

## TECHNICAL NOTE

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# Fluorescence and Structural Degradation in Composite Resins as a Function of Temperature\*

**ABSTRACT:** Detecting composite resin upon postmortem examination can be difficult. Ultraviolet illumination has been suggested to ease location of this material; however, this may not be advisable in incineration situations. Understanding of the chemical and physical properties of resin as a function of temperature is an important parameter in identification of this material in incineration circumstances. Twenty-seven discs of resin, Quixx (Dentsply), Filtek Supreme (3 M), and Tetric Ceram (Ivoclar) were prepared and exposed to increasing heating conditions of 200°C–900°C in 100°C increments for 30 min. Analysis was performed with Fourier transform infrared spectroscopy, ultraviolet-visible light spectrophotometry, scanning electron microscopy/energy dispersive X-ray spectroscopy, optical microscopy, and UV illumination. Characterization of the material occurred at each temperature range. The organic components and the fluorescence properties were lost at temperatures above 300°C. The inorganic component remained through 900°C. This information can aid in detection of resin in high temperature circumstances.

**KEYWORDS:** forensic science, forensic odontology, composite resin, incineration, fluorescence, SEM, FTIR

Detection of composite resin restorations in a victim's dentition can be very difficult. Restorations exhibiting proper shade match and contour configuration may be visually indistinguishable from tooth structure. Thus they can be easily missed upon postmortem dental examination. Omission of these restorations can compromise identification of the victim due to an inconsistent antemortem and postmortem dental comparison.

Composite resins are composed of inorganic filler particles in an organic matrix. The inorganic particles can form 70% or more by weight of the resin mass. These particles are added for reasons such as wear resistance, radiopacity, and polishing capability. The organic component typically consists of a mixture of methacrylates with polymerization inhibitors, initiators, and organic dyes for coloration (1). The methacrylates form the matrix of the resin, with the other components present at low concentrations. Organic fluorophores (compounds that fluoresce) may also be included. Dentin and enamel naturally fluoresce. To mimic the natural appearance of tooth structure, manufacturers have added fluorophores to achieve this effect in resin (2).

Alternative light sources have been used with success in various fields of forensic science. These light sources typically possess the attributes of intense narrow band emission of light used with or without filters to observe the fluorescence properties of a variety of materials.

Inspection of the oral cavity with ultraviolet (UV) light emitting diode flashlights in the 360 nm to 385 nm range can be an adjunctive aid for illuminating resins that may otherwise go unnoticed (3,4). These wavelengths of light will cause the resins to fluoresce,

providing a noticeable contrast between the restorative material and the tooth structure. This makes fluorescence a valuable indicator, especially when many individuals must be identified such as in mass disaster situations. However, it has been documented that these materials lose their fluorescence after exposure to high temperatures (5). As a result, fluorescence may not reveal restorations in cases of incineration. Under these conditions, the use of UV light may not provide a benefit to the examiner.

Fluorescence, defined, is the absorption of light by a substance and the spontaneous emission of light in a longer wavelength within  $10^{-8}$  sec of activation (3,4). This can be more simply described as the emission of a longer wavelength of light when a shorter wavelength is used as an illuminant.

Resins can also change in visual appearance when exposed to high temperatures. They can dislodge from the tooth and in these circumstances, be easily overlooked. It has been documented that resins, even when exposed to cremation conditions, can be identified by brand name (6). The brand of resin detected can be compared to the written documentation in the victim's chart and could be used as an aid in identification (6). The detection and verification of brand of a resin liner placed under an amalgam restoration was pivotal in victim identification in a 1999 murder case (7). Thus, it is important to understand the structural and chemical changes that occur when resin is exposed to high temperatures.

It was one goal of this study to assess the presence of the fluorescent properties of composite resin when exposed to increasing temperatures and to determine the temperature range in which fluorescence is lost. Another goal was to describe physical changes in composite resin as a function of increasing temperature. This information could potentially be used to estimate incineration temperatures and conditions endured by burn victims. It can also be used to help predict the appearance of resins when they have been exposed to heat, thus, aiding location and detection of them.

