

Use of Epoxy–Phenolic Lacquers in Food Can Coatings: Characterization of Lacquers and Cured Films

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ABSTRACT: Liquid and cured epoxy–phenolic lacquers used as can coatings were characterized. Tinplate was used as the base material, which was coated with lacquers of different epoxy to phenolic ratios (EPRs) from a commercial source. Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were used together to obtain helpful information about the degree of curing and the composition of the lacquers. From FTIR analysis, we were able to infer that the lacquers were composed of a high-molecular-weight

diglycidyl ether of bisphenol A type epoxy resin and a resol-type phenolic resin. In addition, from FTIR spectra, we estimated the EPRs of lacquers applied on the tinplate and detected if they had been overcured. The EPRs of the applied lacquers were estimated also from DSC analysis. From TGA, we detected undercuring in the applied lacquers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1448–1458, 2005

Key words: coatings; infrared spectroscopy; calorimetry; thermogravimetric analysis (TGA)

INTRODUCTION

The use of organic coatings is widely used in the production of metallic food containers to protect metal against corrosion and to avoid metal–food contact. Among the organic polymeric coatings, epoxy–phenolic lacquers are often used on tinplate,^{1,2} although waterborne polymer coatings have been playing an increasingly important role as well.^{2–4}

Novolac resins are the reaction products from formaldehyde and excess phenol under acidic catalysis. When novolac resins are cocured with high-molecular-weight solid epoxy resins, the resulting products are coatings with excellent adhesion, film strength, flexibility, and chemical resistance.^{5,6} Resol resins are the reaction products from excess formaldehyde and phenol under basic catalysis. When they are cocured with high-molecular-weight solid epoxy resins, they have even higher crosslinking densities and higher chemical resistance than novolac resins. These types of systems are used almost exclusively as surface coatings and are cured at relatively high temperatures to

yield films with excellent physical properties and chemical resistance.^{7,8} The phenol–formaldehyde resins most commonly used are butylated resol-type resins, which contain phenolic hydroxyls plus etherified and unetherified methylol groups. Epoxy–phenolics are among the most chemically resistant known finishes. Phenolic resins alone give excellent chemical resistance, and crosslinking with epoxy resins improves their adhesion and impact resistance. The main uses for these finishes are as can and drum linings.⁹

It is well known that a lacquer's chemical composition and curing degree are key parameters in can performance. The goal of this study was to characterize epoxy–phenolic lacquers as liquids and to analyze the properties of the applied lacquers as a function of their composition and curing degree.

EXPERIMENTAL

Materials

The base material we used was commercial tinplate, produced by tin electrocrystallization in a phenol sulfonic acid bath (the Ferrostan process). Tinplate samples were coated with epoxy–phenolic lacquers, which were obtained from a commercial source and which had different epoxy to phenolic ratios (EPRs; Table I).

Lacquers were conditioned for application on tinplate by the addition of a solvent (application viscosity = 260 cP). Each lacquer was coated on a tinplate panel

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TABLE I
Resins and Lacquers Studied

Sample	Lacquer type	EPR
Resin 1	Phenolic	—
Resin 2	Epoxy	—
Lacquer A	Epoxy-phenolic	80/20
Lacquer B	Epoxy-phenolic	72/28
Lacquer C	Epoxy-phenolic	64/36

with a #18 coating bar to give a dry film thickness of about $7 \mu\text{m}$ ($\sim 9 \text{ g/m}^2$). Lacquer curing conditions in industry are 200°C for 12 min. The coated samples were cured in a non-forced-air oven at different conditions (curing temperature = 170 – 220°C , curing time = 12–36 min).

Well-known epoxy and resin-type phenolic resins were used for comparison with the commercial ones. Diglycidyl ether of bisphenol A (DGEBA) with an n (polymerization degree) of 0.14 and an equivalent weight of 190 g/equiv of epoxy and a resin synthesized with a formaldehyde/phenol molar ratio (F/Ph) of 1.3 were used as epoxy and phenolic references, respectively.

Methods

IR spectroscopy was performed on the liquid resins and lacquers. Fourier transform infrared (FTIR) spectra were acquired with a PerkinElmer spectrometer (Boston, MA) (model 1600). Liquid samples were set in a cell with NaCl windows and an optical path of 0.025 mm. The acquisition conditions were as follows: spectral width = 600 – 4000 cm^{-1} resolution, accumulations = 4, and resolution = 4 cm^{-1} .

FTIR spectra of the cured lacquers were obtained with a Mattson Genesis II spectrometer (Madison, WI). The coatings were mechanically removed by scraping from the tinplate, mixed with KBr, and then finely ground in an agate mortar to obtain a well-homogenized mixture. This mixture was then submitted to a pressure of 10 tons to make a translucent pellet. Each spectrum was acquired with a spectral width of 600 – 4000 cm^{-1} , 50 accumulations, and a 2 cm^{-1} resolution. For comparison purposes, the spectra were normalized with the intensity of the band at 1610 cm^{-1} . This band was assigned to the stretching $\text{C}=\text{C}$ of the benzene ring, and its intensity was expected to remain constant for all of the samples.¹⁰

