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FTIR ANALYSIS AND THE EFFECTS OF ALKYD/MELAMINE RESIN RATIO ON THE PROPERTIES OF THE COATINGS

Alkyd/melamine resin mixtures are mainly used in industrial baking enamels. The effects of the alkyd/butylated melamine resin ratio (from 90/10 to 50/50) and curing temperature (from 110 to 180 °C) on the crosslinking and properties of the coating are presented in this paper. The curing reactions through functional groups of resins were monitored by FT-IR spectroscopy. The hardness, elasticity, degree of adherence and gloss were also determined. Optimal coating properties could be achieved with an alkyd/melamine resin ratio of 80/20, a curing temperature of 150 °C and a curing time of 20 min.

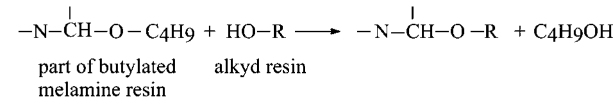
Organic coatings based on alkyd and melamine resins are high-quality industrial finishes. The combination of melamine-formaldehyde resins with suitable alkyd resin in surface coatings yields better hardness, mar and chemical resistance, improves weatherability, and reduces thermal curing times [1]. Alkyd-melamine resin blends are used mainly for the high-quality finishes called "baking enamel" required in the appliance, metal furniture, and automotive fields.

These finishes require exterior durability, gloss, gloss retention, low dirt pickup, color quality and retention, combined with the requisite hardness and toughness. To meet these specifications, many baking enamels are currently being made with blends of alkyd-melamine resin vehicles having a relatively high amino resin content (25–35%), but the ultimate development of these coating properties is, in general, influenced mainly by the alkyd resin used. In order to meet these requirements, especially those of durability and gloss retention, short-oil, nondrying alkyds are used in preference to short-oil, drying alkyd resins in the enamels.

The short-oil alkyd resins containing 38–45% of phthalic anhydride have a higher proportion of hydroxyl groups, which provides compatibility and reactive sites with alkylated melamine-formaldehyde resins. In cases where superior adhesion and impact resistance are required, the short-oil alkyd is based on dehydrated castor oil [2].

The chemistry of the curing process of alkyd-melamine resin systems has been the subject of a vast amount of literature. Wohnsiedler's first detailed study on this subject, published in 1960, showed that the alkyd resins not only exerted a plasticizing function but were also directly involved in the cross-linking of the system. Wohnsiedler considered reactions between hydroxyl groups in the alkyd and hydroxymethyl and alkoxymethyl groups in melamine resin as the most important in cocondensation, but several other possibilities were also indicated.

The curing of alkyd resin by a melamine one is effected over their functional groups (Scheme 1).



Scheme 1. Formation of alkyd-melamine resin.

The self-condensation of melamine resins leads to the formation of methylene linkages between the aminotriazine structures with a simultaneous loss of alcohol and formaldehyde. Wohnsiedler pointed out that transesterification is a predominant curing reaction with hydroxyl/carboxyl-containing polymers [3].

It should be emphasized that co-crosslinking boosts flexibility and weatherability, while self-crosslinking supports hardness and solvent resistance. The aim is to achieve the greatest balance of these properties. When the types of alkyd and melamine resin are defined, optimisation takes place by varying and testing different mixing ratios of both resins. The optimum mixing ratio is influenced by the quantity of functional groups on both resins – the alkyd hydroxyl groups, and the molecular weight of the melamine resin, which is directly related to the quantity of functional groups [4].

The aim of this work was to investigate the effects of alkyd/melamine ratio and curing temperature on the properties of the dry coating film. Primarily, the optimal ratio of alkyd and melamine resin was obtained at constant curing temperature of 140 °C during 20 min. Further, the optimal mixture is cured at elevated temperatures (from 110 to 180 °C) for 20 min. The preparation of the mixture of alkyd based on dehydrated castor oil with melamine resin, as well as their curing reactions and crosslinking, were studied by IR spectroscopy.

EXPERIMENTAL

Materials

Two kinds of resins were used: Epoal 4037 and Melform 45 IX.

