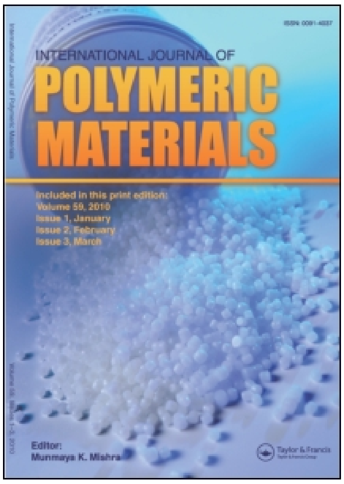

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Reactive Phenol-Functional Polyesters with UV-Absorbing Moiety and their Coating Applications

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Reactive Phenol-functional polyester (PPE) resins have been synthesized using p-hydroxy cinnamic acid (p-HCA) as one of the components, by direct polyesterification reaction. The PPEs have been characterized for relevant physical and chemical characteristics. Various thermosetting coating compositions have been prepared using PPE and melamine-formaldehyde type crosslinking agent. The cured coatings have been found to have excellent mechanical properties. The study shows that PPE-based coatings strongly absorb in the ultraviolet region below 330 nm and their films exhibit superior resistance to accelerated weathering tests.

Keywords: benzoxazoline, phenol-functional, UV-absorption

INTRODUCTION

Polyester resins form one of the most important groups of polymers used for applications such as composites, coatings, adhesives, and sealants, among others due to their versatility and excellent cost-performance benefits. Commercial availability of a wide range of polyester raw materials allows products with diverse properties for a

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variety of end-use applications. In the field of coatings, thermosetting polyesters are widely used in industrial coatings such as automotive coatings, coil coatings, powder coatings, and so on [1]. For such applications, these polymers are expected to give cured films with excellent mechanical properties and often long-term durability in the exterior environment. These properties are generally tailored through polymer design, crosslinking chemistry, and by use of suitable pigments and additives in the coatings.

Conventional polyesters used for coating applications are generally hydroxyl functional resins and are frequently cured by isocyanate or melamine-formaldehyde type crosslinkers. Coatings based on melamine-formaldehyde type crosslinkers are generally required to be cured at elevated temperature. Such coatings form crosslinked structure by formation of imino-ether linkages between polyester chains and crosslinker. Mechanical properties of the films such as hardness or impact resistance can be controlled by controlling the crosslink density of the films [2].

Condensation of phenol-functional resins with melamine-formaldehyde type crosslinkers, in presence of acid catalyst, is believed to result in the formation of heterocyclic 1,3-benzoxazine structure [3–10]. Subrayan and Jones have shown the formation of benzoxazine structure by condensation reaction of 4-substituted phenol with hexakis(methoxymethyl)melamine [11]. The presence of such rigid cyclic crosslinks in polymeric coatings is known to substantially harden the films [12].

The most common chemical processes leading to degradation of coatings are photoinitiated oxidation and hydrolysis resulting from exposure to sunlight, air, and water. In order for polymeric coatings to be exterior durable, they must be resistant to the UV radiation of sunlight. Such coatings are formulated from inherently UV-stable polymers or by using photo-stabilizers as additives.

The goal of the present research was to synthesize functional polymeric systems with potential for formation of rigid crosslinking structures together with photostabilizing capability.

Phenol-functional polyester resins were designed and synthesized using p-hydroxy cinnamic acid (p-HCA) as one of the components along with aromatic and aliphatic dicarboxylic acids and polyol, in a direct polyesterification reaction. p-HCA is known UV-absorbent [13] and it was shown to retain its UV-absorption capability in the cured films. Besides, p-HCA provides phenol functionality that can be used for crosslinking with the melamine-type crosslinkers mentioned earlier. Coating compositions based on these phenol-functional resins were prepared using highly methoxylated methyl melamine as cross linker. The cured film properties, especially their UV absorption characteristics and exterior durability were investigated. The cure reactions of these coatings are schematically illustrated in Figure 1.

