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The use of near-infrared spectroscopy for the cure monitoring of an ethyl cyanoacrylate adhesive

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Abstract

Near-IR reflectance spectroscopy has been used to study the curing of ethyl cyanoacrylate adhesive on polished dental glass and microscope slide substrates. The effects of changing the glue film thickness and the type of substrate on the curing rate have been investigated whilst maintaining a constant humidity. The FTIR spectral data has been used to calculate and plot the extents of cure versus time for various film thicknesses.

Keywords: Cyanoacrylate; Cure monitoring; Near-IR spectroscopy; Film thickness

1. Introduction

Cyanoacrylates are one of many types of synthetic adhesives. They show exceptional adhesion to a wide range of materials such as metals, plastics, rubber, ceramics, woods, and fabrics. Besides their versatility, cyanoacrylates have several other assets. As they are one-part adhesives, no mixing or metering is required and only occasionally are substrate surface primers necessary. They contain no solvents and so, not only is there no need for solvent evaporation, they are also potentially 100% reactive. As only minimal amounts of the adhesive are required for optimal bond strengths to be achieved, cyanoacrylates are an economical adhesive [1]. Due to these unique properties, cyanoacrylates are the focus of this work.

Cyanoacrylates have been developed over the years to suit a continually increasing range of substrates and applications. Cyanoacrylates are ideal as industrial product assembly adhesives due to their ability to rapidly form bonds with many types of materials [1]. They have been used widely in the automotive, electronics, household appliance, home repair, furniture and hobby industries. Another more unusual application is in the detection of latent fingerprints in crime investigations [2–4]. Cyanoacrylates are also bacteriostatic [5] and have therefore found applications in medicine and dentistry. Some examples of such applications are plastic surgery [6], over-the-counter mouth ulcer dressings [7], ophthalmic surgery [8], nailbed repair [9], and post-extraction dressings in dentistry [5].

Recently, cyanoacrylates incorporated into glass-ionomer cement (GIC) formulations have been described [10]. These types of composites could be used for various general adhesive applications, but in particular, show potential as dental restorative cements. These types of cement would represent a new alternative to the already available resin-modified glass-ionomer cements (RMGICs: glass-ionomers modified by the addition of a resin component typically hydroxyethyl methacrylate) but with several advantages. For example, they would show enhanced adhesive properties due to the adhesive nature of the cyanoacrylate in comparison to the (non-adhesive) methacrylate resin. Due to the basic nature of the glass and the nature of the polymerisation reaction, these cements should also not suffer from incomplete polymerisation; a common problem for light-activated RMGICs [11,12]. The need for

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incremental placement by the dentist would thus be avoided. In comparison to GICs, these cyanoacrylate-modified GICs would develop and strengthen more rapidly and again show improved adhesive properties. This study forms part of an ongoing, extensive program of investigation and development of these cement formulations. This work uses infrared spectroscopy to investigate the reaction between a cyanoacrylate adhesive and *planar* dental (GIC) glass, as this will be useful for understanding the more complex bonding that will be occurring between cyanoacrylates and *powdered* dental (GIC) glass. As will be described again later on, the curing of the cyanoacrylate will also be performed on a microscope glass slide substrate to compare the results for a different glass composition.

Cyanoacrylate esters are known to polymerise by both free radical and anionic mechanisms [13]. The latter mechanism has attracted more attention in the field of adhesives due to the ease of initiation and the rapid rates of polymerisation that can occur. Anionic polymerisation can be initiated by mild nucleophiles such as water or alcohols because of the electron withdrawing groups –COOR and –CN groups on the α-carbon atom of the cyanoacrylate ester molecule. These groups not only reduce the electron density on the β-carbon thereby rendering this position susceptible to nucleophilic attack, they also significantly stabilise the anion formed at the α-carbon after such attack, by delocalising the negative charge. In most cases, ambient humidity in the air and moisture on the bonding surface are sufficient to initiate polymerisation within just a few seconds [1].

The mechanism for the anionic polymerisation of cyanoacrylates has been compiled from various literature sources [1,4,14–18] and is shown in Fig. 1. Despite the display of the chain transfer and termination steps in Fig. 1, these steps of the mechanism are much less clear [1] and are often not addressed in the literature [14–16]. However, it is believed a water molecule can react with a ''living'' polycyanoacrylate chain anion, thereby producing an inert polymer chain and a hydroxyl ion which can initiate further polymerisation of any remaining monomer molecules [1,17]. It is thought that the inert or ''dead'' polymer chain may also act as chain transfer agent (not shown in Fig. 1) [19]. Termination occurs when the chain anion reacts with a species such as an acid [1,4,18].

