A FT-IR Analysis Method for Simple Unsaturated Polyesters

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SYNOPSIS

A simple and reliable FT-IR method enabling almost complete qualitative and quantitative identification of the components of unsaturated polyester resins for glass-reinforced laminates is presented. This method is based on percentage transmission ratios of characteristic bands in a single IR spectrum. Coupled with simple chemical tests, such as resin acid number and, when needed, UV-VIS determination of Co(II) curing accelerators, this FT-IR method allows the qualitative and quantitative determination of the various reacted and unreacted components of the resin. Some critical discussion of the advantages of such a method over some conventional tests is presented.

INTRODUCTION

Simple unsaturated polyesters are today the main component of clear glass-fiber-laminated sheets used for building applications. The resins commonly referred to as unsaturated polyesters are mixtures of the linear polymers which result from the esterification of difunctional unsaturated acids or their anhydrides with a glycol, dissolved in a polymerizable monomer, most commonly styrene, which provides crosslinking units to network chains tridimensionally. The two components coreact, and resin sets, upon introduction of a peroxide catalyst and an accelerator, to form a rigid, infusible network.

Such conventional unsaturated polyester resins for glass-fiber laminating are bulk products based on the reaction of maleic and phthalic anhydrides with a glycol, most commonly propylene glycol and/or ethylene glycol. Plasticizers such as methyl methacrylate or butylacrylate are often added. The most common hardener and accelerator used are methyl ethyl ketone peroxide and cobalt(II) naphthenate, respectively. Notwithstanding their simple composition, a scan of the literature did not show any simple method for the "one-step" complete analysis of the composition of such resins. Most polyester analysis appears to be done by polarographic techniques[1] or by hydrolysis of the resin followed by chromatography,[2] both incomplete and fairly cumbersome techniques. Each technique, however, concentrates on a specific functional group in the resin and no allround technique for polyester resin identification could be found.

This article deals with a spectrophotometric method of polyester resin analysis based on FT-IR in which no chemical derivations of the resin are required and identification is obtained from peak ratios and percentage transmissions of bands in a single spectrum. The method was also compared critically to the more conventional tests used in the polyester industry.

EXPERIMENTAL

Resin Synthesis

Resins containing different proportions of propylene glycol, maleic anhydride, and phthalic anhydride and a fixed amount of hydroquinone as a carbon–carbon double bond crosslinking inhibitor were prepared according to the proportions indicated in Table I. Each resin was produced four times to check the reproducibility of the method. The resins were prepared according to the following procedure: propylene glycol, maleic anhydride, phthalic anhydride, and hydroquinone were charged into a flat-bottom glass reactor equipped with a distillation condenser, a thermometer, heating and cooling facilities, and a mechanical stirrer. The apparatus was flushed with

nitrogen and then gradually heated, under continuous mechanical stirring and a slow stream of nitrogen, up to 80°C. Xylene was then added to aid azeotropic distillation of the water produced in the reaction. The reaction mixture was then heated to 180°C and the temperature maintained between 180 and 190°C for the required reaction time, under nitrogen atmosphere and continuous mechanical stirring. Water and xylene were distilled as the reaction proceeded. The reaction mixture was then cooled to 140°C and a set amount (Table I) of distilled styrene containing 0.03% hydroquinone added over a period of 1 min while stirring. The mixture was then rapidly cooled to room temperature to prevent premature crosslinking. A viscous, clear solution of unsaturated polyester, of a very pale yellow color (due to hydroquinone addition) was obtained. Plasticizers, when added, were added at this point.

Room temperature curing of the resins was carried out by adding to 200 parts by mass of the resin 1 part Co(II) naphthenate and 1 part methyl ethyl ketone peroxide. The resins solidified in approximately 1 h at ambient temperature.

Testing

All the spectra were collected on a JASCO 5000 FT-IR. The uncured resin was placed as a smear between two NaCl plates. The spectra baseline was normalized in order for the spectra to be comparable. Scanning was between 4300 and 400 cm^{-1} in percentage transmission mode. Acid numbers for each resin, resin volatile content, and resin refractive indexes were determined according to established standards.[3,4]

Other tests on cured or uncured samples, for correlation purposes, were also carried out. These were gel times of catalyzed resins at 95°C, glass transition temperature determination on hardened samples by both differential scanning calorimetry (30–200°C, 20°C/min) and thermal gravimetric analysis (30–

130°C, 10°C/min) on a Mettler TA 3000 system, and cobalt content analysis by UV-VIS spectrometry in the range 0.672–2.545% Co naphthenate on total resin, at 580 nm on a Cary 2000 spectrometer.

