural rubber latex with hydrogen peroxide and cobalt acetylacetonate at 65°C for 72 hrs. The preparation of acrylated natural rubber was carried out by the reaction of acrylic acid and epoxidized liquid natural rubber (ELNR) prior obtained from LNR with formic acid and hydrogen peroxide in the ratio of 2:1 by weight in toluene at 80°C for 6, 9, 12, 18, and 24 hrs. It was found that the percentage of acrylate grafted onto liquid natural rubber depended on the reaction time. Surface coating was performed by using acrylated liquid natural rubber and 1,6-hexanediol diacrylate (HDDA) or tripropylene glycol diacrylate (TPGDA) as a crosslinker and Irgarcure 184 or Irgarcure 651 as a photoinitiator under UV exposure for 30, 60, and 90 seconds. The hardness test of cured products was investigated using the Pencil hardness test at pencil level of 2B to 6H. It was found that the highest hardness of surface coating was at pencil level of 4H for the product using TPGDA and Irgacure 651 in the ratio of 80:10 parts per hundred of rubber (phr). The cured products were able to resist to 2% H_2SO_4 and distilled water for more than 24 hrs.

Keywords: ultraviolet curing, liquid natural rubber, acrylated liquid natural rubber, surface coating

1. Introduction

Currently, there is general an increasing environmental awareness, which also created a higher interest in natural rubber and its derivatives. The reason is that natural rubber is a renewable resource, whereas its synthetic counterparts are mostly manufactured from non-renewable oil-based resources (Oliveira *et al.*, 2005). Radiation curing has become a well accepted technology with widespread use. It is the polymerization into a three-dimensional network of a chemical system, which is initiated by incident radiation. The major reasons for this development are its unique features, which include solvent-free formulations, high cure speed, low processing temperature, and high quality of products obtained. Notably, radically polymerizing UV-curable formulations are used in a wide variety of applications. These include protective and decorative coating of wood, metal, plastic, paper, and glass fiber coatings (Dietliker *et al.*, 2004). Ultraviolet sensitive polymers with acrylic moieties seem to be good candidates because of their high reactivity on irradiation, moderate coat and low volatility. One method of synthesizing ultraviolet sensitive polymer is the grafting of ultraviolet sensitive units onto other polymer backbones. Photocrosslinkable elastomers with pendant acrylate group have been prepared by ring-opening reaction of epoxidized natural rubber with acrylic acid. The acrylated natural rubber undergoes a fast photocrosslinking polymerization when it is exposed to UV radiation in the presence of an aryl ketone photointiator, with the formation of a three-dimensional polymer network within a few second. The UV-cured polymer becomes totally insoluble in organic solvents and exhibits

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remarkable mechanical properties such as hardness, flexibility, and impact resistance (Le Xuan and Decker, 1993). Rubbers bearing pendant acrylate groups have been synthesized by reacting acrylic acid with epoxidized rubbers. The reaction kinetics, monitored by infrared spectroscopy, follows a first order law when acrylic acid is in excess and second order law under stoichiometric conditions (Decker *et al.*, 1996a). The photoinitiated polymerization of rubbers bearing pendant acrylate groups has been studied by infrared spectroscopy (Decker *et al.*, 1996b). In the presence of a radical photoinitiator, the polymerization develops within a few second of UV exposure to give a totally insoluble crosslinked polymer. Decker *et al*. (1996c) have studied the crosslinking of epoxidized natural rubber by UV-irradiation in the presence of a sulfonium salt. They found that the addition of a radical photoinitiator enhanced the crosslinking polymerization of acrylate monomer. Furthermore, the photocrosslinking reaction of the acrylate epoxidized liquid natural rubber was studied by monitoring the exothermic heat of photocuring of acrylate double bond using a double beam photocalorimeter. It was found that the fast crosslink-ing-polymerization occurred when the rubber was exposed to UV irradiation in the presence of photocleavage initiator and diacrylate monomer (Phinyocheep and Duangthong, 2000).

The objective of this work was to investigate the reaction of ELNR with acrylic acid in toluene for obtaining acrylated liquid natural rubber (ALNR). The ALNR was then performed a photocrosslinking reaction with Irgacure 184 or Irgacure 651 as a photoinitiator in the presence of 1,6-hexanediol diacrylate (HDDA) or tripropylene glycol diacrylate (TPGDA) as a crosslinker under UV irradiation. Surface coating film obtained after UV exposure compared with that before UV exposure was also characterized and a plywood coating application was also studied.