Five techniques were employed. These were Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible light

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\*Presented at the 59th Annual Meeting of the American Academy of Forensic Sciences in San Antonio, TX, February 19–24, 2007.

Received 25 April 2008; and in revised form 8 July 2008; accepted 13 July 2008.

spectrophotometry (UV-VIS), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), optical microscopy, and UV illumination.

The selective absorption of light by composite resins in the UV and infrared (IR) regions of the electromagnetic spectrum make UV-VIS and FTIR valuable techniques for characterization of these materials.

When exposed to increasing temperatures, the changes that take place in the organic molecules and fluorophores found in resins can be determined by visible inspection under UV illumination and by using UV-VIS. By measuring the absorbance of UV and visible light as a function of illuminating wavelength, the resulting spectrum makes it possible to determine the chemical changes taking place in a dental material.

Similarly, FTIR is an analytical method used to measure the wavelength of light that a certain material will absorb in the IR spectral range. This technique produces IR absorption patterns unique to the materials' organic and inorganic components.

SEM/EDS reveals detailed information on surface topography and elemental composition and together with optical microscopy can be used to understand changes in reflectivity and color caused by pyrolysis and subsequent fusing of filler particles.

## Methods and Materials

Three commonly available brands of resin were analyzed: Filtek Supreme (3 M), Quixx (Dentsply), and Tetric Ceram (Ivoclar). The brand of composite resins used in this study and its chemical composition obtained from the manufacturers is shown in Table 1. These three brands were chosen due to their known differences in inorganic filler composition. All three brands were shade A2.

The resins were prepared in 1-cm diameter discs and sandwiched between two glass slides. Nine discs of resin material were prepared for each brand according to manufacturer's instructions. The discs were light-cured for 30 sec.

Each sample was placed in a porcelain crucible and the 27 discs were exposed to temperatures ranging from room temperature to 900°C in 100° increments. As soon as each target temperature had been reached, the samples were placed in the oven for 30 min. They were then removed from the oven and allowed to cool to room temperature.

For each condition, UV-VIS spectra, FTIR spectra, optical and SEM images were recorded. Images of the resins under UV illumination at 365 nm wavelength were also collected. This combination of techniques allowed for characterization of both the organic and inorganic components. The color changes of the materials were also noted before and after the heating procedures mentioned above.

## Analysis Conditions

FTIR analysis was performed on a Digilab FTS 40 Pro using the attenuated total reflectance mode.

For SEM/EDS analysis, samples were carbon coated prior to analysis. SEM analysis was performed at 25 keV, and EDS spectra were collected with livetime of 100 sec, with a takeoff angle of 25°.

Optical images of the surface of the samples were taken with a stereomicroscope equipped with a digital camera.

UV illumination was conducted using a Blak-Ray longwave ultraviolet lamp at a wavelength of 365 nm.

UV-VIS emission spectra of the three brands of resin were taken at the excitation wavelength of 400 nm (435 LPF) showing the fluorescence intensity versus emission wavelength (nm).

## Results

All three of the resin brands showed similar changes at each target temperature. When heated, the organic component of the composite resin tested underwent pyrolysis in a nearly identical fashion. Figs. 1–5, though they depict Quixx, are representative of all three brands. The resins maintained their individual inorganic compositions as illustrated in Table 1. It should be noted that only one shade of resin was used. Apart from obvious visual shade differences, the only difference due to shade would be noted in small peak changes in the fingerprint region of the FTIR spectra. The organic dyes used to create shade form a minor proportion of the organic resin component and thus would not affect the overall appearance of the spectra. After analysis, the findings for the specimens at different temperature increments using the five instrumental techniques were as follows.

## FTIR Analysis

FTIR spectra shown in Fig. 1 demonstrate that as the resins were exposed to increasing temperatures, bond degradation did occur, with peaks associated with organic bonds between 2800 and 3000  $\text{cm}^{-1}$  diminishing in intensity. Thermal decomposition associated with weight loss begins to take place around 200°C. At 200°C and 300°C, a significant decrease in the peaks' intensity occurred, and by 400°C these peaks had completely disappeared, indicating that the organic bonds had been compromised due to the exposure to very high temperatures. Peaks near 1000  $\text{cm}^{-1}$  sustained a relatively uniform intensity until around 900°C, where a reduction was observed. The peaks near 1000  $\text{cm}^{-1}$  are associated with the inorganic filler particles that were able to resist changes when exposed to high temperatures.

