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Determination of extent of reaction in dimethacrylate-based dental composites using solid-state ^{13}C m.a.s. n.m.r. spectroscopy and comparison with *FT*i.r. spectroscopy

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The instrumental conditions required for the determination of the extent of reaction in dimethacrylate-based dental composites using high-resolution solid-state ^{13}C nuclear magnetic resonance (n.m.r.) techniques have been investigated. In the absence of paramagnetic fillers, clearly resolved carbonyl resonances for reacted and unreacted methacrylate groups were observed. The two peaks showed considerably different relaxation times using cross-polarization excitation, and accurate relative intensities could only be obtained using direct excitation of the ^{13}C nuclei with a pulse interval of at least 30 s. Chemical shielding anisotropy spinning sidebands were observed for the reacted peak, but not for the unreacted. A spin-rate-dependent centreband intensity correction factor to account for this difference was evaluated using model triethyleneglycol dimethacrylate materials. The proportion of unreacted methacrylate groups determined using n.m.r. was essentially unaffected by spin rate, dipolar decoupling field strength and temperature, but was only about one-half that determined using infra-red spectroscopy. The origin of the discrepancy is as yet unclear.

(Keywords: solid-state n.m.r.; i.r. spectroscopy; dental materials)

INTRODUCTION

Polymer composites are used in dentistry where good aesthetics are important. Their colour and translucency are good, and they are durable in service. They have also been developed as restorative materials for molar teeth. In order to compete with the hard-wearing characteristics of amalgam, they tend to be heavily loaded with ceramic for this application, a feature that may adversely affect colour and translucency.

Dental polymer composites consist of two principal components, an organic matrix and a powdered ceramic phase, such as quartz or barium aluminoborate silica glass[1]. The diameter of the ceramic particles ranges from 0.04 to 8 μm, and the volume proportion ranges from 25 to 70%. The organic matrix is usually formed by polymerization of aromatic or urethane dimethacrylates, typical examples of which are shown in *Figure 1*. Many composites are made from 2,2-bis[4-(2-hydroxy-3-methacryloylpropoxy)phenyl]propane, commonly known as bis-GMA. Bis-GMA is used because of its large molecular size, which has the effect of reducing the proportion of the molecule that undergoes polymerization, hence ensuring a low overall shrinkage of about 2%. However, bis-GMA has a high viscosity, and low-viscosity monomers such as triethylene glycol dimethacrylate (TEGDMA) are commonly added as diluents. Urethane dimethacrylates, when used in place of bis-GMA, have the advantage that when cured they have reduced sensitivity to water. Urethane dimethacrylate monomers have lower viscosities than bis-GMA, hence lower proportions of diluent are required.

Two types of activation of polymerization are used in these composites. The first method involves free-radical initation (chemical cure, c.c.). The material is supplied as a two-paste system, one containing benzoyl peroxide as free-radical initiator, the other containing an accelerator, typically a tertiary amine such as dimethylaminoethyl methacrylate, which, on mixing the two components, stimulates the fragmentation of the benzoyl peroxide into free radicals at room temperature, thus initiating polymerization of the unsaturated methacrylate groups. The second method is cure by visible light (v.l.c.), using an initiator system comprising an α-diketone, such as camphoroquinone, together with an amine reducing agent. This combination generates free radicals on exposure to light at about 470 nm. V.l.c. composites are supplied as one-pack systems. Since light can penetrate to only a limited depth, care has to be taken to use the material in relatively thin sections, and to irradiate for a

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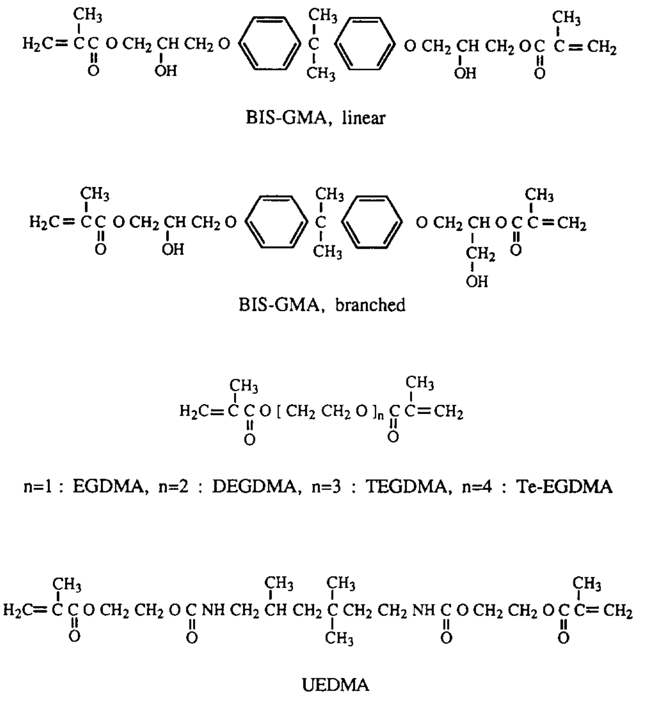

Figure 1 Structures of constituents of materials studied

sufficient time to promote good cure throughout the sample.

The properties and performance of these highly crosslinked materials are critically dependent on the degree of conversion. In normal circumstances, the composites are polymerized *in situ* at body temperature, 37°C. The crosslinking reaction in these dimethacrylate systems is a self-limiting process, and the rate of reaction diminishes virtually to zero when the degree of conversion reaches 60–70%, though some dental procedures do exist that provide for extra-oral curing at elevated temperatures where the degree of conversion may reach 90–95%. Hitherto i.r. spectroscopy has been the principal method of determining this property, by comparing the intensity of the alkene C=C peak at ca. 1640 cm^{-1} to the aromatic C=C peak at ca. 1608 cm^{-1}. However, this method is inappropriate if no aromatic component is present, and there are also considerable problems in defining a suitable baseline and in deciding on a suitable measure of peak intensity (peak height or integral)[2].