2. Materials and Methods

2.1 Materials

Natural rubber latex (HA-NR 60%DRC) was supplied by Pattani Industry, Ltd., acrylic acid AR grade was obtained from MERCK Schuchardt, hydrogen peroxide (H_2O_2) AR grade was obtained from MERCK Schuchardt, cobalt acetylacetonate was obtained from Sigma-Aldrich Chemie, formic acid AR grade was obtained from AnalaR$^{@}$, Terric N-16 as a surfactant, 1,6-hexanediol diacrylate (HDDA) was obtained from Fluka, and tripropylene glycol diacrylate (TPGDA) was obtained from Specialty Chemicals. Irgacure 184 and Irgacure 651 were obtained from Ciba-Geigy, Toluene AR grade was obtained from MERCK Schuchardt, methanol was obtained from MERCK Schuchardt, sodium hydrogen carbonate was obtained from Asia Pacific Specialty Chemicals, ammonium hydroxide, sulfuric acid hydroxide were obtained from Ajax Finechem, and inhibitor-remover was obtained from Aldrich Chemical.

2.2 Preparation of liquid natural rubber

The liquid natural rubber (LNR) was obtained by degradation of 20% DRC natural rubber latex with hydrogen peroxide of 0.5 phr and cobalt acetylacetonate of 1 phr by means of mechanical stirrer in a round bottom flask at 65°C for 72 hrs. LNR was precipitated in methanol and then dried in a hot oven at 40°C. Molecule weight of LNR was determined by GPC (1525, 1717 plus auto sampler and waters 2414 Reflective Index Detector) and its structure was analyzed by FTIR spectroscopy (Nicolet Magna-IR 560 spectrophotometer).

2.3 Preparation of epoxidized liquid natural rubber

Epoxidized liquid natural rubber (ELNR) was prepared by using 10% w/v LNR in toluene. Formic acid and hydrogen peroxide in ratio of 30:60 (mol % with respect to isoprene unit) were added drop wise and stirred at 50°C for 2 hrs. ELNR was then washed in 5.0% $NaHCO_3$ solution, precipitated in methanol and dried at 40°C. ELNR obtained was analyzed by ^{1}H-NMR and FT-IR spectroscopic techniques to calculate the epoxidation level (Burfield *et al.*, 1984).

2.4 Preparation of acrylated liquid natural rubber (ALNR)

Five grams of ELNR was dissolved in 100 ml of toluene in a round bottom flask at 80°C and 100°C and 10 g of acrylic acid was then added drop wise to the solution. The reaction mixture was withdrawn at intervals of 6, 9, 12, 18, and 24 hrs, precipitated in methanol and dried at 40°C. Acrylation reaction profile was determined by using FT-IR spectroscopy and % acrylation was determined by using ^{1}H-NMR (Varian Mercury 300 MHz) spectroscopy.

2.5 Preparation of surface coating

Films of ALNR were coated from a toluene solution on a glass plate containing 20, 40, 60, and 80 phr, and 5 and 10 phr Irgacure 184 or Irgacure 651. Samples were exposed to the radiation of a mercury lamp at room temperature for 30, 60, and 90 seconds.

2.6 Testing of Surface Coating Film

2.6.1 Testing for solution resistance

The coating sample was soaked in 2% H_2SO_4, 2% NH_4OH solution and distilled water at room temperature for 20 mins (level 1), after 2 mins (level 2), 2 hrs (level 3) and 24 hrs (level 4) (ASTM D1647-89).

2.6.2 Pencil hardness test

A complete set will have the following pencil grading, starting with the hardest, 6H, 5H, 4H, 3H, 2H, 2B, 3B, 4B, 5B, and 6B. The “H” stands for “hardness” select soft grade of pencil, e.g. 6B, and was applied to the coated surface. If there is no damage or marring to the surface then this procedure was repeated with the next hardness grade of pencil until there is marring (damage) to the coating. The coating hardness is therefore the last pencil grade which did not damage the coating (ASTM D3363).