FT Raman [4,20], mid-infrared (mid-IR) [15,21–24], electron tunnelling [22] and nuclear magnetic resonance spectroscopy [15] have been used in the past to study the curing process of cyanoacrylates. The quantification of the extent of monomer conversion to polymers with time has been performed previously [4,20,23]. For example, Raman spectroscopic studies [20] have been used to quantify the extent of cure of a (unspecified) cyanoacrylate between an aluminium surface and a glass slide with time. The calculations were based on the changing intensity of the peak of the C–O–C bond at 840 cm^{-1} possibly corresponding to an oxirane ring present as an additive in the adhesive. However, as the role of the additive in the curing mechanism is not exactly known, the change in additive concentration may not be proportional to the change in monomer concentration. A more accurate assessment of monomer conversion may be obtained from the intensities of the peaks corresponding to the C=C or neighbouring bonds (e.g. the C–H bond) because the C=C functionality is disappearing during the polymerisation process.

Other Raman studies have investigated the polymerisation of an ethyl cyanoacrylate sealed with moisture in a glass tube (diameter 4 mm) [4]. It was estimated, based on the disappearance of the C=C bond, that the polymerisation had proceeded to 85% completion after 92 days. The amount of added water in the system, which may affect overall conversion, was not indicated. The limited amount of water in the system possibly prevented complete monomer conversion even after 92 days.

Other mid-FTIR spectroscopic studies [23] of a curing (unspecified) cyanoacrylate on a borosilicate glass disc quantified monomer conversion with time based on the changing peak area corresponding to the C–H (in H_2C=C) bond, and determined the adhesive to be 100% cured in 4–5 min. The high extent of cure (100%) in comparison to that (85%) obtained from the Raman studies [4] described previously may be due to the fact that the cyanoacrylate was spread out on the substrate using a swab, in comparison to being contained sealed in glass tube [4]. Consequently, the cyanoacrylate samples in these experiments had different humidity conditions (or water access), which may explain the difference in results. In addition, the cyanoacrylate studied may have been a different type to that used in the Raman studies [4]. The rapid setting time (4–5 min) was possibly due to the basicity of the glass surface [25] and again the fact that the cyanoacrylate sample may have been spread as a thin film.

Studying the effects of film thickness on the curing of cyanoacrylates whilst maintaining a constant humidity, may provide a better understanding of the overall mechanism and in particular the role of water in the curing process. Ambient humidity in the air and surface absorbed water is usually sufficient to neutralise any acid stabiliser and then to initiate the curing reaction (anionic radical polymerisation). It has been claimed that in order to achieve a fast cure and to obtain a strong bond, a very thin film is required [1]. A thick film of cyanoacrylate between the adherends is known to produce a weak bond because the surface-initiated cure may not extend throughout the entire film thickness. The film thickness is therefore very important, as it determines the bond strength. The effect of changing the film thickness of a curing ethyl cyanoacrylate on an aluminium surface has been studied previously using spectroscopy [21,22] but these studies focused on a cyanoacrylate/oxidised aluminium interface rather than the curing of the entire depth of the cyanoacrylate film. Spectral changes resulting from varying the film thickness were used to derive the vibrational spectrum of the adhesive molecule in the first monolayer and it was