When subjected to increasing temperatures, organic polymers begin the process of pyrolysis. During pyrolysis, bonds in the long chain polymers are broken, leaving free radicals, which combine with oxygen. As the temperature rises, the organic material breaks into successively smaller fragments, leaving the ultimate reaction products  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Breakdown of the bond structure can be characterized by FTIR. The peak near 1700  $\text{cm}^{-1}$  is associated with the carbonyl bond found in the organic matrix of the

TABLE 1—Composite resins used and their chemical composition according to manufacturer.

	Manufacturer	Organic Resin Matrix	Inorganic Fillers
Filtek Supreme	3 M (St. Paul, MN)	Bis-EMA, UDMA, Bis-GMA, TEDGMA	Silicon dioxide nano-silica, zirconium dioxide/silicon dioxide nano-clusters.
Quixx	Dentsply Caulk (Milford, DE)	UDMA, TEGMA, carboxylic acid modified dimethacrylate	Strontium aluminum, sodium fluoride, phosphate silicate glass.
Tetric Ceram	Ivoclar (Amherst, NY)	Bis-GMA, UDMA, TEGDMA	Barium glass, ytterbium trifluoride, dispersed silicon dioxide, spheroid mixed oxide.

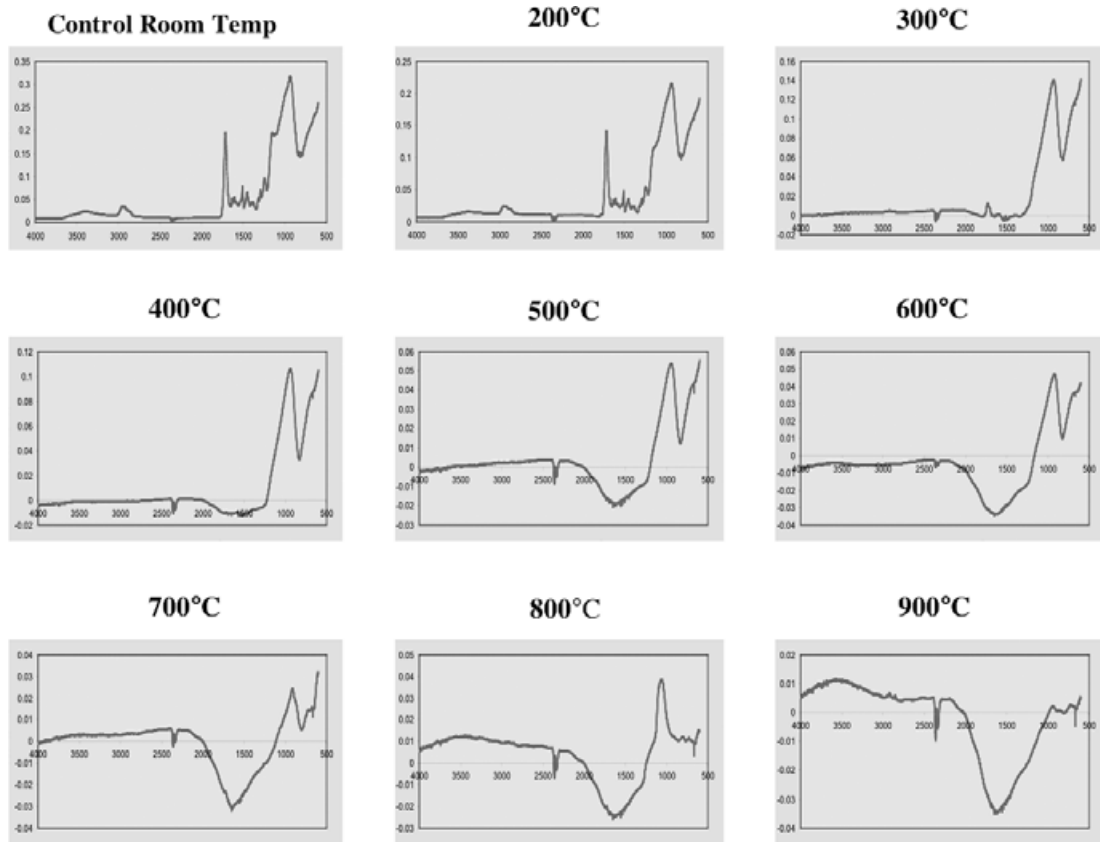


FIG. 1—Quixx (Dentsply) FTIR spectra recorded before and after incineration at a range of increasing temperatures. Note: The Y-axis represents Absorbance and the X-axis represents Wavenumber ( $\text{cm}^{-1}$ ).

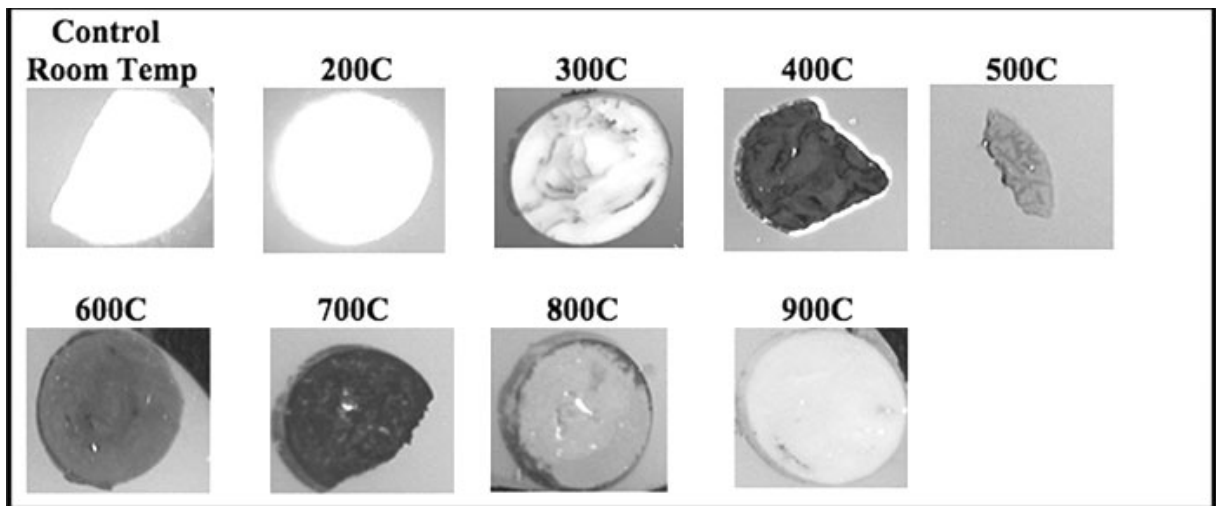


FIG. 2—Pictures of Quixx (Dentsply) resins under UV illumination before and after incineration at a range of increasing temperatures.

composite resin material. As the temperature of exposure increases, this peak diminishes in intensity above 300°C; therefore, a conclusion can be made indicating that degradation of the bonds associated with the organic material occurs above 300°C. At 200°C, the O-H band near the  $3400\text{ cm}^{-1}$  region had already disappeared.

*UV Illumination and UV-VIS Spectrophotometry*

Pictures of the resins under UV illumination were taken before and after incineration at a range of increasing temperatures as shown in Fig. 2. Visible inspection showed that the light beige color of the resin disc seen at room temperature was affected only

