

Process Cure Monitoring of Unsaturated Polyester Resins, Vinyl Ester Resins, and Gel Coats by Raman Spectroscopy

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ABSTRACT: The curing process of unsaturated polyester resins, vinyl ester resins, and gel coats was studied by using a process Raman spectrometer, equipped with a remote fiber-optic probe. The resins were cured and Raman spectra were recorded during the curing reaction. The spectral changes were identified and, from the intensities, the cure process could be monitored. Gel times given by the resin suppliers correlated well with the Raman results. It could also be seen that the curing process continues for a long time, up to several weeks. Postcuring will finally complete

the curing process. White and lightly colored gel coats could easily be monitored by Raman spectroscopy, but fluorescent problems were encountered with heavily colored pigments. The curing of laminates containing 50–70 wt % glass fiber mat could also be followed by Raman spectroscopy. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1285–1292, 2004

Key words: composites; curing of polymers; Raman spectroscopy; resins; gel time

INTRODUCTION

The curing reaction is a fundamental stage in the processing of thermosets into composites. During the curing the thermoset is crosslinked and transforms into an insoluble and infusible rigid material. To achieve good quality of the product the curing reaction must proceed in a controllable manner. It is also necessary to carefully follow and check the degree of curing or conversion after the processing of the composite product. There are several techniques available to characterize the curing reaction.¹ They can be divided into methods based on changes in physical properties of the thermoset and methods based on changes in chemical properties of the thermoset.

Physical properties, which change during cure, include shear modulus, hardness, dielectric constant, and viscosity. The composite processing industry uses several empirical techniques based on these properties for cure monitoring. The simplest method is to follow the cure with a stopwatch while mixing a standard amount of thermoset in a beaker; this method gives the gel time. Hardness is another method to determine

the degree of cure in laminates, for example, by using the Barcol impressometer. Among the chemical techniques, differential scanning calorimetry (DSC) is the most important. DSC involves the measurement of the overall heat of reaction (exothermal heat), which is liberated in the crosslinking reaction of the thermoset.

Spectroscopic methods, such as FTIR spectroscopy, are widely used to monitor the progress of fast and complex reactions. FTIR has also been used to monitor the curing reaction of thermosets. The disadvantages are that FTIR equipment is rather expensive and that data analysis is more time consuming and less qualitative. FTIR is also limited to mainly slow reactions at atmospheric conditions. The sample path lengths must be rather short and the sample preparation must be made with care. Remote analysis during processing conditions involving high temperatures or high pressures is also not possible with conventional FTIR instruments.

Raman spectroscopy is an established spectroscopic technique, which recently has become more popular because of developments in instrumentation. In composites a rather common application for Raman spectroscopy is to measure local strains in the polymer matrix.² In Raman spectroscopy a laser beam is used to energetically excite the functional groups in the sample, and the shift of the scattered light compared to the incoming light is used to generate the spectra. Raman spectroscopy has several advantages over infrared (IR) spectroscopy. The spectra produced are well resolved and can easily be quantified. Raman

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spectra can be recorded from almost any sample, without tedious sample preparation. The measurement time is very short; a spectrum can be collected after a measurement of only a few seconds for an optimal sample. It is also possible to use fiber optics for the detection probe, thus making it possible to do on-line measurements from a remote distance, from as far as 10 to 20 m. The laser signal can also be collected through glass windows, thus enabling cure monitoring of a closed molding process.^{3,4}

For thermosets Raman spectroscopy has mainly been used to analyze the structures and curing reaction of urea-formaldehyde and melamine-formaldehyde resins.^{5,6} The residual melamine content in melamine-formaldehyde resins has also been determined.⁷ Very strong Raman signals are produced by C=C double bonds and by aromatic groups, both of which are present in unsaturated polyester and vinyl ester resins. This was used in an earlier study where crosslinked unsaturated polyesters were characterized by Raman spectroscopy.⁸ The optical levitation technique in combination with Raman spectroscopy was used for *in situ* and real-time investigations of the crosslinking of unsaturated polyesters in single microdroplets.⁹ Quantitative determination of the degree of unreacted groups, photocured acrylates, and methacrylates was also done by Raman spectroscopy.¹⁰ Fiber-optic Raman spectroscopy with multivariate analysis was used for *in situ* analysis of epoxy polymers and composites, in which the degree of cure was determined.^{11,12} The isothermal curing mechanisms of unsaturated polyesters were studied in detail by modulated temperature DSC, rheometry, and Raman spectroscopy.¹³ The filler content in calcium carbonate/polyethylene composites was also determined by Raman spectroscopy. The selected band ratio had a good linearity with the volume ratio of filler and matrix at filler contents up to 75 wt %.¹⁴

The aim of this study was to investigate the curing process of unsaturated polyester resins, by using a process Raman spectrometer, equipped with a remote fiber-optic probe. A further aim was to demonstrate the practical applicability of Raman spectroscopy on the process monitoring of composites. The Raman spectrometer used is especially suitable for on-line measurements under process conditions.¹⁵ The curing of vinyl ester resins and gel coats was also studied. The remote fiber-optic probe could be used to monitor the curing at different points in a laminate under real-time processing. The technique should be especially interesting for closed-molding techniques because the Raman signal can be collected through glass windows in the mold, or through the plastic vacuum bag.

