The Effect of Alkyd Resins on the Properties of AA-NC Semi-IPNs as Binders in Wood Finish

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ABSTRACT: Wood coatings of AA-NC semi-interpenetrating polymer networks (semi-IPNs), made from acid curing amino-alkyd resins (AA) and nitrocellulose (NC), were prepared by sequential polymerization method. To investigate the effects of oil length on the properties of AA-NC semi-IPNs, three grades of alkyd resins (Alkyd) containing 38, 48, and 58% oil were synthesized with phthalic anhydride, glycerol, and soybean oil, employing alcoholysis method. The butylated urea formaldehyde resin (UF) and melamine formaldehyde resin (MF) were also prepared in this study. The AA-NC semi-IPNs were maintained at a weight ratio of AA : NC of 25 : 75, where the AA was the composition of MF : UF : Alkyd of 7.5 : 22.5 : 70 (by weight), and 10% of *p*-toluene sulfonic acid solution (concentration, 25% in isopropyl alcohol) based on the weight of amino resins was added as acid catalyst. The properties of coatings such as viscosity, drying time, and gel time, and the properties of films including adhesion, hardness, abrasion resistance, impact resistance, tensile strength, released formaldehyde, lightfastness, solvent resistance, and durability were examined. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1923–1927, 2004

Key words: coatings; films; blends; networks

INTRODUCTION

Among the common resins used in wood coatings, nitrocellulose (NC) has the highest hardness, fastest drying rate, and excellent compatibility with other resins. Wood coatings containing nitrocellulose as the film-former have good clarity in popular media and low sheens and give a finishing to the appearance of the wood that appeals to most people. Polymer blending is a useful technique to obtain properties not readily achieved in homopolymers.[1] The semi-interpenetrating polymer networks (semi-IPNs) are a special type of polymer blends that consist of an intimate mixing of linear polymer with a crosslinked polymer and have unique properties that cannot be achieved with a single polymer alone.[2–4] They can be obtained either by crosslinking of a functionalized polymer with a linear polymer blend or by polymerization of a multifunctional monomer dispersed in a linear polymer. The PU-NC semi-IPNs,[5–8] and PE-NC semi-IPNs,[9–10] based on the linear NC blended with polyurethane (PU) and unsaturated polyester resins (PE), respectively, used as wood coatings were previously investigated by the author. The results indicated that the semi-IPNs wood coatings containing NC could be synthesized readily and some properties including pot-lift, drying time of coatings and hardness, tensile strength, and durability of films were better than those of PU and PE.

Acid curing amino-alkyd resins (AA) for wood coatings are made with oil-modified alkyd resins in combination with butylated urea formaldehyde resin (UF) or melamine formaldehyde resin (MF), possess high solid content, film thickness, outstanding heat, and chemical resistance, are cheap in price, and are one of the important resins used on wood furniture. They are accelerated for air-drying by the addition of acid catalysts such as *p*-toluene sulfonic acid. However, because of pollution problems caused by the evolution of released formaldehyde from amino resins, more attention has been paid to reduce the amount of formaldehyde evolved from the cured film. The objective of this series of research is to prepare AA-NC semi-IPNs for wood coatings, not only to enhance the properties of AA but also to reduce formaldehyde emissions by blending AA with NC.

Alkyd resins, one of the components of AA, are products derived from the polycondensation of a polybasic acid (i.e., phthalic anhydride), and a polyhydric alcohol such as glycerol modified with oil. Thus, soybean oil has been shown to give good drying rates and good color retention and therefore the standard alkyds are usually soybean alkyds. Alkyd resins are excellent film formers and possess outstanding elasticity, adhesion, gloss, and durability in outdoor exposure. However, they have some flaws; namely: they need high oven temperature or long times to cure; they are too soft; they turn yellow when exposed to

light; and for certain applications, their alkali resistance is too low. An example is amino resin, which is the other component of AA; the most commonly used are UF and MF. They are products of reaction between formaldehyde and urea or melamine under alkaline conditions which initially produces methylol groups. This methylol urea or melamine may then be reacted with *n*-butanol to yield butylated amino resins for manufacturing solvent-borne coatings. They possess high hardness and lightfastness and need only low curing temperature in the presence of some acid, but are too brittle for practical use and do not have enough adhesion.