For comparison the FT-IR spectra of one of the polyesters prepared is compared with the FT-IR spectra of the components from which the resin was produced; the values of % transmission are in brackets.

Polyester resin: 3424(66.7), 3084(48.0), 3062(48.8), 3030(49.3), 2970(20.0), 2880(45.4), 2368(75.3), 2338(77.5), 1949(76.2), 1721(0.4), 1632(48.3), 1601(53.9), 1580(52.6), 1545(73.8), 1495(34.6), 1475(32.7), 1452(35.8), 1408(32.7), 1377(17.2), 1354(17.1), 1276(0.6), 1197(21.2), 1125(7.7), 1075(9.6), 1040(30.3), 1021(27.4), 980(20.7), 911(27.0), 876(34.7), 843(69.8), 812(62.6), 777(12.0), 743(33.3), 700(10.8), 667(60.0), 650(58.1), 429(0.2), 416(0.0).

Maleic anhdride (reflectance spectrum): 3932(82.8), 3754(82.5), 3589(81.7), 3429(76.2), 3058(25.4), 2900(24.5), 2794(26.1), 2688(29.5), 2607(22.0), 2508(25.6), 2425(25.1), 2302(34.1), 2169(37.4), 2045(43.7), 1892(40.8), 1816(50.5), 1707(15.2), 1632(16.2), 1586(0.0), 1466(10.1), 1437(11.7), 1266(3.7), 1221(25.2), 988(28.9), 938(20.8), 870(15.8), 785(53.1), 610(22.6).

Phthalic anhydride (reflectance spectrum): 3908(85.4), 3755(86.6), 3600(78.9), 3087(23.8), 3021(26.1), 2898(28.2), 2653(34.5), 2531(39.5), 2342(80.5), 2263(68.4), 2167(69.2), 2033(68.7), 2055(68.9), 2012(62.1), 1933(63.8), 1897(58.3), 1848(27.6), 1767(11.4), 1634(0.1), 1592(33.6), 1501(58.0), 1464(46.6), 1407(19.1), 1351(41.1), 1277(5.4), 1165(58.3), 1109(54.2), 1073(50.6), 1003(57.6), 972(52.2), 907(3.0), 837(47.4), 799(28.7), 743(37.5), 713(34.0), 677(46.6), 642(67.2), 561(55), 546(53.3), 423(50.5).

Styrene: 3084(52.5), 3062(53.2), 3030(52.3), 3012(57.7), 2364(71.1), 1823(72.1), 1723(69.6), 1632(60.8), 1603(71.2), 1575(68.0), 1543(74.8), 1495(46.2), 1450(62.8), 1412(67.2), 1290(69.5),

Table I Molar Proportions of All Ingredients for Resin Synthesis 1–11

Component	1	2	3	4	5	6	7	8	9	10	11
Propylene glycol	1.05	1.05	1.05	1.05	1.75	1.3	1.05	1.05	1.3	1.05	1.05
Maleic anhydride	0.5	0.5	0.25	0.75	0.5	0.5	0	1	0.5	0.9	0.1
Phthalic anhydride	0.5	0.5	0.75	0.25	0.5	0.5	1	0	0.5	0.1	0.9
Hydroquinone	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
Xylene	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Styrene	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96

1203(74.0), 1083(66.7), 1021(66.7), 992(47.3), 909(34.7), 777(25.6), 698(19.2), 431(0.4).

Propylene glycol: 3800(71.8), 3746(69.5), 3196(2.6), 2974(4.7), 2934(5.8), 2366(69.7), 1655(67.9), 1460(18.0), 1412(18.1), 1379(15.8), 1334(22.4), 1292(25.8), 1234(32.2), 1139(6.9), 1046(0.9), 992(21.6), 924(19.2), 839(16.0), 803(43.8), 420(0.5).

Butylacrylate: 3658(61.5), 3640(58.9), 3626(59.8), 3442(48.0), 3109(47.3), 3040(38.6), 2936(0.7), 2878(1.8), 2368(61.8), 1937(57.0), 1717(0.2), 1638(6.1), 1622(9.9), 1514(56.7), 1466(4.6), 1410(0.8), 1265(0.9), 1183(0.1), 1122(27.9), 1065(0.7), 1023(19.2), 973(1.1), 911(43.3), 861(47.6), 812(2.5), 739(45.5), 665(44.3).