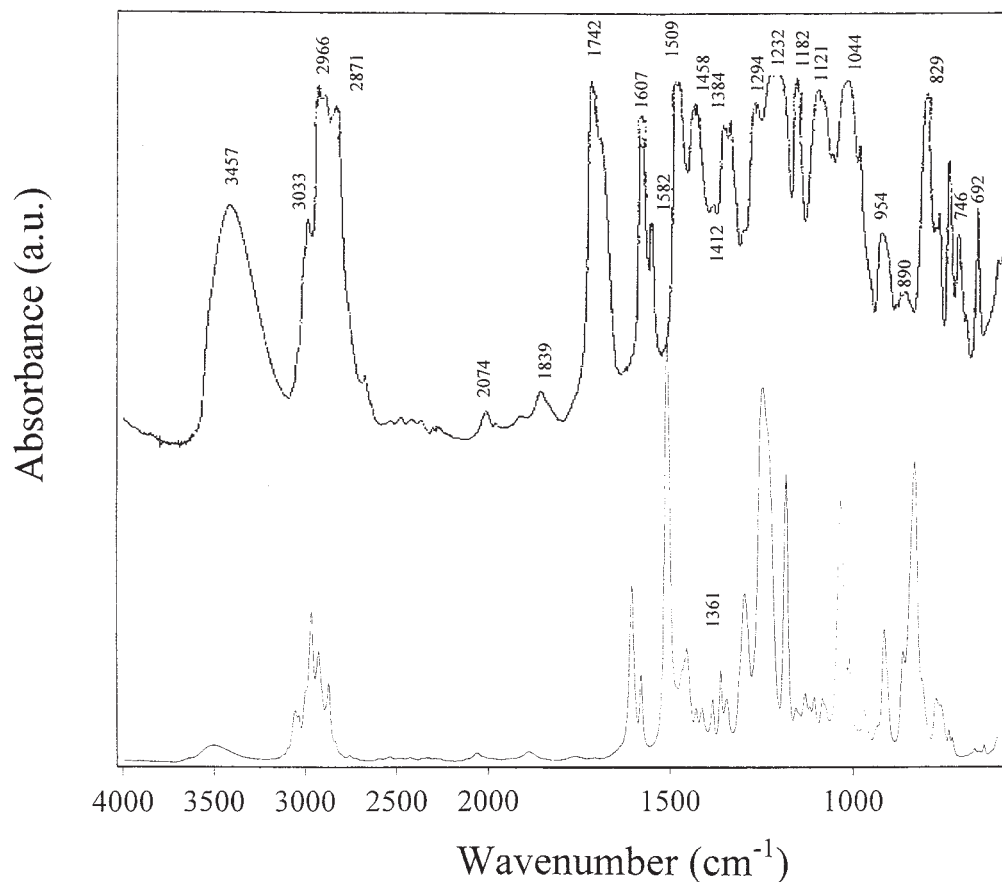


Figure 1 FTIR spectra of the liquid epoxy resin used in the (—) lacquers and (---) DGEBA ($n = 0.14$, molecular weight = 190 g/equiv of epoxy).

TABLE II
IR Absorption Assignments of an Epoxy Resin

Wavenumber (cm ⁻¹)	Assignment ¹²⁻¹⁴
3494	ν (OH)
3033	ν (φ -H) arylene- ν_{as} (CH ₂) epoxy
2998 _{sh}	ν_s (CH ₂) epoxy
2966	ν_{as} (CH ₃) + ν_{as} (O-CH ₂)
2871	ν_s (CH ₃)
2074 _w	φ , disubstituted
1889	φ , disubstituted
1742	ν (C=O), R-COO-R
1607, 1582, 1509	ν (C=C) phenylene
1458	ν (C=C) φ + δ_{as} (CH ₃)
1412	δ (CH) epoxy
1384-1360	δ_s (CH ₃) gem dimethyl
1294	ν (C-O) + ν (C-C)
1248 _{st}	ν (φ -O)
1232 _{sh}	δ (φ -H) in plane
1182	δ (φ -H) in plane ν (C-C) de Ar-C-Ar C
1121	ν (C-O) and ν (O-H) ν (C-C) aliphatic chain
1044	ν (φ -O-C)
954	δ (φ -H) out of plane
915	Epoxy ring
829	δ (φ -H) out of plane
800-690	(CH ₂) _n δ (φ -H) out of plane (φ monosubstituted)

ν = stretching; φ = benzene ring; as = antisymmetric; sh = shoulder; s = symmetric; δ = deformation; st = strong.

Differential scanning calorimetry (DSC) experiments were performed with both liquid and cured lacquers in a Shimadzu DSC-50 (Tokyo, Japan) thermal analyzer. The temperature was raised by 10°C/min from room temperature to 300°C in a N₂ flow.

Thermogravimetric analysis (TGA) was carried out in a Shimadzu electrobalance. Experiments were conducted at a constant heating rate of 10°C/min from room temperature to 900°C in a N₂ flow. About 2 mg of cured lacquer (removed from the tinplate) was loaded into the container.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of the liquid epoxy resin used in the lacquer formulation and the reference DGEBA. To determine the type of epoxy used, these spectra were compared. The molecular weight of the DGEBA was lower than the molecular weight of the epoxy resins usually used as coatings.

Table II shows the IR characteristic bands of a DGEBA resin. Comparison of the spectra (Fig. 1) suggested that both resins were derived from bisphenol A and epichlorohydrin. However, some differences arose. The intensity of the characteristic band of the

epoxide ring at 915 cm⁻¹ was lower in the spectrum of the epoxy resin, indicating that it was a high-molecular-weight resin. In addition, the band at 3457 cm⁻¹, assigned to the secondary hydroxyl group, was higher for the studied epoxy resin. This was probably due to the higher content of hydroxyl groups in the high-molecular-weight resin. In both spectra, bands that corresponded to the gem dimethyl group (1384 and 1361 cm⁻¹) were observed. These results suggest that the liquid epoxy resin used in the lacquers should have been a high-molecular-weight DGEBA type. The high intensity band at 1742 cm⁻¹, corresponding to carbonyl group stretching in an ester group, was probably due to an organic solvent added to the commercial epoxy resin.

Figure 2 shows the FTIR spectra of a resol-type phenolic resin with a F/Ph of 1.3 and the phenolic component of the lacquers. The assignment of the bands is listed in Table III. The intense band at 1037 cm⁻¹, attributed to primary alcohols (methylol), suggested that the phenolic component of the lacquer was a resol-type resin. The intensity of this band is lower for novolac-type phenolic resins.¹⁰ The bands between 2800 and 2970 cm⁻¹ were higher for the lacquer's phenolic resin than for the resol. These bands probably appeared because the phenolic resin was a butylated resol-type resin.

The FTIR spectra of the liquid epoxy-phenolic lacquers studied (Fig. 3) showed the same characteristic bands and were very similar. So, it was not possible to estimate the lacquer composition through the FTIR spectra of the liquid epoxy-phenolic lacquers in the studied range of EPRs.