EXPERIMENTAL

Materials

A standard orthophthalic unsaturated polyester; ENDUR M 105 TB, and a white gel coat, Maxguard NP, from Neste Polyester (Helsinki, Finland), were used. Colored gel coats blended from the white gel coat were further analyzed. A vinyl ester, Dion 411-C50 (Dow Chemicals, Midland, MI), was also used in this study. All resins were preaccelerated with cobalt octoate. Butanox M50 (Akzo Nobel Nederland, Arnhem, The Netherlands) was used as an initiator for the polyester and gel coat, whereas Butanox LPT, also from Akzo Nobel, was used as an initiator for the vinyl ester. For laminate preparations a chopped strand glass fiber mat, with a surface weight of 450 g/m² from Ahlstrom Glassfibre (Helsinki, Finland), was used. Laminates with 50, 60, and 70 wt % glass fiber content were prepared from the unsaturated polyester.

Raman spectrometer

A prototype process Raman spectrometer (RAMSTAS), developed by VTT Electronics (Oulu, Finland), was used in this work. This instrument is rugged and portable and was especially developed for process analysis. The spectrometer consists of a semiconductor diode laser, a spectrograph, a CCD detector, a fiber-optic probe, and a process PC (see Fig. 1). The length of the fiber-optic probe was 2 m, thus making remote process measurements possible. A housing protects the spectrograph and the CCD camera. The PC has a user interface, which uses the LabVIEW-based data acquisition and analysis software (National Instruments Corp., Austin, TX). The specifications of the Raman spectrometer are shown in Table I.

Raman measurements

Before spectral analysis the initiator was added, and the solution was effectively mixed for 1 min. The samples were cured in reusable circular Teflon molds ($\phi = 30$ mm). For the unsaturated polyester and the vinyl ester 4 g of the resin mixture was transferred into the mold, which gave a 4 mm sample thickness of the cured specimen. For the gel coat samples 0.4 g was used, which gave a 0.5 mm thickness of the cured specimen. These sample thicknesses correspond to typical thicknesses present in lamination and spraying of polyesters, vinyl esters, and gel coats. All measurements were done at 23°C, under atmospheric conditions. Raman spectra were also measured for styrene, and for a sample of the unsaturated polyester containing no styrene, which had been obtained by evaporating the styrene.

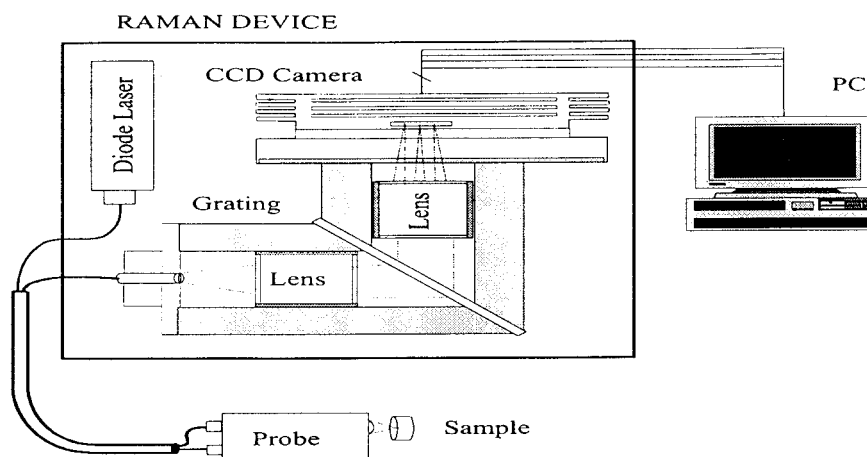


Figure 1 Schematic diagram of the RAMSTAS process Raman spectrometer.

The Raman signal acquisition time was 1 s during the first 2 h of measurements; after this the acquisition time was increased to 10 s. Acquisition times as long as 30 s were necessary when measuring samples cured over 1 week, and the laminates. The laser beam was focused on the sample surface where the Raman intensity is the strongest. After 2 weeks of curing at room temperature, the samples were postcured in an oven for 24 h at 50°C and reanalyzed. It was assumed that the postcuring would give fully cured samples.

The obtained Raman spectra were analyzed by integrating the band areas of the desired bands. Matlab software (MathWorks, Natick, MA) was used for the data evaluation.

Differential scanning calorimetry

Isothermal DSC scans at 25°C were performed on a Mettler Toledo STAR^c System (Stockholm, Sweden). The resins were mixed with the methyl ethyl ketone (MEK) peroxide initiator and placed in sealed DSC pans. The time when the crosslinking reaction exotherm reached its maximum was detected and compared to the Raman analysis.