Methyl methacrylate: 3766(69.5), 3720(70.1), 3698(67.8), 3626(65.6), 3426(57.8), 3110(53.2), 2990(16.3), 2960(5.3), 2934(19.8), 2852(42.8), 2556(70.9), 2366(68.1), 2126(71.9), 1997(66.2), 1893(63.4), 1721(0.1), 1638(3.6), 1549(66.2), 1516(61.2), 1439(0.5), 1404(23.1), 1379(23.3), 1325(0.2), 1305(0.5), 1164(0.0), 1019(13.1), 986(23.4), 944(2.6), 816(6.5), 654(26.8), 592(31.2), 470(0.3), 424(0.5).

DISCUSSION

The determination of unreacted anhydrides in polyester resins offers a rather difficult analytical problem. Resins of the type described always contain free carboxylic groups on the polyester molecules as well as free acid groups. Both interfere with the common acidimetric method used for analysis of anhydrides. Notwithstanding that a potentiometric titration method has been proposed for their analysis, which allows for the simultaneous determination of acid anhydrides, free acids, and carboxyl end groups, this does not allow the determination of the resin composition. However, all the different components of the resin present characteristic bands in the IR region.[5] The variation of the different components in the resin preparation allowed the identification of the relevant IR bands the variation of which can be used for both the qualitative and quantitative determination of the composition of the resin.

The phthalic component exists as different isomers, all with bands in the 1710–1750 cm^{-1} region (C=O) and in the 1250–1300 cm^{-1} region (C—O—). The ortho-disubstituted ring of phthalic anhydride presents a very characteristic band, sensitive to quantitative variations in anhydride content, at 740–

745 cm^{-1}. This band is characteristic of unreacted phthalic anhydride. Isophthalic and terephthalic residues can easily be distinguished by the IR bands at 665–685 and 870–880 cm^{-1}, respectively, bands which increase in intensity (lower % transmission) as the % of these components increase.

Dibasic acids are the polyesters components which are perhaps easier to identify by IR spectrometry. Characteristic features are the bands at 1724 cm^{-1} from C=O groups, at 1282 cm^{-1} from C—O—C linkages, and the aromatic nuclei bands at 1600 and 1575 cm^{-1} (doublet), 1163, 1070, 741, and 704 cm^{-1}. The aromatic nuclei of the resin derive from phthalic anhydride and styrene. The 1724 and 1282 cm^{-1} bands are the more intense ones and are found in all polyesters spectra. Because they are so intense, they often can mask bands belonging to other components.

The unsaturation in the polyester resin can be detected on the basis of the C=C band at 1639 cm^{-1}. This band represents free, unreacted maleic anhydride and it is observed to vary with the length of the reaction time of the resin. The unsaturation in the polymer itself is instead characterized by the small band at 1354 cm^{-1}.

As a result of the well-defined anhydrides and anhydride residues bands (maleic and phthalic), various bands ratios can be examined. Four bands were selected, namely, the 745 cm^{-1} free phthalic anhydride band, the 1070–1100 cm^{-1} band representing the polymerized phthalic anhydride residue, the 1354–1380 cm^{-1} band of the polymerized maleic anhydride residues, and the 1630–1647 cm^{-1} band representing free maleic anhydride. In the resins preparations the phthalic : maleic anhydrides molar ratio was varied (cf. Table I) while the glycol concentration remained constant. The bands ratios which showed good correlation with the molar ratios of the anhydrides and their residues are shown in Figures 1–4. From these ratios variation the relative proportions of phthalic to maleic anhydride in their different states, polymerized (in the resin skeleton) or unreacted, can be determined. The results were later found to be reliable independently of the spectra baseline due to relative ratios having been used. The curves obtained are only valid in the range 90 : 10–10 : 90 phthalic : maleic.