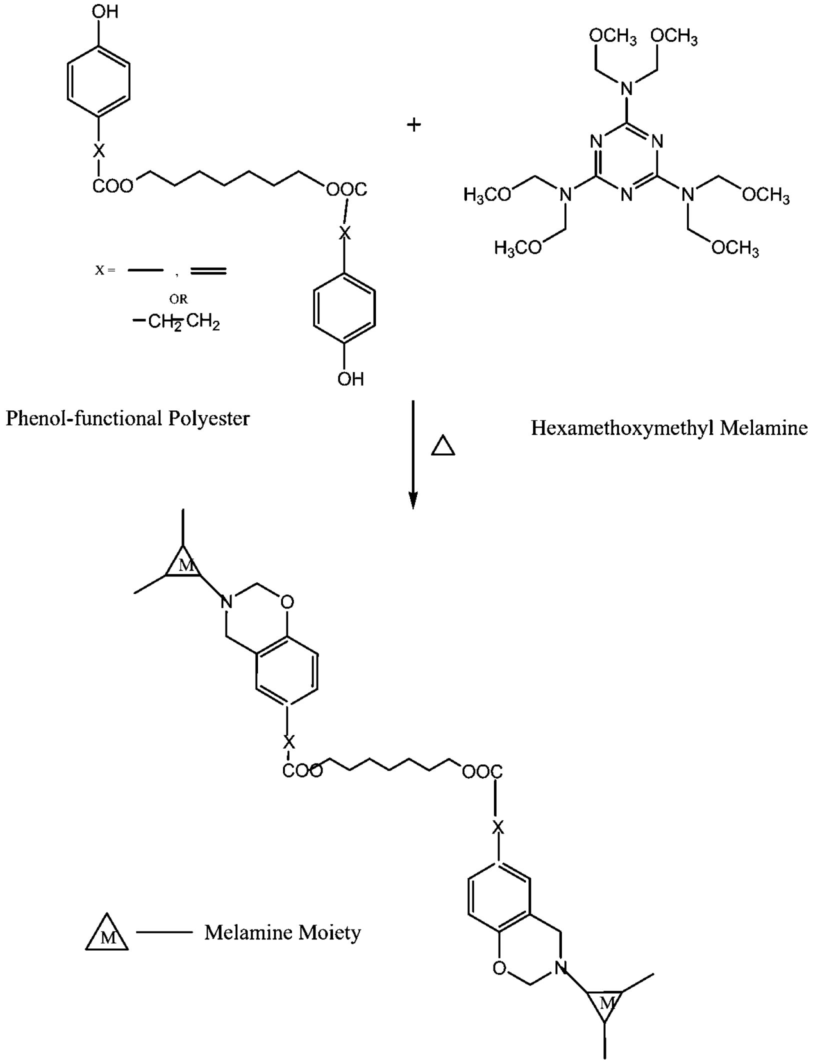

FIGURE 1 Cure reactions of phenol-functional resins—formation of benzoxazoline linkages.

EXPERIMENTAL

Materials

Purified 4-hydroxy cinnamic acid (p-HCA) was supplied by DuPont. All other chemicals and reagents used were procured from Sigma-Aldrich and used without any purification or treatment. A commercial polyester resin, Setal-26-1023, was procured from Akzo-Nobel Resins, USA. Highly methoxylated methyl melamine formaldehyde resin, Cymel 303, and acid catalyst (p-toluenesulfonic acid), Cycat-4040, were procured from Cytec Industries, USA. Steel panels used for studying film properties of coatings cold rolled steel panels, 6″ × 4″, with 0.032″ thickness and having no pretreatment. The panels were procured from Q-Panel Company.