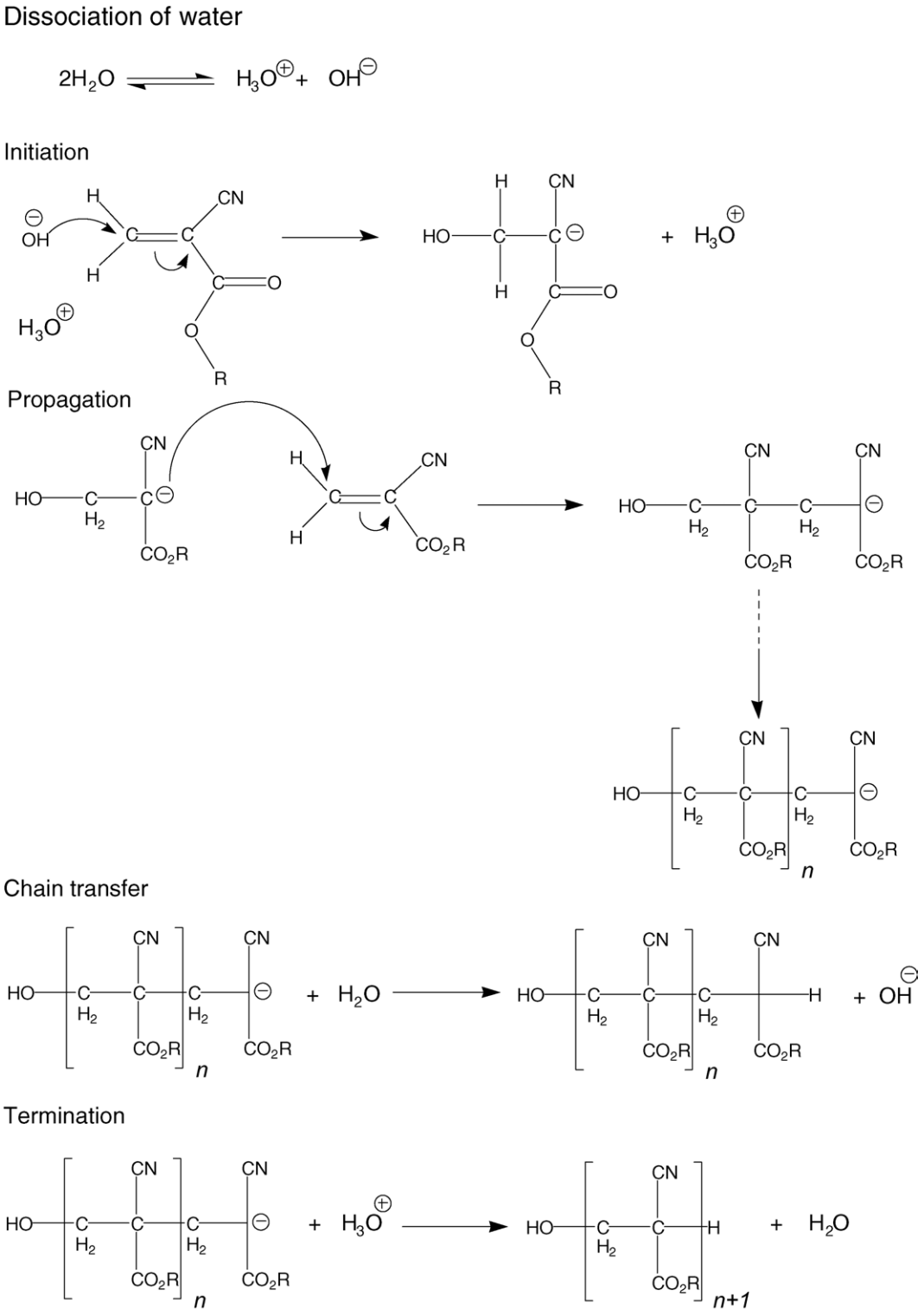

Fig. 1. Anionic polymerisation of cyanoacrylates initiated by mild nucleophiles [1,4,14–18].

concluded that there might be hydrogen-bonding occurring between the surfaces. To date there appear to be no studies quantifying the effect of the cyanoacrylate film thickness on the extent of cure of the cyanoacrylate. This study therefore aimed to find a quantitative correlation between cyanoacrylate film thickness and extent of cure with time.

The nature of the substrate the cyanoacrylate is bonding to may significantly affect the cyanoacrylate curing process. As clear from the above, only a limited number of different cyanoacrylate curing substrates have been investigated and these were isolated studies, which cannot be reliably compared due to different experimental conditions. This

study therefore aims to investigate the curing of ethyl cyanoacrylate on two types of substrate: a planar dental glass (KG 23) disc and a standard glass microscope slide. As mentioned previously, a knowledge of how cyanoacrylates cure on planar dental glass will be useful for understanding the more complex bonding that will be occurring between cyanoacrylates and powdered glass. In addition, cyanoacrylates are known to show poor durability when bonding to planar glass. This is believed to be due to the basic nature of the glass causing rapid cyanoacrylate curing which leads to high stress in the bond line, and therefore renders the cyanoacrylate at the bond line particularly susceptible to chemical or physical degradation [25]. The comparison of cyanoacrylates curing on these two different compositions of glass in this study may further clarify this theory.