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Epoal 4037, a short-oil phthalic alkyd resin containing 37 mass% of dehydrated castor oil, produced by "Epoxid" (Priboj, Serbia), was used as 55–60% solution in xylene/*n*-butyl alcohol mixture. The characteristics of the resin were: acid number = max. 25 mg KOH g^{-1}; viscosity at 20 °C: 160–200 s^{-1}.

Melform 45 IX, a middle-esterified melamine-formaldehyde resin, produced by "Spolchemie" (Czech Republic), was used as a 50–55% solution in xylene/isobutyl alcohol (1:2) mixture. The characteristics of the resin were: acid number = 0,1 mg KOH g^{-1}; viscosity at 23 °C: 120 s^{-1}.

The commonly used pigment is titanium dioxide (TiO_2, rutile).

Preparation of the resin mixture

A specific quantity of the alkyd (based on dried mass) was mixed with an adequate quantity of melamine resin and homogenized at room temperature. The mixture of solvents xylene/butyl alcohol (3:1) was added to control the viscosity. Several experimental metallic panels were smeared with a thin layer of the resin mixtures (a film thickness of 20 and 50 μm) in different alkyd/melamine weight ratio (from 50/50 to 90/10). The films were cured at constant temperature of 140 °C for 20 min. After the examination of physical and mechanical properties of each coated panel, we determined the optimal alkyd/melamine ratio. Optimal coating properties could be achieved with an alkyd/melamine ratio of 80/20 at constant curing time of 20 min. Curing of chosen sample (80/20) was carried out at temperatures from 110 to 180 °C for 20 min.

The designations and the compositions of the samples are presented in Table 1.

Determination of the properties of the dry coating film

The degree of grind fineness of liquid dispersions of pigments in the range 0–15/20/50/100 μm was determined by the method JUS H.C8.052 using a hardened steel instrument – grindometer.

The hardness of the coating film was determined by the standard method JUS H. C8. 055 using a Koning's bell-clapper. The bell-clapper was placed on a panel with a coating film at an angle of 6° and left to oscillate. The elapsed time (s) until the measured amplitude of the oscillation decreased to 3° is defined as the hardness.

The drawing elasticity was determined by the standard method JUS H. C8. 050 using Erichsen's cupping test for numerical evaluation of the quality of stamping lacquers and plastic coatings on semi-spherical standard cup. An experimental metallic panel was compressed with a semi-sphere like cup. The distance from the zero position of cup to the moment when the film cracks is defined as the drawing elasticity (in mm).

The bending elasticity was determined using the T-BEND method (ICI PVM 64/14/Y2). The cured panel was held with a clamp (final 2 cm) and bent at an angle of 90° with the coating facing outwards (that is 0T according to the adopted nomenclature). Then the panel was removed from the clamp, the edging was bent by hand, then it was put in the clamp again and made a bending of 180° (0.5T). The result was noted as the smallest bending which was made until the film cracks and separates from the panel. For the description of the size of the bending the nomenclature is used in the following order: 0T<0.5T<1T<1.5T<2T<2.5T.

The gloss of the coating film was determined by the method ICI PM 64/18/5 with the laboratory instrument using an optical system of lamp/lens and the photocell, at an angle of 60°.

The degree of film adherence to the panel was measured by the standard method JUS. H. C8. 059, with scale from GT-0 to GT-5. The coated film was cut with cross hatch cutter into small square areas (1×1 mm). The degree of film adherence is the best if none of them separates from the panel. That value is denoted as GT-0.

Infrared analyses were performed using a BOMEM Hartmann & Braun MB-100 model FT-IR spectrophotometer by the method of KBr pellets. The FT-IR spectra of coating film were recorded by scratching paint from the microscope slides (1 mg) and mixing it with 150 mg of KBr. The spectra were recorded in the region 400–4000 cm^{-1}, but for the purpose of this work only spectra from 500 to 2000 cm^{-1} are presented. All the spectra were baseline corrected. FT-IR spectroscopy was employed to study the curing reaction and cross-linking of alkyd/melamine resin blend.