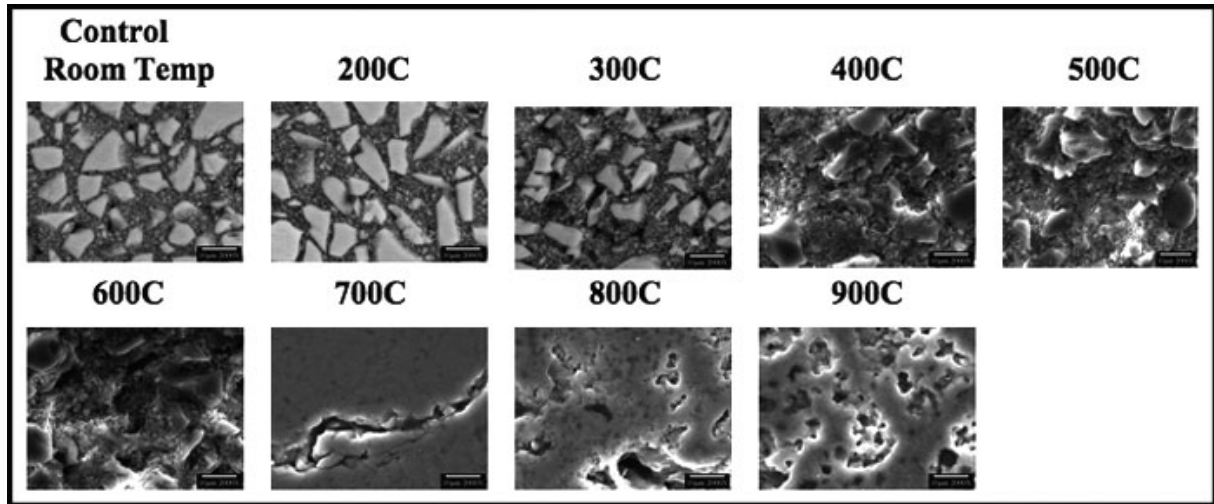


FIG. 3—SEM images of Quixx (Dentsply) resins before and after incineration at a range of increasing temperatures.

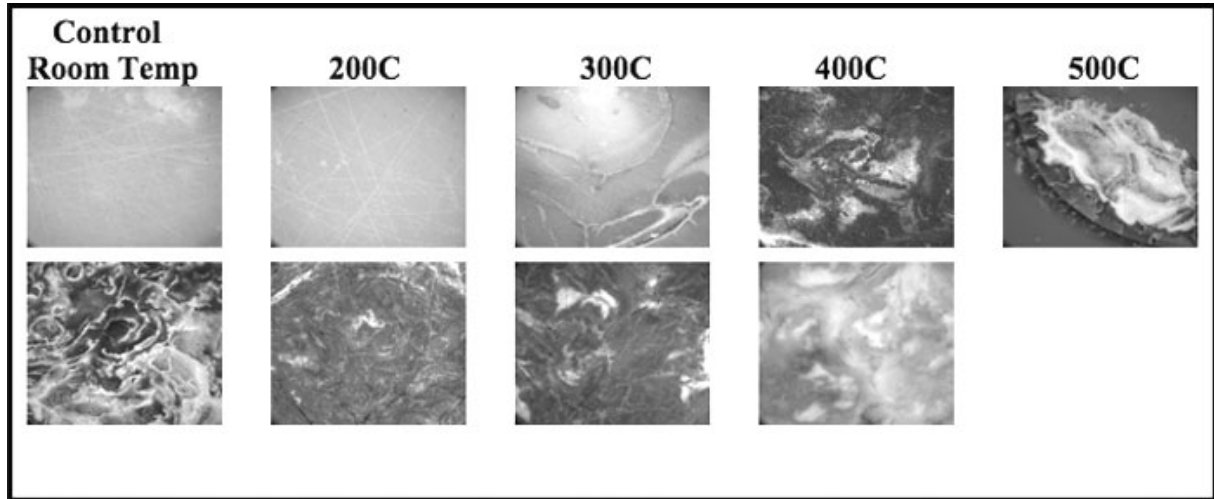


FIG. 4—Images taken by an optical microscope show the surface and color changes that took place as the Quixx (Dentsply) resins were heated to different temperatures.

at temperatures exceeding 200°C. The composite resin material had turned to a black color and appeared charred when exposed to temperatures from 300°C to 700°C. However, once the incineration temperature had reached 800°C and higher, the resins showed a tendency to lighten again to a chalky white color. Exposure to such high temperatures made the resins very brittle and fragile. Shrinkage associated with weight loss occurred as the incineration temperature increased. The majority of decomposition occurred between 200°C and 500°C suggesting that this temperature range may be associated with the breakdown and volatilization of organic materials present (8).