From the four transmission ratios obtained (Figs. 1–4), not only the proportion of each polymerized to each unreacted anhydride can be calculated, but also the proportions of maleic anhydride to phthalic anhydride used by the manufacturer at the beginning of the reaction, giving some insight in the method of preparation of the resin. It must be pointed out
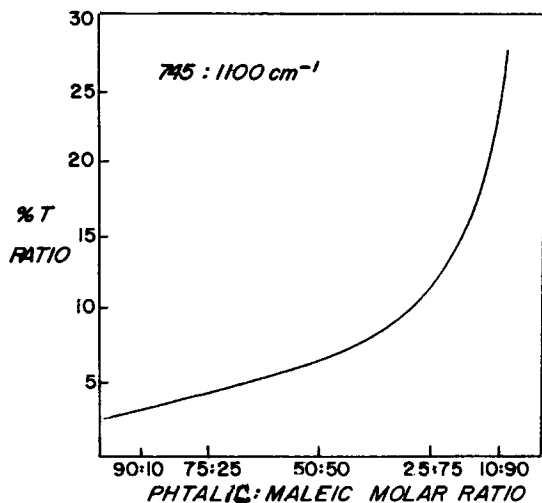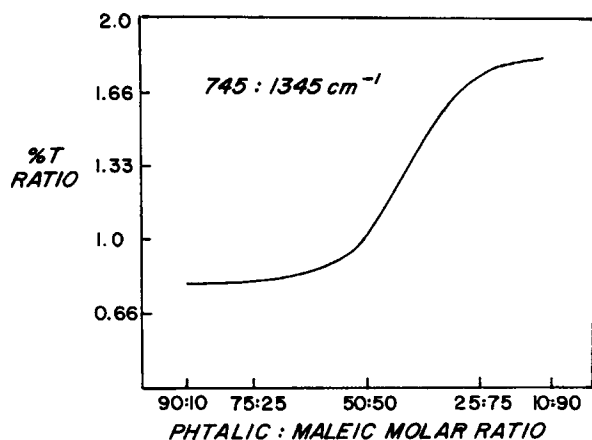
Figure 1 Percentage normalized IR transmission ratio as a function of the initial molar percentages of phthalic and maleic anhydrides in the reaction mix indicated by the ratio of the bands of unreacted and polymerized phthalic anhydride (745 : 1100 cm^{-1}).
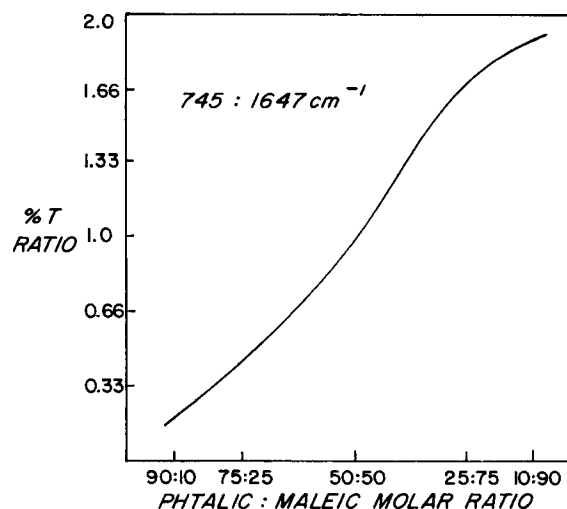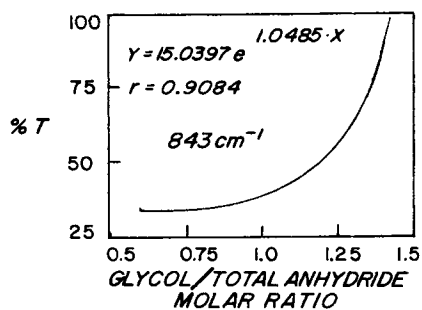
clearly that the values on the x axis of Figures 1–4 represent the initial molar ratio of phthalic : maleic anhydrides used to prepare the polyesters by the manufacturer. For this purpose the acid number of the resin must be obtained as well as the theoretical value of the acid number when all the anhydrides were in their unreacted state. Thus,

$$A/B \times 100 = C \qquad (1)$$

where A = acid number of resin, B = acid number

Figure 3 Percentage normalized IR transmission ratio as a function of the initial molar percentages of phthalic and maleic anhydrides in the reaction mix indicated by the ratio of the bands of unreacted phthalic and maleic anhydrides (745 : 1647 cm^{-1}).

of anhydrides totally unreacted, and C = % free anhydrides in the resin. Then, from the percentage transmission ratios in Figures 3, 4, and 1, the percentual initial molar ratio of phthalic to maleic anhydride used to manufacture the resin is obtained, as indicated by the ratios of the free phthalic to free maleic bands, free maleic to polymerized maleic band, and free phthalic to polymerized phthalic band. The percentual ratio from Figure 3 is multiplied by $C/100$ [from eq. (1)] while the percentual ratios from Figures 4 and 1 are multiplied by $(1 - C/100)$, this to give the correct weight of total un-