In our previous article,[11] the synthesis and characteristics of AA with various amino/soybean short-oil modified alkyd resin (Alkyd) ratios were examined. The results indicated that the AA resin, based on MF : UF : Alkyd with a weight ratio of 7.5 : 22.5 : 70, had the shortest drying time, the best bending strength, and hardness of films and also had good properties of impact resistance and abrasion resistance of film. Also, AA-NC semi-IPNs containing various amounts of AA/NC were prepared by sequential polymerization and the properties of coatings and films were examined.[12] Quality of AA-NC semi-IPNs coatings was better than that of AA and the properties are better with increasing NC content. To explore and better understand the application of AA-NC semi-IPNs as wood coatings, three different oil length alkyds (short-oil, medium-oil, and long-oil modified alkyd) as the constituent of semi-IPNs, respectively, were further investigated in this research.

EXPERIMENTAL

Materials

Soybean oil (Taiwan Sugar Co., Kaohsiung, Taiwan) contains predominantly linoleic and oleic acids,[13] had the specific gravity of 0.971 at 25°C, acid value of 1.90 (mg KOH g^{-1}), saponification value of 198 (mg KOH g^{-1}), and iodine value of 128 (g I_2 per 100 g). Laboratory-grade phthalic anhydride (Shimakyu, Osaka, Japan), glycerol (Shimakyu), litharge (Kanto, Tokyo, Japan), and xylene (Shimakyu) were used in the preparation of the alkyds. Laboratory-grade urea (Shimakyu), melamine (Shimakyu), formaldehyde (concentration, 24%; Union Chemical Work, Hsin-chu, Taiwan), and *n*-butanol (Shimakyu) were used in the preparation of butylated UF and MF. Nitrocellulose (ICI, Taoyuan, Taiwan) had the viscosity of 1/2s (falling ball viscometer) and solid content of 40% (solvent methyl ethyl ketone). All reagents were used directly from the suppliers without further purification. The specimens tested for wood coatings include hard maple(*Acer* sp.) with moisture content of 10%, glass, Teflon panels, and white cardboard. They were treated according to different testing requirements.

TABLE I
Recipe for the Preparation of Soybean Oil Modified Alkyd Resins

Ingredients	Alkyd resins		
	Short-oil	Medium-oil	Long-oil
Soybean oil (%)	38.00	48.00	58.00
Phthalic anhydride (%)	40.00	34.00	29.00
Glycerol (%)	22.00	18.00	13.00

Preparation of alkyd resins

Three samples of alkyd resins formulated to have oil content of 38% (short-oil), 48% (medium-oil), and 58% (long-oil) were prepared with soybean oil, phthalic anhydride, and glycerol (according to the recipe shown in Table I) by using the alcoholysis method.[14] The reaction was carried out in a 1-L round-bottom flask fitted with motorized stirrer of variable speed, nitrogen gas inlet tube, thermometer, and Dean and Stark apparatus carrying a water-cooled condenser. In each preparation, the monoglyceride was first prepared by heating the soybean oil to 230–250°C, the litharge (0.03% based on the weight of the oil), and then the glycerol was added, and the mixture was reheated to 230–250°C. When three volumes of methanol per volume of alcoholysis mixture gave a clear solution, the monoglyceride was cooled down to about 180°C and then a known amount of phthalic anhydride and xylene (10% by weight of total ingredients charged) was added. The reaction temperature ranged from 210 to 250°C, and sampling was carried out at 30 min intervals to determine the acid value of the reaction mixture. When the acid value reached 15, the reaction was stopped and the mixture was cooled down to room temperature. The speed of the stirrer was kept at 400 rpm throughout the duration of the reaction.

