NOTES

Completion of Unsaturated Polyesters Analysis by FTIR

INTRODUCTION

Recently, an FTIR method for the one-step quantitative analysis of simple unsaturated polyester resins was reported.[1] In this method, only the relevant propylene glycol and ethylene glycol IR bands were identified and the amount of these two glycols in the resin quantified by FTIR spectrophotometry. Equally, quantification by FTIR bands intensity variation was not carried out for styrene or some common styrene derivations. Styrene is the most commonly used reactive monomer in unsaturated polyesters. However, when a slower rate of resin cross-linking is required, steric hindrance is introduced by the use of *para*-methylstyrene and *ortho*-methylstyrene. This note briefly deals with the identification of IR bands of a few glycols commonly used in polyester resins relevant to their quantification by FTIR, with quantification of neopentyl glycol, and with the quantification in the resin of styrene and its derivatives.

EXPERIMENTAL

The resins for examination by FTIR were prepared as already reported.[1] All the FTIR spectra were initially collected on a JASCO 5000 FTIR, but as a zooming facility was needed to observe some of the small variations in the percentage transmission of the bands involved, a Mattson Galaxy 4020 FTIR with a zooming facility was used. All the quantitative relationships were based on direct absorbance. Attenuated total reflection FTIR was used on samples held in a reflection attachment of $50 \times 6 \times 5$ mm of the liquid resins. Spectra base lines were normalized for the spectra to be comparable. Scanning was initially in the 3700 and 700 cm^{-1} and later concentrated on the relevant bands for quantification of the materials. The FTIR spectra of the main quantified components are reported for comparison purposes, listing bands in cm^{-1} and % transmission in parentheses:

Neopentyl glycol: 3674 (64.2), 3593 (51.3), 2979 (10.0), 2890 (24.4), 1474 (55.6), 1389 (42.8), 1262 (65.4), 1185 (70.3), 1092 (26.3), 1042 (19.5), 915 (58.2).

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

Para-methylstyrene: 3086 (68.5), 3044 (70.1), 3017 (60.7), 3005 (61.3), 2980 (67.0), 2947 (76.0), 2920 (65.4), 2860 (80.4), 1630 (40.3), 1513 (17.3), 1451 (59.2), 1404 (46.5), 1115 (42.1), 1032 (45.8), 1018 (45.2), 990 (9.1), 903 (4.6), 822 (2.9), 793 (51.5), 729 (29.4), 712 (53.8).

Ortho-methylstyrene: 3082 (65.3), 3057 (70.1), 3025 (74.0), 3005 (87.3), 2974 (68.0), 2945 (72.9), 2920 (82.2), 1630 (39.5), 1601 (68.4), 1574 (62.1), 1435 (28.4), 1441 (21.6), 1375 (42.5), 1302 (67.2), 1028 (46.4), 889 (3.5), 774 (5.5).

Polyester resin, 50/50 diethylene glycol/neopentyl glycol with styrene: 2938 (30), 2306 (33.5), 2875 (37.9), 1733 (4.4), 1721 (0.7), 1644 (25.6), 1632 (32.5), 1599 (56.9), 1578 (59.3), 15555 (75.9), 1544 (75.6), 1434 (37.5), 1475 (23.8), 1450 (21.3), 1394 (15.0), 1374 (8.1), 1286 (1.3), 1257 (0.7), 1241 (1.9), 1212 (2.5), 1135 (6.9), 1171 (3.0), 1156 (0.9), 1132 (1.3), 1123 (1.8), 1113 (2.8), 906 (4.4), 781 (0.1), 734 (8.1), 688 (6.3), 673 (16.3), 656 (13.4).

Polyester resin, 50/50 bisphenol A/diethylene glycol in styrene: 3063 (43), 3023 (45), 3000 (53), 2956 (31), 2340 (32), 2314 (46), 2875 (49), 2855 (51), 2367 (55), 2359 (63), 2328 (71), 1851 (54), 1773 (22), 1727 (0.4), 1711 (5), 1696 (5), 1641 (34), 1620 (30), 1602 (18), 1586 (16), 1508 (6.5), 1493 (12), 1475 (23), 1438 (15), 1383 (16), 1370 (17), 1360 (14), 1304 -1109 (3-5), 1088 (4.8), 1047 (6), 1016 (8.5), 1000 (7), 984 (6.5), 906 (4), 828 (2), 781 (1), 703 (1.5), 688 (0.7), 672 (6), 656 (5.5), 641 (3).

Polyester resin, 50/50 neopentyl glycol/propylene glycol in styrene: (1900–1200 cm^{-1} range): 1806 (72), 1729 (4), 1722 (1), 1705 (3), 1644 (33), 1632 (40), 1560 (58), 1577 (56), 1558 (75), 1541 (76), 1528 (76.5), 1434 (30), 1474 (25), 1450 (22), 1374 (9), 1230–1225 (2–4).