Figure 2 Percentage normalized IR transmission ratio as a function the initial molar percentages of phthalic and maleic anhydrides in the reaction mix indicated by the ratio of the bands of unreacted phthalic anhydride and polymerized maleic anhydride (745 : 1354 cm^{-1}).
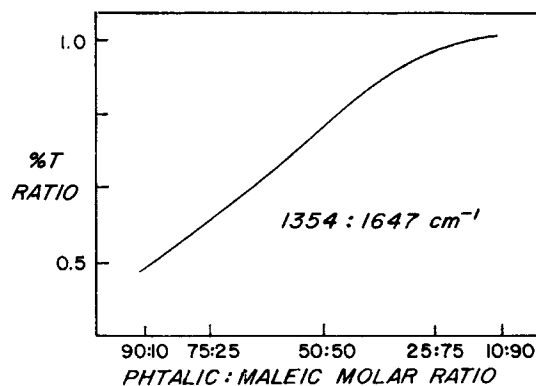
Figure 4 Percentage normalized IR transmission ratio as a function of the initial molar percentages of phthalic and maleic anhydrides in the reaction mix indicated by the ratio of the bands of polymerized and unreacted maleic anhydride (1354 : 1647 cm^{-1}).
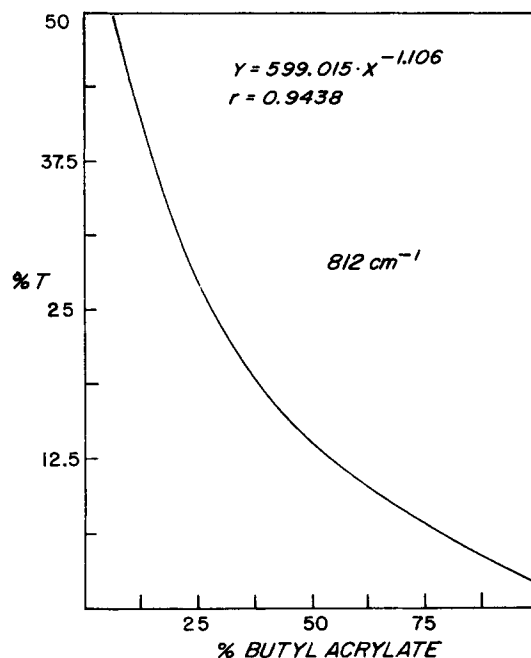
reacted to total polymerized material. Summing the three correctly weighed ratios and dividing by 3, the original relative proportions of the two anhydrides at the beginning of the reaction are obtained. It must be clearly pointed out here that the band at ± 1354 cm^{-1} representing the polymerized maleic anhydride residue is barely observed in resins of initial phthalic: maleic ratios of 90 : 10 and sometimes is completely masked. It is clearly seen in resins of initial phthalic : maleic ratios of 50 : 50 (to this effect cf. Figures 9 and 10).

Glycols have substantially different spectra and this characteristic allows distinction between propylene and ethylene glycols in the resin. Both glycols absorb strongly in the 3200–3500 cm^{-1} range due to their hydroxy groups. However, propylene glycol has a strong characteristic band at 839–845 cm^{-1} and at 1379 cm^{-1}, which can be used for identification. Its band at 2374 cm^{-1} is, however, often masked by C=O and styrene bands and cannot be used reliably for identification. Ethylene glycol most characteristic band, usable for identification is that at 884 cm^{-1}. The propylene glycol band at 845 cm^{-1} was selected to quantify the proportion of this component. On a normalized baseline there is an increase in percentage transmission proportional to the amount of glycol present. The results are shown in Figure 5, the best fit being exponential with a coefficient of correlation r = 0.9084. There are also indications that the intensity of the alcohol band at approximately 3450 cm^{-1} is proportional to the degree of polymerization of the resin in the range 5–8 h reaction time, giving an exponential fit, reaction time (h) = 1.138 $e^{0.0459(\% \text{ transmission})}$ with coefficient of correlation r = 0.989; it also correlates well with the acid number values, although the amount of data needs to be more substantial to confirm this trend.