Preparation of UF resin

The 2 mol formaldehyde (in the form of a 24% solution) was first put in a 1-L round-bottom flask and was neutralized with 1*N* NaOH solution before the addition of urea. Then, 1 mol urea was added and dissolved; the mixture was brought to pH 8.6–8.8 by the addition of 1*N* NaOH solution, and 2 mol *n*-butanol was added with heating and stirring. The resultant mixture was heated under reflux to 70°C within 30 min and maintained for 1 h. Thereafter, the temperature was raised to 85°C and maintained for 20 min. At the end of the reaction, the mixture was cooled to about 25°C, and the pH was adjusted to 4.5–5.0 by adding 1*N* CH_3COOH solution. The mixture was reheated to 85°C and maintained for about 1 h. Toluene (25% by weight of total ingredients charged) was em-

ployed as the azeotropic solvent as an aid to removing water during the reaction. When this was done, the mixture was cooled down to 25°C and was brought to pH 8.0–8.2 by the addition of 1N NaOH solution. The resultant UF resin had a viscosity of 21.7 cps at 25°C and solid content of 26.6%.

Preparation of MF resin

The MF resin was prepared following the procedure used for UF resin. However, the molar ratio of melamine : formaldehyde : n-butanol was 1 : 5 : 5, and the reaction temperature was 90–100°C. The resultant MF resin had a viscosity of 278 cps at 25°C and solid content of 35.1%.

Preparation of AA-NC semi-IPNs

The AA-NC semi-IPNs can be obtained by crosslinking of alkyd resin with amino resin (i.e., MF, UF), using p-toluene sulfonic acid as catalyst + linear polymer (i.e., NC) blend. The alkyd resin, NC, and amino resin were maintained at a weight ratio of AA : NC of 25 : 75, where the AA was the composition MF : UF : Alkyd of 7.5 : 22.5 : 70 (by weight), and the alkyd resins were the short-oil, medium-oil, and long-oil alkyd. Three different AA-NC semi-IPNs coatings were prepared with the three different alkyd resins. In each preparation, first, the calculated amounts of UF and MF were mixed in 1-L four-necked flask at room temperature and the mixture was stirred for 30 min, followed by the addition of the NC and stirring for 30 min. Then, calculated amount of alkyd resin was added and stirred for another 30 min. The solid content of the synthesized compounds was maintained at 40% by adding the thinner (compositions based on the weight ratio of methyl ethyl ketone : n-butanol : butyl acetate : xylene of 10 : 35 : 20 : 35). Finally, 10% of p-toluene sulfonic acid solution (concentration 25% in isopropyl alcohol) as acid catalyst was added to the synthesized compounds based on the weight of amino resin and the mixture was stirred for another 10 min. The speed of the stirrer was kept at 1000 rpm throughout the duration of the reaction.

The resultant coatings were kept at room temperature until all bubbling ceased and were then applied on the different kinds of substrates with film applicators. The thickness of wet film was adjusted to 200 μm, and 100 μm for drying time test. All finished specimens were conditioned at room temperature for 1 week before testing.

Characterization

Tests of viscosity for wood coatings were carried out on a Gardner bubble viscometer at 25°C. Drying time tests of coatings was performed on a three-speed B. K.

drying time recorder at the conditions of 25°C and 65% relative humidity (RH). The gel time of each coating was identified by its flowing characteristics at room temperature.

The adhesion property of the tested films on wood panels was determined by crosscut method according to CNS K 6800. The hardness of the tested films was investigated on a König hardness tester (Braive Co.) according to DIN 53157, and at least five points were tested for each specimen. The abrasion resistance of the tested films was measured in terms of the weight loss per 1000 revolutions on a Taber Model 503 Abraser and the CS-10 wheel was used. The impact resistance of the tested films was determined based on the height of striking of the coated wood panels that do not crack on a known falling weight of 500 g by using a DuPont Impact Tester IM-601. The tensile strength and elongation at break of tested films were carried out on an Schimadzu Eztest Main instrument. All tested specimens were prepared as a specified shape, typically a dog bone, according to ASTM D638. The sample was clamped at one end and pulled at a 5 mm/min of elongation until the center of specimen failed and five samples were tested for each treatment. The released formaldehyde of the tested films was measured according to CNS-1349.

The lightfastness of the tested films was determined by using a SUGA Weather Meter. The light source was applied as carbon arc, and its black panel temperature was adjusted to 50 ± 2°C. After 100 h exposure, the ΔL^* (brightness difference), ΔE^* (color difference), and ΔYI (change in yellowness) of the specimens were measured at five different points for each specimen by using a color and color difference meter (Minolta CR-200).

