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The Noise in Measurements of Degree of Conversion of (Meth)Acrylates by FTIR-ATR

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Abstract: Noise frequently appears on FTIR-ATR spectra of a cured (meth)acrylic material during determination of its double bond conversion. The goals of this work were to investigate the source of the noise and to find an effective way to reduce it. Two methacrylate-based dental composites, one unfilled methacrylate resin blend, and one acrylate resin system were used as the materials to be tested. Uncured and visible light cured specimens were mounted on an FTIR-ATR and their IR spectra were taken. The characteristics of the spectra were analyzed along with those of other solids and liquids. It was found that the origin of the noise is IR absorption bands of water adsorbed on the surface of the solid specimens. Among several remedies, digital subtraction of the water absorption baseline is demonstrated to be a flexible, easy-to-implement, and time-saving method to reduce or even eliminate the noise of the sample spectrum. Noise reduction improves the quality of FTIR-ATR spectra and makes the measurement of double bond conversion more accurate.

Keywords: FTIR-ATR; Methacrylates; Acrylates; Polymerization; Degree of conversion; Noise reduction

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INTRODUCTION

Because of its direct measuring nature, relatively simple sample preparation, and fast data generation, Fourier transform infrared (FTIR) spectroscopy has been widely used in methacrylate-based dental materials^[1–12] and other acrylic polymers^[13–19] to determine the degree of conversion (DC) of aliphatic double bonds during polymerization. An attenuated total reflectance (ATR) attachment to FTIR extends its measuring capability onto the sample surface as well as into the deep bulk (by grinding away the surface).^[9–12,15–19] FTIR-ATR is more versatile than transmission FTIR because it eliminates the need of KBr (NaCl) plates,^[2–6] sectioning of thin wafers,^[1,2] or cure of the material in a thin film form.^[3–8] This simplifies sample preparation and, more importantly, allows the resin to be cured under conditions closer to practical cases. For instance, the curing conditions for a dental resin composite as a thin film are different from those as a thick restorative—the DC of the former may not truthfully represent that of the latter. FTIR-ATR can also be employed in real-time monitoring,^[15,16] depth profiling,^[17] and simultaneous measurements with another technique.^[18]

Unfortunately, application of FTIR-ATR to the measurement of double bond conversion is often plagued by a high level of noise in the wave numbers of interest, as was found by the present authors and other researchers.^[20] Some examples are shown in Figure 1 with cured methacrylates. Depending on the measured material and DC, the noise may interfere with the signal slightly to severely, making quantification of DC difficult or even impossible.

Based on the fact that the typical noise is associated only with FTIR-ATR—it does not appear in transmission FTIR—it was hypothesized that the noise did not occur randomly but came from an identifiable source. Therefore, investigation of the noise was worthwhile in order to improve the accuracy of FTIR-ATR measurements. The first goal of this work was to search for the origin of the noise. Its identification would enrich our understanding of FTIR-ATR itself. Once the origin had been found, the second goal was to look for a simple and effective way to reduce or even eliminate the noise. This would improve the accuracy of the measurement, which would help expand the application of this technique in polymer chemistry and benefit industries using (meth)acrylates as the monomers, such as dental materials and coatings.

EXPERIMENTAL SECTION

Materials

Visible light curable materials included two hybrid dental resin composites: Z100TM shade A2 (3M, St. Paul, Minn., Lot 9PP) and RenewTM shade A2 (Bisco, Schaumburg, Ill., Lot 19991004), an acrylic resin system,