Synthesis of Phenol-Functional Polyester Resins (PPEs)

The experimental process for synthesis of PPE-II resin is described in what follows. The polycondensation reaction was carried out in a 1-L, 4-neck round bottom flask equipped with (1) a heating mantle, (2) a mechanical stirrer, (3) a thermometer, (4) a steam jacketed bubble reflux condenser packed with ceramic saddles, and (5) a nitrogen sparg tube. A Dean-Stark Trap with a chilled water condenser was fitted on top of the steam-jacketed column. For synthesis of PPE-II resin, p-HCA (1.849 moles), adipic acid (0.851 mole), phthalic anhydride (0.851 mole), and neopentyl glycol (2.870 moles) were charged under stirring. The temperature of reaction mixture was slowly raised to 122°C and phosphorous acid (1.0% based on total charge) was added as catalyst. 2,6-di-tert-butyl-4-methoxyphenol (0.20% based on total charge) was added to the reaction to prevent polymerization through the double bond of the p-HCA. Reaction temperature was then raised slowly to 220°C and maintained at 210–220°C. Xylene in combination with a nitrogen sparge was used to azeotropically remove water from the reaction as it was formed. The water was removed using a Dean-Stark trap allowing the xylene to be recycled into the reaction. The reaction temperature was controlled by controlling heat supply and/or or controlling xylene content in the reflux. The reaction was continued until an acid number value of less than 1.0 for carboxylic acid was obtained.

PPE-I resin was prepared by using exactly identical process as described earlier using the composition – p-HCA 34.1%, Azelaic acid 36% and Neopentyl glycol 29.9% by weight.The characteristics of the phenol-functional polyester resins are listed in Table 1.

TABLE 1 Characteristics of Phenol-Functional Polyester Resins

Properties	PPE-I	PPE-II
Phenolic –OH Number*	118.0	127.0
Acid number	0.8	1.2
Molecular wt.—Mn	1160	1220
Mw	2154	2562
Polydispersity Index	1.857	2.1
Color	Light yellow and clear	Light yellow and clear

*Number of mgs of KOH equivalent to phenolic –OH groups present in 1.0 g of sample.

Coating Composition

Thermosetting coating compositions using PPE resins as primary binders were prepared by mixing, in varying amounts, PPE resin, Cymel 303 (melamine type crosslinker, Ex Cytec Industries), and Cycat-4040 (p-tolune sulfonic acid catalyst, 40% in isopropanol, Ex.Cytec Industries). Solvent, a mixture of xylene and n-butyl alcohol (90:10 wt/wt) was used to maintain percent non-volatile content of all the formulations at 70% by wt. Compositions were allowed to stand for 24 h before application to make films. A control coating was formulated using commercial polyester resin Setal-26-1023 (Akzo Nobel Resins). All the coatings were applied on mild steel panels using block applicator such that their dry film thicknesses were approximately 1.0 mil. Films were cured, after a 30-min flash-off time, in an air-oven for specified temperature and time. Film properties of the coatings were evaluated after aging the cured panels for a minimum of 48 h.

Characterization

The PPE resins were characterized for various properties using physical, chemical, FT-IR spectroscopy (Figures 2 and 3) and UV-visible spectroscopy. The cured films of the coatings were characterized for, besides primary film properties (Tables 2 and 3), their UV-absorption and accelerated weathering (Figures 4–7) to study their exterior durability properties (Table 4).

RESULTS AND DISCUSSION

Synthesis of PPE Resins

The literature gives some references of synthesis of phenol-functional polyester resins [14–17]. It was found that the processes described in many of these patented literature were difficult to reproduce. It is