The vast majority of the reported cyanoacrylate curing studies [15,21–23] have been carried out in the mid-IR range, showing fundamental absorptions. To date there have been no infrared spectroscopic studies of curing cyanoacrylates performed using near-infrared (near-IR) reflectance spectroscopy. Near-IR spectroscopy has recently become a popular technique and it has various advantages over mid-IR spectroscopy [26–28]. The presence of the fundamental bands in mid-IR sometimes hampers the identification of the absorption bands of interest. In contrast, the near-IR region is dominated by overtones and combination bands, which can be isolated more easily. In addition, the lower intensity of the near-IR bands may be used as an advantage because it is often difficult to obtain on-scale mid-IR spectra [29,30].

Near-IR spectroscopy has recently been used to monitor the curing of unfilled [28,31–35] and filled [34,36–39] dental resins. The majority of the dental resins studied in this way have been standard methacrylate mixtures, Bis-GMA/TEGDMA [28,31,34,36–39]. The majority of previous studies obtained spectra using standard spectrometers with enclosed sample compartments. Only limited studies [34,37,38] to date have involved near-IR spectroscopy using fibre optics and these were using different arrangements to that used in this study. As opposed to the studies referenced above, which used *transmission* spectroscopy, this current cyanoacrylate study uses an optical fibre probe to obtain *transflectance* [40] measurements. The general set-up for transflectance measurements is such that the incident light passes through the sample of interest, reflects off for example an aluminium plate, and then travels back through the sample before reaching the detector. Recording NIR transmission spectra for liquids or gels would be awkward, especially for cyanoacrylates due to the need for filling and emptying the cuvettes. By using transflectance, the need for a mould or cuvette to contain the liquid can be avoided.

Near-IR spectroscopy has been the chosen technique for this study because of the above-mentioned advantages and due to the following other practical advantages: working in the mid-IR region requires long, tedious sample preparation in comparison with near-IR; and the near-IR optical fibre probe (connected to a spectrometer) is flexible and relatively small in size, thus making the near-IR apparatus readily portable, and more convenient to use than a standard mid-IR spectrometer. Its portability is particularly convenient for the humidity effect studies. To help identify and confirm peaks in the near-IR spectra, mid-IR studies were also undertaken.

2. Experimental

2.1. Materials

The ethyl cyanoacrylate used in this investigation was commercially obtained and is known under the trade name of Loctite Super Glue Control Liquid (product code: 0158589) [41]. The material was used as received. A fresh sample was used each time for each test. Attempts to establish the detailed composition of the adhesive using ^{1}H NMR spectroscopy and mass spectrometry have so far been unsuccessful due to the very complex spectra obtained in both cases. Besides the major peaks representing the cyanoacrylate functional groups/bonds, there were numerous (weak) peaks present, indicating there to be a mixture of additives present in only very small concentrations. This analysis will require further investigation.

2.2. FTIR spectrometer–near-infrared

A Bruker Matrix-F FTIR Spectrometer [42] with a standard reflectance optical fibre probe [43], provided by Bruker Optics Limited, UK [42], was used for the tests. The FTIR spectrometer operated in the near-IR region of 4000–10,000 cm^{-1} using a white light source and a TE-InGaAs detector, along with a CaF_2 beamsplitter. Reflectance spectra were collected at 4 cm^{-1} resolution. The collection time of each spectrum was 30 s and one spectrum was collected every minute for 100 min.

The substrates used were KG23 dental glass and standard microscope glass slides. The main components of the KG23 glass (indicated as mass%) are: silica (42.4%), alumina (28.3%), strontia (13.6%) and fluoride (8.4%). Present in smaller amounts are calcium oxide, soda, phosphorous pentoxide, barium oxide and zinc oxide [44]. The microscope glass slides were provided by Chance Propper Ltd. [45]. The composition of the microscope slides was determined using an Energy Dispersive X-ray (EDX) Spectrometer (Oxford Instrument INCA 4.04). The main elements contained in the glass (indicated as mass%) were found to be: oxygen (53.14%), silicon (30.74%), and sodium (9.56%). Present in smaller amounts are calcium, magnesium, aluminium, and potassium.