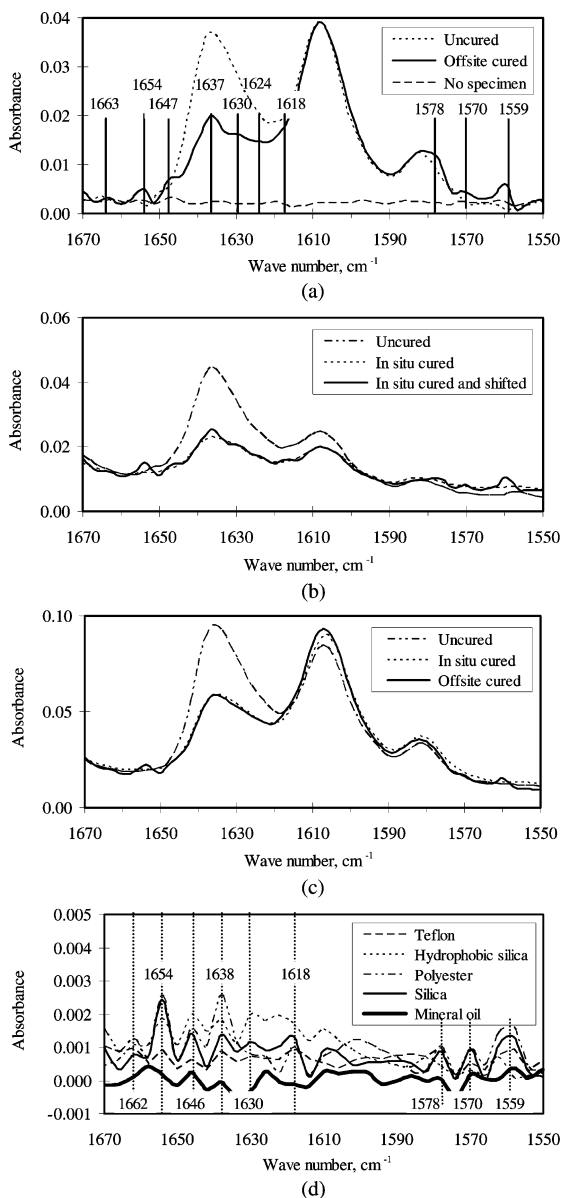


Figure 1. FTIR-ATR spectra of (a) Renew A2: the cured sample shows a number of reproducible noise bands and the bands interfering with the estimation of the aliphatic peak are those at 1654, 1647, 1637, 1630, 1624, and 1618 cm⁻¹; (b) Z100; (c) bis-GMA/TEGDMA blend; and (d) other solids show similar noise bands at identical wave numbers but the liquid does not.

BisCoverTM (Bisco, Lot 0300007729), and an experimental resin blend consisting of bis-phenol A glycidyl dimethacrylate (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) (62:38 by weight) (Esstech, Essington, Penn.) plus 0.30 wt% camphorquinone (Hampford Research, Stratford, Conn.) and 1.0 wt% ethyl 4-dimethylaminobenzoate (Lancaster Synthesis, Windham, N.H.). A VIPTM quartz-tungsten-halogen curing unit (Bisco) was used for irradiation in the 400–500 nm range. Other materials for FTIR measurements were mineral oil (Aldrich, Milwaukee, Wis.), Teflon tapes (Mil Spec, Taiwan), polyester films (Fisher Scientific, Pittsburgh), microscope cover glass (Fisher Scientific), hydrophobic silica (SIP-22, Degussa, Ridgefield Park, N.J.), hydrophilic silica (Aerosil[®] OX-50, Degussa), and colloidal silica suspension (Ludox TM-50, a DuPont product from Aldrich).

Instrument

FTIR measurements were conducted with Spectrum 1000 FTIR spectrometer (Perkin Elmer, Norwalk, Conn.) with a Golden Gate single reflection diamond ATR (P/N10500 series, Graseby Specac, Smyrna, Ga.). The diamond prism measured 2.0 mm × 2.0 mm, with an active measuring area of 2.0 mm × 0.6 mm.

