Evaluation of the Amount of Residual Monomer on UDMA-Based Resins by FTIR

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The purpose of this study was to establish a method using FTIR to evaluate the polymerization characteristics of UDMA-based resins. Three kinds of experimental UDMA-based resins were prepared with various molar fractions. IR spectra of the cured film specimens were measured with FTIR before and after extracting residual monomer from each specimen by MeOH. From the IR spectra, the changes in the number of double bonds were measured, with the NH absorbance peak as an internal standard, and the amounts of residual monomers (RM) were calculated. The MeOH-immersed specimens were analyzed by HPLC. The RM measured by FTIR were compared with those measured by HPLC. The RM measured by HPLC were more than those by FTIR. Since these differences could be due to the difference in the area measured, this FTIR estimation method of residual monomers in cured resins using the NH absorbance peak as an internal standard could be an appropriate method when the resin monomer does not contain aromatic compounds.

Key words: UDMA-based resin, FTIR, Residual monomer

INTRODUCTION

Most commercially available composite resins are BisGMA/TEGDMA-based. The authors have already established a method to evaluate the polymerization characteristics of these resins by Fourier transformed infrared spectrometer (FTIR)\(^1\). In this method, the changes in the number of double bonds are measured using the aromatic absorbance peak as an internal standard. The amounts of residual monomer (RM) are measured by high performance liquid chromatography (HPLC)\(^2,3\). The degree of conversion (DC) is measured by infrared spectroscopy\(^4-12\) or differential scanning calorimetry (DSC)\(^13-15\). The cross-linked network structure cannot be evaluated from either the RM values or DC values. In addition, the methods by HPLC or DSC cannot evaluate the RM or DC of a whole specimen. Light-cured materials have a three-dimensional distribution of polymerization characteristics, since polymerization of light-cured resin depends upon the degree of light intensity. HPLC and DSC cannot evaluate these distributions. Our method using FTIR can evaluate these distributions and the cross-linked structure on BisGMA-TEGDMA resins\(^1\).

Laboratory-cured composites for crown and bridge are mainly based on a TEGDMA/UDMA monomer\(^16\). Recently, the application of UDMA-based resins to restorative materials has increased\(^17\). Most of these resins do not contain aromatic moieties in their structure, and a method using FTIR for evaluating the
characteristics of polymerization on UDMA-based resins that do not contain aromatic compounds has not yet been established.

Some reports describe an FTIR method using the carbonyl peak as an internal standard\textsuperscript{11,12}. The carbonyl peak is quite sharp and has a strong intensity. The large value of absorbance associated with the carbonyl peak suggests that its concentration is so large that it is outside the limits of the validity of Beer's law. Consequently, in these reports, cured resin specimens were ground with a mortar and pestle to produce a fine powder, and the resulting powder was mixed with IR-grade KBr and pressed into a transparent pellet. However, heating due to the grinding action might have enhanced the degree of conversion\textsuperscript{6}.

The purpose of this study was to establish a method involving an appropriate peak as an internal standard to evaluate the polymerization characteristics of experimental UDMA-based resins.

**MATERIALS AND METHODS**

**Experimental light-cured composite**

The monomers used were di(methacryloyxethyl)trimethyl hexamethylenediurethane (UDMA; Negami Chemical Industrial Co. Ltd., Ishikawa, Japan), 2,2-bis[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane (BisGMA; Polysciences, Inc., Warrington, PA, USA) triethylene glycol dimethacrylate (TEGDMA; Shin-nakamura Chemical Co., Wakayama, Japan) and 2,2-bis(4-methacryloxypolyethoxyphenyl)propane (BisMPEPP\textsubscript{2,6E}; Shin-nakamura Chemical Co., Wakayama, Japan). UDMA/BisGMA, UDMA/TEGDMA, UDMA/BisMPEPP\textsubscript{2,6E}-based resin composites were prepared with various molar fractions. To prepare the resin for light-curing, 0.5 mol% of camphorquinone (CQ; Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan) and 0.5 mol% 2-dimethylamino ethylmethacrylate (DMAEMA; Wako Pure Chemical Industry, Osaka, Japan) were dissolved in the monomer mixture; 50 wt% of the quartz filler (Fuselex X; Tatsumori Ltd., Tokyo, Japan) treated with silane coupling agents was added to the monomer mixture.