RESULTS AND DISCUSSION

Mechanical analysis

The determined properties of dry coating films (the hardness, elasticity, degree of adherence and gloss) are

Table 1. Designations and formulations of the prepared resin mixtures

Number of sample	Alkyd/melamine resin ratio	Resin content at completing	Dry resin content	Factor *A*/*M*[a]
1	50/50	25.37/31.47	17.0/17.0	1.0
2	60/40	30.44/25.18	20.4/13.6	1.5
3	80/20	40.60/12.60	27.2/6.8	4.0
4	90/10	45.67/6.30	30.6/3.4	9.0

[a]Factor *A*/*M* is obtained from the alkyd and melamine resin ratio (counted according to the dry resin content)

given for the samples of thickness 50 μm (Table 2) and for the samples of thickness 20 μm (Table 3).

The results of the samples with the thickness of the dry coating film about 50 μm show a poor adherence, but they also show the satisfactory values of the hardness, elasticity, degree of adherence and gloss. Then we made further investigations with the panel of average thickness of applied film of 20 μm.

As expected, the hardness of the coating films increases with increasing the ratio of melamine resin in the blend in accordance with literature data for some alkyd/melamine resin blends [5–7]. The functionality of the melamine resin (containing three methylol groups) is higher than that of the alkyd resin which results in the formation of a more cross-linked coating film at higher ratios of melamine in the blend. The minimal acceptable value for the hardness is 40 s according to the standard method JUS H. C8. 055.

The minimal value for the drawing elasticity is 6 mm according to the standard JUS H. C8. 050. In the cases of the samples with the less melamine resin ratio (mostly between 8 and 9) the investigated coating films have satisfactory values. The drawing elasticity is appreciably less in the cases of the samples with larger melamine resin ratio.

The values for the film adherence (GT-0 for samples 3 and 4) are excellent except for the samples with the larger melamine resin ratio (GT between 1 and 3 for samples 1 and 2). The results for the gloss have satisfactory values.

Analyzing the physico-mechanical characteristics of all samples (Figure 1), with different thicknesses the sample ALK-MF was chosen (80-20) as the one with the best characteristics for the determination of the optimal curing rating.

Determination of the optimal curing condition

The hardness of the coating films of sample ALK-MF (80-20) increases with the increase of curing temperature (Figure 2).

The drawing elasticity decreases with the increase of curing temperature as shown in Table 4.

The values of the film adherence (GT-0 for all curing temperatures) and gloss are excellent.

Table 2. Physical properties of alkyd-melamine resin films; the thickness of the dry coating film is 50 μm (t = 140 °C, τ = 20 min)

Number of sample	Hardness, s	Drawing elasticity, mm	Gloss, %	Adhesion (GT)	T-BEND (T)
1	143.5	3	81.9	3	0
2	143.5	4	82.6	0	0
3	72.8	8	82.0	0	0
4	25.9	9	80.9	0	0

Table 3. Physical properties of alkyd-melamine resin films; the thickness of the dry coating film is 20μm (t = 140 °C, τ = 20 min)

Number of sample	Hardness, s	Drawing elasticity, mm	Gloss, %	Adhesion (GT)	T-BEND (T)
1	147.00	2	75.36	2 – 3	2.0
2	150.85	5	74.35	1 – 2	2.0
3	111.65	8	75.36	0	1.5
4	59.85	8	77.17	0	0.5

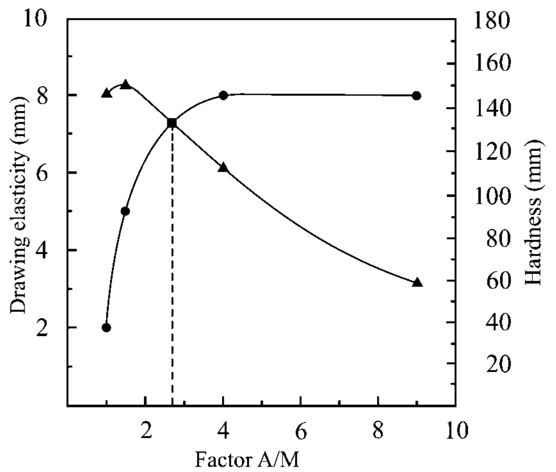


Figure 1. Dependence of the hardness and elasticity of the film thickness of 20 μm on A/M ratio (t = 140 °C, τ = 20 min) and determining the optimal A/M ratio (the point of the curves cut).