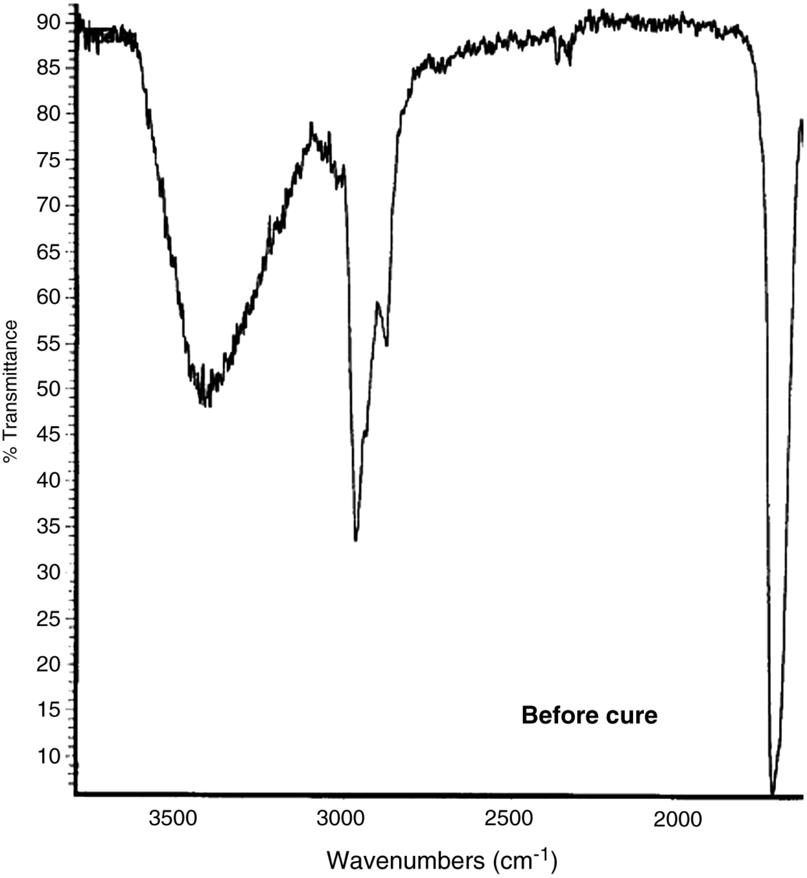

FIGURE 2 FT-IR spectrum of PPE coating—before cure.

necessary to find conditions that strongly favor esterification of p-HCA over potential competing reactions, decarboxylation of p-HCA and esterification of its phenol group. The authors therefore developed the process described in this article and studied its reproducibility. This process was found to be fairly reproducible for various polyester compositions studied. In this process, Phenol-functional polyester resins were synthesized by direct esterification process. The resins were synthesized using 10% excess hydroxyl equivalents over carboxylic acid equivalents to drive the reaction toward completion. Water of reaction was azeotropically removed using xylene. The progress of reaction was followed by monitoring carboxylic acid group concentration by pH metric titration. Carboxylic acid was

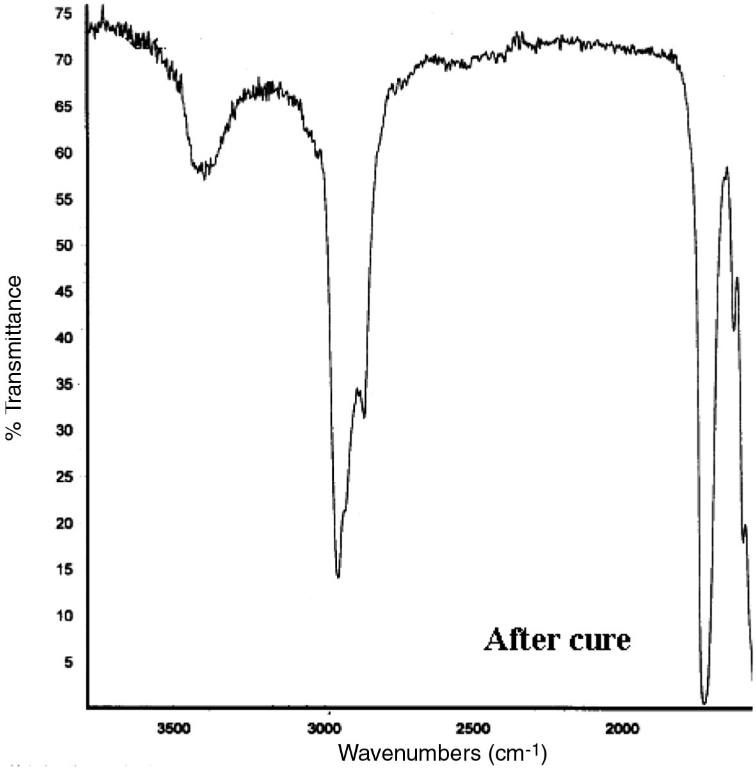

FIGURE 3 FT-IR spectrum of PPE coating—after cure.