DISCUSSION

It is of interest to examine the resin when this is composed of a single glycol or of two glycols in combination. Glycols

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are generally characterized between 1500 and 600 cm^{-1}. However, there are many strong bands in this region that may mask the characteristic bands of a glycol. For example, the diethylene glycol (DEG) CH$_2$—O—CH$_2$ stretch transmits at 1150–1060 cm^{-1}; this can in no way be identified accurately. Nevertheless, some peaks can be attributed to a particular glycol. A peak at 1450 cm^{-1} in neopentyl glycol (NPG) resins is characteristic of NPG and represents the CH$_3$—C, C—H stretch. It is not detected in any other glycol spectra. 1,3- and 1,4-Butandiol can also be clearly distinguished using FTIR. 1,3-Butandiol contains one secondary alcohol and one primary alcohol, whereas 1,4-butandiol contains two primary alcohols. The secondary alcohol is clearly visible between 1340 and 1360 cm^{-1} in the 1,3-butandiol spectrum. The 1,4-butandiol contains a —CH$_2$—CH$_2$— link; this characteristically absorbs at 1480–1400 cm^{-1} and is not seen in the 1,3-butandiol spectrum.

Various glycol combination resins were synthesized to evaluate influence on the FTIR identification of the various components. The total glycols-to-anhydrides-to-styrene molar ratio was kept constant at 1.3 : 1.0 : 0.96. The glycol combinations were all 50/50 blends. The FTIR analysis of these glycol combination resins show that although a glycol mix is present individual glycols can be identified.

The IR of the resin containing 50/50 DEG/NPG clearly distinguishes between the two glycols. The CH$_3$—C stretch of NPG shows an unmasked peak at 1450 cm^{-1}. The —CH$_2$— groups in DEG absorb between 1480 and 1440 cm^{-1}. The —CH$_2$—O—CH$_2$— group cannot be detected as it transmits between 1150 and 1060 cm^{-1} where very intense transmissions from other groups occur, masking any characteristic peaks.

The 50/50 bisphenol A/DEG resin spectrum appears to be slightly different from characteristic polyester spectra as a result of the aromatic rings in bisphenol A. Nevertheless, a distinction between the two glycols can be made: The DEG —CH$_2$— group (1480–1440 cm^{-1}) and the —CH$_2$—O—CH$_2$— group (1150–1060 cm^{-1}) are clearly visible to distinguish DEG. The bisphenol A also has some characteristic peaks. Its CH$_3$—C stretch can be detected between 1470 and 1435 cm^{-1}. The 1 : 4 distribution of the aromatic rings is visible at 1070–1000 cm^{-1} and at 860–

800 cm^{-1}. The peaks at 1225–1175 cm^{-1} and 1125–1090 cm^{-1} are not visible due to strong transmissions of other groups in the same wavenumber ranges. Its phenol groups transmit strongly at 1410–1310 cm^{-1}.

Propylene glycol (PG) and NPG can be detected in a resin containing a 50/50 mix. The NPG CH$_3$—C IR signal is clearly detectable at 1450 cm^{-1}, whereas propylene glycol can be identified by the peak at 1379 cm^{-1}.

Table I is a summary of the IR glycol identification bands when in combination. Should a combination of NPG and bisphenol A be made, it would be difficult to isolate the characteristic C—CH$_3$ peak at 1450 cm^{-1} as both components contain this group.

The spectra of the NPG resins containing 1.3, 1.2, 1.0, and 0.86 mol of NPG (maintaining a 50/50 maleic/phthalic anhydride ratio) were used to quantify NPG. The peaks that quantitatively represent NPG occur at 1392 cm^{-1} [—C—(CH$_3$)$_2$ stretch] and 1039 cm^{-1} (C—O stretch of primary alcohol). There are other peaks that quantitatively represent NPG; these are, however, masked by stronger peaks and, thus, they are not easily usable for quantification.

Linear regressions of the absorbance of the resins at 1039 and 1392 cm^{-1} yielded the following relationships:

1039 cm^{-1} band molar proportion NPG

$$= 1.312 \times \text{absorbance} - 0.4585,$$

1392 cm^{-1} band molar proportion NPG

$$= 1.6186 \times \text{absorbance} + 0.2091,$$

with coefficients of correlation of .9757 and .999 for the 1033 and 1392 cm^{-1} IR bands and the results obtained as molar ratio to total anhydride content.