High-resolution solid-state n.m.r. spectroscopy is now a standard characterization tool in many areas of chemistry, including polymer science[3–5], the most common nucleus studied being the ubiquitous ^{13}C isotope. Using this technique, it is possible to obtain chemical structural information similar to that given by solution-state n.m.r. for systems where the use of the solution state is impossible, either because it is the properties of the solid state itself that are of interest, or because the materials under investigation are totally insoluble without chemical degradation, as in the present work. Magic-angle spinning (m.a.s.) and dipolar decoupling (d.d.) during acquisition are used to remove (or substantially reduce) severe line-broadening effects encountered in the 'normal' spectra of static solid samples, while the cross-polarization (c.p.) technique is used to enhance the sensitivity. However, in quantitative applications of c.p./m.a.s./d.d. n.m.r. spectra, several potential problems must be addressed: (i) spinning sidebands arising from chemical shielding anisotropy (c.s.a.); (ii) relaxation phenomena during the c.p. process; and (iii) interference between molecular motion and both m.a.s. and d.d., which may lead to severe line broadening.

In m.a.s. n.m.r. of solids, nuclei having a non-zero c.s.a. produce a centreband/sideband pattern, the intensities of which depend on the magnitude of the spinning frequency relative to the dispersion of resonance freqencies. In ^{13}C n.m.r. of rigid materials, these sidebands typically are large for unsaturated nuclei, but small, often negligible, for saturated nuclei. The sidebands are reduced by sufficiently rapid molecular motion, being eliminated entirely by fast isotropic rotation. Although they may be substantially reduced by several techniques[6,7], thus simplifying the spectrum, the remaining centreband intensities are not quantitatively reliable.

In the c.p. technique, the detected signal depends on the time constants for three spin relaxation processes during the c.p. stage, termed the contact time: (a) growth due to transfer of magnetization from ^{1}H to ^{13}C (time constant T_{CH}); and (b) decay due to relaxation of ^{1}H and ^{13}C in the rotating frame (time constants $T_{1\rho H}$ and $T_{1\rho C}$ respectively). Normally the condition $T_{CH} \ll T_{1\rho H}, T_{1\rho C}$ is fulfilled. However, all three time constants depend on molecular structure and dynamics, so that differential relaxation of structurally distinct nuclei may lead to inaccurate quantification. In addition, the intensity depends on the ^{1}H longitudinal relaxation time T_{1H}, which governs the recovery of the ^{1}H magnetization during the recycle interval between time-averaged spectrum acquisitions, T_{rec}, though this factor can be eliminated providing the condition $T_{rec} \geqslant 5T_{1H}$ is fulfilled. The difficulties associated with differential relaxation during c.p. may be circumvented by using the standard method of excitation in solution-state pulsed n.m.r., viz. a pulse at the resonance frequency of the observed nucleus combined with m.a.s. and d.d. to remove line broadening. This technique is referred to as single-pulse excitation (s.p.e.). The disadvantages of s.p.e. are that the sensitivity gain of c.p. is lost, and that the repetition rate of the pulses is governed by the longitudinal relaxation time of the ^{13}C nuclei, T_{1C}, which is normally significantly greater than T_{1H}. However, peak intensities in s.p.e. spectra are quantitatively reliable, provided $T_{rec} \geqslant 5T_{1C}^{max}$, where T_{1C}^{max} is the largest value of T_{1C} for the peaks of interest.

The influence of molecular motion may be significant when the average motional frequency matches either the m.a.s. frequency or the resonance frequency of the protons in the d.d. field[8]. Under these conditions, the efficiency of the line-narrowing techniques is very much reduced, and the ^{13}C peaks may be severely broadened. Whether either of these effects is operative may be checked by varying the m.a.s. or d.d. frequency, or by varying the sample temperature.

The objective of this work was to investigate the practicality of high-resolution solid-state n.m.r. techniques for characterizing highly crosslinked dental composites based on dimethacrylate monomers, particularly with a view to determining the proportion of unreacted methacrylate groups for comparison with the i.r. method. Several proprietary composite products were examined, as well as model materials prepared from the single-monomer triethylene glycol dimethacrylate, using both c.p. and s.p.e. excitation tecnques for a wide range of instrumental conditions. A few reports of high-resolution solid-state n.m.r. studies on dimethacrylate systems have been published[9–12], but only the c.p. technique was used, and although the spectra were analysed quantitatively, no systematic investigation of the effects of excitation technique or of instrumental conditions appeared to have been made.

EXPERIMENTAL

Materials

Two proprietary composite resins and two bonding agents were investigated. Details of the sources, constituents, physical form and curing method of the materials are listed in *Table 1*. The systems were mixed according to the manufacturers' instructions, and polymerized in a plastic disc mould. The dimensions of circular specimens were 3 mm in diameter and 2 mm in thickness. For visible-light-cured systems, the specimens were polymerized by illuminating the resin-filled plastic disc with visible light from a Coltène[R] lamp, Coltolux curing unit model 204, for 60 s on both sides of the specimens. The specimens were further cured for 24 h at ambient temperature. For chemically cured systems, the resins were mixed in equal proportions and cured in the same mould for 24 h at room temperature. All samples were ground using a pestle and mortar into a fine powder suitable for m.a.s. n.m.r.

In addition, model samples were prepared from TEGDMA alone using v.l.c. by a 50/50 (by weight) mixture of *dl*-camphoroquinone and 2-(dimethylamino)-ethyl methacrylate, the initiator mixture being incorporated in the monomer at 2 wt%. These materials were supplied by Aldrich Chemical Co. Ltd, and were used as received.

N.m.r. spectroscopy

^{13}C m.a.s. spectra were obtained using a Varian Associates Unity 300 spectrometer operating at 75.5 MHz and equipped with a Doty Scientific Industries 7 mm high-speed m.a.s. probe. The normal radiofrequency field strength used for cross-polarization and dipolar decoupling was ca. 50 kHz. Spectra were obtained using both c.p. and s.p.e. excitation with m.a.s. and d.d. Spectrum deconvolution was performed using manufacturer-supplied software. For operation at ambient temperature, separately regulated bearing and drive air supplies were used. For spectra run at −20°C, the probe was operated using a single input stream of cooled nitrogen gas, which supplied both bearing and drive functions. The maximum spinning rate at −20°C was limited to ca. 3 kHz.