TABLE 2 Composition and Properties of Coatings

Properties	PPE-I		PPE-II		Polyster control
Rensin/Melamine* ratio	85/15	80/20	85/15	80/20	80/20
Dry Film Thickness (DFT) mils.	1.05	1.05	1.05	1.1	1.2
Film appearance	clear and colorless	clear and colorless	clear and colorless	clear and colorless	clear and colorless
Pencil hardness	H	2H	2H	3H	4H
Impact resistance (Ibs × inch)					
Direct	140	140	140	140	140
Reverse	140	140	140	120	140
Adhension (Cross-hatch)	4B	4B	5B	4B	2B
MEK Double-rubs (Passes)	25	50	25	50	50

*Cured@130°C, for 30 min.

TABLE 3 Composition and Propeties—PPE-II Based Coatings

Composition properties	PPE-II based coatings				Polyster control
PPE-II/Melamine (wt. ratio)	70/30		60/40		80/20
Cure schedule	130°C for 30 min	180°C for 20 min	130°C for 30 min	180°C for 20 min	130°C for 30 min
Dry Film Thickness (mils)	1.1	1.1	1.05	1.1	1.15
Film appearance	clear and colorless	clear and yellowish	clear and colorless	clear and yellowish	clear and colorless
Pencil hardness	9H	9H	9H	9H	4H
Impact Resistance (Ibs × inch)					
Direct	140	20	40	20	140
Reverse	120	5	10	5	140
Adhension (Cross-hatch)	5B	2B	5B	3B	2B
MEK Double-rubs (Passes)	150	>200	>200	>200	50

distinguished from acidity from phenolic groups and that of the catalyst, by the differences in their pKa values.

Characteristics of the PPE

Table 1 shows the characteristics of phenol terminated polyester resins. The two resins prepared for the study primarily differ in their

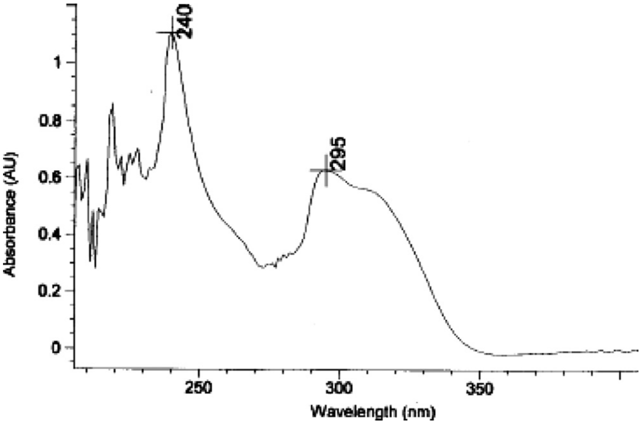

FIGURE 4 UV-absorption spectrum of p-HCA.

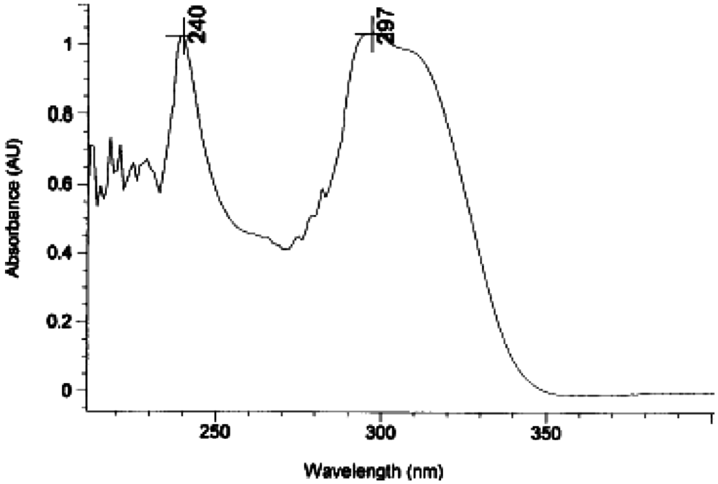

FIGURE 5 UV-absorption spectrum of PPE-II resin.