Crosslinking reactions between phenolic and epoxy resins are a combination of reactions through the secondary hydroxyls of the epoxy resin, through self-condensation, and perhaps, to a limited extent, through reactions with the epoxide ring.^{5,7} The stoichiometry of the reaction of epoxy with a phenolic resin is not well defined. On baking at temperatures between 180 and 200°C, several reactions can take place, including not only reactions between the phenolic hydroxyl and the epoxy group, to form a secondary hydroxyl and an ether group, but also further reaction between the phenolic methylol groups and the secondary hydroxyl groups of the high-molecular-weight epoxy resin to form an ether linkage. In addition, side reactions occur between the resol molecules themselves via the methylol groups.⁷

To study the crosslinking reaction, it is necessary to measure the change of the absorbance peak height at 915 cm⁻¹ in the FTIR spectra. However, this is not feasible because of the low intensity of this band, which is caused by the low quantity of epoxy groups in the high-molecular-weight epoxy resin. For phenolic resins, however, oxidative degradation reactions usually take place during the curing process, leading

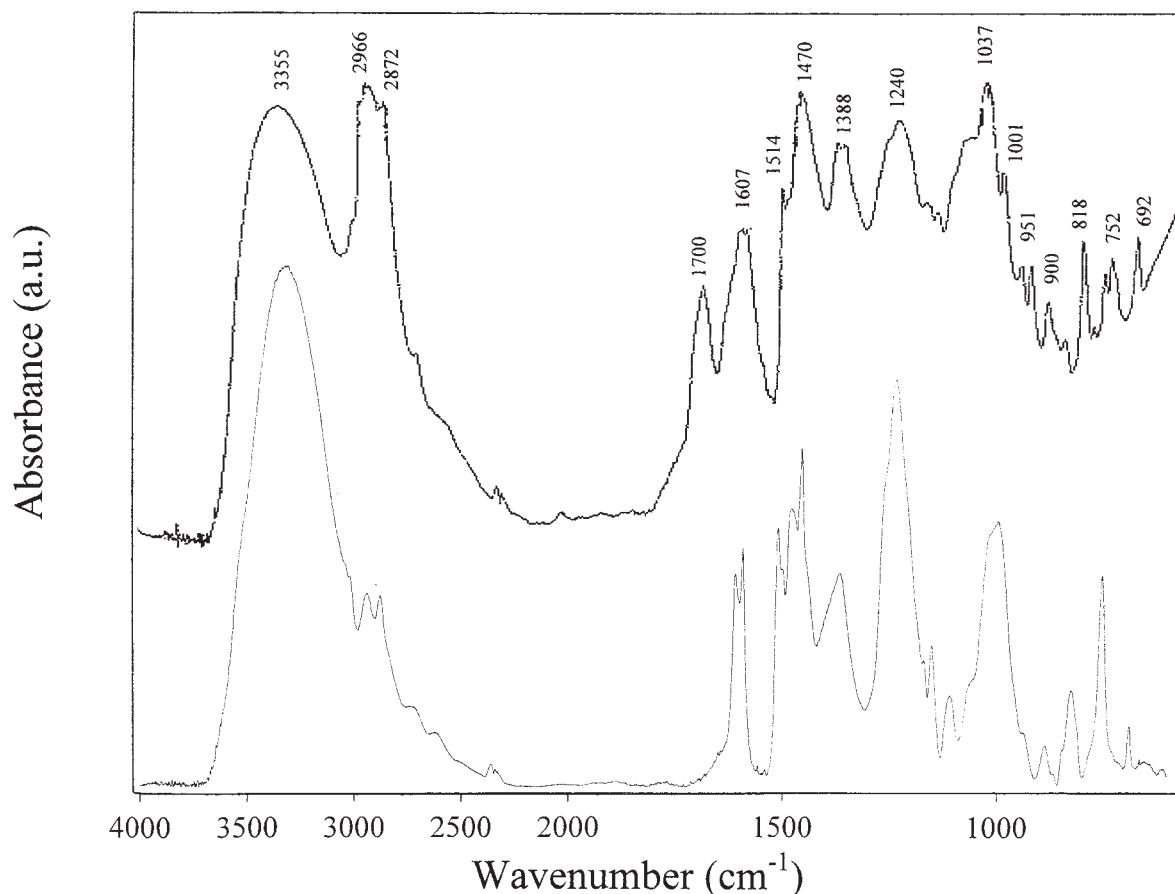


Figure 2 FTIR spectra of (—) a resol with a F/Ph of 1.3 and (---) the phenolic component of the lacquers.

to the formation of benzophenone (1638 cm^{-1}), quinone (shoulder at 1650 cm^{-1}), and carboxylic acid and aldehyde groups (1712 cm^{-1}).¹¹ As explained later, the

bands associated with these compounds gave valuable information regarding the composition and curing degree of the applied lacquers.

TABLE III
IR Absorption Assignments of a Resol-Type Phenolic Resin

Wavenumber (cm^{-1})	Assignment ^{10,15,16}
3600–3400	ν (OH) phenol and methylol (free and intramolecular hydrogen bonded)
3400–3200	ν (OH) phenol (intermolecular hydrogen bonded), broad band
3000	ν (φ -H)
2966	ν (CH_2) in-plane aliphatic
2872	ν (CH_2) out-of-plane aliphatic
1712	ν (C=O) carboxylic acid, aldehyde
1655	ν (C=O) quinone
1638	ν (C=O) benzophenone
1607–1513	ν (C=C) benzene ring
1470	δ (C-H) (methylene bridges)
1387–1366	δ (O-H) phenol
1240	ν (C-O) out-of-phase (phenol)
≈ 1100	ν (φ -O-C), ν (C-O-C) aromatic-aliphatic ethers
1037–1001	ν (C-O) + δ (O-H) primary alcohol
900	δ (φ -H) out-of-plane (1,2,4,6- tetrasubstituted φ)
818	δ (φ -H) out of plane (1,4-disubstituted φ and 1,2,4-trisubstituted φ)
752	δ (φ -H) out of plane (1,2-disubstituted φ and 1,2,6-trisubstituted φ)
692	δ (φ -H) out of plane (monosubstituted φ)

ν = stretching; φ = benzene ring; δ = deformation.