2.3. FTIR spectrometer–mid-infrared

A Bruker Vector 22 FTIR spectrometer was used for monitoring the curing of ethyl cyanoacrylate in the mid-IR region. In this case, the FTIR spectrometer was configured to

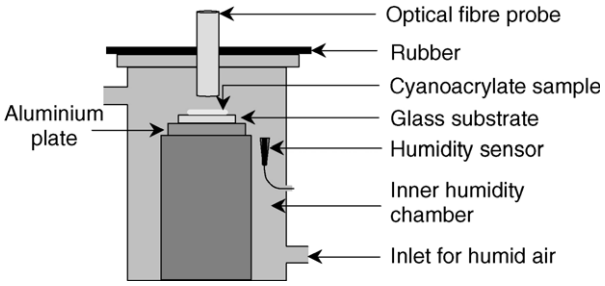

Fig. 2. Overall experimental set-up for controlling the humidity surrounding the curing cyanoacrylate sample during near-IR spectroscopic studies.

operate in the mid-IR region of 400–4000 cm^{-1} using a DTGS detector and a KBr beamsplitter with multilayer coating. The tests were carried out in the main bench compartment, in transmission using 1 mm thick KBr windows. The collection time of each spectrum was 30 s and one spectrum was collected every minute for 100 min.

2.4. Near-infrared experimental set-up

A schematic diagram of the overall experimental set-up is given in Fig. 2. A lab-built humidity chamber [46] was used to control the humidity during the cure tests. The arrangement consisted of a reflectance optical fibre probe connected to the FTIR spectrometer, a glass slide used as a substrate for the curing cyanoacrylate sample, and an aluminium plate placed under the glass slide, required for reflection.

All different film thickness experiments were carried out at 40% relative humidity and room temperature (averaging 22.5 °C).

3. Results and discussion

3.1. Mid-infrared spectra

For clarity, only the mid-IR spectra recorded every minute between 0 and 5 min and finally at 100 min are displayed in the graphs (Figs. 3, 4 and 6). These particular spectra were chosen because they gave the clearest indication of how the peaks were changing during the curing process. The ambient temperature was 23 °C, the relative humidity was 57% and the cyanoacrylate film thickness was 0.325 mm.

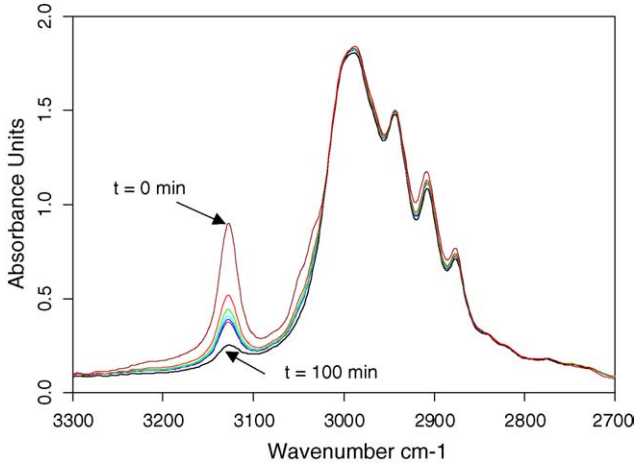

Fig. 3. Mid-IR transmission spectra of the curing cyanoacrylate system in region A (only spectra recorded every minute between 0 and 5 min and finally at 100 min are displayed).

Mid-IR peak assignments of the cyanoacrylate system are presented in Table 1.

The three wavenumber regions of particular interest in the mid-IR spectra are: 2700–3300, 2200–2300, and 1500–1900 cm^{-1}. In order, these will be referred to as regions A–C, and are shown in Figs. 3, 4 and 6, respectively.

Fig. 3 shows the detailed structure of the changing spectra as a function of time in region A. Peaks corresponding to the –C=C– stretching vibrations of the vinyl structures (=CH–, $=CH_2$) at 3130 cm^{-1} and the –C–H stretching vibrations (symmetric and asymmetric) of the methyl and methylene ($-CH_2-$, $-CH_3$) groups between 2800 and 3050 cm^{-1} can be seen. As mentioned earlier, the C=C bond is of great importance for cyanoacrylate cure monitoring because this functionality is disappearing during the formation of polymer chains from monomer units (see Fig. 1).