The solvent resistance of tested films was measured by putting each weighted film into 100 mL ethyl acetate for 48 h. To remove the remnant solvent, the soaked film was further dried in an oven at 80°C for 24 h. The weight retention of tested film was calculated as the solvent resistance. The hot and cold cycle tests of the films were carried out on hard maple wood coated with different synthesized wood coatings. One test cycle of the specimens consisted of placing them in a −20°C refrigerator for 2 h and then transferring them to a 50°C oven for another 2 h. Twenty test cycles were performed on the coated specimens, and the gloss of the films was also measured during the test cycles by using Pacific Scientific Glossgard II 60° Gloss Meter, and the gloss retention was calculated. The cycle number was recorded if the films were cracked.

RESULTS AND DISCUSSION

Coating properties of AA-NC semi-IPNs

The coating properties of AA-NC semi-IPNs with different oil length alkyd resins are shown in Table II.

TABLE II
Properties of AA-NC Semi-IPNs Coatings

Sample code	Viscosity (Gardner, 25°C)	Drying time (min)	Gel time (day)
S-AANC	Y	1.5	68
M-AANC	Z-1	1.0	43
L-AANC	W	1.0	30

The AA-NC semi-IPN coating containing medium-oil alkyd resin (i.e., M-AANC) has the highest viscosity value of Z-1, corresponding to 27.0 P, while that containing the long-oil alkyd resin (i.e., L-AANC) showed the lowest viscosity value of *W*, corresponding to 10.7 P. As per our previous article,[11] the drying time of acid curing AA, with the compositions MF : UF : short-oil alkyd resin of 7.5 : 22.5 : 70 (by weight), was 4 h. Blending AA with NC to form AA-NC semi-IPNs reduces the drying time significantly from 4 h to 1.5 min. Furthermore, the M-AANC and L-AANC took only 1 min to dry. Among the tested coatings, the AA-NC semi-IPNs coating containing short-oil alkyd resin (i.e., S-AANC) had the longest gel time of 68 days, and the M-AANC and L-AANC were 43 and 30 days, respectively, indicating that the AA-NC semi-IPNs coatings could be kept at a flowing condition for more than 30 days even by adding *p*-toluene sulfonic acid catalyst. The results indicated that all of the AA-NC semi-IPNs coatings in this study dried very rapidly and had long pot-life, suited for wood finishing.

Mechanical properties of AA-NC semi-IPNs films

Mechanical properties of AA-NC semi-IPNs films with different oil length alkyd resins are listed in Table III. The best order of adhesion was 10, followed by 8, 6, 4, 2, and 0. The results showed that the S-AANC had the best adhesion of 8, while the M-AANC and L-AANC had the same order of 6. The S-AANC had the highest value of hardness at 190, and the L-AANC had the lowest one at 152, which may be owing to the long-oil alkyd resin having the presence of a larger number of saturated fatty acids such as palmitic acid and stearic acid[15] and imparts a soft character to the alkyd resin, which in turn influences the hardness of AA-NC semi-IPNs films. By comparison with the

weight loss of abrasion resistance property of AA-NC semi-IPNs films, the medium-oil alkyd resin containing film had the least weight loss of 30.7 mg per 1000 cycles (i.e., it had the best abrasion resistance). This was probably due to its better interpenetration between AA and NC than that of containing short-oil and long-oil alkyd resins.

The height of impact resistance property of M-AANC and L-AANC were of the same value of 10 cm, and those had better impact resistance than that of S-AANC of 5 cm. Among all of the AA-NC semi-IPNs films, the highest tensile strength was observed to be 384.5 kgf cm^{-2} for the coating containing medium-oil alkyd resin. However, the elongation at break of M-AANC is slightly inferior to that of S-AANC.