RESULTS AND DISCUSSION

Unsaturated polyester resin

The spectral changes in the unsaturated polyester attributed to the curing reaction can clearly be seen in

TABLE I
Specifications of the Raman Device

Parameter	Value
Laser wavelength	830 nm
Laser power at sample	200 mW
Spectral range	2000–200 cm^{-1}
Spectral resolution	$\leq 8 \text{ cm}^{-1}$
Spot size at sample	0.6 mm

Figure 2, where the Raman spectra for the unsaturated polyester resin is compared to the Raman spectra for styrene, and the Raman spectra for the same unsaturated polyester with no styrene. The main spectral changes originate from the styrene component in the resin, and the intensity of several strong bands will decrease during the cure (marked with arrows in the figure). The Raman spectra in the 1800–1400 cm^{-1} region for uncured and cured samples are shown in more detail in Figure 3, and the interpreted bands are listed in Table II.

In this area all necessary peaks for the cure monitoring can be assigned. The increase of the spectral slope is attributed to fluorescence of the sample, and it is thus necessary to use separate baselines for the functional groups when calculating their intensity. The intensity of the vinyl C=C band at 1630 cm^{-1} , originating from the double bond in styrene, decreases

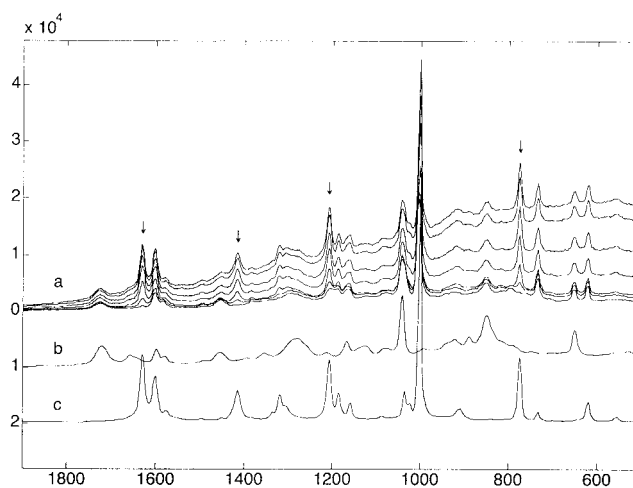


Figure 2 Change in the Raman spectrum during cure of the unsaturated polyester resin (a). The origin of the bands can be seen by comparing to the Raman spectra for the unsaturated polyester resin containing no styrene (b) and styrene (c).

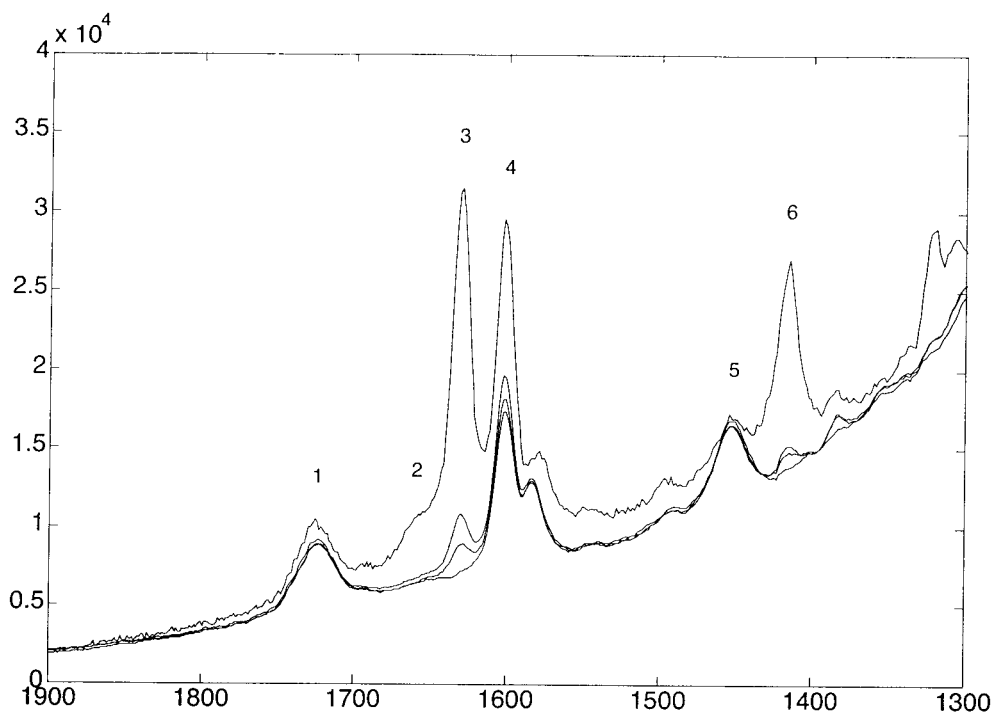


Figure 3 Raman spectrum of the unsaturated polyester before the start of the curing reaction, 30 h and 14 days after the start, and after a 24 h postcuring at 50°C (from top to bottom). The resin was cured with 2 wt % MEK peroxide. The peak assignments are shown in Table II.