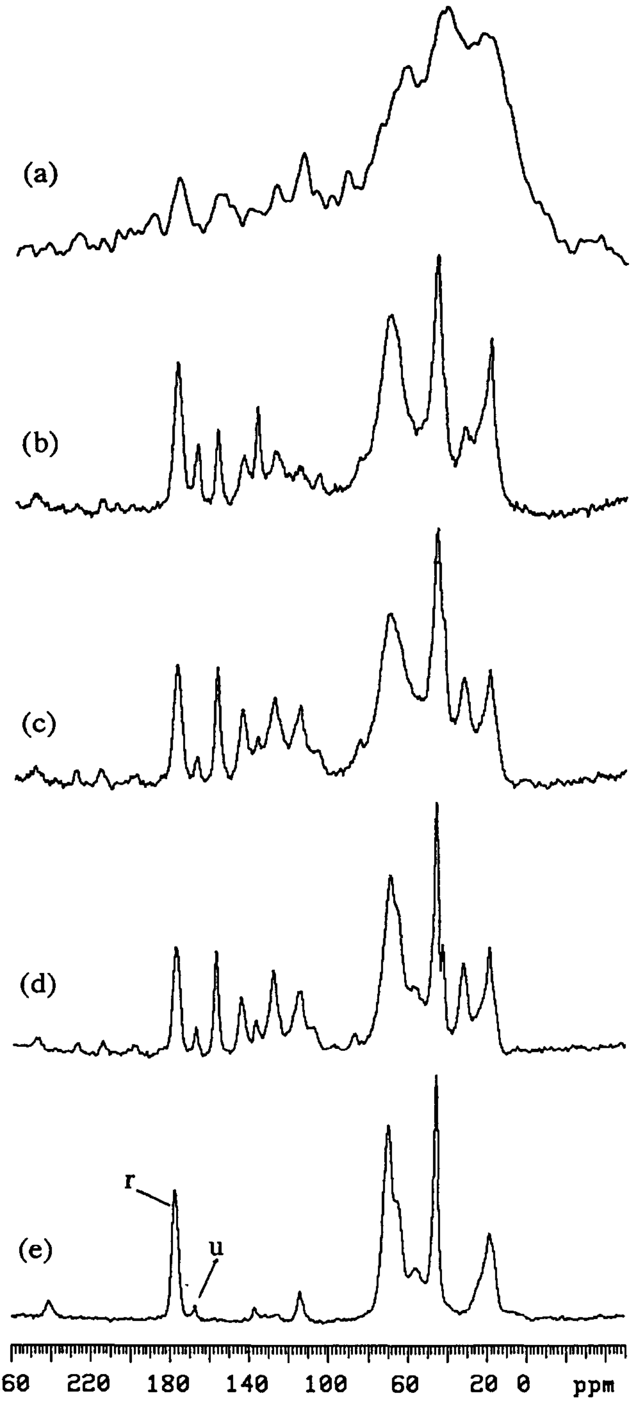

Figure 2 ^{13}C c.p. spectra of materials prepared by v.l.c.: (a) Tetric; (b) Z100; (c) Duo Bond; (d) Coltène bonding agent; (e) TEGDMA. In (e), the labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively. All spectra were obtained using a contact time of 2 ms, a pulse interval of 3 s, and a spin rate of 5.1 to 5.3 kHz

Table 1 Proprietary materials used in this study

Product	Batch	Type	Cure[a]	Principal components[b]	Manufacturer
Tetric	580040	Single paste; filled	V.l.c.	Bis-GMA, TEGDMA, UEDMA, YbF_3	Ivoclar-Vivadent, Liechtenstein
Z100	93B02A	Single paste; filled	V.l.c.	Bis-GMA, TEDGMA, ZrO_2/SiO_2	3M Health Care, UK
Duo Bond	050290-16	Two liquids	V.l.c., c.c.	Bis-GMA, TEGDMA	Coltène AG, Switzerland
Coltène bonding agent	–[c]	Single liquid	V.l.c.	Bis-GMA, TEGDMA	Coltène AG, Switzerland

[a] V.l.c. = visible-light cure; c.c. = chemical cure
[b] See *Figure 1* for abbreviations and structure
[c] Sample supplied in bulk by manufacturer

I.r. spectroscopy

Transmission *FT*i.r. spectra were obtained using a Perkin–Elmer model 1710 spectrometer. Monomer spectra were recorded as one scan over the range 650 to 4000 cm^{-1} using a drop of the resin smeared between NaCl plates. For the sample supplied as a pair of pastes, the individual components were examined separately to avoid polymerization, which takes place on mixing. For polymerized resins, ca. 2 mg of the powdered resin was pressed into a pellet with approximately 70 mg of i.r.-grade KBr. Spectra were obtained by time-averaging 30 scans over the range 650 to 4000 cm^{-1}.

RESULTS AND DISCUSSION

Comparison of c.p. and s.p.e. ^{13}C n.m.r. spectra

Figure 2 shows ^{13}C c.p./m.a.s. spectra using comparable conditions for the five v.l.c. systems examined. All except the Tetric proprietary composite give reasonably well resolved spectra. The observation of very broad peaks for Tetric was attributed to the presence of paramagnetic YbF_3 as a filler, which rendered the n.m.r. technique useless as a measure of residual unsaturation; this system was not therefore studied further. The peaks in the remaining materials were too complex to assign in detail except for the carbonyl peaks at 168 and 178 ppm, which were assigned to unreacted and reacted methacrylate groups respectively. These peaks are well resolved from each other, and moreover are not overlapped by spinning sidebands from aromatic peaks provided the spin rate is greater than ca. 5.3 kHz. This method potentially therefore offers an excellent way of determining residual unsaturation if suitable quantitative n.m.r. conditions can be found.

Recognizing the sensitivity advantages of the c.p. technique, we first investigated the effect of varying the contact time. *Figure 3* shows the variation of the carbonyl peaks with contact time for Coltène bonding agent, results that were typical of the other samples also. It is apparent that, whereas the intensity of both reacted and unreacted carbonyl peaks passes through a maximum, as expected, the time constants are not the same for the two peaks. The relative intensity of the peaks depends strongly on the contact time, so that this method is inappropriate as an absolute method of determining residual unsaturation. The fact that the unreacted peak develops over a longer timescale than the reacted peak is consistent with greater mobility of the unreacted group at the end of a chain.