Photo Cure of Specimens

For in situ cure, a resin composite paste was placed on the ATR diamond prism and covered with a clear polyester film (0.25 mm thick). It was slightly compressed into a disk 0.2–0.4 mm thick and about 5 mm in diameter via a glass plate. After the glass plate was removed, the paste with the film was irradiated directly from above for 40 s at 500 mW/cm². For off-site cure, the resin composite paste was sandwiched between two polyester films and compressed into a disk 1 mm thick and about 5 mm in diameter between two glass plates. The top glass plate was removed and the paste was irradiated directly from above for 40 s at 500 mW/cm². The unfilled resins, either the bis-GMA/TEGDMA blend or BisCover, were sandwiched between two polyester films and irradiated for 30 s at 200 mW/cm², producing polymer disks 0.10 mm thick and 12 mm in diameter. All the specimens were allowed to post-cure for 10 min before their IR spectra were taken.

Mounting of Specimens

Before each new specimen was mounted, the diamond prism was wiped clean with acetone-soaked Kimwipes EX-L tissues. For liquid specimens, a drop was deposited and spread on the prism with a disposable pipette. For powder specimens, about 10 mg of material was heaped on the prism

and compressed into a loosely packed cake by a sapphire anvil via a screw clamp with a pressure of 0.6 GPa. For uncured composite pastes, roughly 20 mg of material was placed on the prism and lightly pressed to force an intimate contact. For in situ cured composites, the cured specimen was left on the prism undisturbed or slightly compressed with the sapphire anvil via the screw clamp to create some shifting (see below for the reason). For off-site cured composites and unfilled resins, the specimen, with the protective polyester films removed, was placed on the prism and compressed with its top surface against the prism by the sapphire anvil via the screw clamp with a pressure of 0.6 GPa. No polishing was performed since the surface was very smooth and glossy. For transmission FTIR measurements on the unfilled resins, the uncured resin was spread on a NaCl plate into a thin coat about 0.1 mm thick. The plate was then clamped onto the sample holder with the coat directly in the path of the IR beam. The thin film of cured resin, with the protective polyester films removed, was directly clamped onto the sample holder.

Measurements

FTIR spectra were taken by scanning the specimens 10 times over the 1670–1550 cm^{-1} wave number range with a resolution of 4 cm^{-1} . The background was taken in the same manner only without a specimen on the prism. The background was remeasured every 30 min to minimize the effect of fluctuation of CO_2 in air. The relative double bond concentration of the methacrylates was represented by the height of the absorption band at 1637 cm^{-1} for the aliphatic (H_{al}) and at 1608 cm^{-1} for the aromatic (H_{ar}).^[11] (It was 1634 cm^{-1} and 1582 cm^{-1} , respectively, for BisCover, an acrylate system.) The aromatic band served as an internal standard.^[5] The DC was calculated from the following equation:^[5]

$$DC(\%) = \frac{H_u - H_c}{H_u} \times 100$$

where H_u is H_{al}/H_{ar} of the uncured sample, and H_c is H_{al}/H_{ar} of the cured sample.

Every sample was measured at least three times. The DC data were analyzed by one-way ANOVA with Fisher's least significant difference procedure with a 95% confidence level.

RESULTS AND DISCUSSION

Source of the Noise

Figure 1 shows some typical noise-bearing FTIR-ATR spectra. Table I summarizes the characteristics of the noise bands and their implications.

Table I. Characteristics of the noise bands and their implication and explanation