Fig. 4 shows the detailed structure of the changing spectra as a function of time in region B. The peak within this region corresponds to the –C≡N stretching vibration. It can be seen that the –CN peak starts at 2240 cm^{-1} and then shifts during

Table 1
Major mid-IR peak assignments for cyanoacrylate system

Wavenumbers (cm^{-1})	Peak assignments and comments
3130	=C–H stretching vibrations of vinyl structures ($=CH_2$, =CH–)
3080–2800	C–H stretching vibrations (symmetric and asymmetric) of $-CH_2-$ and CH_3- groups
2240	–C≡N stretching vibration shifts to 2248 cm^{-1} along with a change in shape. This might be due to conjugation effects between the –C≡N and C=O/C=C bonds
1747	–C=O stretching absorption
1615	C=C stretching vibration (this vibration absorbs more strongly because the groups attached to the C=C bond are not symmetrical, and therefore lead to a strong dipole momentum. The conjugation effects between the C=C and C=O/C≡N bonds leads to this lower frequency of vibration (normally present between 1630–1670 cm^{-1})
1500–1350	CH_2 and CH_3 scissoring and bending region

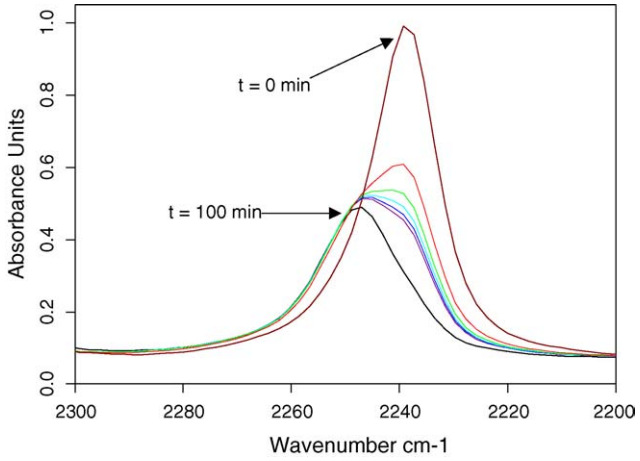

Fig. 4. Mid-IR transmission spectra of the curing cyanoacrylate system in region B (only spectra recorded every minute between 0 and 5 min and finally at 100 min are displayed).

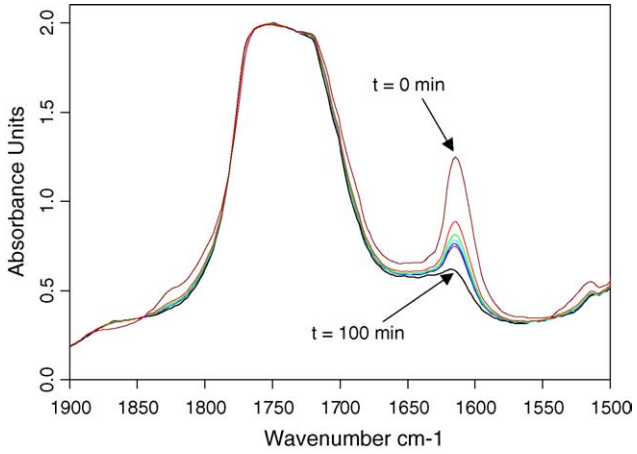

Fig. 6. Mid-IR transmission spectra of the curing cyanoacrylate system in region C (only spectra recorded every minute between 0 and 5 min and finally at 100 min are displayed).

the cure process to 2248 cm^{-1}. At the same time, the peak intensity is changing. To quantify this change, the peak area throughout the cure was calculated. The normalised –CN peak area as a function of time is presented in Fig. 5.

The shift of the peak as well as the change in shape has been noticed previously [4], and it was thought to be associated with the loss of conjugation between the –C≡N, C=C and C=O groups and with the presence of the –CN groups in two distinct environments in the system. Another possibility is that after nucleophilic attack (in the initiation step), the –COOR and –CN groups significantly stabilise the anion formed at the α-carbon by delocalising the negative charge. The shift of the –CN peak could also be a consequence of intra- and intermolecular hydrogen bonding. It is not clear at this stage if the decrease in –CN peak area is a consequence of one of the above-mentioned phenomena, or if it is related to a chemical reaction.

Fig. 6 shows the detailed structure of the changing spectra as a function of time in region C. Here peaks corresponding to the –C=O stretching vibration at 1747 cm^{-1} and the C=C stretching vibration at 1615 cm^{-1} can be seen.

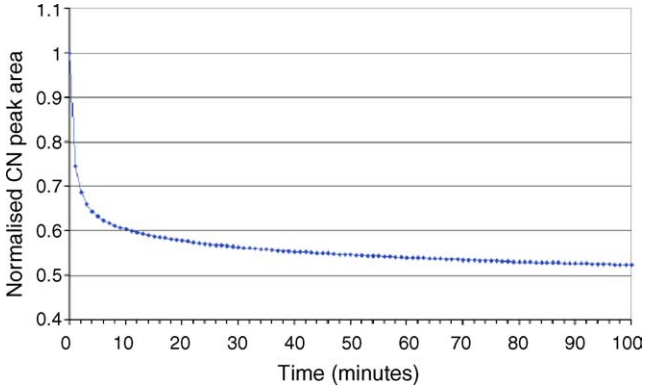

Fig. 5. Graph showing the area of the peak corresponding to the C≡N bond (at 2240 cm^{-1}) decreasing with time.