to approximately one tenth after 30 h, and the postcuring diminishes the band completely. The vinyl C—H band at 1410 cm^{-1} originating from styrene also decreases, and can hardly be seen in the postcured sample. The intensity of the carbonyl at 1730 cm^{-1} does not change, and this signal can therefore be used as an internal standard. The intensity for the saturated C—H band at 1460 cm^{-1} increases slightly because the vinyl C—H groups are transformed into saturated C—H groups during the crosslinking reaction. The intensity of the aromatic C=C band at 1600 cm^{-1} also decreases, but not so much as for the C=C band. This is partly attributed not only to evaporation of styrene from the open mold during the beginning of the crosslinking reaction, but also to changes in the spec-

tral environment of the styrene molecule during the curing reaction.

A more quantitative picture of the spectral changes during the curing process is obtained by plotting the ratio of the C=C band intensity and the C=O band intensity. This is shown in Figure 4, where the resin was cured with 2 wt % MEK peroxide. Up to 20 min the ratio is constant, and the crosslinking has not started. The crosslinking reaction then proceeds rap-

TABLE II
Raman Bands for the Spectra from the ENDUR M 105 TB Resin

Peak number	Wavenumber (cm^{-1})	Assignment	Component
1	1730	C=O	UP
2	1660/1645	C=C <i>trans/cis</i>	UP
3	1630	C=C vinyl	Styrene
4	1600/1580	C=C aromatic	UP and styrene
5	1460	C—H saturated	UP
6	1410	C—H vinyl	Styrene

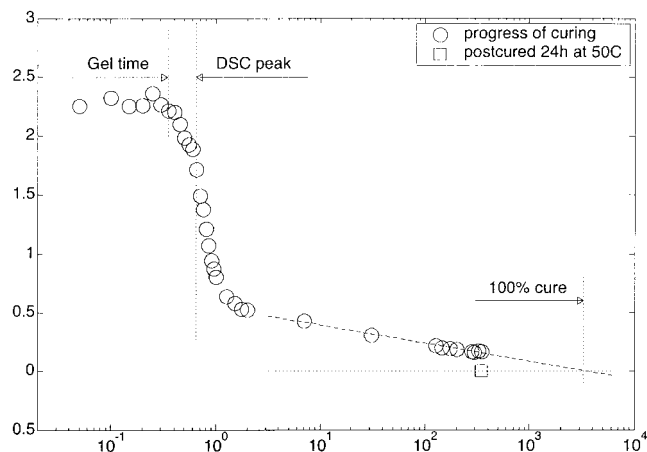


Figure 4 Raman band ratio C=C/C=O for the unsaturated polyester. The resin was cured with 2 wt % MEK peroxide. The gel time given by the supplier and the time for the DSC exotherm maximum are marked.

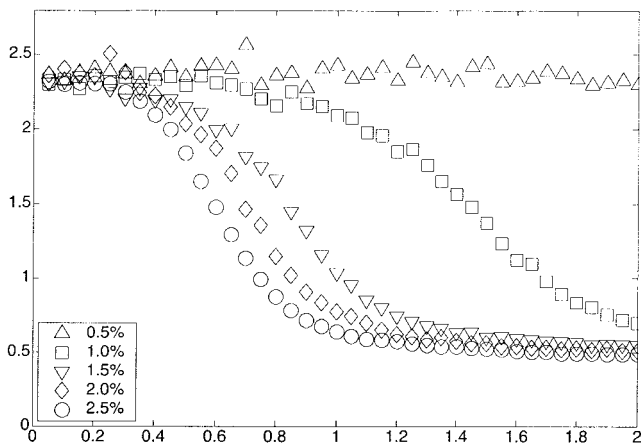


Figure 5 Raman band ratio C=C/C=O for the unsaturated polyester initiated by 0.5, 1.0, 1.5, 2.0, and 2.5 wt % MEK peroxide.

idly after achieving the gel point, and within 2 h approximately 80% of the double bonds have reacted. The gel time given by the resin supplier (20 min) coincides very well with the gel point detected by Raman. After this point the crosslinking reaction is very slow, and it is still possible to detect unreacted C=C bonds 350 h after the start of the crosslinking reaction. The crosslinking reaction is obviously a two-stage reaction with a fast reaction during the gelation, and a slow diffusion-controlled reaction during the vitrification. Postcuring at 50°C for 24 h finally com-

TABLE III
Comparison of the Gel Times Using Different Amounts of Initiator for ENDUR M 105 TB Given by the Supplier and Estimated from the Raman Measurements

MEK peroxide (wt %)	Gel time from Raman data (min)	Gel time given by supplier (min)
0.5	ND	Not given
1	42	40
1.5	24	25
2	18	20
2.5	15	Not given

pletes the crosslinking reaction. By extrapolation it can be estimated that the resin would achieve 100% curing after 3500 h, if the reaction proceeds at room temperature. The time when the exothermal DSC peak reaches a maximum is also shown in Figure 4. This point occurs at the same time as when the crosslinking reaction proceeds most rapidly according to the Raman analysis.