3. Results and Discussion

3.1 Preparation of LNR

The number-average molecular weight ($\overline{Mn}$) and the weight-average molecular weight ($\overline{Mw}$) of LNR were 19,700 and 59,800 g.mol $^{-1}$ compared to those of original natural rubber were 412,300 and 2,833,380 g.mol $^{-1}$, respectively. LNR with brown color and low viscosity was obtained by chain scission of natural rubber in the presence of hydrogen peroxide and cobalt acetylacetonate. The degradation of natural rubber was obtained from catalytic effect of Co^{2+} on decomposition of hydrogen peroxide to form hydroxyl radical and then abstract allylic proton of NR and obtained LNR with ketone and carboxylic chain end *via* hydroperoxide (Shelton, 1971; Stivala *et al.*, 1983). The possible structure of LNR is given by :

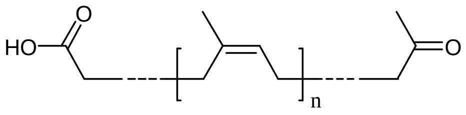

Figure 1 shows a FTIR spectrum of liquid natural rubber by degradation of natural rubber latex with hydrogen peroxide in the presence of cobalt acetylacetonate. The absorption bands at 3400 cm^{-1} (OH stretching), 1720 cm^{-1} (C=O stretching), 1660 cm^{-1} (C=C stretching), 1440 cm^{-1} (C-H bending of CH_2), 1375 cm^{-1} (C-H bending of CH_3), and 835 cm^{-1} (=C-H out of plane deformation) were found.

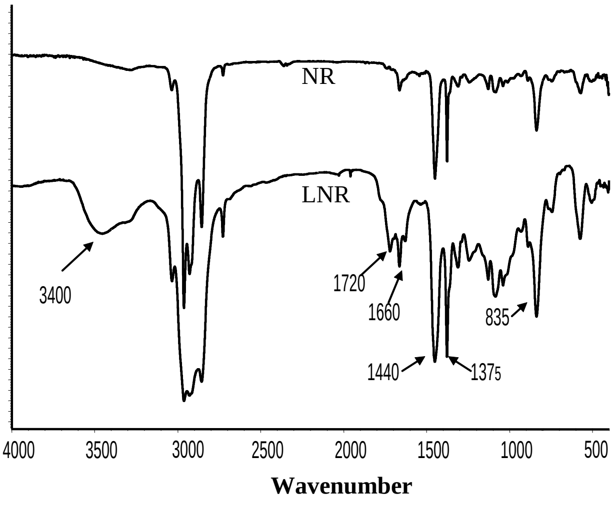

Figure 1. FTIR spectroscopy of natural rubber (NR) and liquid natural rubber (LNR).

3.2 Preparation of ELNR

FTIR spectrum of epoxidized liquid natural rubber obtained from the reaction of LNR with formic acid and hydrogen peroxide is shown in Figure 2.

From the FTIR spectrum, the principal absorption bands at 3400 cm^{-1} (OH stretching), 1720 cm^{-1} (C=O stretching), 1375 cm^{-1} (C-H bending of CH_3), 835 cm^{-1} (=C-H out of plane deformation) (Ng and Gan, 1981; Gelling, 1991) as well as 1251, 870 cm^{-1} (epoxy ring) appeared. The ^{1}H-NMR signal of ELNR is shown in Figure 3.

The epoxidation level was calculated from the integrated area of proton peaks obtained from the ^{1}H-NMR spectrum appearance of olefinic proton (5.14 ppm) and the appearance of a methine resonance (2.70 ppm) due to the

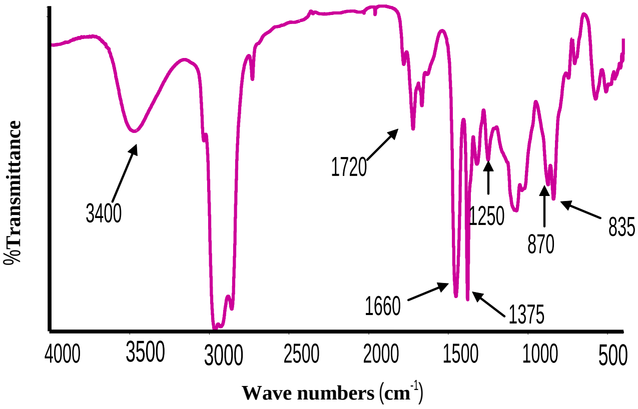

Figure 2. IR spectrum of epoxidized liquid natural rubber (ELNR) at 2 hrs at 50°C.