**Preparation of specimen**

A schematic diagram showing the preparation of the specimen is shown in Fig. 1. The composite resin paste was interposed between two polyester strips together with a 40 µm spacer. These were then pressed between two glass slide plates. The material was exposed to visible light from the light curing unit (New Light VL-Ⅱ, GC Corp., Tokyo, Japan) for 30 s. This unit was selected because the light intensity was constant with time\textsuperscript{18}. For each test section, the exposure light was taken as the incident light intensity after 30 s from the time the lamp was switched on\textsuperscript{18}. The irradiation period was then applied after a 30 s exposure.

The specimens were stored at 37°C in the dark for 24 h without being removed from the strips. Five specimens were prepared for each condition.
Determination of amount of residual monomer using FTIR measurement

At 24 h after the irradiation period, the infrared (IR) spectra of the specimens were recorded by FTIR (JIR-100, JEOL Co. Ltd., Tokyo, Japan). The specimens were weighed and immersed in 10 ml methanol to extract residual monomers at 23°C in the dark. After 30 days’ extraction, each specimen was removed and freed of solvent. IR measurement was then repeated. MeOH immersed specimens were subjected to further analysis using high performance liquid chromatography (HPLC). The IR spectra were measured to evaluate the quantities of carbon-carbon double bonds remaining in the specimens before and after extracting any residual monomer by MeOH. From the IR spectra, the changes in the numbers of double bonds were measured using the NH absorbance peak at 3373 cm⁻¹ or the aromatic absorbance peak at 1608 cm⁻¹ as an internal standard. For TEGDMA 100% resin, the peak intensities at 1637 cm⁻¹ were corrected by the thickness of the specimens.

Spectra of the resin pastes were obtained immediately after the resin pastes had been pressed into a thin film between two KBr-disks.

In these IR spectra, two absorbance peaks appeared in the range 1600-1650 cm⁻¹ and two absorbance peaks in the range 3000-4000 cm⁻¹ (Fig. 2). The peak at 1637 cm⁻¹ was assigned to the C=C stretching vibration of the methacryloyl groups and that at 1608 cm⁻¹ to the stretching vibration of the aromatic rings. An appropriate baseline was drawn, and these two absorption peaks were separated into two Lorentzian curves. The peak at 3373 cm⁻¹ was assigned to the N-H stretching vibration of the urethane groups and that at 3463 cm⁻¹ to O-H stretching vibration (Fig. 2). An appropriate baseline was drawn within the range. The absorption intensity was determined from the areas under the peaks.

The amounts of residual monomers (RM) were calculated using the following equation:

\[ \text{RM} (%) = \left| \frac{(c-e)}{c} \right| \times \left| \frac{bc}{ad} \right| \times 100 \]

Where the intensities a-e are defined as follows:
Fig. 2 Typical IR spectrum in the range 2400-4000 cm$^{-1}$

The band at 3373 cm$^{-1}$ was assigned to N-H vibration and that at 3463 cm$^{-1}$ to O-H vibration.

In b) and c), these bands were overlapped.

a: C=C absorbance peak at 1637 cm$^{-1}$ of resin pastes;
b: NH absorbance peak at 3373 cm$^{-1}$ or aromatic absorbance peak at 1608 cm$^{-1}$ of resin pastes;
c: C=C absorbance peak at 1637 cm$^{-1}$ of cured resin before extraction;
d: NH absorbance peak at 3373 cm$^{-1}$ or aromatic absorbance peak at 1608 cm$^{-1}$ of cured resin before extraction;
e: C=C absorbance peak at 1637 cm$^{-1}$ of cured resin after extraction.

The amount of the eluted components that have double bonds can be calculated by the equation under the assumption that these are monomers.