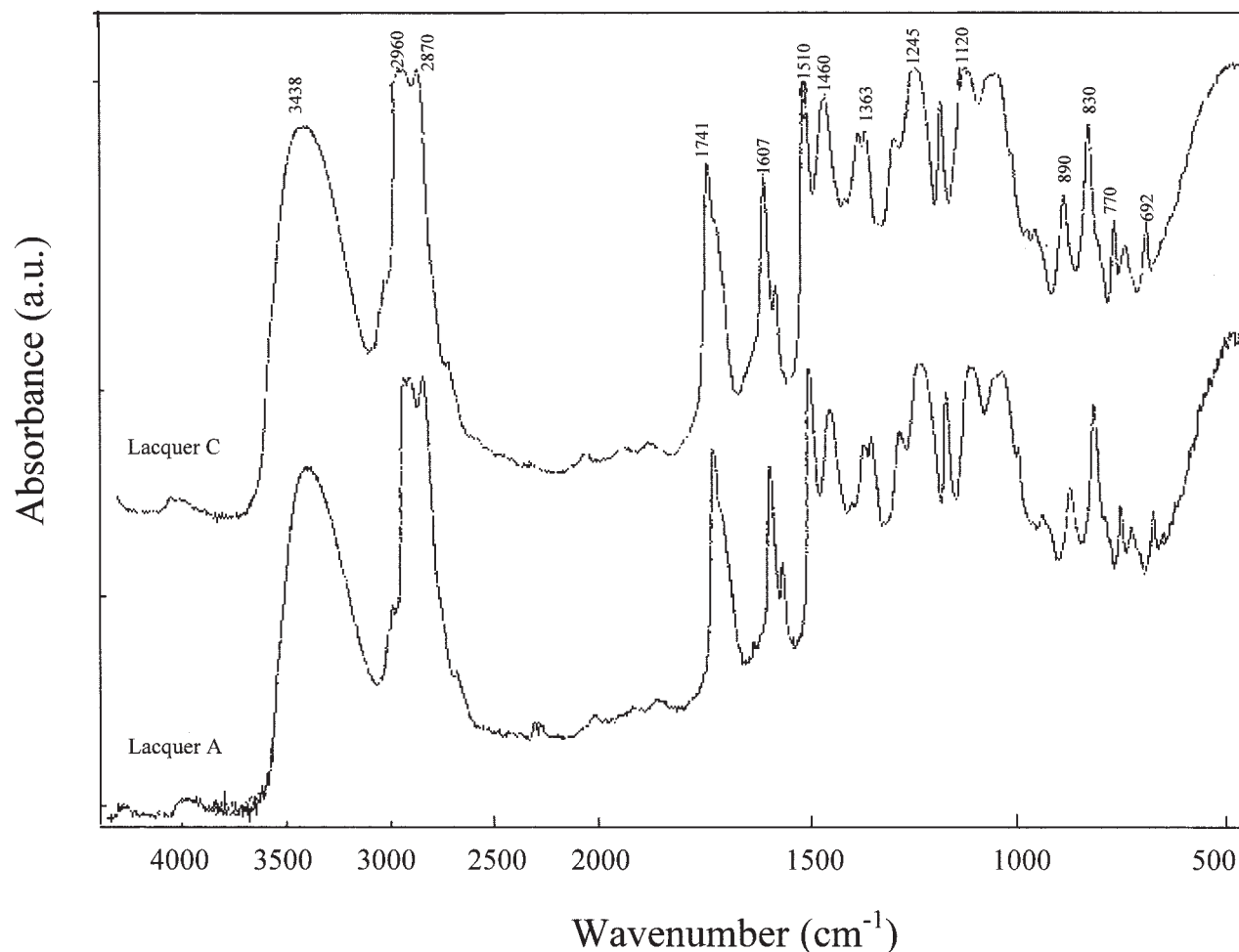


Figure 3 FTIR spectra of the liquid epoxy-phenolic lacquers A and C.

The effect of temperature on the structure of the cured lacquers was studied by the curing of lacquer B for 12 min at different temperatures: 170, 200, and 220°C. As the FTIR spectra show (Fig. 4), the band at 1712 cm^{-1} did not appear when the lacquer was cured at temperatures up to 200°C. Instead, the band at 1638 cm^{-1} appeared in the lacquer cured at the three temperatures used. These observations suggest that the oxidation of the methylene bridges to form benzophenone occurred first; then, the quinone-type compounds, carboxylic acid, and aldehyde groups from the methylol oxidation appeared; and further, the degradation of the benzophenone occurred.

The three lacquers were overcured at 200°C for 36 min, and we compared the obtained FTIR spectra (Fig. 5). The characteristic band of the methylene bridges of the phenolic resin (1460 cm^{-1}) increased with the phenolic content in the lacquer. In addition, the band at 1638 cm^{-1} diminished with the phenolic content, and the bands at 1655 and 1712 cm^{-1} increased in the same way. This was consistent with degradation reactions of the phenolic resin previously described.

To analyze changes in their chemical structures, lacquers A, B, and C were cured at 200°C for different times: 12 min (standard time) and 36 min (overcured). The normalized FTIR spectra are shown in Figures 6–8.

When the region between 700 and 1800 cm^{-1} of the spectra in Figures 6–8 were compared, the band at 1636 cm^{-1} , due to the benzophenone compounds, appeared in the spectra of the three lacquers in the studied conditions. However, the appearance of the band at 1712 cm^{-1} , due to carboxylic acid and aldehyde groups, depended on the formulation and degree of curing of the lacquer. For lacquer A, this band was absent for both normal and overcured samples. However, for lacquer B, the band only appeared when it was overcured for 36 min and had a low intensity of approximately 0.3, and for lacquer C, it showed up in the FTIR obtained at the two different times. For the overcured lacquer C, the intensity of this band (0.83) was higher than for the normal cured lacquer C (0.2) and was even higher than the band for the overcured lacquer B (0.3). Then, it was possible to estimate the