composition, whereas their molecular weights and phenolic hydroxyl number are comparable. The presence of free phenol functionality, arising from use of p-HCA is confirmed both by FT-IR and by chemical method involving pH-metric titration. The pH metric titration method was used to determine phenolic hydroxyl number, to avoid interference by carboxylic acid groups. The phenolic hydroxyl numbers

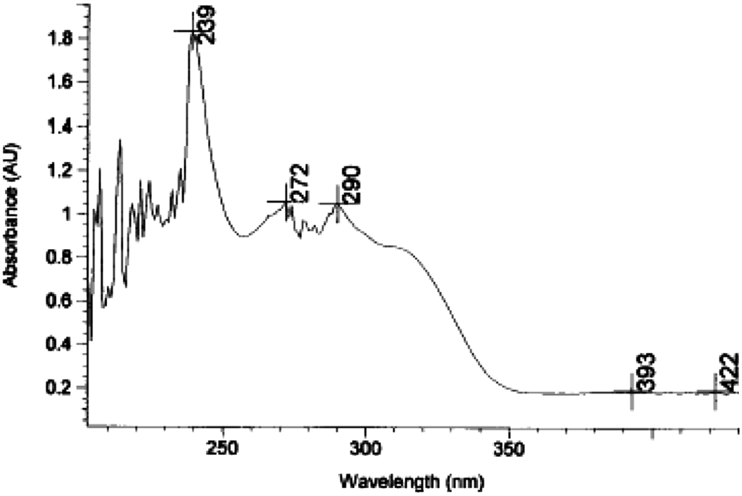

FIGURE 6 UV-absorption spectrum of cured coating of PPE resin.

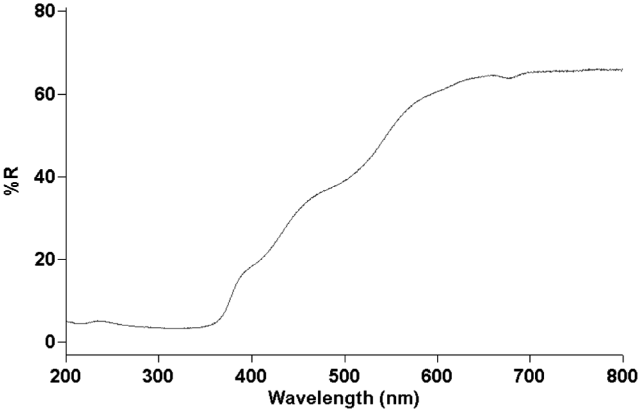

FIGURE 7 UV-reflectance spectrum of cured film of PPE-II-based coatings.

for both the resins are fairly close to the theoretically calculated numbers. The polydispersity index for these resins, in the range of 1.8–2.1 is not unusual for such condensation polymers.

In order to derive UV-absorption characteristics of PPEs, the synthetic strategy has been designed to retain the ethylenic unsaturation of p-HCA, which is responsible for UV-absorption. However, under the conditions of polyesterification, the possibility of partial loss of this unsaturation can not be ruled out. 2,6-Di-tert-butyl-4-methoxyphenol

TABLE 4 Accelerated Weathering Test Results

Properties Identity	Gloss% (60°)	Color change	Film intergrity
PPE-II/Melamine (80/20)*			No visible damage or loss of adhesion
Before exposure	92	Colorless	
After exposure	92	Significant yellowing Delta b = 36.2 (BYK Gardner ColorGuide^{TM})	
Polyester control (80/20)*			No visible damage or loss of adhesion
Before exposure	92	Colorless	
After exposure	88	No apparent change in color Delta b = 1.1 (BYK Gardner ColorGuide^{TM})	

*Cured at 130°C for 30 min.

was incorporated during the synthesis as free radical inhibitor. The analysis of reaction mixture at the intermediate stages indicated no decarboxylation of p-HCA under the conditions of processing.