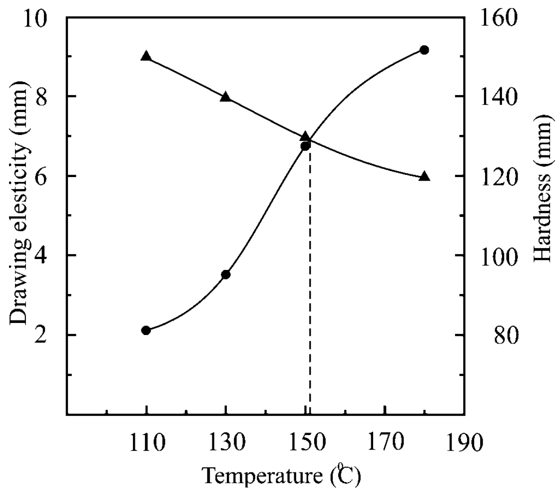


Figure 2. Dependence of the hardness and elasticity of the optimal chosen sample III (80:20) on temperature, and the selection of the optimal curing temperature (cut point curves).

Table 4. Properties of coating films of alkyd-melamine sample (80-20) at different curing temperatures, a curing time of 20 min and the thickness of the dry coating film is 20 μm

Curing temperature, °C	Hardness, s	Drawing elasticity, mm	Gloss, %	Adhesion (GT)	T-BEND (T)
110	81.2	9	70.0	0	1.0
130	95.2	8	77.7	0	1.5
150	126.7	7	75.6	0	1.5
180	151.9	6	73.6	0	2.5

FT-IR studies of the curing of alkyd/melamine resins mixtures

The FT-IR spectra of alkyd resin, amino resin and alkyd amino resin are given in Figure 3. As a rough estimate, we can assume that the peak absorbance for a particular functional group should reflect the extent of reaction of the functional group [8]. The peaks due to the free carboxyl and hydroxyl groups in the alkyd resin are observed at 1730 cm^{-1} from ν(C=O) and 1270 cm^{-1} from δ(OH), respectively [9]. The peaks due to the free methylol and butylated methylol groups in amino resins are observed at 1375 cm^{-1} from ν_{as}(C–O) and 1081 cm^{-1} from ν_s(C–O), respectively [10]. The intensity of these peaks is transformed in alkyd–amino resin due to the reaction between free carboxyl and hydroxyl groups of al-

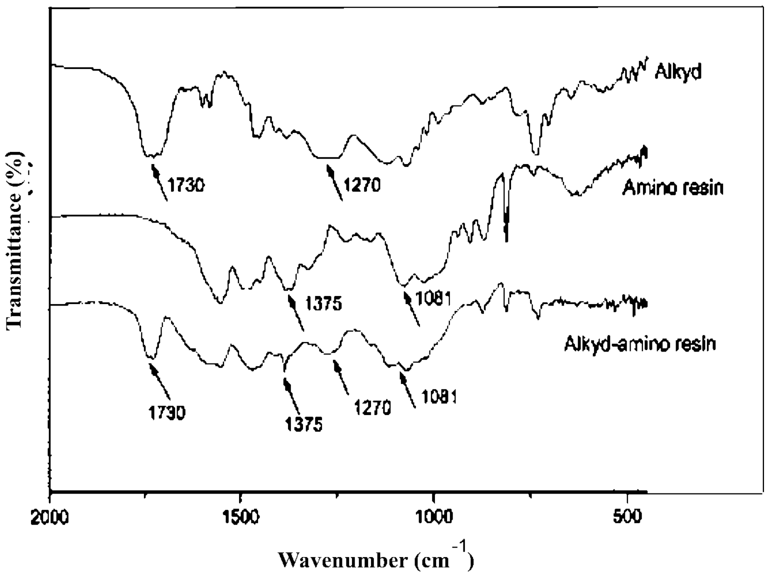


Figure 3. FT-IR spectra of alkyd, amino and alkyd-amino resins [11].

kyd resin and free methylol and butylated methylol groups of amino resins.