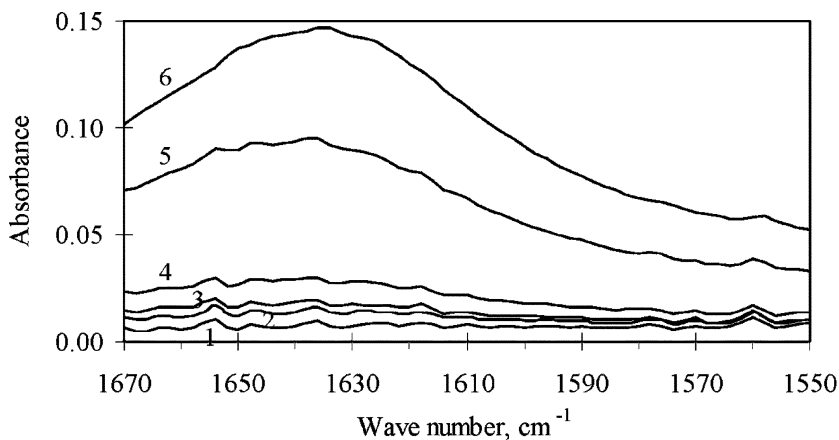
No.	Source	Characteristics	Implication	Explanation
1	Figures 1(a) and 1(c)	They become prominent only when there is a solid specimen on the diamond prism.	Not from an instrumental origin	No specimen, no adsorbed water, no water bands
2	Figures 1(a), 1(b), and 1(c)	There are no typical noise bands for an uncured composite paste or a liquid resin.	Related to the contact between the specimen and the prism, a better contact resulting in lower noise	No solid substrate, no adsorbed water
3	Figures 1(b) and 1(c)	There are usually no typical noise bands for an in situ cured composite. But they will appear when the specimen is slightly shifted on the prism.		In situ cure preserves the intimate contact of the specimen to the prism; a gap forms once the cured specimen is shifted, allowing water to get in
4	Figures 1(a) and 1(c)	Off-site cured specimens always have the noise.		Adsorbed water always present
5	Figures 1(a) and 1(c)	A hard specimen such as a cured composite has higher noise than a soft specimen such as a cured unfilled resin.		A soft solid has better contact to the prism due to its higher deformation
6	Figure 1(a)	They consistently appear only at certain wave numbers.	Not random noise	Since it is water bands, the noise appears systematically rather than randomly
7	Figure 1(d)	In addition to cured composites and resins, all other tested solids display the similar noise features but the liquid does not.	From a ubiquitously present source	In ambient conditions, every solid sample adsorbs water so they all have the water bands

As for the source of noise, one temptation is to associate it with the intrinsically weak signals of FTIR-ATR measurements because FTIR-ATR usually has an absorbance range of 0.01 to 0.1 versus that of at least 0.1 to 1 for its transmission FTIR counterpart. However, the low signal is highly unlikely to be the cause for the following reasons. A weak signal, per se, does not necessarily mean the presence of strong noise. It is the signal-to-noise ratio that matters. A spectrum with a weak signal should be usable as long as the noise is much weaker. In Figures 1(a) and 1(c), the IR spectra of the in situ cured specimens have similarly low absorbance to those of the off-site cured specimens, yet they do not bear the typical noise.

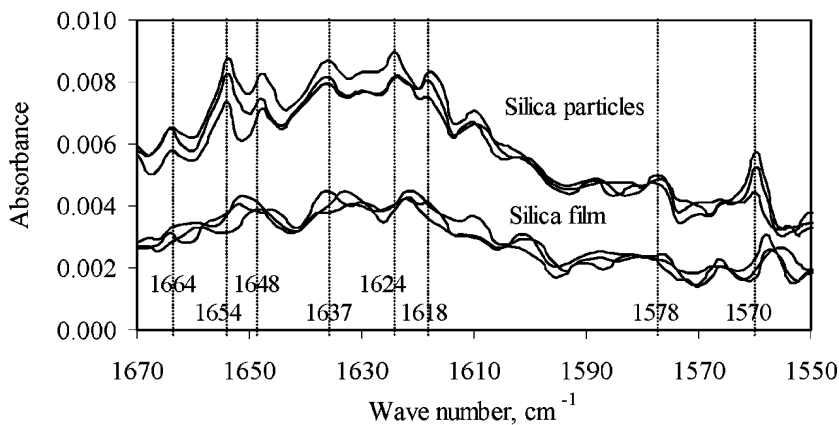
Since the noise does not preexist with the solids (the in situ cured specimens in Figures 1(b) and 1(c)), it must be acquired during the measuring process. A most plausible culprit is water, which is ubiquitously present and has IR absorption in the region where double bonds are measured. Although water may come from four possible sources (water in the specimen, water vapor in air, liquid water, and adsorbed water), all but one can be eliminated based on the experimental observations.