Of interest was the attempt at quantification of styrene, p-methylstyrene, and o-methylstyrene. A comparison between styrene and p-methylstyrene clearly shows the strong transmissions of the p-methylstyrene at 825 and 1113 cm^{-1}. It also transmits strongly at 1512 cm^{-1}. These are all a result of the 1 : 4 disubstitution on the aromatic ring. These peaks can be clearly detected irrespective of the MA : PA ratio in the resin. A resin containing p-

Table I Glycol Identification Ranges When in the Presence of Other Glycols

Resin	Glycol	Wavenumber Range	Identification
50/50 Molar DEG/NPG	DEG	1475	—CH$_2$—
	NPG	1450	—C—CH$_3$
50/50 Molar DEG/bisphenol A	BIS A	1070–1000	1,4-Disubstitution
	DEG	1475	—CH$_2$—
50/50 Molar PG/NPG	PG	1374–1379	—CH—CH$_3$
	NPG	1450	—C—CH$_3$

Table II Quantification of p-Methylstyrene in Unsaturated Polyester Resins

p-MethylStyrene in Resin (%)	Absorbance at 1512 cm^{-1}	Absorbance at 825 cm^{-1}
0	0.002	−0.040
0.3832	0.012	0.030
0.6108	0.006	0.014
1.2793	0.006	0.000
1.6650	0.014	0.041
2.0325	0.018	0.045
2.2415	0.026	0.073
3.2664	0.037	0.096
5.2392	0.057	0.225
5.9173	0.065	0.220
11.0948	0.124	0.417
12.0488	0.131	0.399
14.2579	0.145	0.501
18.3477	0.198	0.577
20.5751	0.203	0.610
24.5547	0.236	0.689
30.3647	0.270	0.737
35.0126	0.290	0.847
40.7790	0.320	0.825

methylstyrene is noticeably different from a resin containing styrene as the peaks at 825 and 1512 cm^{-1} transmit sharply and strongly. It is for this reason that the peaks at 825 and 1512 cm^{-1} are selected for the quantification of p-methylstyrene.

The quantification was performed by adding between 0 and 40% p-methylstyrene to an unsaturated polyester after manufacture. The experimental absorbance results obtained for these two IR bands are shown in Table II and yield the following relationship:

[1512 cm^{-1} band]p-methylstyrene(%)

$$= 119.05 \times absorbance - 1.441.$$

With coefficient of correlation of .9887. The variation of the band at 825 cm^{-1} gives more accurate results in the range up to 25% p-methylstyrene in which linear regression gives a coefficient of correlation of .9869 according to the following expression:

[825 cm^{-1} band[p-methylstyrene(%)

$$= 32.5733 \times absorbance - 0.2248(0–25\% range).$$

Methylstyrene can be distinguished from p-methylstyrene and styrene by using FTIR. A characteristic band at 729 cm^{-1} is indicative of the 1,2-disubstitution on the aromatic ring. However, 1, 2 disubstitution bands are known to occur between 770 and 725 cm^{-1}. The 1,2-disubstitution on the phthalic anhydride ring also absorbs in this range. Nevertheless, it is possible to distinguish between bands with different 1,2-substituents in this range. The phthalic anhydride aromatic ring contains highly polar substituents that cause the band to shift to higher wavenumber ranges (e.g., 773 cm^{-1}). The o-methylstyrene contains nonpolar substituents that absorb at the low end of the wavenumber range. The unsaturation present also favors absorption at the low end of the wavenumber range (e.g., 729 cm^{-1}). In this way, misinterpretation of the 1,2-aromatic o-methylstyrene with the 1,2-disubstituted phthalic anhydride peak is avoided. However, the peak at 729 cm^{-1} is not clearly visible and is masked by a styrene peak absorbing at 700 cm^{-1}. Nevertheless, changes in absorbances in the sum of these two peaks are detected as the amount of o-methylstyrene increases, but, due to juxtaposition of the two peaks, no easily quantifiable trends can be detected and, hence, the 729 cm^{-1} peak is not suitable for quantitative analysis when styrene is present.

Styrene in polyester resins can be identified by a variety of bands.[1] The bands at 1431, 906, and 630 cm^{-1} show particularly small quantitative trends in styrene concentration. The band with the higher correlation coefficients (= .9339) and thus most suitable for styrene quantification is the one at 1431 cm^{-1} that gives the linear relationship

Styrene(%) = 82.65 × absorbance − 37.240

Table III The Quantification of Styrene

Styrene in Resin (%)	Absorbance at 1491 cm^{-1}	Absorbance at 906 cm^{-1}	Absorbance at 630 cm^{-1}
3.0501	0.467	1.556	0.605
6.9692	0.547	1.656	0.775
11.9399	0.621	1.811	0.657
15.3499	0.658	1.683	0.708
18.2208	0.608	1.674	0.725
19.5861	0.707	1.993	0.812
21.6914	0.719	1.929	1.019
Linear correlation coefficient	0.9339	0.7626	0.6970

The results obtained with the three bands are shown in Table III. The last monomer of interest that can be quantified is isophthalic acid. The presence of isophthalic residue in the resin can be quantified from the absorbance bands at 1280 and 729 cm^{-1}.

At 1280 cm^{-1}, the relationship is

Conc Iso-phthalic (%) = 2.642 $\times$ absorbance $-$ 0.9062

with a correlation coefficient of .9242.

At 729 cm^{-1}, the relationship is

Conc Iso-phthalic (%) = 4.250 $\times$ absorbance $-$ 0.9299

with a correlation coefficient of .9508.

References

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