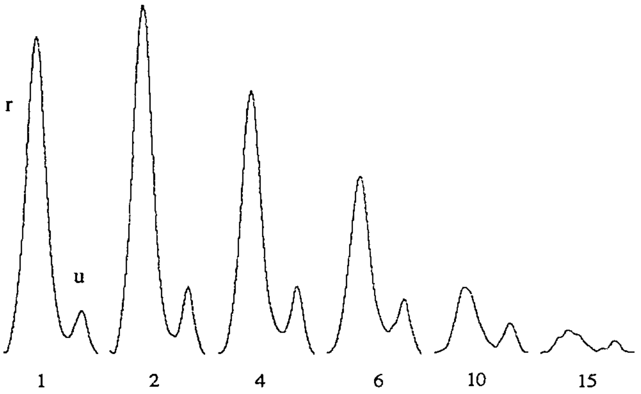

Figure 3 Variation of the carbonyl region with contact time (ms) in c.p. spectra of Coltène bonding agent. The labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively

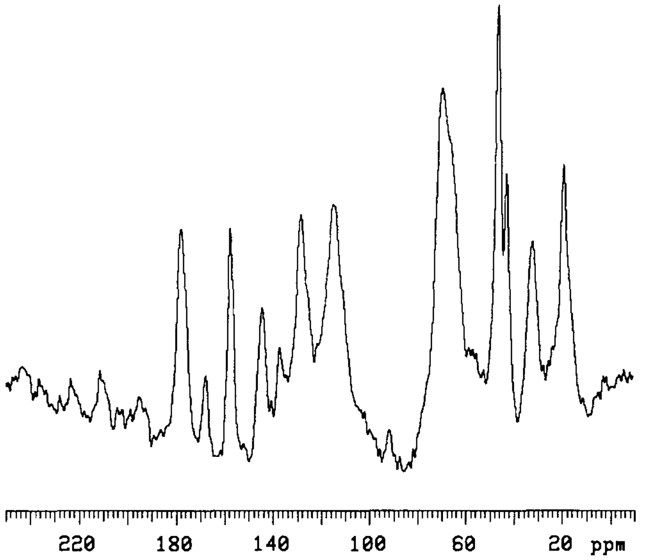

Figure 4 ^{13}C s.p.e. spectrum of Coltène bonding agent. The pulse interval was 32 s and the spin rate was 5.5 kHz

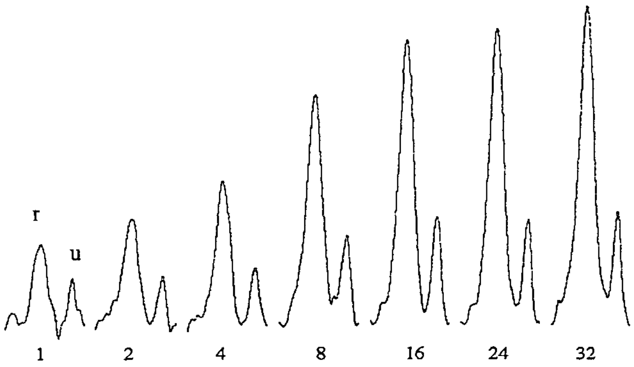

Figure 5 Variation of the carbonyl region with pulse interval (s) in s.p.e. spectra of Coltène bonding agent. The labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively

Turning attention to s.p.e. excitation, *Figure 4* shows the s.p.e. spectrum of Coltène bonding agent. Compared with the c.p. spectrum in *Figure 2d*, a broad background resonance is apparent in the s.p.e. spectrum. This arises from ^{13}C nuclei in the Kel-F polymer in which the m.a.s. probe assembly was housed. Kel-F is a non-protonated poly(chlorofluoroethylene), so ^{13}C resonances are not excited by c.p. from protons. Hence the background peaks do not appear in c.p. spectra. However the Kel-F peaks are excited by s.p.e. pulses, although broadening by ^{13}C–^{19}F dipole–dipole interactions and ^{13}C c.s.a. is not removed by m.a.s. or proton d.d. and the background peaks appear as poorly resolved baseline undulations. Fortunately, the background peaks do not interfere significantly with the observation of the carbonyl resonances.

Figure 5 shows the variation of the carbonyl region with the pulse interval for s.p.e. spectra. Both reacted and unreacted peaks approach an asymptote as the interval increases, as expected. The time constant for the reacted peak (ca. 10 s) is longer than that for the unreacted (ca. 4 s); these values were typical of the other materials also. From these results, it is apparent that the relative intensity of the two carbonyl peaks reaches a constant value for pulse intervals of ca. 30 s or greater. It is noteworthy that the relative intensity of the unreacted peak is significantly greater in the s.p.e. spectra than in the c.p. spectra in *Figure 3*. This indicates that the unreacted carbonyl resonances are not cross-polarized as effectively as the reacted groups, a difference that is also attributable to greater mobility of unreacted chain ends.

The number of time-averaged pulse repetitions required to obtain an adequate signal-to-noise ratio for the carbonyl peaks depends on the concentration of carbonyl groups in the whole sample, which depends on the chemical structure of the components and the amount of filler present. For the unfilled model TEGDMA samples, which have the highest carbonyl concentration, ca. 500 pulses were required, giving a total s.p.e. experimental time of ca. 4.5 h for a pulse interval of 30 s. For the unfilled proprietary systems studied, the components of which have a higher average molar mass than TEGDMA, ca. 1500 pulses were required, giving a total s.p.e. experimental time of ca. 8 h. For the filled Z100 sample, ca. 5000 pulses were required, giving a total s.p.e. experimental time of ca. 28 h.

C.s.a. spinning sidebands in n.m.r. spectra

The spectra presented in *Figures 2* and *4* show spinning sidebands from the carbonyl and aromatic resonances. For accurate quantification of the unreacted content, it is necessary to include the sideband intensities. In the proprietary materials, at the spin rates achievable with the instrumentation employed, the lower-frequency sidebands of the carbonyl peaks were obscured by the aromatic centreband resonances and (in s.p.e. spectra) by the probe background resonances. However in the model TEGDMA spectra both low- and high-frequency carbonyl sidebands are clearly observable, so this system was used to investigate the sideband patterns of the reacted and unreacted carbonyl peaks in detail, and to obtain an estimate of the sideband contribution to the total carbonyl intensity. For these purposes, c.p. spectra were used, with the consequent sensitivity advantage, since it turned out that it was the rigid reacted carbonyl for which an intensity correction was required, and the sideband pattern for a rigid nucleus is the same for both c.p. and s.p.e. excitation.