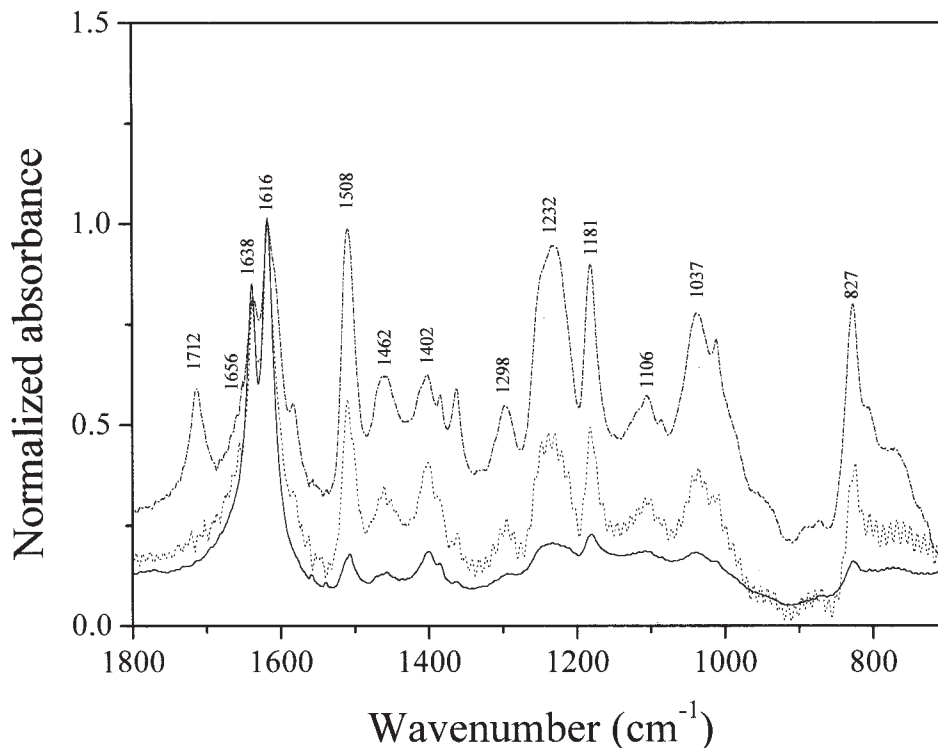


Figure 4 Normalized FTIR spectra of the lacquer B cured for 12 min at (—) 170, (···) 200, and (— · —) 220°C.

composition of the epoxy-phenolic lacquer by curing it at 200°C during different times and analyzing the band at 1712 cm^{-1} in the FTIR spectra. If a low inten-

sity band appeared at 1712 cm^{-1} in the FTIR spectra when the lacquer was cured for 12 min, the lacquer's EPR was 64/36. If in the FTIR spectra of a lacquer

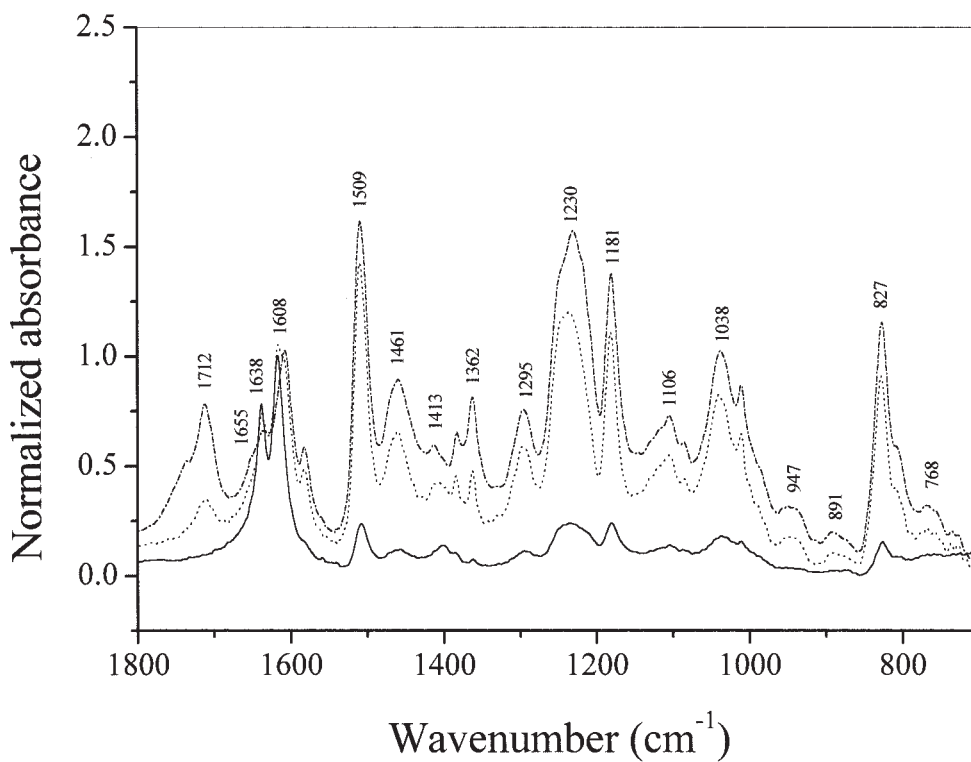


Figure 5 Normalized FTIR spectra of lacquers (—) A, (···) B, and (— · —) C overcured at 200°C for 36 min.

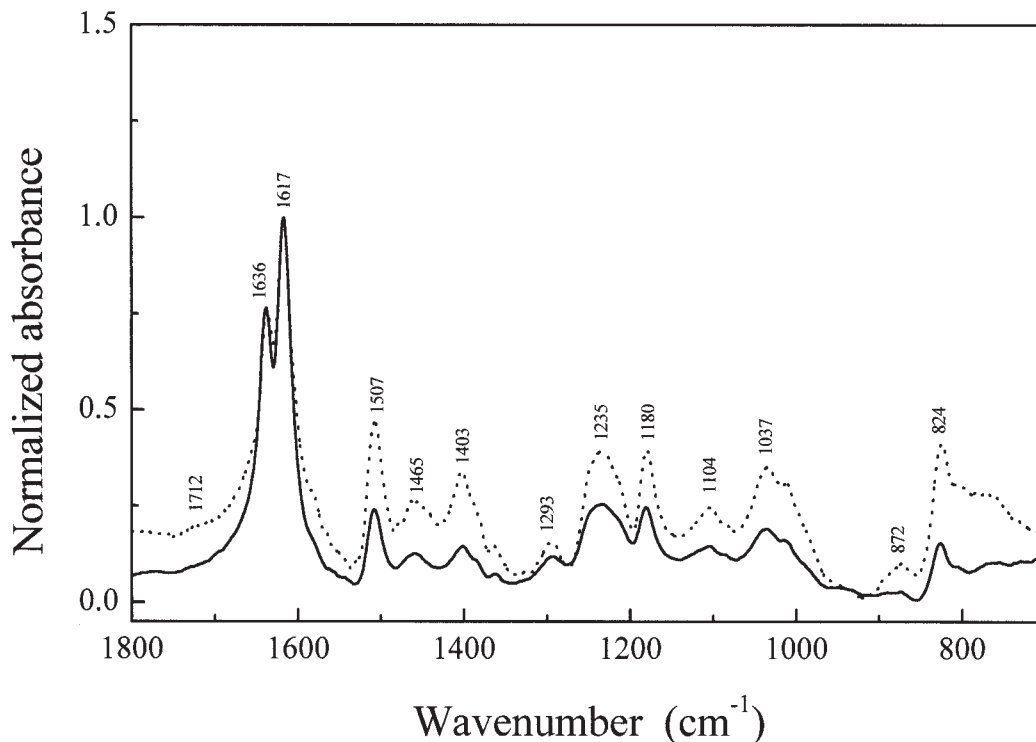


Figure 6 Normalized FTIR spectra of lacquer A cured at 200°C for (···) 12 and (—) 36 min.