First, because the FTIR spectra of uncured specimens did not have the noise, Figures 1(a)–1(c), the water concentration in the specimens should have been below the detecting level. So it is not the water in the specimen. Second, water vapor in air cannot be the source either. The FTIR-ATR spectrum was generated by subtracting a background spectrum from the one with the specimen. Taken without a specimen on the diamond prism, the background spectrum already included IR absorption of water vapor in air above the prism. With a specimen in place, the open space above the prism was considerably reduced if the contact was poor or virtually nonexistent if the contact was good. In either case, smaller water vapor bands should have been detected for the sample spectrum. In other words, the background spectrum should have stronger water absorption than the sample spectrum. After subtracting the background, the resultant spectrum should have dips rather than humps at the locations where the in-air-water bands appear, although most of them may be too weak to be discernable. That is exactly what is observed for most uncured composites, which often show a small dip at the wave number 1654 cm^{-1} , where the most predominant noise band lies in the region (Figure 1(a)).

Third, the evidence in Figure 2 can eliminate the possibility of free liquid water. With a thick film of deionized water on the diamond prism, the spectrum of Figure 2(a) contains a huge broad band without many fine features. This is the characteristic water band due to the H-O-H bending vibration at 1640 cm^{-1} .^[21] When the puddle of water was gradually compressed into a thin film under a clean cover glass, some of the typical noise bands appeared. As the film thickness got smaller under



(a)



(b)

Figure 2. FTIR-ATR spectra of (a) 1: dry cover glass, 2: damp cover glass, 3–5: arbitrary thickness of a liquid water film between a cover glass and the prism—the lower the number, the smaller the thickness, and 6: water only; and (b) colloidal silica films and their crumbled powders.

higher pressure, the finer bands became stronger while the broad band became weaker. Note that even in the absence of the air gap, the typical noise was still present. Finally, without liquid water, the spectrum of the macroscopically dry glass showed features identical to those of the other solids in Figure 1(d).

Another piece of evidence comes from Figure 2(b), which displays two groups of spectra from the same material, thin films of coalesced silica particles, produced by depositing a colloidal silica suspension on the

prism and evaporating the water dispersant. Still containing some residual water, the silica films produced spectra with the broad band of liquid water but no typical noise bands (the lower group of spectra). Once the film was crumbled into small powders (the upper group), the characteristic noise bands appeared, together with the liquid water band. The inference of Figure 2(b) is that it is how well the specimen contacts the prism that determines if the noise bands appear.

Through the elimination of three possible sources of water, only one water source remains. It is consequently hypothesized that adsorbed water on the specimen surface absorbs IR and produces the bands that we call "noise." Experimental supports for the hypothesis are plentiful. For example, there are no "noise" bands if there is no solid surface for water to adsorb on (Spectrum 1 in Figure 2(a)) or no space between the solid and the prism for it to remain (lower group of spectra in Figure 2(b)). Again, the water adsorbed on the prism has already been included in the background and will not appear in the sample spectrum. The water adsorption mechanism can satisfactorily explain all the characteristics listed in Table I, and the explanations are given in the table.

IR absorption of bound water has been investigated.^[22] Both strongly bound water and less firmly bound water on methylcellulose produce a combined band in the region from 1580 to 1700 cm^{-1} , corresponding to the bending mode of water molecules. This band is also well represented in this work by bands centered at around 1654 in Figures 1 and 2.