Mean values for each condition are shown.
Determination of the amount of residual monomer using HPLC measurement

50 μL of each MeOH solution immersed specimen was analyzed by HPLC using a 4.6 mm φ × 150 mm HPLC column (Zorbax ODS, Du Pont Company, USA) and a guard column attached to an HPLC system (LC-3A, Shimadzu Co., Kyoto, Japan). Compounds were eluted at a flow rate of 1 mL/min using the solvent, MeOH:H₂O=70:30 or 75:25. MeOH:H₂O=75:25 was used only on UDMA/BisMPEPP₂₆E. Using an ultraviolet spectral detector, the elution of each compound was monitored by absorbance at 230 nm. The amount of each eluted monomer in each MeOH solution was determined by an absolute calibration method and the amount of residual monomer was calculated.

The amounts of residual monomer determined by FTIR were compared with those by HPLC. The validity of this method using the NH absorbance peak as an internal standard was examined.

Statistical analysis

Differences in the amounts of residual monomer measured between by FTIR and by HPLC were statistically compared by Student's t-test at significance values of P<0.05 and P<0.01.

RESULTS

The amounts of residual monomers using both FTIR and HPLC measurements on UDMA/BisGMA, UDMA/TEGDMA and UDMA/BisMPEPP₂₆E are shown in Tables 1-3, respectively. The superscripts in Tables indicate that there was no significant difference between the values measured by FTIR and those by HPLC. When the aromatic peak was used as an internal standard, there was no significant difference between the values by FTIR and those by HPLC for BisGMA 100, UDMA/BisGMA=4/6, UDMA/BisMPEPP₂₆E=2/8, 4/6, 6/4 and 8/2 (at P<0.01). When the NH peak was used, there was no significant difference for UDMA/BisGMA=4/6, TEGDMA 100

<table>
<thead>
<tr>
<th>Table 1 Comparison of the amounts of residual monomer (%) measured by FTIR with those by HPLC on UDMA/BisGMA resins</th>
</tr>
</thead>
<tbody>
<tr>
<td>UDMA / BisGMA</td>
</tr>
<tr>
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<tr>
<td></td>
</tr>
<tr>
<td>0 / 100</td>
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<tr>
<td>20 / 80</td>
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<tr>
<td>40 / 60</td>
</tr>
<tr>
<td>60 / 40</td>
</tr>
<tr>
<td>80 / 20</td>
</tr>
<tr>
<td>100 / 0</td>
</tr>
</tbody>
</table>

n=5

a : using the peak at 1608 cm⁻¹ as an internal standard
b : using the peak at 3373 cm⁻¹ as an internal standard
* : no significant difference from the value by HPLC (P<0.01)
** : no significant difference from the value by HPLC (P<0.05)
Table 2 Comparison of the amounts of residual monomer (%) measured by FTIR with those by HPLC on UDMA/TEGDMA resins

<table>
<thead>
<tr>
<th>UDMA/TEGDMA</th>
<th>FTIR</th>
<th>HPLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 / 100</td>
<td>23.1±6.4*</td>
<td>31.5±1.5</td>
</tr>
<tr>
<td>20 / 80</td>
<td>4.7±2.2</td>
<td>9.8±1.4</td>
</tr>
<tr>
<td>40 / 60</td>
<td>5.5±0.3</td>
<td>7.2±0.8</td>
</tr>
<tr>
<td>60 / 40</td>
<td>5.9±0.2</td>
<td>9.5±1.4</td>
</tr>
<tr>
<td>80 / 20</td>
<td>7.6±0.2</td>
<td>13.7±3.3</td>
</tr>
<tr>
<td>100 / 0</td>
<td>8.1±0.7</td>
<td>13.4±0.6</td>
</tr>
</tbody>
</table>

n=5
*: no significant difference from the value by HPLC (P<0.01)

Table 3 Comparison of the amounts of residual monomer (%) measured by FTIR with those by HPLC on UDMA/BisMPEPP2.6E resins