The effect of different amounts of peroxide on the crosslinking reaction can be easily studied with Raman spectroscopy, as shown in Figure 5. The sample initiated with 2.5 wt % MEK peroxide has the shortest initiation time and the fastest rate, whereas the sample initiated with 1 wt % MEK peroxide has a longer initiation time and slower rate. A sample initiated with 0.5 wt % MEK peroxide did not react at all during

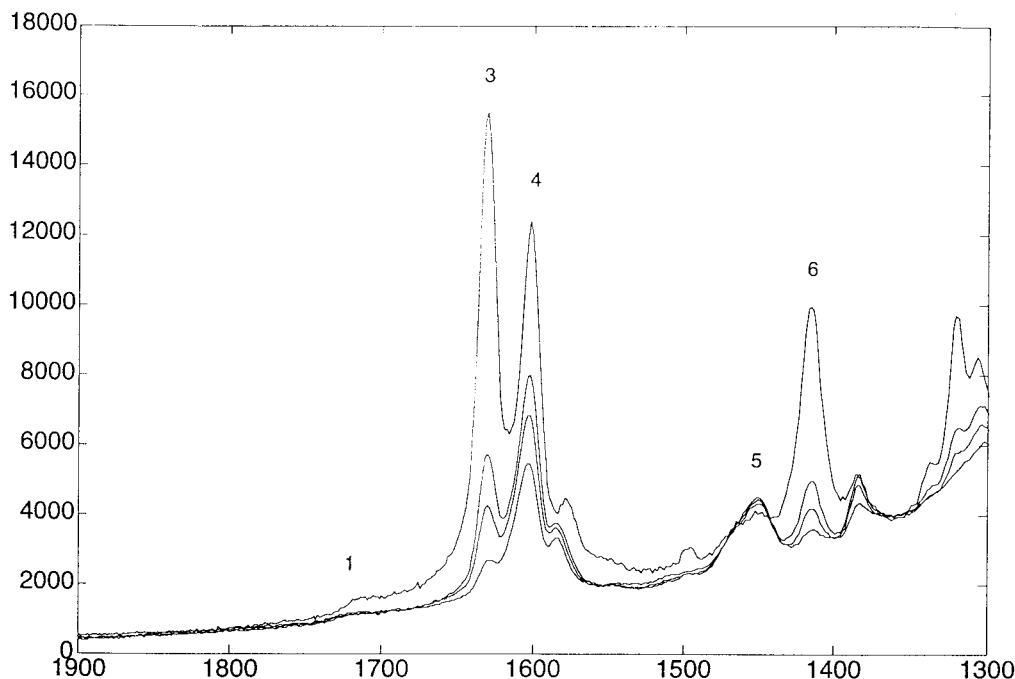


Figure 6 Raman spectra of the vinyl ester resin before the start of the curing reaction, 30 h and 14 days after the start, and after a 24 h postcuring at 50°C (from top to bottom). The resin was cured with 2 wt % MEK peroxide. The peak assignments are shown in Table II.

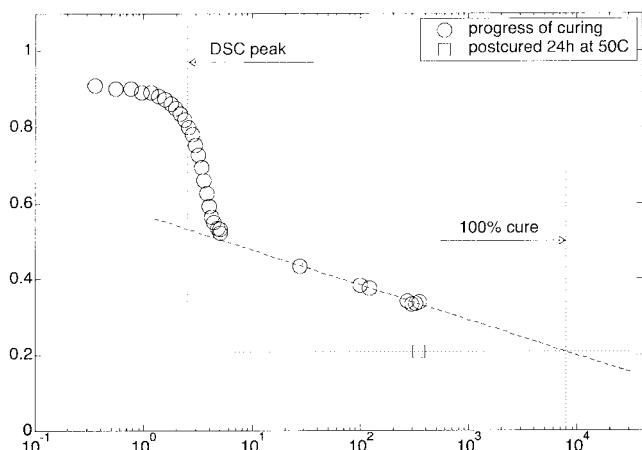


Figure 7 Raman band ratio C=C/aromatic ring for the vinyl ester. The resin was initiated with 2 wt % MEK peroxide.

the first 2 h according to Raman analysis; the crosslinking reaction started after 4 h and needed 30 h to transform into a solid sample. The gel times for the resins given by the supplier correlate very well with the Raman data (see Table III), in which the gel time from the Raman data was taken as the point where the C=C/C=O intensity ratio starts to decrease. The Teflon mold gives a band at 730 cm^{-1} ; this signal could be seen in all measured spectra. It remains stable during the curing reaction, so the signal can be used as a mark of the depth of the Raman laser radiation

penetration. Measurements of clear samples showed that the Raman laser intensity does not noticeably decrease up to a depth of 5 mm from the focus.