Reduction of the Noise

The noise bands at 1638 cm^{-1} , and 1630 cm^{-1} to a lesser extent, overlap with the band at 1637 cm^{-1} for the aliphatic double bond. Note the asymmetry of the aliphatic double bond peak at 1637 cm^{-1} and two small humps at the right-hand side, Figure 1(a). Because of its addition to the band, the noise erroneously increases the double bond concentration, causing an underestimation of DC. Therefore, reducing the noise not only makes the spectrum look better and easier for quantification, it also makes the DC higher and the measurement more accurate.

The simplest way to exclude water absorption is to cure the specimen in situ. This is likely to preserve the intimate contact between the specimen and the prism so that no water can enter the interface, Figures 1(b) and 1(c). This approach, however, can prevent the noise from occurring only under the right conditions. It is not always possible to guarantee a tight interface once a composite paste is cured. On many occasions, the noise appears even after in situ cure. Polymerization shrinkage is presumably responsible for the breaking up of the interface. The dimensional

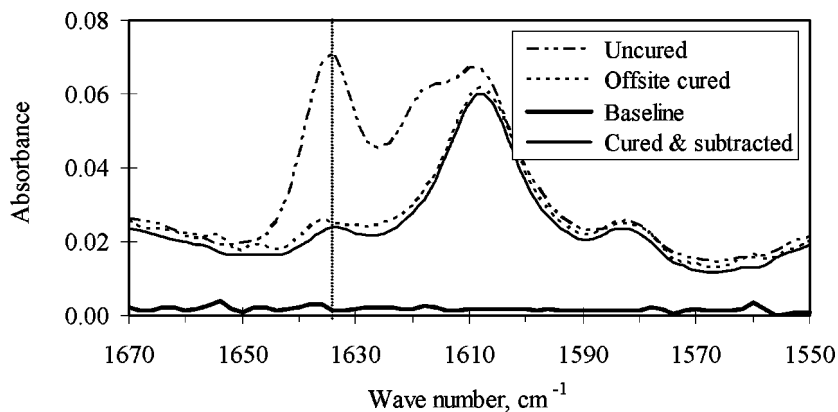
change of the curing specimen alters the registry previously presented at the interface so that the specimen could slightly separate from the prism. Use of a thin film of specimen can often significantly reduce the level of noise. Because of its higher flexibility, a thinner specimen can better preserve the contact. Despite this precaution, however, the in situ curing technique still has two drawbacks that limit its applications. One is that it cannot be applied to an off-site cured specimen, which is how most specimens are prepared. The other is that it cannot measure DC of the bulk material or the surface, cured in air or covered with other materials.

An attempt was made to displace adsorbed water by immersing the specimen in the following liquids with ascending hydrophilicity: mineral oil, polytetrahydrofuran, PEG 300, and glycerin. None of these could reduce the noise bands. The reason is thought to be that the liquids with low hydrophilicity cannot remove water from the solid surface, while those with high hydrophilicity may contain too much water themselves.

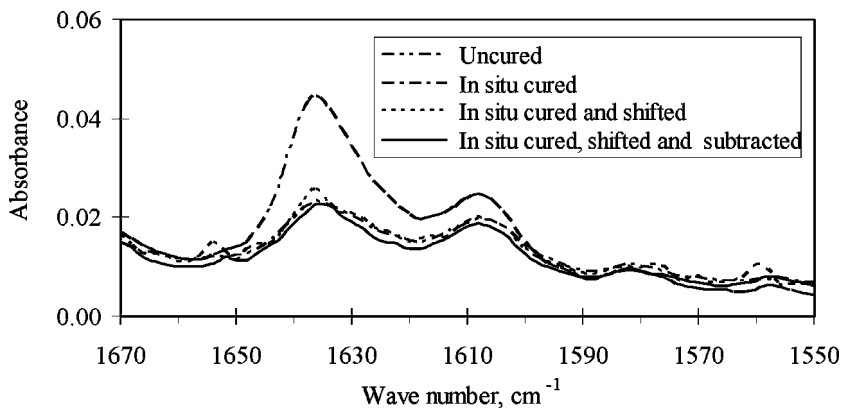
A straightforward approach is probably to build a chamber around the specimen on the prism and use pure dry nitrogen to purge it to remove adsorbed water. An added advantage of using nitrogen is that the clean gas also makes the background more stable because of the absence of CO₂ and hydrocarbons. However, purging requires capital expenditure and complicates the measuring procedure. The time spent on purging can be another disadvantage.