FT-IR spectra of alkyd-amino resins for samples ALK-MF (60-40) and ALK-MF (50-50) are given in Figure 4. The intensity of the peaks in the samples with the larger melamine resin ratio (40 and 50) in alkyd resin is observed at 1730 cm^{-1} from ν(C=O), 1270 cm^{-1} from δ(OH), 1375 cm^{-1} from ν_{as}(C–O) and 1081 cm^{-1} from ν_s(C–O).

The FT-IR spectra of the alkyd amino resin with smaller melamine resin ratio are given in Figure 5.

The ratio of area of selected peaks was taken for the determination of the curing reactions. The values for these peak areas are given in Table 5. The analysis of peak areas indicates a larger percent of production of ether and ester links which results in the formation of a more crosslinked coating film at higher melamine ratios (60 and 50%) in the blend.

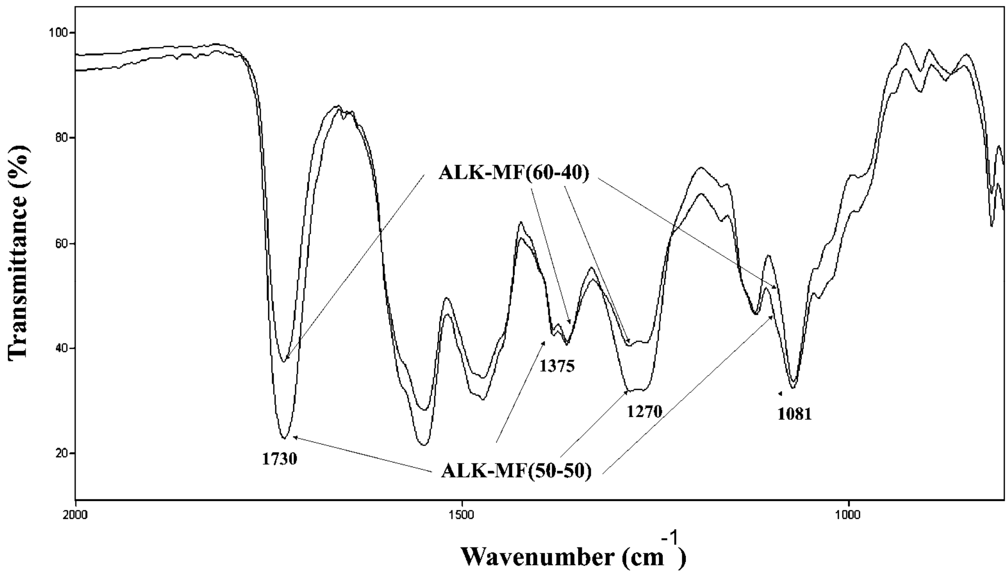


Figure 4. FT-IR spectra of alkyd-amino resins, ALK-MF (60-40) and ALK-MF (50-50).