<table>
<thead>
<tr>
<th>UDMA / BisMPEPP2.6E</th>
<th>FTIR</th>
<th>HPLC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₆H₄ᵃ</td>
<td>NHᵇ</td>
</tr>
<tr>
<td>0 / 100</td>
<td>15.9±1.2</td>
<td>17.4±4.2**</td>
</tr>
<tr>
<td>20 / 80</td>
<td>14.0±3.3*</td>
<td>18.3±1.7*</td>
</tr>
<tr>
<td>40 / 60</td>
<td>16.6±1.8**</td>
<td>9.3±5.0**</td>
</tr>
<tr>
<td>60 / 40</td>
<td>9.6±5.2**</td>
<td>11.2±0.4</td>
</tr>
<tr>
<td>80 / 20</td>
<td>12.3±0.6**</td>
<td>8.1±0.7</td>
</tr>
<tr>
<td>100 / 0</td>
<td></td>
<td>13.4±0.6</td>
</tr>
</tbody>
</table>

n=5
ᵃ: using the peak at 1608 cm⁻¹ as an internal standard
ᵇ: using the peak at 3373 cm⁻¹ as an internal standard
*: no significant difference from the value by HPLC (P<0.01)
**: no significant difference from the value by HPLC (P<0.05)

UDMA/BisMPEPP₂₆E=2/8, 4/6 and 6/4 (at P<0.01). In general, the amounts of residual monomer measured by HPLC were more than those by FTIR.

The amounts of residual monomer measured using the NH peak or the aromatic peak were compared by Student’s t-test at P<0.05. There was no significant difference except for UDMA/BisMPEPP₂₆E=8/2, UDMA/BisGMA=4/6 and 2/8.

DISCUSSION

The amounts of residual monomer in cured resin were measured by HPLC. The degree of conversion, i.e. the percentage of reacted double bonds, has often been evaluated in the relevant literature. However, it is necessary to determine both the amount of residual monomer and the degree of conversion in order to estimate the cross-linked structure, because various properties of a resin system are significantly dependent upon the cross-linked density and structural quality of the network formed during polymerization. Both the amount of residual monomer and the degree of conversion should be evaluated by the same means. In addition, the amount of residual...
monomer and the degree of conversion are heterogeneous in light-cured resins, since light of a certain intensity is required to activate polymerization. Since the IR spectra of microareas could be measured with an FTIR equipped with a microscopic unit, the distribution of the amount of residual monomer and the degree of conversion could be evaluated.

When the amounts of residual monomer measured by HPLC were compared with those by FTIR, the former was generally more than the latter. These differences could be due to the differences in the area measured. By HPLC method, the amount of residual monomer from the whole specimen is evaluated, since the specimen is immersed in solvent and the solvent is analyzed by HPLC. By FTIR method, the irradiation position of infrared ray is only a part of the specimen, the center 5 mm of the specimen in this study. Therefore, HPLC measured the whole specimen of about 13 mm diameter and the area measured by FTIR method was the center (about 5 mm diameter) of the specimen. Radiation through the light guide (13-mm diameter) of the light unit, polymerizing the specimen, has a distributed light intensity, because the light source is a point source. The light intensity is strongest at the center and decreases toward the perimeter. Therefore the polymerized specimens have a distribution of polymerization characteristics such as degree of conversion, amount of residual monomer, number of pendant double bonds, in accordance with the incident light intensity.

Especially regarding UDMA:BisGMA = 20:80, the value determined by FTIR using 3373 cm\(^{-1}\) was significantly more than that by HPLC. This might be because the NH absorbance peak and the OH absorbance peak were overlapped (Fig. 2). In UDMA/BisGMA, the greater the ratio of BisGMA, the greater the OH absorbance peak. These two absorbance peaks in the range of 3000-4000 cm\(^{-1}\) could not be separated into two Lorentzian curves by using the program equipped with FTIR, since two peaks did not appear. If these peaks cannot be separated, the aromatic peak should be used as the internal standard on UDMA/BisGMA. If a higher level program was used, these two peaks might have been separated, and the NH absorbance peak could have been used as the internal standard.

BisMPEP2.6E, which has aromatic rings and no hydroxyl groups, was used in order to investigate whether or not the NH absorbance peak can be used as an internal standard, since the OH peak and NH peak overlapped. On UDMA/BisMPEP2.6E, the value determined using 3373 cm\(^{-1}\) as the internal standard was similar to that using 1608 cm\(^{-1}\). These data did not differ greatly from the values determined by HPLC.

The results indicated that FTIR estimation of residual monomer using the NH absorbance peak as an internal standard could be an appropriate method when a resin monomer does not contain aromatic compounds.

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References