Composition and Film Properties of Coatings Based on PPE

Table 2 shows the film properties of the elevated temperature cured films of PPE-based coatings. Both the PPE resins are formulated with highly methylated methylolmelamine (Cymel 303) crosslinker at resin/crosslinker weight ratio of 85/15 and 80/20. In commercial polyester/melamine coatings it is customary to use such ratios to get balanced film properties. The control coating employs Polyester/melamine weight ratio of 80/20. The results indicate that both PPE-I and PPE-II have comparable film mechanical properties with those of the control. In general, the PPEs show slightly lower hardness compared to the control sample. This difference may be attributed to the difference in their chemical structure and/or to the extent of curing under the conditions employed.

As indicated earlier, the crosslinking reaction between phenol-functional resins with melamine type crosslinkers is known to produce heterocyclic benzoxazine ring structure at elevated temperature cure. It has been found that phenolic groups are participating and consumed during the curing process. Figures 2 and 3 show FTIR spectra for coatings before and after cure. Note the substantial reduction of intensity for $-$OH stretch at 3345 cm^{-1} after curing. It is also important to note that under the conditions of cure, all the phenolic $-$OH groups are not used up. The stoichiometry of such reaction, assuming fairly high extent of reaction, would be 2 methoxy groups (of melamine resin) for each phenolic group. Based on this calculation, formulations based on PPEs would require PPE/melamine resin ratio of up to 60/40 by wt. Therefore, it was thought interesting to formulate compositions with higher melamine content (up to 40% by wt) and study their film properties. Table 3 shows the film properties of coatings formulated at resin/melamine resin weight ratio of 70/30 and 60/40. These coatings were formulated at two different catalyst levels and cured at two different cure schedules to study the effect of these factors on the extent of crosslinking and hence their film properties. PPE-II was selected as a representative resin for this study. Table 3 shows the film properties of compositions cured at two different schedules.

The results in Tables 2 and 3 indicate that increasing melamine content above 20% by wt. substantially changes the properties of the coatings. As expected, film hardness and solvent resistance (which is indicative of degree of crosslinking) have increased, whereas impact resistance has dropped considerably. This can be attributed to several factors such as increased degree of crosslinking, formation of very rigid heterocyclic ring formation, and the presence of more rigid self-condensed melamine resin in the cured film, among others. A comparison of properties of the films cured at higher temperature (180°C for 20 min) indicates that there is definite additional crosslinking taking place at this temperature. This additional crosslinking is believed to be responsible for film embrittlement and hence the coatings show poor impact resistance. The reduction of adhesive properties at higher temperature-cure might be due to the increased cohesive strength resulting from the aforementioned crosslinking reactions.

UV-Absorption Characteristics

p-HCA is a known UV-absorber having characteristic absorption at 240 nm and 295 nm. UV-absorption spectra of p-HCA (Figure 4) and p-HCA-based Polyester (Figure 5) were recorded from their dilute solutions in tetrahydrofuran (THF). For cured films, being insoluble in THF or any other suitable solvent, a fine dispersion of powdered cured film was prepared in THF and its absorption spectrum was recorded (Figure 6).

The results show characteristic absorption peaks for p-HCA based polyester and their cured films at nearly the same wavelength, corresponding to those for pure p-HCA. This clearly establishes that the unsaturation of p-HCA is retained not only during the synthesis of these polyester resins but also in their elevated temperature-cured films. Figure 7 shows UV-reflectance spectrum of cured PPE-II coating, which clearly demonstrates the UV-screening characteristic of these coatings. These results also confirm the retention of unsaturation in the cured films. These results indicate that cured films of p-HCA, besides having excellent mechanical properties, have UV screening capabilities, below 330 nm. This makes these polyesters useful for many coating applications because UV-radiation in the range of 295–330 nm are the ones that are most damaging to the polymeric films when exposed to sunlight.

Accelerated Weathering

In order to study the exterior durability properties, the selected coatings based on p-HCA containing polyesters and a control counterpart were subjected to an accelerated weathering test (ASTM D 5894-96) involving cyclic exposure to UV radiation followed by condensing humidity. The film properties, before and after the test were evaluated and compared (Table 4).