Figure 6 compares TEGDMA c.p. spectra as a function of spin rate. The two features of significance for the present purpose are these:

(i) The sidebands of the unreacted peak are negligible compared with those of the reacted peak. This presumably arises from averaging of the c.s.a. of the unreacted groups by molecular motion, and is consistent with the slower rate of cross-polarization described above.

(ii) At spin rates of ⩾5.2 kHz, which are necessary to avoid overlap of aromatic sidebands with carbonyl peaks (see above), the second- and higher-order sidebands of the reacted peak are negligible.

Interference between molecular motion and m.a.s. or d.d.

The c.p. and s.p.e. spectra discussed above demonstrate the considerable difference in mobility between reacted and unreacted carbonyl groups. Because of the heterogeneous structure of these crosslinked materials, each type of group will almost certainly experience a distribution of dynamic environments. There remains a

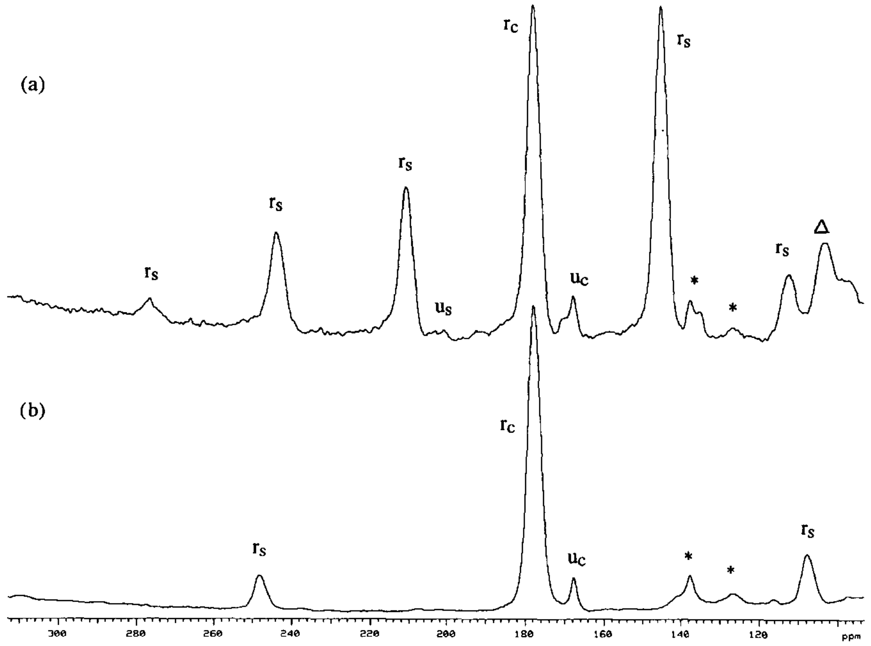

Figure 6 Olefinic/carbonyl region of c.p. spectra of TEGDMA at spin rates of (a) 2.5 kHz and (b) 5.3 kHz. The labels r_c, r_s, u_c and u_s indicate the centreband and sidebands of carbonyls in reacted and unreacted methacrylate groups. The stars indicate peaks from the olefinic carbons in unreacted groups, and the triangle indicates a sideband from the aliphatic carbons

possibility that some nuclei may have a motional frequency matching the m.a.s. or d.d. frequency, such that the resulting line broadening renders them invisible. This possibility was investigated by running spectra under a variety of conditions.

The effect of m.a.s. frequency was investigated using spectra run at different spinning frequencies such as those shown in *Figure 6*. It was found that within experimental error the ratio of the total integrals (centreband + sidebands) of unreacted and reacted carbonyl peaks was independent of spin rate. The effect of decoupling field strength is illustrated in *Figure 7*, which compares centreband carbonyl s.p.e. spectra of a TEGDMA sample obtained with the normal decoupling field (*Figure 7a*) and a decoupling field lower by 5 dB (*Figure 7b*). The reacted carbonyl peak is noticeably broad for the lower field, but the unreacted carbonyl is much less affected. Using spectrum deconvolution techniques (see below and *Figure 9*) for the centreband spectra shown, the proportions of the unreacted carbonyl peak were found to be 18% and 19% for the lower and higher decoupling fields respectively. The decoupling fields used in this work therefore have an insignificant effect on the carbonyl intensities.

The molecular motional frequencies depend on temperature. *Figure 8* compares centreband carbonyl s.p.e. spectra of a TEGDMA sample run at ambient temperature and at $-20°C$ with a spinning rate of 2.7 kHz. At the lower temperature there is some broadening of the unreacted carbonyl peak, but the relative integrals of the two peaks are essentially unaffected by temperature. It thus appears that the normal conditions for s.p.e. acquisitions on the instrument used in this work give a reliable estimate of the extent of reaction in these materials.

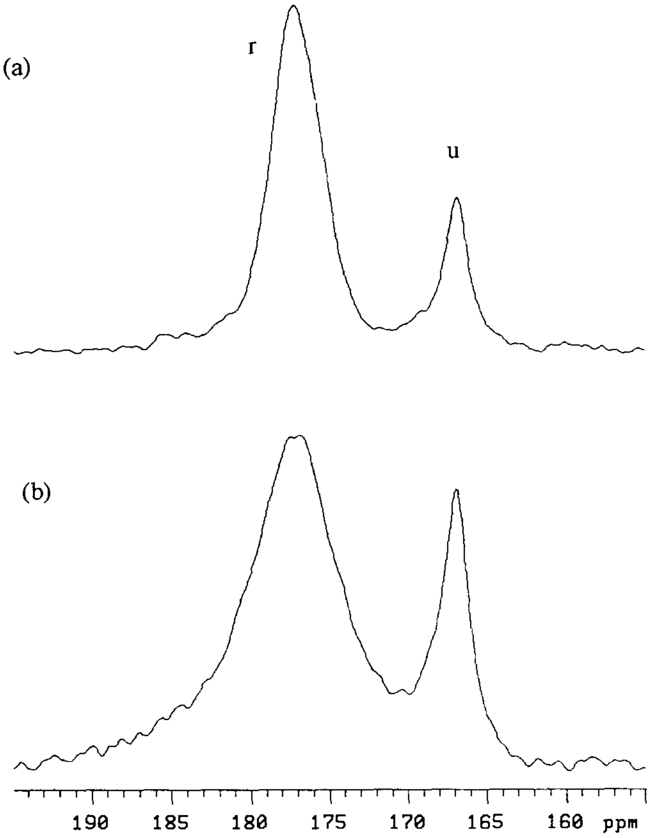

Figure 7 Carbonyl region of s.p.e. spectra of TEGDMA at (a) normal d.d. field strength and (b) a d.d. field strength reduced by 5 dB. The spin rate was 5.0 kHz. The labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively

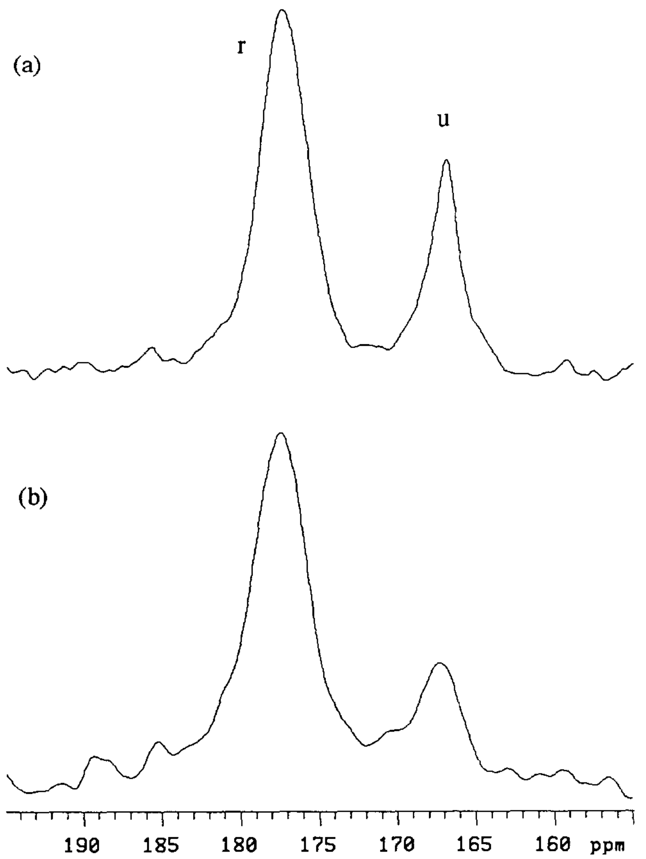

Figure 8 Carbonyl region of s.p.e. spectra of TEGDMA at (a) ambient temperature and (b) $-20°C$. The spin rate was 2.7 kHz. The labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively

Determination of unreacted content by n.m.r.

Determination of the proportion of unreacted methacrylate groups proceeded in two stages: (a) determination of the relative intensities (i.e. integrals) of the reacted and unreacted carbonyl centreband peaks in s.p.e. spectra; (b) determination of the relative intensities of the reacted carbonyl sidebands.

Because there was some overlap between the reacted and unreacted carbonyl peaks, and also because of the presence in the proprietary composites of an aromatic quaternary peak close to the high-frequency side of the reacted peak, the first stage was accomplished using deconvolution of the carbonyl centreband region into two peaks (TEGDMA) or three peaks (composites). A typical example of the latter is shown in *Figure 9*. A Lorentzian lineshape was assumed for each component, but the fitting process was allowed unconstrained iteration on the frequency, peak height and linewidth. The proportion of the unreacted carbonyl centreband was then obtained from the integral of that component relative to the total carbonyl centreband integral.

The relative intensity of the reacted carbonyl sidebands was obtained to sufficient accuracy by integration of the

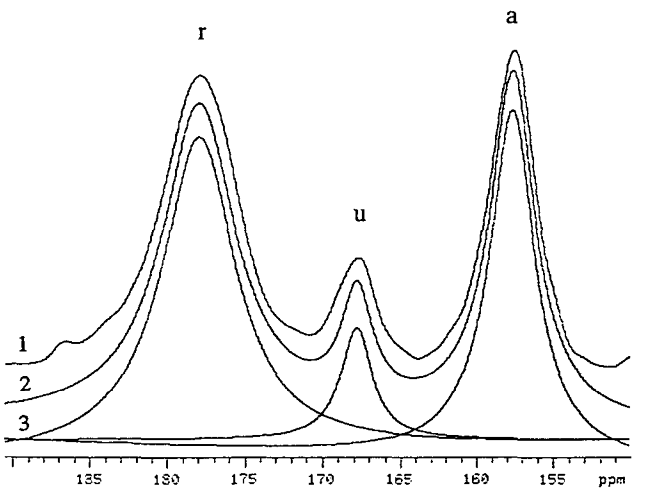

Figure 9 Deconvolution of the carbonyl centreband peaks in the s.p.e. spectrum of Coltène bonding agent run with a pulse interval of 32 s: (1) the experimental spectrum; (2) the simulated composite lineshape; (3) the individual components. The labels r and u indicate carbonyl peaks from reacted and unreacted methacrylate groups respectively, and the label a indicates an aromatic carbon resonance

Table 2 Proportion of unreacted methacrylate groups in systems studied

		Unreacted groups (mol%)	
System	Cure	N.m.r.	I.r.
TEGDMA	V.l.c.	6	–
Duo Bond	V.l.c.	19	40
	C.c.	26	44
Coltène bonding agent	V.l.c.	15	37
Z100	V.l.c.	40	70

centreband and sideband peaks in c.p. spectra of model TEGDMA samples. Since the sideband intensity depends on the spin rate, spectra were run at a range of spin rates and a centreband correction factor C, defined as:

$$C=\frac{I_{\mathrm{cb}}+I_{\mathrm{ssb}}}{I_{\mathrm{cb}}}$$

was evaluated as a function of spin rate. I_{cb} is the integral of the reacted carbonyl centreband peak and I_{ssb} is the combined integral of the first upper and lower reacted carbonyl sidebands. The variation of C with spin rate is shown in *Figure 10*. There is some scatter in the points, which reflects the difficulty in accurately integrating sidebands with a low signal-to-noise ratio. Correction factors from *Figure 10* were then used to correct the intensity of the reacted carbonyl centreband peak in the proprietary materials, this procedure implying that the sideband pattern is of the same form as in TEGDMA alone. Results are listed in *Table 2*.