The presence of styrene can also be detected by its numerous characteristic sharp bands. These are
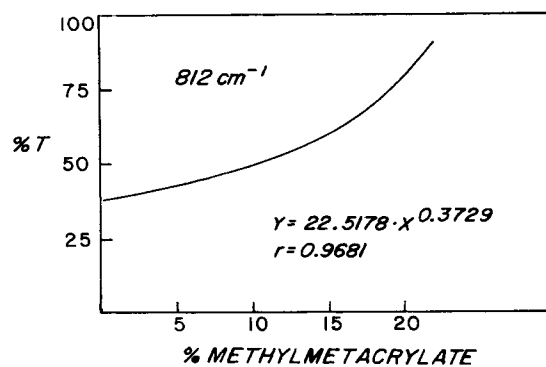

Figure 6 Percentage normalized IR transmission at 812 cm^{-1} as a function of butyl acrylate concentration (y = 599.015 $x^{-1.106}$; r = 0.9439).

at 698, 777, 909, 992, 1021, 1412, 1452, 1495, 1545, 1576, 1603, 1632, 3030, and 3084 cm^{-1}. Because styrene is always present in large quantities, 30–45% of total resin, it can always be detected easily by IR spectrometry although the variations in bands intensities at such large concentrations are too small to describe quantitatively the styrene present to an adequate level of reliability. A residual volatiles content test, a very simple test, is in this case the best approximation of the amount of styrene present. FT-IR is then only an excellent method for the


Figure 5 Percentage normalized IR transmission at 843 cm^{-1} as a function of the ratio of propylene glycol to total anhydrides content (y = 15.0397 $e^{1.0485x}$; r = 0.9084).

Figure 7 Percentage normalized IR transmission at 812 cm^{-1} as a function of methyl methacrylate concentration (y = 22.5178 $x^{0.3729}$; r = 0.9681).
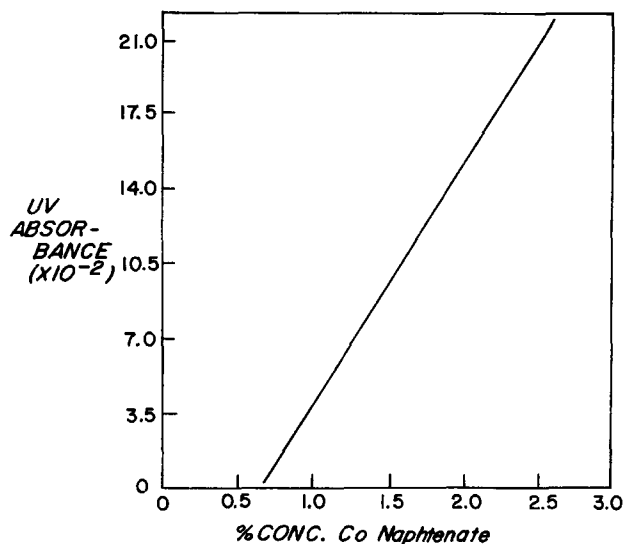
Figure 8   UV absorbance ($\times 10^{-2}$) at 580 nm as a function of percentual Co naphthenate concentration.

qualitative detection of the presence of styrene but needs to be coupled with a simple residual volatiles content test for styrene quantification. This method is then simpler, cheaper and faster than gas–liquid chromatography, where the resin needs to be dissolved in methyl ethyl ketone.