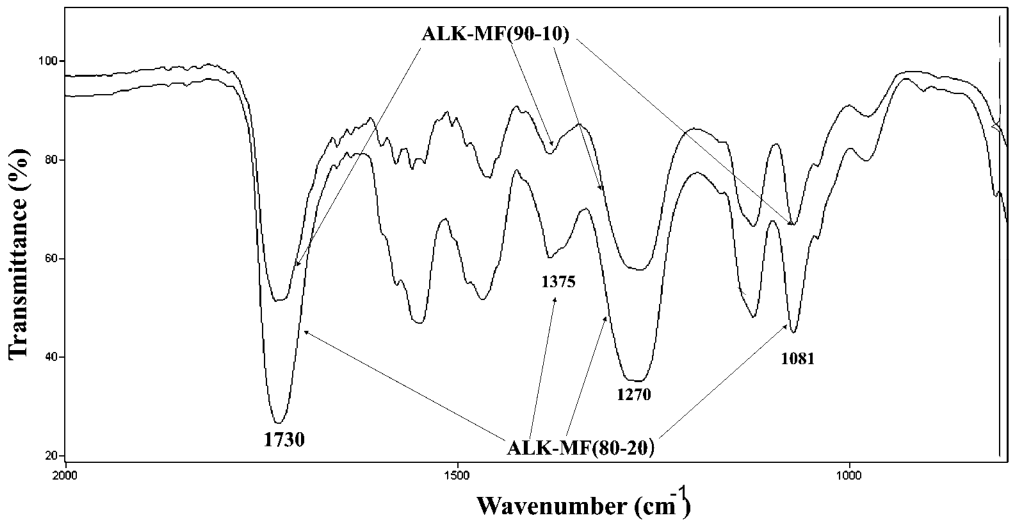


Figure 5. FT-IR spectra of alkyd-amino resins, ALK-MF (80-20) and ALK-MF (90-10).

Table 5. The ratio of area of selected peak of alkyd resins with different ratio of melamine resin

Sample	ν_{as}(C–O)	ν_s(C–O)	ν(C=O)	δ(OH)
ALK-MF (50-50)	6.39	5.04	26.89	18.39
ALK-MF (60-40)	4.85	4.04	17.02	10.02
ALK-MF (80-20)	3.53	3.82	25.65	20.56
ALK-MF (90-10)	1.21	1.90	13.65	11.76

In the cases of samples with the smaller melamine resin ratio (20 and 10%) in the blend a greater reduction of line areas is obtained which is due to the ether link. In the cases of samples with alkyd and melamine resin ratio of 80:20 the areas are increased due to ester link which indicates that they are responsible for the best physico-mechanical properties of this sample [12]. The uttermost decrease of areas i.e. the least crosslinking of alkyd-melamine resins is obtained in the case of the alkyd-melamine sample with a 90:10 ratio.

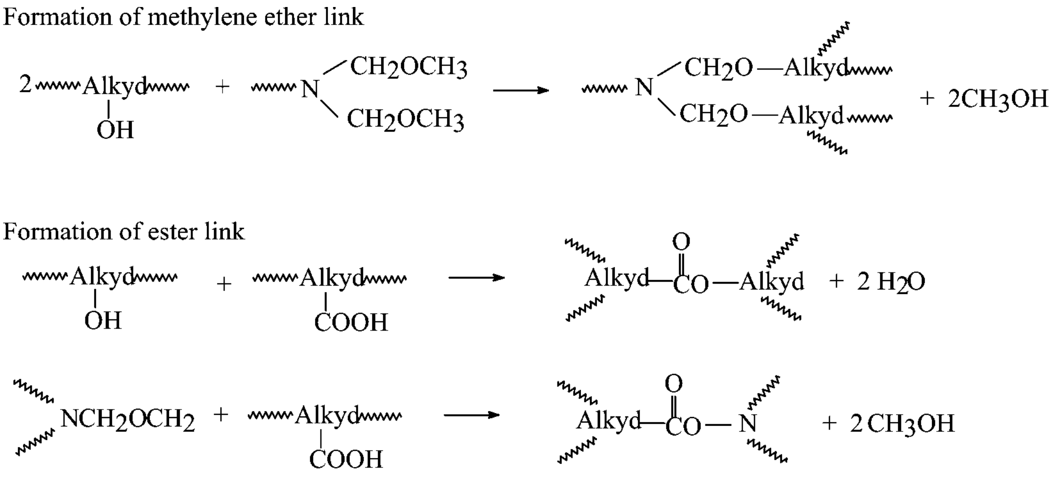
Both alkyd and melamine resins are complex mixtures, in which each components can undergo a variety of reactions (Scheme 2). Some of the crosslinking reactions are reversible, so that bonds might break and reform many times during cure of a coating, causing network structure to change continuously throughout the process [13].