I.r. spectra

The i.r. method for determining residual unsaturated groups in dental materials has recently been discussed in detail[2], so only two example spectra, those of the Coltène bonding agent material before and after polymerization, are presented here (*Figure 11*). The peaks used in the analysis are the methacrylate C=C absorbance at 1640–1635 cm^{-1} and the aromatic C=C absorbance at 1610–1605 cm^{-1}. The aromatic peak originates from the aromatic rings in the bis-GMA molecule, the amount of which remains unchanged during the polymerization. The percentage of unreacted methacrylate groups was obtained as previously[2] by comparing the ratio of the methacrylate and aromatic absorbances before and after polymerization according to:

$$\%\ \text{unreacted}=\frac{100\times[A_{\mathrm{meth}}/A_{\mathrm{arom}}]_{\mathrm{polymer}}}{[A_{\mathrm{meth}}/A_{\mathrm{arom}}]_{\mathrm{monomer}}} \qquad (1)$$

where A_{meth} and A_{arom} are the absorbances of the methacrylate and aromatic bands respectively. Note that this relation assumes that the ratio of extinction coefficients is unaffected by the polymerization, i.e.

$$[\varepsilon_{\mathrm{meth}}/\varepsilon_{\mathrm{arom}}]_{\mathrm{monomer}}=[\varepsilon_{\mathrm{meth}}/\varepsilon_{\mathrm{arom}}]_{\mathrm{polymer}} \qquad (2)$$

Figure 12 shows the expansion of these peaks for Coltène bonding agent, together with the baseline used to measure the absorbances as peak heights. For the Duo Bond material, which has two monomer components, it was found that the ratio $A_{\mathrm{meth}}/A_{\mathrm{arom}}$ was almost the same for each component. Since the two components are mixed in equal amounts, for this system equation (1) was replaced by the expression:

$$\%\ \text{unreacted}=\frac{100\times[A_{\mathrm{meth}}/A_{\mathrm{arom}}]_{\mathrm{polymer}}}{\frac{1}{2}\{[A_{\mathrm{meth}}/A_{\mathrm{arom}}]_{\mathrm{A}}+[A_{\mathrm{meth}}/A_{\mathrm{arom}}]_{\mathrm{B}}\}}$$

where the subscripts A and B denote the two monomer components. Values of the unreacted methacrylate content obtained in this way are given in *Table 2*.

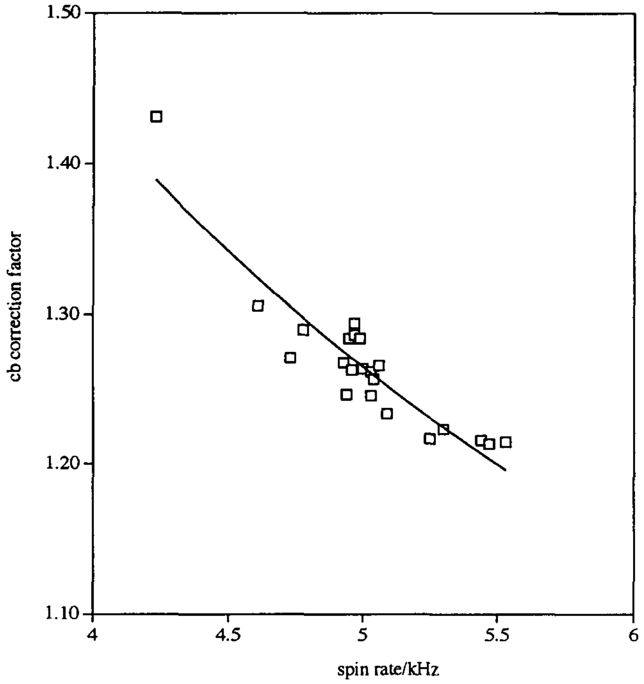

Figure 10 Variation of the reacted carbonyl centreband correction factor with spin rate for TEGDMA. The curve is for eye guidance only

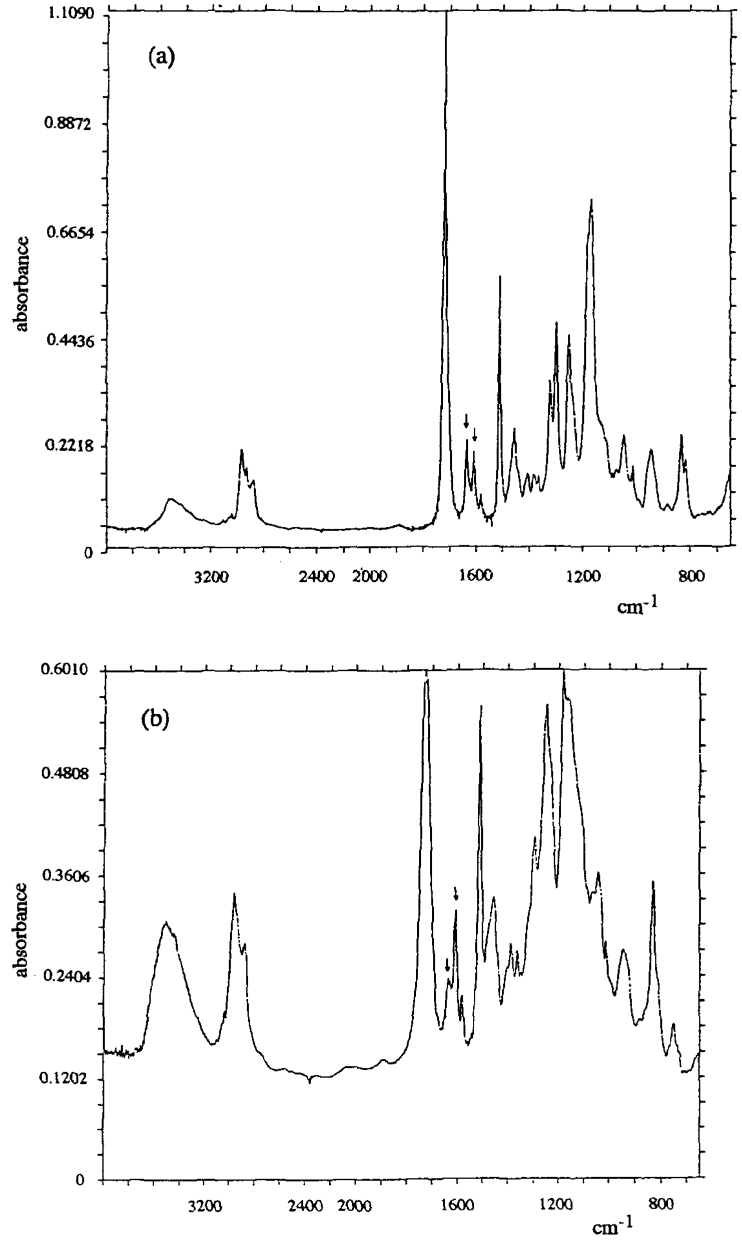

Figure 11 Transmission i.r. spectra of Coltène bonding agent (a) before and (b) after polymerization. The arrows indicate the methacrylate C=C absorption at 1639 cm^{-1} and the aromatic C=C absorption at 1610 cm^{-1}