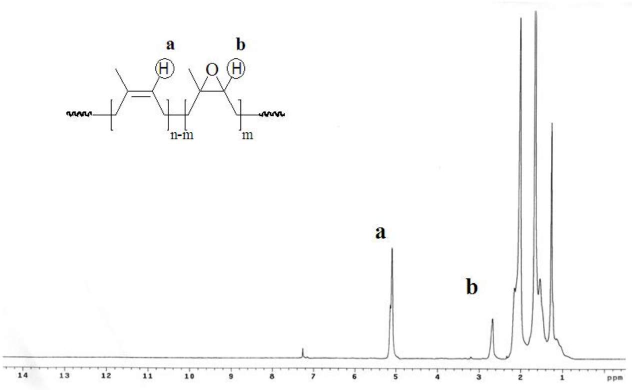

Figure 3. ^{1}H-NMR signal of epoxidized liquid natural rubber (ELNR) ($CDCl_3$ as solvent).

proton attached to the oxirane ring as shown in the following relationship (Burfield *et al.*, 1984).

$A_{2.70}$: Integration area of proton adjacent to epoxide ring at 2.70 ppm.

$A_{5.14}$: Integration area of olefinic proton at 5.14 ppm in isoprene units.

The mole % epoxide of ELNR obtaining from LNR with formic acid and hydrogen peroxide in toluene at 50°C for 2 hrs was found to be 25.

3.3 Preparation of ALNR

The reaction diagram of acrylation reaction of ELNR with acrylic acid is represented in Figure 4. The IR spectrum of ALNR obtained from the reaction of ELNR and acrylic acid at 1:2 weight ratio in toluene at 80°C for various times and principal characteristics of FTIR absorption bands of ELNR and ALNR are shown in Figure 5 and Table 1, respectively.

We observed a decrease of the absorption bands of the epoxy group (1250 and 870 cm^{-1}) and an increase of the absorption bands of the acrylate function, mainly at 1403 cm^{-1} ($=CH_2$ deformation), due to strong absorption bands of C-H bending in CH_3, which remained constant after acrylation. The changes in the absorption band intensity during the acrylation reaction have been consequently monitored from the ratio of optical density (OD_x / OD_{1375}) (Figure 6) as mentioned previously (Le Xuan and Decker, 1993). However, the progress of acrylation reaction was monitored by using peak area ratio of epoxide to methyl group (Phinyocheep and Duangthong, 2000).

The acrylation level was calculated from the integrated area of proton peak as shown below :

$$\%\text{Acrylation} = \frac{A_{6.42}}{A_{6.42} + A_{5.14} + A_{2.70}} \times 100$$

where $A_{6.42}$ is the integration area at 6.42 ppm (H of 1-ethylene, *cis*), $A_{5.14}$ is the integration area 5.14 ppm (olefinic proton) and $A_{2.70}$ is the integration area at 2.70 ppm (proton adjacent to epoxide ring).

The acrylation percentage at 80°C, for 6, 9, 12, 18, and 24 hrs was found to be 0.12, 0.25, 0.13, 1.10, and 0.14, respectively. The ^1H-NMR signal of ALNR is shown in Figure 7.

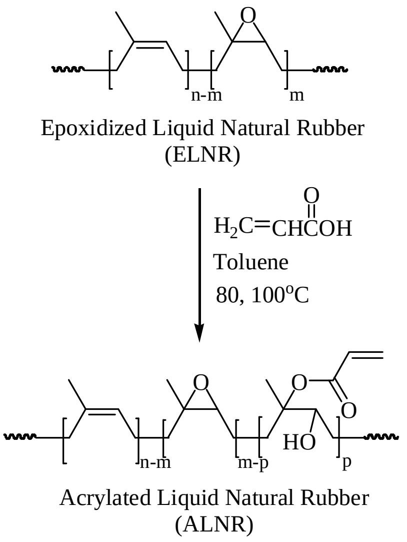

Figure 4. Acrylation reaction of epoxidized liquid natural rubber (ELNR) with acrylic acid.

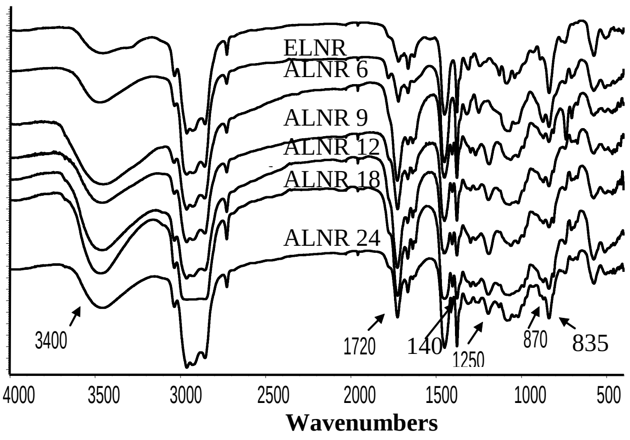

Figure 5. Infrared spectra of liquid natural rubber (LNR), epoxidized natural rubber (ELNR) and acrylated liquid natural rubber (ALNR) for 6, 9, 12, 18, and 24 hrs at 80°C.