Vinyl ester resins

The Raman spectrum of the vinyl ester resin is very similar in the region $1800\text{--}1400\text{ cm}^{-1}$ to the spectrum for the unsaturated polyester (see Fig. 6). The only difference is the very weak carbonyl signal, which is attributed to the chemical structure of the vinyl ester. All other peaks can be assigned to the same functional groups as in the unsaturated polyester. The main backbone of vinyl esters consists of a bisphenol A polyether, with only two carbonyl groups for each polymer chain, whereas in unsaturated polyesters there are two carbonyl groups for each repeating unit. The aromatic band at 1600 cm^{-1} was thus used as an internal standard, although this peak is not completely constant because of the evaporation of styrene. The curing reaction is illustrated by plotting the ratio of the C=C band intensity and the C=C aromatic band intensity, as shown in Figure 7. The reaction proceeds in a similar way as for the unsaturated polyester.

Gel coats

Gel coats are typically applied as thin films ($100\text{--}800\text{ }\mu\text{m}$ thickness) and the sample thickness was therefore $500\text{ }\mu\text{m}$. The spectrum of the white gel coat is shown

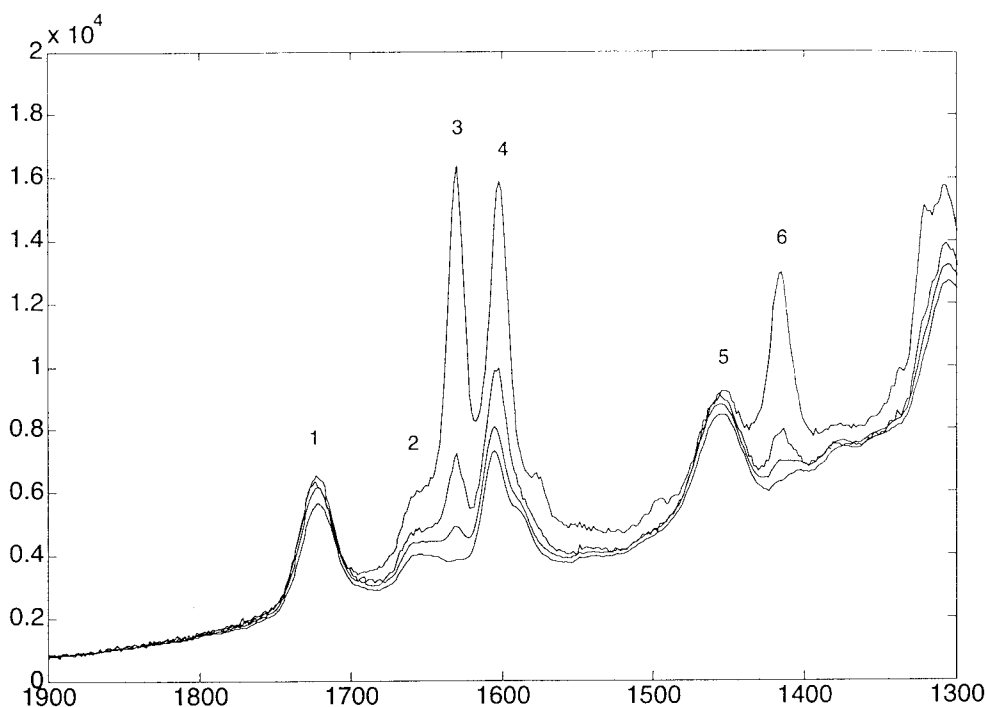


Figure 8 Raman spectra of the white gel coat before the start of the curing reaction, 2 h, 30 h, and 14 days after the start (from top to bottom). The gel coat was cured with 1 wt % MEK peroxide. The peak assignments are shown in Table II.

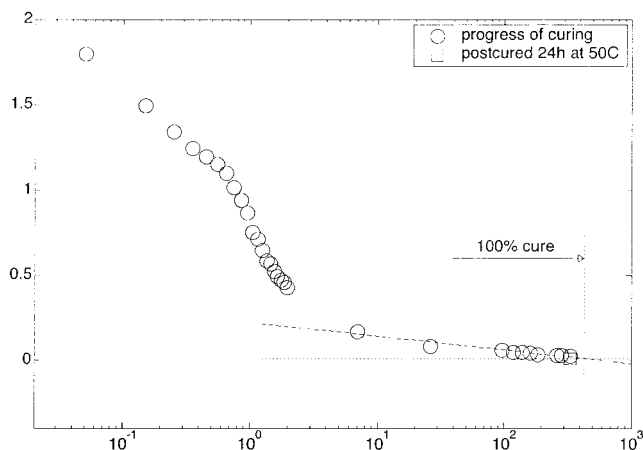


Figure 9 Raman band ratio $C=C/C=O$ for the white gel coat. The gel coat was initiated with 1 wt % MEK peroxide.