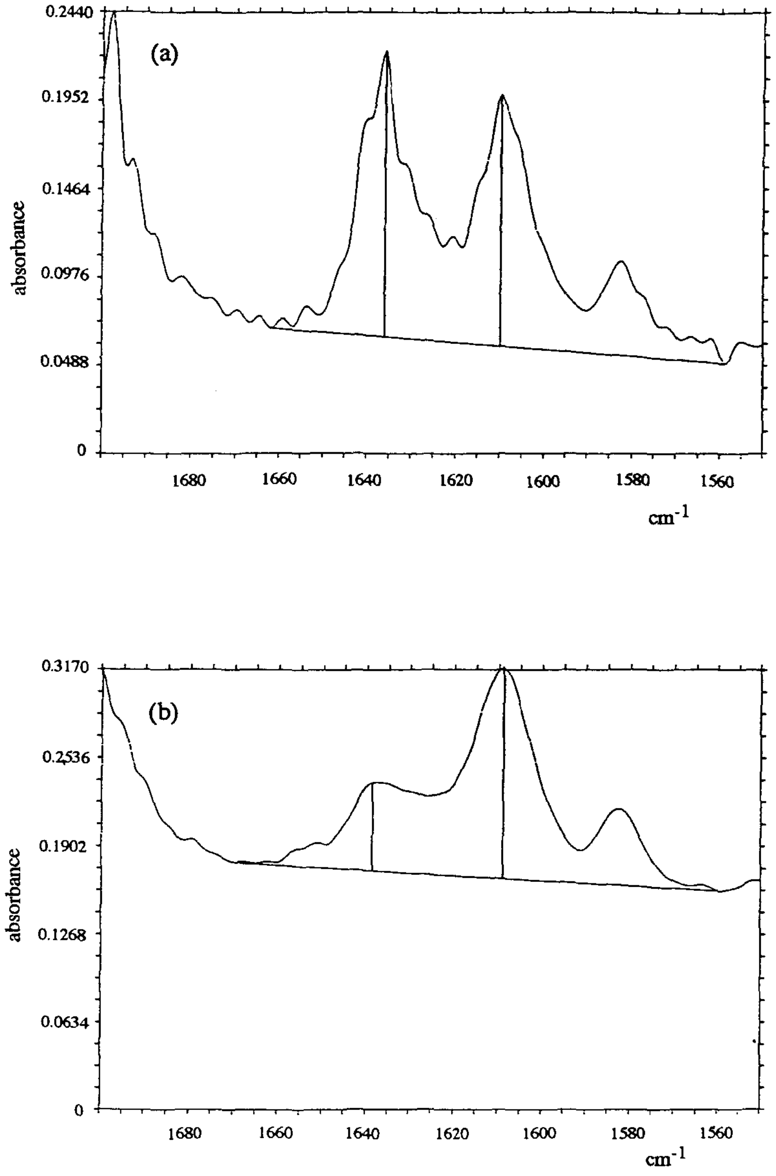

Figure 12 Transmission i.r. spectra of Coltène bonding agent over the region 1550 to 1700 cm^{-1} (a) before and (b) after polymerization. The method of measurement of peak absorbances is indicated

Comparing the methacrylate contents from the two techniques, it is seen that the i.r. and n.m.r. results for different samples parallel each other, but the i.r. results are about a factor of 2 greater than the n.m.r. results. The origin of this serious discrepancy is unclear. The i.r. results reported here are similar in magnitude to those reported elewhere for a larger range of composites[13], and the i.r. experimental and data processing procedures used here are consistent with those used in previous work. Since a finely ground powder was used for both i.r. and n.m.r., the discrepancy cannot be accounted for by a difference in effective sampling volume between the two techniques, though it may be that the i.r. method is more responsive to surface layers. In the n.m.r. analysis, spinning sidebands of the unreacted carbonyl peak were neglected, but even if they were the same magnitude as those of the reacted carbonyl peak, the unreacted methacrylate content would increase by only some 30%. It is clear that because of the importance of a reliable measurement of the extent of reaction for characterizing the network and understanding the properties of these systems, further work is necessary to resolve the conflict. Several avenues are worthy of exploration. First a thorough investigation of alternative i.r. or Raman methods using the wealth of other information in the vibrational spectrum should be made. Secondly, a comparison of i.r. and n.m.r. methods using model composites with known structure (e.g. by using pure poly(methyl methacrylate) with known amounts of a dimethacrylate monomer) should be carried out. In particular this would allow a test of the validity of assuming equation (2). Finally, a study of the extent of reaction in an unground thin film should be performed in order to study the effect of the grinding process on the n.m.r. results and to obtain an accurate i.r. transmission spectrum representative of the whole sample.

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Note added in proof

After acceptance of this paper, the following closely related papers were published:

Horák, D., Straka, J., Schneider, B., Lednický, F. and Pilař, J. *Polymer* 1994, **35**, 1195. A ^{13}C c.p./m.a.s. n.m.r. study of poly(ethylene dimethacrylate). Differential relaxation of reacted and unreacted carbonyl peaks was observed, and taken quantitatively into account by fitting intensities as a function of contact time to a biexponential growth/decay expression[5].

Kalachandra, S., Turner, D. T., Burgess, J. P. and Stejskal, E. O. *Macromolecules* 1994, **27**, 5948. Analysis of residual monomer in poly(methyl methacrylate) by ^{13}C c.p./m.a.s. n.m.r. Differential relaxation was not examined.

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