cured for 12 min this band did not appear, to estimate the EPR of the lacquer, it was necessary to measure the intensity of this band when the lacquer was cured for 36 min.

In addition, from the FTIR results and the knowledge of the EPR of a lacquer, it was possible to esti-

mate if it was overcured. Depending on the lacquer composition, it was necessary to consider the spectra in Figures 6–8 and to analyze the absence or presence and height, for lacquer C, of the band at 1712 cm^{-1} . So, from the FTIR results, it was possible to determine the EPR and the overcuring of a lacquer.

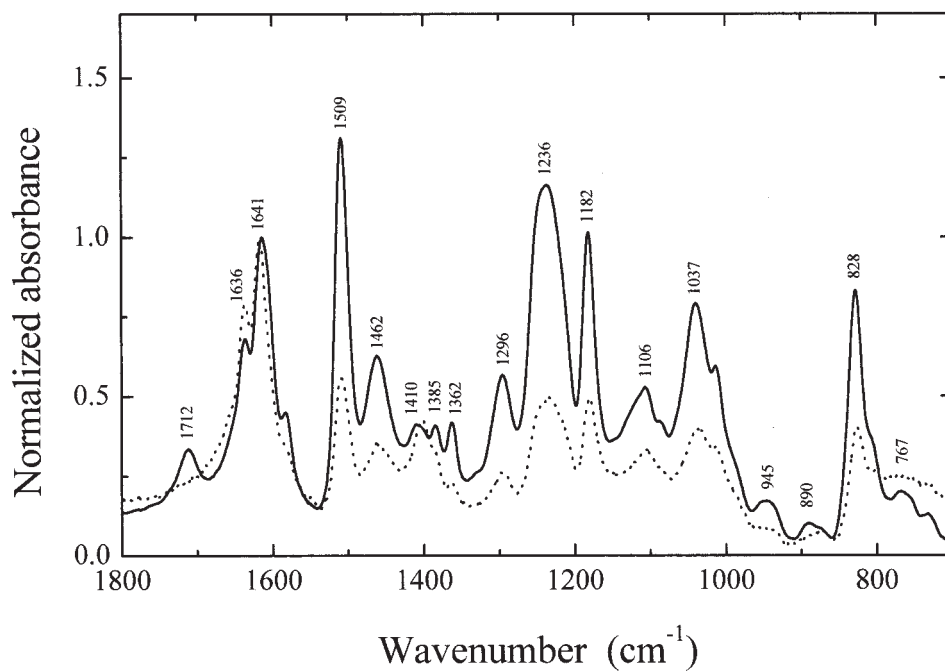


Figure 7 Normalized FTIR spectra of lacquer B cured at 200°C for (···) 12 and (—) 36 min.

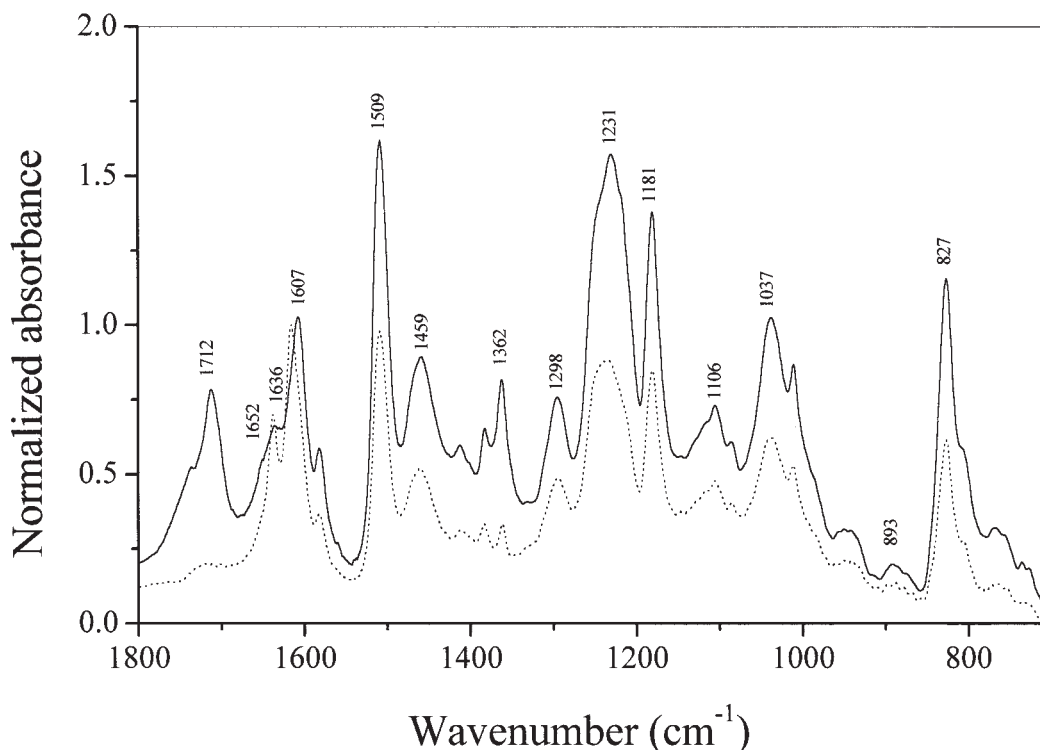


Figure 8 Normalized FTIR spectra of lacquer C cured at 200°C for (···) 12 and (—) 36 min.