in Figure 8, and the peak ratio $C=C/C=O$ during curing is shown in Figure 9. The changes can be interpreted in the same way as for the unsaturated polyester resin. The crosslinking reaction starts almost immediately (12 min) after adding the peroxide, which can be seen as a decrease in the peak ratio. This compares well with the gel time given by the supplier, 7 min. After the gel time the reaction proceeds more slowly initially, but after 30 min the reaction rate increases. The slower initial reaction rate is possibly attributable to the smaller sample volume compared to the unsaturated polyester. The temperature increase resulting from the exothermal reaction will be lower in a smaller sample volume than that in a larger sample, which will affect the reaction rate. Gel coats are pigmented unsaturated polyesters, and the pigments will affect the Raman spectra. In the white gel coat the TiO_2 pigment will give two strong bands at 600 and 450 cm^{-1} , but these will not disturb the measurements. A series of colored gel coats based on the white gel coat were also analyzed. Yellow, brown, blue, and red gel coats were analyzed; of these Raman spectra could be recorded from only the yellow gel coat. The addition of color dyes prevents the penetration of the laser beam into the sample and can also cause fluorescence.

Unsaturated polyester laminates

The Raman spectrum of an unsaturated polyester laminate containing 50 wt % chopped strand mat glass fiber is shown in Figure 10. The glass fiber luminescence causes an increased baseline below 1400 cm^{-1} , but the bands around 1600 cm^{-1} are clearly visible. Cure monitoring of laminates can therefore be done, and an example is shown in Figure 11. The laminate starts to cure around 20 min after the addition of the MEK peroxide, and the curing reaction continues for

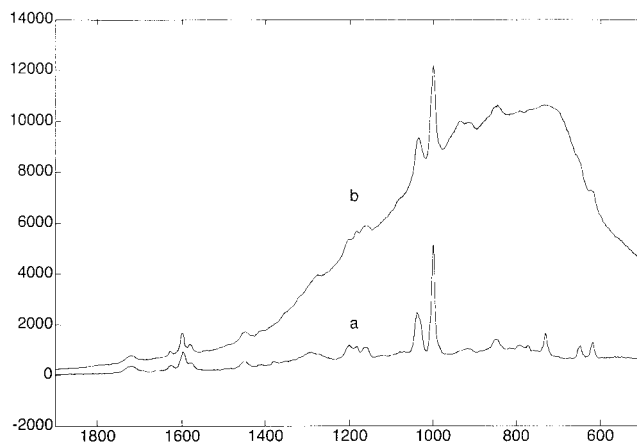


Figure 10 Raman spectra of the neat unsaturated polyester (a) and the unsaturated polyester laminate containing 50 wt % chopped strand mat glass fiber (b).

40 min. At this point the laminate has been transformed into a solid, but it can be seen that the curing is not complete. Unreacted $C=C$ bonds can still be detected up to 350 h after the start of the curing process. Postcuring at 50°C finally completes the crosslinking reaction. Usable Raman spectra with reduced resin bands can be collected from laminates with up to 70 wt % glass fiber content, which is shown in Figure 12. The measurement time was 30 s. Carbon fibers strongly absorb light, and with this Raman setup no spectra could be recorded.

CONCLUSIONS

The curing of unsaturated polyesters can easily be monitored by using Raman spectroscopy. By following the spectral changes during curing, a detailed picture of the curing process is obtained. The styrene

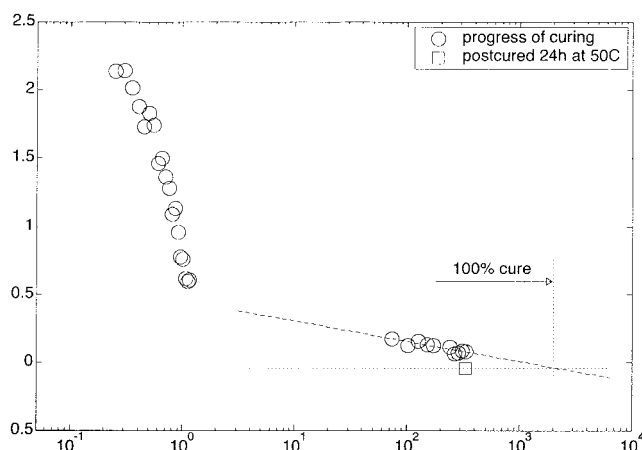


Figure 11 Raman band ratio $C=C/C=O$ for the unsaturated polyester laminate with 50 wt % glass fiber. The resin was initiated with 2 wt % MEK peroxide.