Table 1. Principal characteristics of FTIR absorption bands of epoxidized natural rubber (ELNR) and acrylated liquid natural rubber (ALNR).

ELNR		ALNR	
Wave number (cm^{-1})	Vibration	Wave number (cm^{-1})	Vibration
1250	epoxy	1250	epoxy
870	epoxy	870	epoxy
1721	C=O stretching	1721	C=O stretching
1375	C-H bending of CH_3	1375	C-H bending of CH_3
835	=C-H out of plane deformation	835	=C-H out of plane deformation
		1403	$=CH_2$ deformation

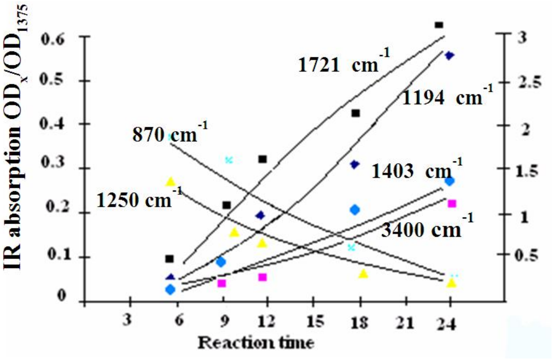

Figure 6. Variation of the different IR absorption bands of liquid natural rubber (ELNR) during the acrylation reaction at 80°C.

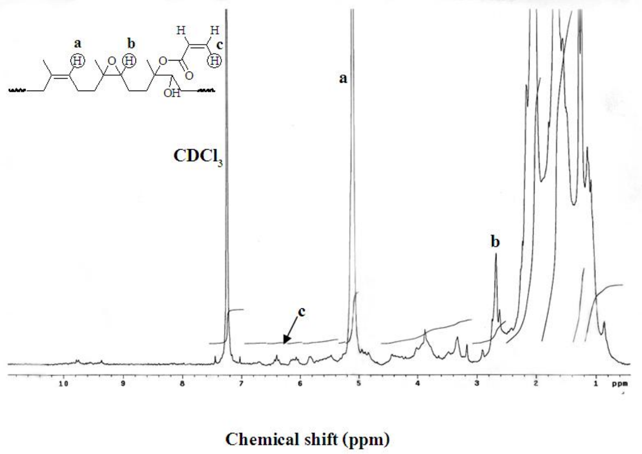

Figure 7. ^{1}H-NMR signal of acrylated liquid natural rubber (ALNR) (CDCl$_3$ as solvent)

3.4 Preparation of surface coating

For laboratory testing of surface coating films, samples were prepared on glass plates from ALNR, 5 and 10 phr Irgacure 184 or Irgacure 651 and 20, 40, 60, and 80 phr HDDA or TPGDA under UV exposure for 30, 60 and 90 mins. The results showed that a clear hard coating film was found when using 10 phr Irgacure 651, 80 phr TPGDA under UV exposure for 30 mins. In our work, ALNR with around 19,700 was easier to collide with longer product chain TPGDA than HDDA. In contrary, Phinyocheep and Duanthong (2000) reported that HDDA was better than TPGDA as a crosslinker due to the latter possessing a longer product chain between acrylate function causing the probability of a collision between the radical and acrylate function to decrease.

ALNR undergoes fast radical crosslinking when exposed to UV radiation together with HDDA or TPGDA as a crosslinker in the presence of a photoinitiator, Irgacure 184 or Irgacure 651. The photoinitiators produce radicals by fragmentation in the photo-exited state, and initiates radical. Crosslinking reaction leads to formation of an insoluble coating, and chains are joined together to form a three dimensional network (Dufour, 1993). The possible mechanism for insoluble coating product from ALNR, TPGDA, and Irgacure 651 after UV exposure is represented in Figure 8 and the coating film samples on plywood from suitable formula TPGDA and Irgacure 651 in ratio 80:10 phr are demonstrated in Figure 9.