Visible inspection using UV illumination and also the UV-VIS spectrometer showed that the resins lost their fluorescence above 300°C. The loss of fluorescence above 300°C can help to indicate the temperature of victim exposure. Inspection of the dentition using UV light would reveal to the eye whether or not that temperature had been reached. All of the composites fluoresced at low temperatures, but the intensity of fluorescence

was different for each resin. In order of increasing intensity, Filtek had the lowest intensity followed by Quixx and Tetric Ceram.

As the fluorescing molecules undergo pyrolysis, the fluorescent property is lost. This was measured by UV-VIS spectrophotometry as shown in Fig. 5. This technique can determine without question whether any fluorescent properties remain. All of the composites fluoresced with a broad emission range at low temperatures, resulting in an intense blue/green color. The emission maxima for all three materials were centered around the 450–475 nm wavelength range, but fluorescence continued up to 600 nm. This resulted in an overall blue/green color.

This study indicates that the fluorescence property of the resins disappeared above 300°C. It should also be noted that while fluorescence was lost at temperatures above 300°C there was an initial increase in fluorescence from room temperature to 200°C. This is very likely due to the conversion of the unreacted double bonds in the polymerized material.

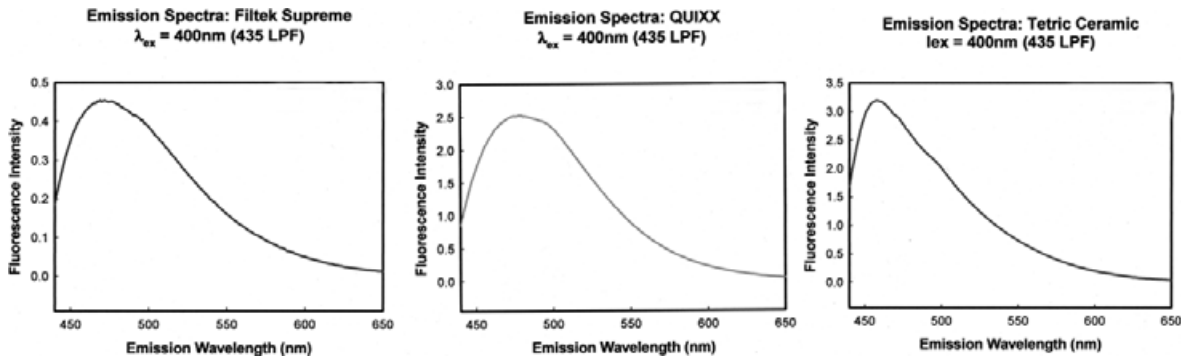


FIG. 5—UV-VIS spectra of the resins show fluorescence intensity versus emission wavelength (nm).

### SEM/EDS Analysis

Secondary electron microscopy images were taken by SEM at 2000 $\times$  magnification as shown in Fig. 3. These images revealed the microstructural changes that took place in the resins.

Above 300°C, the organic matrix disappeared resulting in a friable assembly of filler particles. At 700°C, the particles fused together in a single glassy mass. Above 700°C, porosity developed in the resins, indicating that there was a volatile component in the glass. This coincided with the FTIR results that showed the apparent and sudden decrease in the inorganic peaks intensity near the 1000  $\text{cm}^{-1}$  region. At 900°C, the resins appeared to be vitrified masses.

As the temperature increased, the inorganic material eventually melted and fused. Although the SEM images are necessarily qualitative, they nonetheless characterize the structure. This information could be useful in locating incinerated resins by gaining knowledge of the structural degradation of dental resin, and thus, their microstructural presentation in high temperature situations.

Pyrolysis of the organic component of the resin does not affect the inorganic filler particles. SEM/EDS allowed for individual characteristic classification based on the elemental composition of the inorganic filler particles.