3.2. Near-infrared spectra

Once the mid-IR spectra of the cyanoacrylate system were fully understood, the peak assignments of the near-IR spectra were carried out. For clarity, only the near-IR spectra recorded at 0, 20, 40, 60, 80 and 100 min are displayed in the graphs (Figs. 7 and 8). These particular spectra were chosen because they gave the clearest indication of how the peaks were changing during the curing process. The ambient temperature was 23 °C, the relative humidity was 40% and the cyanoacrylate film thickness was 0.07 mm.

Near-IR spectra peak assignments of the cyanoacrylate system are presented in Table 2.

The two wavenumber regions of particular interest in the near-IR spectra are: 5500–6500 and 4400–5500 cm^{-1}. In order, these will be referred to as regions D and E, and are displayed in Figs. 7 and 8, respectively.

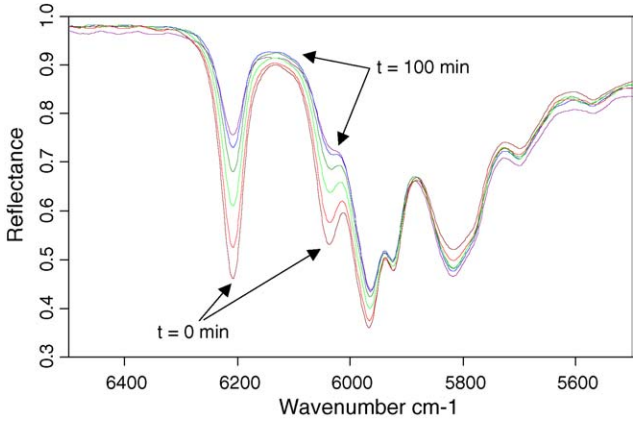

Fig. 7. Near-IR reflectance spectra of the curing cyanoacrylate system in region D (only the spectra recorded at 0, 20, 40, 60, 80 and 100 min are displayed).

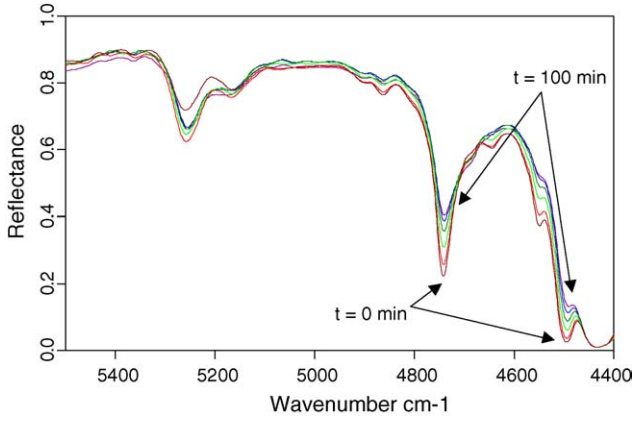

Fig. 8. Near-IR reflectance spectra of the curing cyanoacrylate system in region E (only the spectra recorded at 0, 20, 40, 60, 80 and 100 min are displayed).

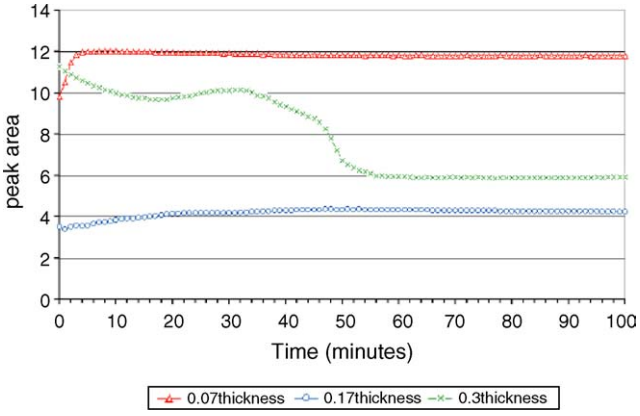

Fig. 9. Area of peak corresponding to aliphatic C–H bond (5810 cm^{-1}, used for normalisation) throughout curing of various films thicknesses of ethyl cyanoacrylate on dental glass disc.