The FT-IR spectra of sample ALK-MF (80-20) cured at different temperatures are given in Figure 6. In the case of sample ALK-MF (80-20) changes of peak areas are expected with the increase of temperature [8]. Considering all other physico-chemical properties which deteriorate at higher temperature the optimal temperature for curing is 150 °C.

On the basis of the obtained experimental results, and taking into consideration the economic factor, it can be seen that suitable coating properties could be achieved with an alkyd/melamine resin ratio of 80/20, a curing temperature of 150 °C and a curing time of 20 min. Curing temperatures above 150 °C are technologically unfavorable.

CONCLUSION

Curing of alkyds based on semi-drying oils (dehydrated castor oil) with melamine resin when made into baking enamel was investigated. The film elasticity can be reduced and hardness can be increased by higher amount of melamine resin. The minimum level of melamine resin for complete cross-linking for alkyds based on dehydrated castor oil is 20%.



Scheme 2. Various reactions between the alkyd and melamine resins [8].

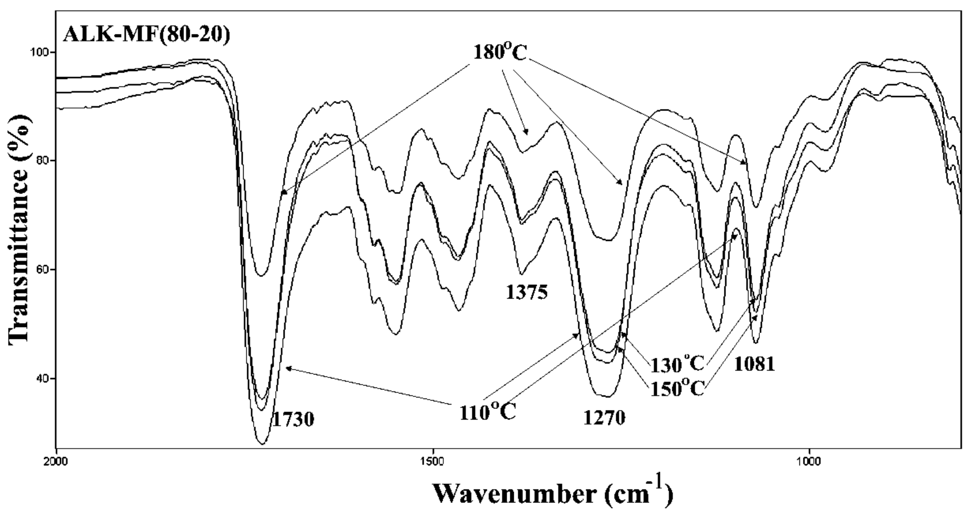


Figure 6. FT-IR spectra of enamel of ALK-MF (80-20) cured at 110, 130 150 and 180 °C.

According to the FT-IR analysis degree of curing increases with the increase of ratio of melamine resin in the resin blend, and with curing temperature. The hardness of a coating film increases with the increase of degree of curing while the elasticity slightly decreases. Favourable coating properties could be achieved with an alkyd/melamine resin ratio of 80/20, a curing temperature of 150 °C, and a curing time of 20 min.

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IZVOD

FTIR ANALIZA I UTICAJ ALKID/MELAMINSKOG ODNOSA SMOLA NA OSOBINE PREMAZA

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(Stručni rad)

Smeša alikidna/melaminska smola se obično koristi u pečenim industrijskim emajlima. U ovom radu predstavljen je uticaj masenog odnosa alkidna/butilovana melaminska smola (od 90/10 do 50/50) i temperature (od 110 do 180 °C) na umrežavanje i svojstva premaza. Reakcije umrežavanja preko funkcionalnih grupa smola su posmatrane FT-IR spektroskopijom. Takođe su određene tvrdoća, elastičnost, stepen prijanjanja i sjaj. Optimalne osobine umrežavanja su dobijene pri odnosu alkidna/melaminska smola 80/20, na temperaturi umrežavanja 150 °C u vremenu od 20 min.

Ključne reči: Alkidna smola modifikovana melaminom • Umrežavanje • FT-IR • Osobine premaza

Key words: Melamine modified alkyd resin • Curing • FT-IR • Coating properties