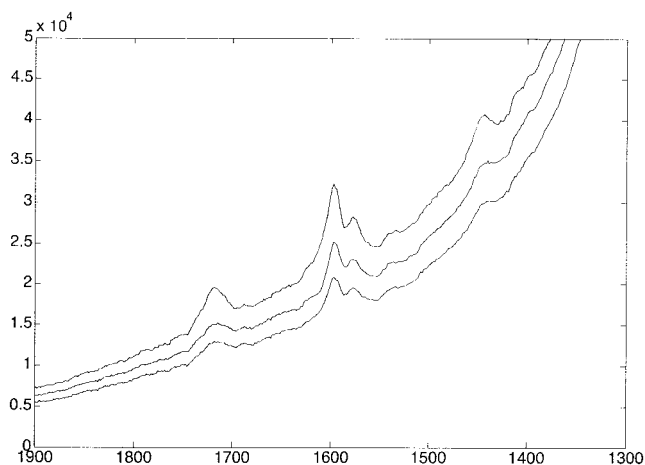


Figure 12 Raman spectra for cured unsaturated polyester laminates with 50, 60, and 70 wt % glass fiber content (from top to bottom). The measuring time was 30 s.

C=C band at 1630 cm^{-1} obviously decreases during the curing, and postcuring diminishes the band completely. The styrene C—H band at 1410 cm^{-1} also decreases, and can as well be used for the cure monitoring. The carbonyl band at 1730 cm^{-1} remains constant, and this band is therefore used as an internal standard. The aromatic band at 1600 cm^{-1} also decreases, which is attributed to styrene evaporation and changes in the spectral environment. By plotting the ratio of the C=C band intensity and the C=O band intensity a quantitative picture of the cure process is obtained. The gel time given by the resin supplier correlates well to the time when the ratio starts to decrease rapidly. It can also be seen that the curing process proceeds for a long time, up to several weeks. Postcuring will finally complete the curing process. Vinyl esters behave in the same way as unsaturated polyesters, and the curing can be monitored in the same way. The biggest spectral difference is the much smaller intensity of the carbonyl band, and the aromatic band is instead used as an internal standard. Heavily colored gel coats cannot be measured because of the pigments that absorb the laser beam and also

cause fluorescence. White and lightly colored (such as yellow) gel coats can easily be monitored by Raman spectroscopy. The curing of laminates containing 50 wt % glass fiber mat could easily be monitored by Raman.

This study shows that Raman spectroscopy has a great potential for process cure monitoring of unsaturated polyesters and vinyl esters. By using a remote fiber-optic probe it is possible to collect on-line data about the crosslinking reaction. Processing techniques such as RM, vacuum infusion, and pultrusion should benefit by using Raman as a cure monitoring technique. However, improvements in research methodology and in data analysis need to be accomplished to achieve quick and easy method for common use.

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References

- Willoughby, B. G. Cure Assessment by Physical and Chemical Techniques, Rapra Review Reports 68; Rapra Technology: Shawbury, UK, 1993.
- Nielsen, A. S.; Pyrz, R. *Compos Sci Technol* 2002, 62, 19.
- Pelletier, M.; Davis, K. *Int Lab* 1996, 11, 11.
- Lewis, I. R.; Howell, G. M. *Handbook of Raman Spectroscopy*; Marcel Dekker: New York, 2001.
- Hill, C. H.; Hedren, A. M.; Myers, G. E.; Koutsky, J. A. *J Appl Polym Sci* 1984, 29, 2749.
- Scheepers, M. L.; Gelan, J. M.; Carleer, R. A.; Adriaensens, P. J.; Vanderzande, D. J. *Vib Spectrosc* 1993, 6, 55.
- Scheepers, M. L.; Meier, R. J.; Markwort, L.; Gelan, J. M.; Vanderzande, D. J.; Kip, B. J. *Vib Spectrosc* 1995, 9, 139.
- Koenig, J. L.; Shih, P. T. *J Polym Sci* 1972, 10, 721.
- Musick, J.; Popp, J.; Trunk, M.; Kiefer, W. *Appl Spectrosc* 1998, 52, 692.
- Jöhnck, M.; Müller, L.; Neyer, A.; Hofstraat, J. W. *Polymer* 1999, 40, 3631.
- Aust, J. F.; Booksh, K. S.; Stelman, C. M.; Parnas, R. S.; Myrick, M. L. *Appl Spectrosc* 1997, 51, 247.
- Chike, K. E.; Myrick, M. L.; Lyon, R. E.; Angel, S. M. *Appl Spectrosc* 1993, 47, 1631.
- van Assche, G.; Verdonck, E.; van Mele, B. *Polymer* 2001, 42, 2959.
- Pakjamsai, C.; Suwanprateeb, J. *J Appl Polym Sci* 2000, 78, 1947.
- Niemelä, P.; Suhonen, J. *Appl Spectrosc* 2001, 55, 1337.