In the FTIR spectra shown in Figures 6–8, the characteristic band of the methylol group of the phenolic resin, at 1037 cm^{-1} , is superimposed to the band at 1040 cm^{-1} due to the ether bridges of the epoxy resin. During crosslinking reactions, if the methylols of the phenolic resin react with the secondary OH of the epoxy resin to form an ether bridge, the band at 1037 cm^{-1} should be reduced, and the band at 1040 cm^{-1} should increase. Therefore, these bands were not useful for the study of the evolution of the reactions.

Next, mixtures of the liquid epoxy and phenolic resins were analyzed by DSC. In the first sweep, mixtures were heated to 300°C, and the analysis showed exothermic and endothermic peaks. The exothermic peaks due to the evaporation of water, free formaldehyde, and solvents added to the epoxy appeared between 100 and 150°C. The endothermic peaks appeared at higher temperatures ($\sim 230^\circ\text{C}$) and were attributed to the crosslinking reaction of the phenolic resin. In the second sweep, there was no evidence of residual heat, but the glass-transition temperature (T_g) was clearly seen (Fig. 9), with its value depending on the lacquer formulation. The higher the content of phenolic resin in lacquer formulation was, the higher the T_g was (Fig. 9).

DSC analysis of the lacquers applied on the tinplate and cured at commercial conditions showed a clear glass transition in the second sweep. As for the mixture of liquid resins, T_g increased with increasing proportion of phenolic resin in the lacquer formulation

(Table IV). T_g obtained for the lacquers was higher than that obtained for the mixtures. This could have been due to the presence of metallic additives in the lacquers.

Lacquers cured for 12 min at different temperatures were studied by DSC to try to estimate their curing degree, but the results were similar in all of the cases. Therefore, DSC analysis was useful for the estimation of the composition of the lacquers from the T_g values but not their curing degrees.

TGA was carried out to determine the weight loss of the lacquers cured at different times and temperatures. Figure 10 shows the TGA thermograms for lacquer B cured at different temperatures and times. The lacquer cured at 200°C for 12 min showed the same behavior as the one cured for 36 min at the same temperature up to 384°C. From this temperature on, the lacquer cured for 12 min degraded in high proportion, achieving a lower final residual weight. When the curves of the lacquer B cured at different temperatures during the same time were compared, we observed that when the lacquer was cured at 170°C, the degradation started at a lower temperature. TGA showed that the lacquers cured at a low temperature lost weight faster than lacquers cured at higher temperatures and longer times. These results could be explained through consideration that the crosslinking reactions occurred to a lower extent when baking was carried out at lower temperatures and times. As a consequence, there was a higher content of methylols

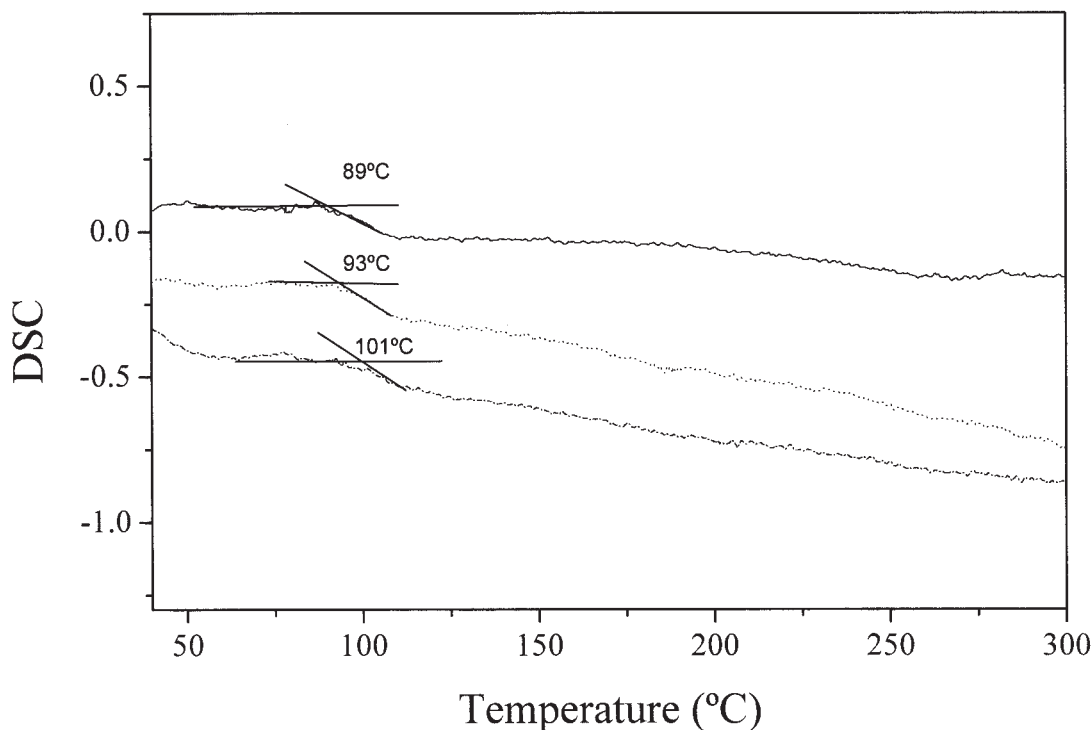


Figure 9 Second sweep of the DSC analysis of the liquid epoxy-phenolic lacquers: (—) A, (···) B, and (-·-·-) C.

and pendant chains that could degrade easily in a resin with a lower crosslinking. So, by analysis of the temperature at which the lacquer began to degrade, it was possible to determine if it was cured at normal conditions or if it was undercured at a lower temperature.

Figure 11 shows the thermograms for lacquers A, B, and C cured at 200°C for 12 min. The most resistant lacquer at low temperatures was lacquer A. The addition of the phenolic component resulted in a lower resistance to temperature due to the loss of oligomers present in the resin. At temperatures higher than 420°C, there was an increase in resistance for lacquer C. This behavior was expected because the phenolic resin was more resistant to higher temperatures than the epoxy resin. However, finally, lacquer B had a higher residual weight content. The higher residual weight obtained for lacquer B could have been affected by the quantity of fillers present in the lacquers that could have been different in the three lacquers

studied. It was not very clear in the comparison between the three lacquers. In summary, TGA may have been useful for the detection of undercuring, but it could not be used to determine the lacquer composition.