In order to optimize the chemical and physical properties of polyesters, methyl methacrylate or butylacrylate are sometimes added as resin plasticizers. The characteristic bands of methyl methacrylate are the strong 592 cm^{-1} band and the 812 cm^{-1} band. The former is often masked by the overlapping aromatic bands range and thus cannot be used for methyl methacrylate detection. The 812 cm^{-1} band needs then to be used; although this band can be used for quantification of the acrylate present, it does not distinguish between methyl methacrylate and butylacrylate. Thus, the presence of this band will point to the presence of an acrylate and be able to quantify its amount, but will not distinguish what type of acrylate is present. The percentage transmission changes of the 812 cm^{-1} band were studied with changes in the amount of plasticizer used in the resin. The curves of % transmission as a function of % acrylate content with their best fit regression analysis for both types of acrylates are shown in Figures 6 and 7. It is important to note that in the case of the butylacrylate (Fig. 6) the 812 cm^{-1} band % transmission decreases as the % of acrylate increases. This trend is correct showing increase of intensity (decrease in % transmission) of the acrylate band with increasing % butylacrylate. This is the reversal of what noticeable with methyl meth-
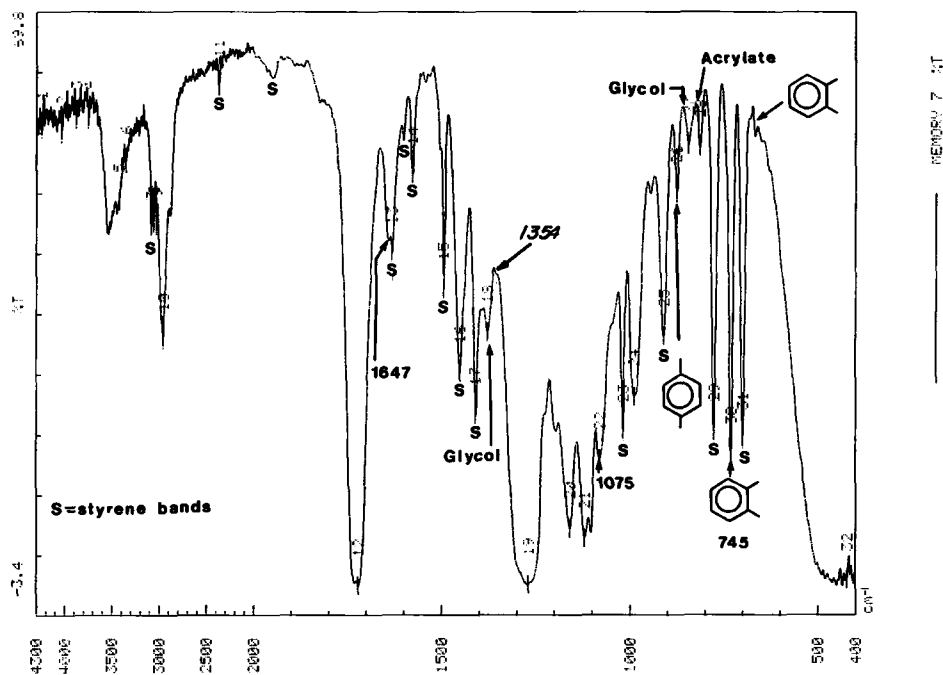
Figure 9   FT-IR spectrum of a commercial unsaturated polyester resin of 90 : 10 phthalic : maleic initial molar ratio, 1.05 propylene glycol/total anhydrides molar ratio, showing presence of phthalic, terephthalic, and isophthalic residues and containing 9.5% butylacrylate. Note the almost completely hidden band at 1354 cm^{-1} (maleic shoulder).
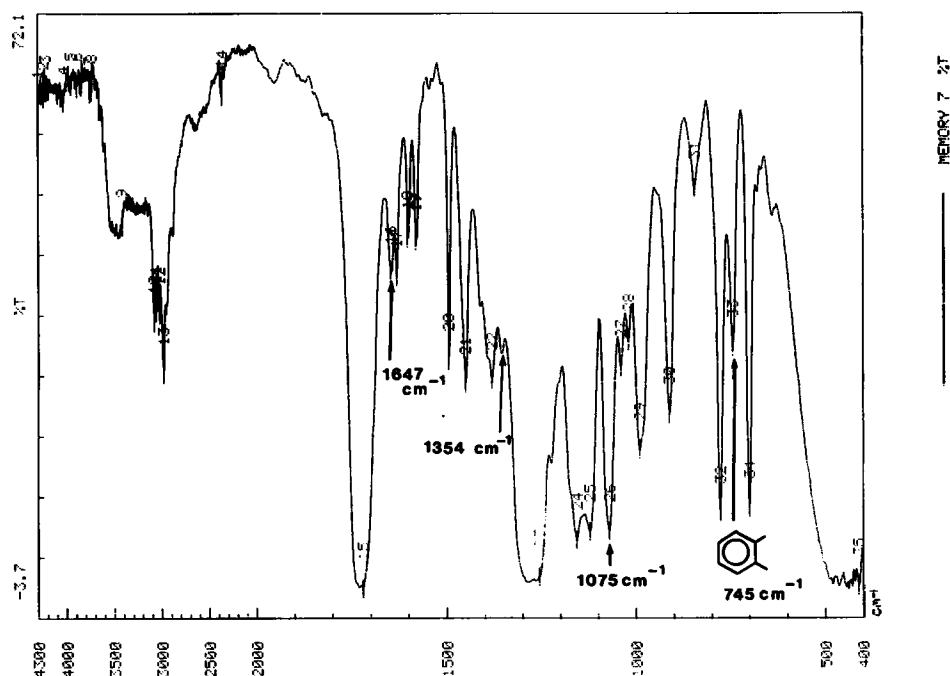
Figure 10   FT-IR spectrum of a commercial unsaturated polyester resin of 50 : 50 phthalic
: maleic initial molar ratio, 1.30 propylene glycol/total anhydrides molar ratio, showing no
presence of terephthalic residues and containing no acrylates. Note the clearly visible 1354
cm⁻¹ band.

acrylate. No explanation can be afforded for the reverse trend of the methyl methacrylate band.