The primary reason for drop in gloss of a coating exposed to exterior environment is the surface degradation of the coating due to its interaction with the damaging UV radiation. In Table 4, the gloss values of the coatings, before and after the exposure, indicate that p-HCA containing coatings have excellent gloss retention properties, as compared to the control. This can be attributed to the UV absorption characteristic of p-HCA-based coatings. However, coatings based on p-HCA show significant yellowing as compared to the control. The authors believe that yellowing tendency of these coatings might be due to the presence of free phenolic groups, which are known to oxidize upon exposure to the exterior environment.

CONCLUSIONS

This study shows that it is possible to synthesize polyester resins containing reactive phenol-functional groups using p-HCA as one of the components, by direct polyesterification reaction. These phenol functional resins can be cured by conventional melamine-formaldehyde crosslinkers to yield films with excellent mechanical properties. It has been found that the UV absorption characteristic of p-HCA can be retained both in the derived phenol-functional polyester resins as well as in their cured films, which strongly absorbs UV below 330 nm wavelength. The properly formulated coatings, besides superior mechanical properties, show excellent resistance to accelerated weathering, which makes them useful and important candidates for industrial coating applications. However, p-HCA-based coatings show significant yellowing during accelerated weathering.

REFERENCES

[1] Deligny, P., Tuck, N., and Oldring, P. Eds., (2002). *Resins for Surface Coatings*, Vol. II, Second Edition, Wiley, Chichester, UK, pp. 119–130.

[2] Wicks, Z. W. Jr., Jones, F. N., and Pappas, S. P. (1999). *Organic Coatings: Science and Technology*, Second Edition, SPE Monograph, Wiley & Sons, New York, pp. 246–257.

[3] Braun, D. and Unvericht, R., *Angew. Makromol. Chem.* **226**, 183 (1995).

[4] Tomita, B. and Matsuzaki, T., *Ind. Eng. Chem. Prod. Res. Dev.* **24**, 1 (1985).

[5] Tomita, B., *Polym. Prepr.* **24** (2), 165 (1983).

[6] Von Lampe, I., Reinhardt, M., Lorkowski, H.-J., and Schnabel, W., *Angew. Makromol. Chem.* **214**, 197 (1994).

[7] Braun, D. and Ritzert, H. J., *Angew. Makromol. Chem.* **125**, 27 (1984).

[8] Sato, Y., Aizawa, T., Hirai, Y., Nagase, H., Numata, S., and Yoshimura, Y., *Jpn. Kokai Tokkyo Koho JP 09,278,985, 1997, Chem. Abstr.* **128**, 13757 (1998).

[9] Thackeray, J., Orsula, G., Rajaratnam, M., Sinta, R., Herr, D., and Pavelchek, E., *Proc. SPIE-Int. Soc. Opt. Eng.* **1466**, 39 (1991).

[10] Schreiber, H., *Ger. Offen.; Chem. Abstr.* **105**, 44103 (1986).

[11] Subrayan, R. and Jones, F., *Chem. Mater.* **10**, 3506 (1998).

[12] Wicks, Z. W., Jones, F. N., and Pappas, S. P. (1999). *Organic Coatings Science and Technology*, Second Edition, SPE Monograph, Wiley & Sons, New York, p. 464.

[13] Natella, F., Nardini, M., Felice, M., and Scaccini, C., *J. Agric. Food Chem.* **47**, 1453 (1999).

[14] Yezrielev, A. I., Wellman, W. E., Kowalik, R. M., Knudsen, G. A., and Romanelli, M. G., U.S. Patent 5,210,155 (1993).

[15] Yezrielev, A. I., Wellman, W. E., Kowalik R. M., Knudsen G. A., and Romanelli, M. G., U.S. patent 5,453,469 (1995).

[16] Yezrielev, A. I., Wellman, W. E., Kowalik, R. M., Knudsen, G. A., and Romanelli, M. G., U.S. Patent 5,631,330 (1997).

[17] Kuo, T. and Powell, J. E. G., U.S. Patent 5,416,187 (1995).