CONCLUSIONS

FTIR, DSC, and TGA techniques were used together to obtain valuable information about the composition and curing degree of epoxy-phenolic lacquers.

FTIR results of the liquid resins suggest that the epoxy resin used in the lacquers was a DGEBA type with a high molecular weight, and the phenolic component was a resol-type resin. It was not possible to estimate the lacquer composition through the FTIR spectra of the liquid epoxy-phenolic lacquers in the studied range of EPRs. However, FTIR analysis of the cured lacquers applied on the tinplate was sensitive to the EPR and may have also been useful for determining whether lacquers were overcured. However, due to the complexity of the FTIR spectra and the overlapping of bands, it was not possible to follow the evolution of crosslinking reactions between both resins.

When mixtures of liquid epoxy and phenolic resins were heated to 300°C, DSC analyses in the first sweep showed evidence for the evaporation of solvents. The second sweep clearly showed the glass-transition temperature (T_g). The higher the amounts of phenolic

TABLE IV
Effect of EPR on T_g for Lacquers Cured at 200°C
for 12 min

Lacquer	EPR	T_g (°C)
A	80/20	94
B	72/28	98
C	64/36	107

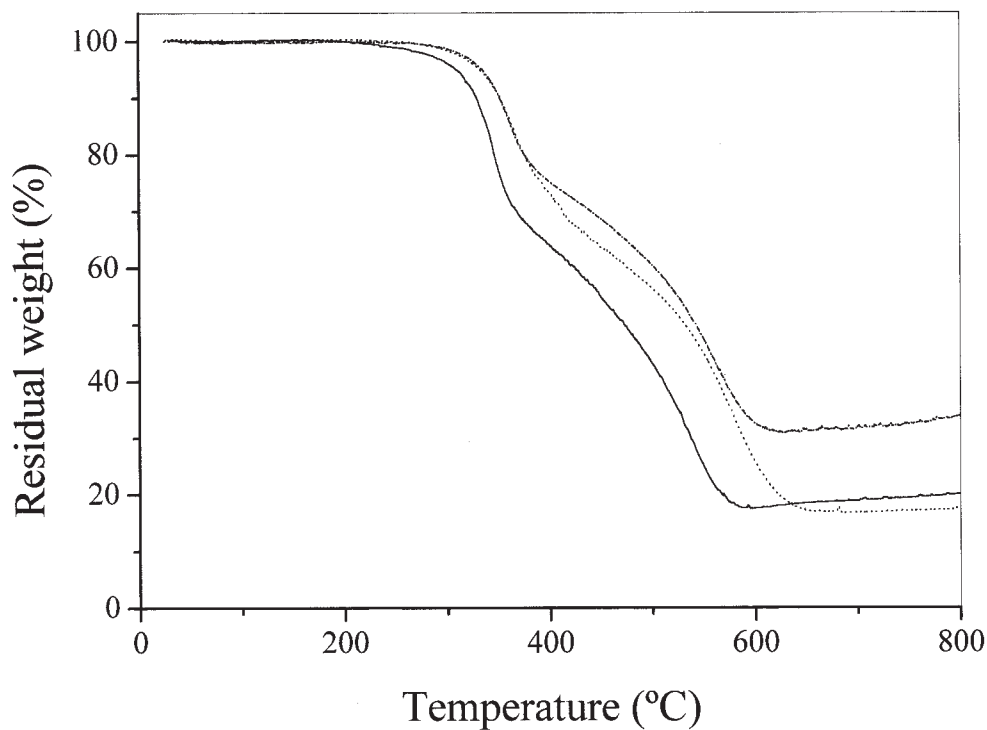


Figure 10 TGA thermograms of lacquer B cured at (—) 170°C for 12 min, (···) 200°C for 12 min, and (— · —) 200°C for 36 min.

resin was in the mixture, the higher the value of the T_g was. In addition, T_g was clearly observed in the second sweep when cured lacquers were analyzed by DSC. The value of T_g increased with phenolic content,

so the EPRs of the cured lacquers applied on the tinplate could be estimated by DSC analysis.

Undercuring of the applied lacquers could be inferred from TGA. Lacquers cured at low temperatures

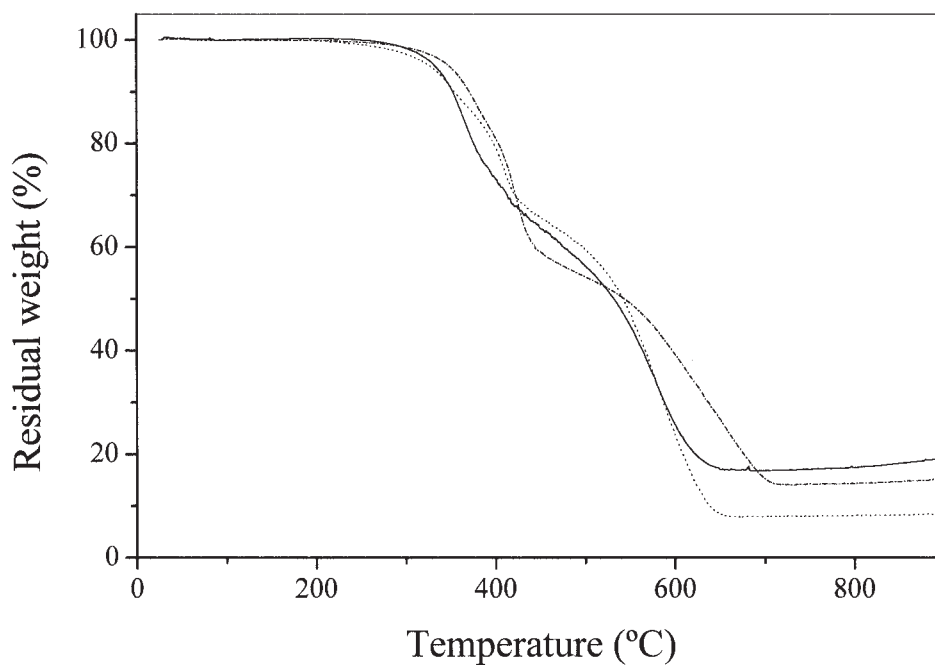


Figure 11 TGA thermograms of the lacquers cured at 200°C for 12 min: (— · —) A, (—) B, and (···) C.

lost weight faster than lacquers cured at higher temperatures and longer times.

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