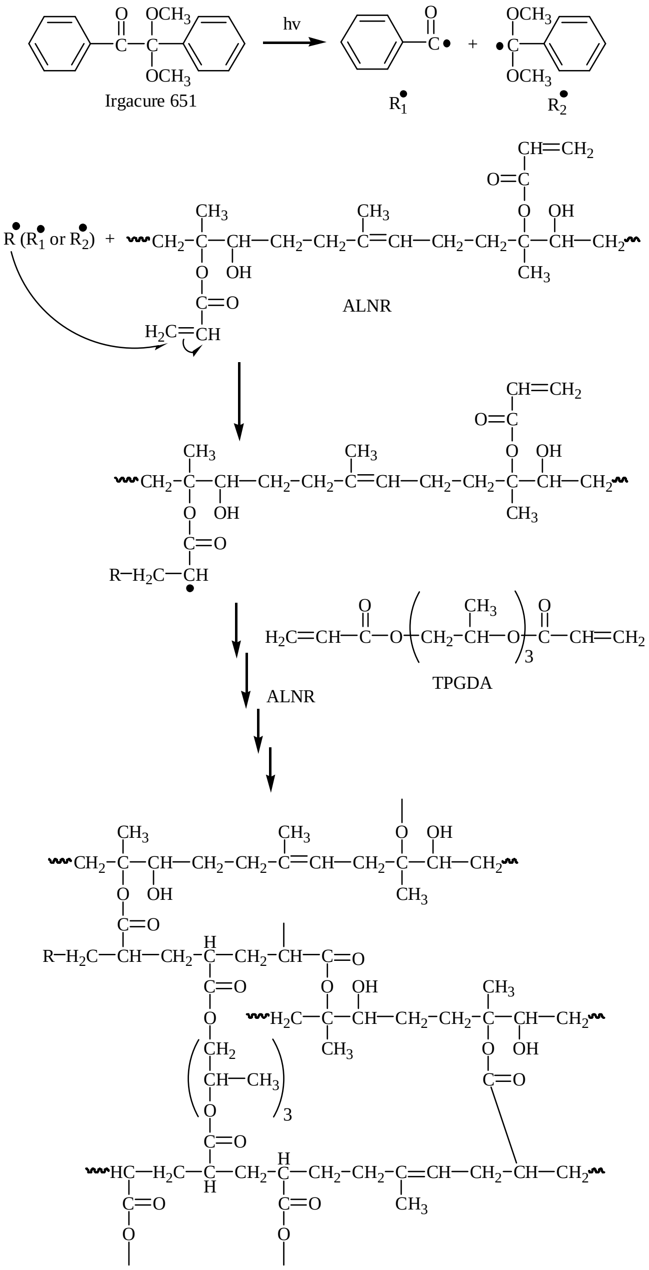

Figure 8. Proposed mechanism in preparation of coating product from acrylated liquid natural rubber (ALNR), TPGDA, and Irgacure 651 under UV exposure.

3.5 Properties of surface coating

3.5.1 Hardness test

From the pencil hardness test it was also found that the

Figure 9. Coating film samples on plywood (2.5x8.0 cm) prepared from optimum formulation: ALNR, TPGDA and Irgacure 651 in ratio 100:80:10 by weight.

highest hardness of a surface coating was at pencil level 4H for products using 80 phr TPGDA and 10 phr Irgacure 651 under UV exposure for 90 seconds. The result showed that the hardness increases with exposure time (Le Xuan and Decker, 1993), with the amount of crosslinkers and photoinitiators.

3.5.2 Solution resistance

Acid-base resistant tests of coating product samples were performed in 2% H_2SO_4, 2% NH_4OH and distilled water. It was found the products were resistant to 2% H_2SO_4 and distilled water in level 4, whereas cured products were resistant to 2% NH_4OH in level 2 due to cured products possesses components of the ester group ,which was able to hydrolysis in base medium.

4. Conclusion

The grafting of acrylate group onto an epoxidized liquid natural rubber was accomplished by producing of the photocrosslinkable rubber. Acrylated liquid natural rubber (ALNR), a photocrosslinkable material, can be prepared from epoxidized liquid natural rubber and acrylic acid at 80°C. The appropriate surface coating material was obtained by mixing of ALNR with 80 phr tripropylene glycol diacrylate and 10 phr Irgacure 651. The formation of a three-dimensional polymer network leads to hardness film after 90 mins of UV irradiation. The highest hardness of surface coating on plywood was found at pencil level of 4H. The plywood coating obtained was to be stable in 2 % H_2SO_4 for more than 24 hrs.

Acknowledgements

The authors gratefully acknowledge the Thailand Research Fund (TRF) for financial support under TRF-Master Research Grants (Year 2006) and the Faculty of Science and Technology, Prince of Songkla University, Pattani Campus, for its permission to use laboratory facilities.

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