Although physically removing adsorbed water is formidable, as demonstrated above, it was found that it is relatively simple to do it digitally using computer software. An easily implemented technique is to use the water absorption baseline subtraction (water subtraction). The baseline is a spectrum measured from a solid that had nothing but the water bands in the wave number range of interest. Many solids can serve as the candidate for the baseline material, such as those in Figure 1(d). In this study, hydrophilic silica powder was preferred because of its relatively strong water bands. During the water subtraction process, reduction of the most predominant water band at 1654 cm⁻¹ of the sample spectrum is monitored. The computer program can progressively increase or decrease the magnitude of the water bands of the baseline to match those of the specimen until the pairs cancel one another. Because of the sophistication of the software, the whole subtraction operation usually takes less than 10 s. In principle, the subtraction is similar to the subtraction of water background with an aqueous solution,^[21] only this time a relatively small baseline is being subtracted so the introduction of a potential error is not as a big concern as in the solution case.

Figure 3 displays representative spectra before and after water subtraction for BisCover and Z100. Water subtraction corrects the symmetry of the aliphatic band of the cured specimens and centers it with that of the uncured specimens. Table II presents the calculated DC data for



(a)



(b)

Figure 3. Noise reduction by water baseline subtraction of (a) BisCover and (b) Z100. The calculated DC is 42%, 35%, and 40% for the in situ cured, in situ cured and shifted, and in situ cured, shifted, and subtracted techniques, respectively.

Table II. Comparison of degree of conversion of unfilled resins ($n = 3$)

Unfilled resin	DC without water subtraction, %	DC with water subtraction, %	DC from the transmission mode, %
Bis-GMA/ TEGDMA	55.8 (0.5)	58.1 (0.3) ^a	57.8 (0.9) ^a
BisCover	80.9 (1.0)	88.4 (2.3) ^a	86.8 (1.0) ^a

^aThese values in this row are statistically equivalent ($p < 0.05$).

the two unfilled resins. Without the interference of water bands, the DC of the bis-GMA/TEGDMA resin blend is more than 2% higher and closer to that from the transmission measurement. As can be envisaged, when the band of aliphatic double bond becomes smaller, for example, due to the presence of more filler or higher conversion, the deviation due to water interference increases because the signal gets weaker while the noise remains more or less constant. This is indeed the case demonstrated in Table II. BisCover, a multifunctional acrylate-based resin, can reach a DC higher than 80% after cure, and its DC after water subtraction is almost 10% higher than that before water subtraction.

Finally, water subtraction on the spectra of Z100 in Figure 1(b) resulted in a new spectrum in Figure 3(b). Similar to the above resin cases, the water subtraction treated spectrum yields a DC similar to the in situ cured one and is 7% higher than the untreated. With the conversion only about 40%, the 7% absolute difference is equivalent to a 20% increase in the relative DC. In principle, when a perfect match is found, all the water bands of the specimen should disappear after water subtraction. Practically, due to noises from other sources, the treatment seldom removes all the water bands: the extent of removal depends on the quality of both specimen and baseline spectra.

CONCLUSIONS

IR absorption of water adsorbed on cured (meth)acrylates produces extraneous bands, seen as “noise,” in their double bond concentration measurements using FTIR-ATR. A simple and effective way to reduce the “noise” is subtraction of a baseline containing only water absorbance bands from the sample spectrum. This not only improves the quality of the spectrum but also systematically results in a higher and more accurate degree of conversion.

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