### Optical Microscopy

Images taken by optical microscopy show the surface and color changes that took place in the resins (Fig. 4). Below 300°C, the surface appeared to be smooth and had a uniform grayish white color. At 300°C, the heat began to affect the appearance and composition of the resins as the surface began to crack and the color changed to reddish-orange. At 400°C the color of the resins changed to a charred black color and the surface became porous. After being exposed to temperatures from 500°C to 800°C, the resins became a lighter gray color with white swirls, and the surface became vitrified. Above 800°C, the surface of the resins became porous again, and the dark color began to subside as it transformed to a light gray color again. These changes were consistent with the sequence of organic pyrolysis followed by fusing and melting of the inorganic components.

### Discussion

Identification of victims of high temperature situations can be very difficult, especially when traditional means of determining identity cannot be employed such as DNA and fingerprint analysis.

Dental X-ray comparison may not be possible if the structural relationship of the jaws have been destroyed. Teeth can dislodge from the bone, enamel tends to fracture, and shrinkage of incinerated bone and teeth can be as high as 20–25% (5,6). Under these circumstances, the nonbiologic material present within the individual may provide the best clues for establishing identity. The oral cavity is a rich source of nonbiologic material.

There has been a 30% decrease in amalgam placement in the last 10 years as more restorations are being performed with composite resin (4). Therefore, it is important to detect the presence of composite resin and understand its chemical and physical changes in response to heat.

The effects of fire on teeth and dental materials are influenced by the temperature applied and by the duration of exposure. Other factors such as the protection of teeth by tissues of the oral cavity, the use of accelerants or any fire-extinguishing chemicals can also play a role in varying the temperature reached during a fire and its effect on composite resins (8). Other situations, if involving accelerants and combustion can raise the temperature of exposure up to 800°C–1100°C (9). Though most house fires seldom reach temperatures in excess of 649°C, this temperature is still high enough to cause the loss of fluorescent properties of the resin (10).

As the fluorescing molecules undergo pyrolysis, the fluorescing property is lost. This occurs at a fairly low temperature, 300°C, as shown by UV illumination. Though UV light is an excellent method to detect composite resin in a nonincinerated individual, it may be essential for the examiner to discontinue the use of UV light for inspection of the dentitions of victims of fire fatalities. In these circumstances, the resin will not show a contrast from the tooth structure, leading investigators to possibly believe that a resin is not present, when in fact it is.

Traditional inspection with X-radiography and tactile sensation would be the best means of evaluation for composite resin under these circumstances, as the radiopacity of the resins will be maintained. Radiopacity of the material is determined by the addition of heavy elements in the inorganic filler particles. The composition of the inorganic filler particles is unaffected by high temperature situations and radiopacity is an excellent means of composite detection in these circumstances (5).

Changes to the overall appearance of the resin can be characterized. With increasing temperatures, the change to the composite resin can become drastic. Based on the observed color changes that took place as the resins were heated, exposure to temperatures below 300°C showed no color change from the light beige color seen at room temperature. However, exposure to temperatures from 300°C to 700°C showed that the resins turned to a charred black material, and above 800°C, the resins showed an ability to turn to

a chalky white color. This information could help investigators to search for the correct color of resin material when looking through charred remains and ashes, as the color would vary depending on the temperature the fire may have reached.

It is recognized that this study is limited to three resin brands currently available in the United States. However, the analysis demonstrated that resins respond to heat in a similar fashion. It is also of interest to note that while the organic components broke down in a similar fashion, the inorganic filler composition remained unchanged, thus allowing for distinction of resin brand.

As with any forensic evidence, the more tests one can run, the more reliable the conclusions will be. In this study, five such techniques were used to analyze changes in restorative resin properties. In order for composite resin to be used as an aid in victim identification, it must be located. From this information, it is hoped that the task of correlating dental composite resins found at a crime scene with existing dental records will assist in identifying unknown remains.

#### *Acknowledgments*

Support for this work was given by Peter Bush, BS and Raymond Miller, DDS of the South Campus Instrument Center, University at Buffalo, School of Dental Medicine and the Chemistry Department at Buffalo State College.

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