In some resins Co(II) in the form of cobalt naphthenate is added to the resin independently of its addition immediately before resin curing. In the resins where Co(II) is present its percentage cannot be determined by IR but rather by UV-VIS spectrometry at 580 nm. The graph of absorbance vs. cobalt naphthenate concentration shown in Figure 8 can be used for the determination of the Co(II) content of the resin between the limits indicated. This is definitely a easier procedure than wet-ashing techniques with strong oxidizing agents as used in the polyester industry. It is also interesting to critically compare the confidence limits of the FT-IR method with other methods used in polyester resins analysis, in particular, refractive index, glass transition temperature, and acid number determination.

As regards glass transition temperature, measured by both thermogravimetric analysis and differential scanning calorimetry, these could be useful for the determination of the % acrylate plasticizer in the resin. However, the T_g values obtained for different percentages of plasticizer lie very close together; an accurate value of the % plasticizer cannot be easily obtained from these readings because their tendency to fluctuate with sample size and sample preparation

renders the experimental error too significant for the nearness of the values obtained (see Table III).

The refractive index at 25°C gives instead more acceptable results; the relationship between % acrylate and refractive index value (see Table IV) could be explained by a logarithmic curve fit $y = 642.2444 - 1508.956 \ln x$ with $r = 0.9844$. Unfortunately, when two commercial resins not used for the fit and known to contain 8 and 10% butylacrylate, respectively, were measured against this, the results were of 3.9 and 4.3%, against FT-IR obtained values of 7.7 and 9.5%. The refractive index then cannot be used as the values obtained, for the small variations of plasticizer introduced, are too close together and the experimental error becomes too large. The refractive index can be used if the differences in plasticizer content are greater than 9% because the ratios would then be further apart (e.g., comparing resins with 6, 15, and 30% butylacrylate). However, the FT-IR analysis appears always to produce more reliable results for any range of percentage plasticizer added.

In conclusion FT-IR is shown to be a simple and reliable "one-step" method for the almost complete identification of the components proportions of laminating polyester resins. FT-IR coupled with simple, routine, chemical tests, such as the acid

Table II   FT-IR Spectra Peak Assignments

Peak (cm^{-1})	Assignment
3400–3600	Free OH (unreacted glycol)
3030–3094	Aromatic CH (styrene)
3000	Ortho disubstituted aromatic ring
2970	Propylene glycol (characteristic)
2300	Styrene
1950	Vinyl (styrene)
1700–1800	Overlap—acrylate/cyclic anhydride (C=O stretch)
1647	C=C unsaturation, free maleic double bond
1632	Styrene
1601	Aromatic ring—styrene
1580	Aromatic ring—styrene
1545	Styrene
1490–1520	Ortho disubstituted aromatic ring
1495	Free styrene
1452	Styrene
1379	Propylene glycol
1354	C=C—polymerized maleic anhydride
1230–1330	Overlap—acrylate, ester, anhydride (C=O stretch)
1125	Acrylate
1075	Reacted phthalic anhydride
1040	Glycol
1020	Styrene
960–970	Trans alkene
911	Free styrene
870	Para disubstituted aromatic ring (terephthalic residue)
843	Glycol
812	Acrylate
777	Styrene–aromatic ring–polymer
730–743	Ortho disubstituted aromatic ring (phthalic residue)
700	Styrene–aromatic ring–monomer
670	Meta disubstituted aromatic ring (isophthalic residue)
600	Aromatics

number of the resin, results in the complete identification of a laminating polyester resin. The attractiveness of this approach is that a single FT-IR spectrum of the resin is needed for its characterization.

Table III   A Comparison between Gel Time (at 93°C) and Glass Transition Temperature

Resin	Sample Mass (g)	Gel Time (s)	T_g (°C)
1	10	94.0	37.0
2	10	228.8	40.1
3	10	243.3	—
4	10	63.5	30.8
5	10	52.0	31.5
6	10	80.0	35.9
7	10	10 min	
8	10	Gel at room temp	36.5
9	10	110	34.4
10	10		37.3

Table IV   Refractive Indexes at 25°C at Varying Amounts of Butyl Acrylate and Varying the Resin Reaction Time

Sample	Refractive Index
10% BA 2 h	1.5179
10% BA 5 h	1.5189
10% BA 6 h	1.5193
10% BA 8 h	1.5190
0% BA 5 h	1.5328
6.284% BA 5 h	1.5230
10.248% BA 5 h	1.5188
15.420% BA 5 h	1.5131
30.496% BA 5 h	1.5021

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