Other properties of AA-NC semi-IPNs films

The released formaldehyde, lightfastness, solvent resistance, and hot and cold cycle tests of AA-NC semi-IPNs films are listed in Table IV. As we have previously reported,[12] the released formaldehyde of AA was 8.2 ppm. In this study, we hoped to enhance the properties of AA by blending with NC; meanwhile, the use of a low amount of AA results in the release formaldehyde into the environment also will be expected. The results indicated that using the weight ratio of AA : NC of 25 : 75, the released formaldehyde could be significantly reduced from 8.2 to 3.1 ppm (S-AANC), and the lower the oil content of the alkyd resin, the lower the formaldehyde emitted. The lightfastness of the AA-NC semi-IPNs films with different oil length alkyd resins after exposure to a carbon arc for 100 h are also summarized in Table IV. The ΔL^*, ΔE^*, and ΔYI of AA and NC were -1.98, 44.33, and 54.86, as well as -0.98, 11.3, and 17.33, respectively, as presented in our previous article.[12] The lightfastness of AA was inferior to that of NC, while it can be improved by blending AA with NC to form the AA-NC semi-IPNs as shown in this study. Generally, among all tested films, the S-AANC had the lowest value of ΔL^*, ΔE^*, and ΔYI of -0.80, 39.10, and 48.38, respectively, indicating that the AA-NC semi-IPNs containing short-oil alkyd resin had the best lightfastness.

The weight retention of films after dipping in ethyl acetate for 48 h are shown in Table IV. As we have

TABLE III
Mechanical Properties of AA-NC Semi-IPNs Films

Sample code	Adhesion	Hardness (König, s)	Abrasion resistance (mg per 1000 cycles)	Impact resistance (cm)	Tensile strength (kgf cm^{-2})	Elongation at break (%)
S-AANC	8	190	32.4	5	203.9	4.34
M-AANC	6	166	30.7	10	384.5	3.13
L-AANC	6	152	53.3	10	349.4	2.92

TABLE IV
Properties of AA-NC Semi-IPNs Films

Sample code	Released formaldehyde (ppm)	Lightfastness			Solvent resistance	Hot and cold cycles
		ΔL^*	ΔE^*	ΔYI	Weight retention (%)	Gloss retention (%)
S-AANC	3.1	−0.80	39.10	48.38	36.9	95
M-AANC	3.7	−0.66	43.58	54.66	54.2	100
L-AANC	4.3	−1.51	40.33	50.18	28.1	99

previously reported,[12] the weight retentions of AA was 76.3% at the same test condition. Theoretically, the weight retention of the film is about 19.1% (76.3 × 25%) in the AA-NC semi-IPNs with the composition AA : NC of 25 : 75, and all of the films in this study had a higher weight retention value than 19.1%, indicating an entanglement occurred between AA and NC in all of the AA-NC semi-IPNs. The results of interpenetrating between AA and NC of the AA-NC semi-IPNs coating containing short-oil alkyd resin also had been proved by solvent extraction and Fourier transform infrared (FTIR) analysis, as presented in our previous report.[12] Furthermore, among all AA-NC semi-IPNs films, the maximum weight retention was observed at 54.2% for the medium-oil alkyd resin containing film, indicating that the best solvent resistance was achieved by this formulation. In addition, the worst solvent resistance was found at 28.1% for the film containing long-oil alkyd resin. This was probably due to its poor interpenetration between AA and NC, which makes it easy to dissolve in the ethyl acetate solvent.

For all AA-NC semi-IPNs films after 20 hot and cold cycle tests, no film cracking was found on coated wood panels and the gloss retention of all specimens were retained at above 95%, especially 100% for M-AANC, indicating that all of the AA-NC semi-IPNs films had excellent durability.

CONCLUSION

In this study, three kinds of alkyd resins with various oil lengths were synthesized by alcoholysis method, and three types of AA-NC semi-IPNs were prepared by sequential polymerization method from different oil lengths of alkyd resins for application in wood coatings. Among all AA-NC semi-IPNs, the short-oil alkyd resin coating had the best adhesion, the highest hardness, the lowest released formaldehyde, and the best lightfastness. The AA-NC semi-IPNs with medium-oil alkyd resin had the best abrasion resistance, the best tensile strength, and the best solvent resistance. All AA-NC semi-IPNs had a short drying time of 1.5 min as well as a long pot-life of coatings of more than 30 days, and their films showed excellent durability of gloss retention. From these results, it can be concluded that the AA-NC semi-IPNs with medium-oil alkyd resin have excellent performance and a balanced effect on the properties of coatings and films and can readily be used for wood coatings.

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