Fig. 7 shows the detailed structure of the changing spectra as a function of time in region D. This region displays peaks corresponding to the first overtone of the =C–H stretching vibration of the vinyl structures at 6207 cm^{-1} and the first overtones of the C–H stretching vibrations of the methyl and methylene structures between 5600 and 6000 cm^{-1}. The 6207 cm^{-1} peak will be used for the determination of the extent of cure.

Fig. 8 shows the detailed structure of the changing spectra as a function of time in region E. The peak at 5257 cm^{-1} corresponds to the first overtone of the –CN functional group.

3.3. Film thickness effects

The FT-NIR data was analysed by plotting and comparing extents of cure against time for each film thickness. The extent of cure throughout each cure experiment was calculated using Eq. (1) shown below:

$$\alpha_t = \left(1 - \frac{(A_{H_2C=C}/A_{C-H})_t}{(A_{H_2C=C}/A_{C-H})_{t=0}}\right) \times 100 \quad (1)$$

where α_t is the extent of cure at time t, $A_{H_2C=C}$ is the area of the C–H (in H_2C=C) peak at 6207 cm^{-1}, and A_{C-H} is the is the area of the C–H peak at 5810 cm^{-1}.

For the near-IR data, the C–H bond (peak at 6207 cm^{-1}) directly linked to the C=C (i.e. H_2C=C) bond was chosen to quantify the extent of cure. To compensate for any changes in path length due to physical processes such as shrinkage or variations in temperature, the peak corresponding to the aliphatic C–H bond (peak at 5810 cm^{-1}) was used an internal standard. The use of this C–H bond peak to normalise the data with has been used previously in mid-IR spectroscopic studies [4,23]. Figs. 9 and 10 show plots of the C–H bond peak areas throughout the curing of the various film thickness of adhesive on dental glass and microscope glass slide substrates, respectively. It can be seen that most of the plots display a relatively constant peak area for the C–H bond throughout the curing process. Any small changes could be due to physical processes such as shrinkage, the sample settling down (flow) or variations in temperature. However, for both substrates, there is one plot that shows a significantly decreasing C–H bond peak area; on dental glass it is the 0.3 mm thick film and on the microscope glass slide it is the 0.25 mm thick film. These anomalous results have not affected the overall results at this stage but will be the subject of further investigation.

The curing of several different thicknesses of cyanoacrylate film was monitored using near-IR spectroscopy and plots of extent of cure versus time for KG 23 glass and microscope glass slide substrates are shown in Figs. 11 and 12, respectively. It is important to remember that, as this is a transflectance technique, the infrared light travels through the entire film thickness therefore and so the information collected is an average of the fast (adhesive/air; substrate/adhesive) and slow (central) curing areas.

For both substrates, it can be seen that that the thicker cyanoacrylate films require more time, in comparison to thinner films, to reach an equivalent extent of cure. For

Table 2
Near-IR peak assignments for cyanoacrylate system

Wavenumbers (cm^{-1})	Peak assignments and comments
6207	First overtone of C–H stretching vibrations of vinyl structures (=CH_2, =CH–)
6015–5600	First overtone of C–H stretching vibrations (symmetric and asymmetric) of –CH_2– and CH_3– groups
5257	First overtone of –C≡N stretching vibration

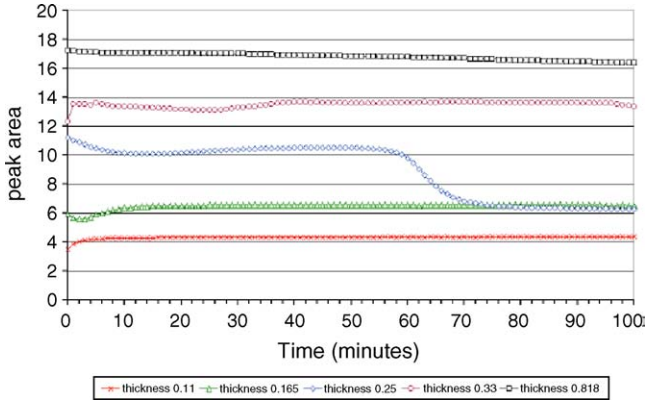

Fig. 10. Area of peak corresponding to aliphatic C–H bond (at 5810 cm^{-1}, used for normalisation) throughout curing of various films thicknesses of ethyl cyanoacrylate on microscope slide glass.

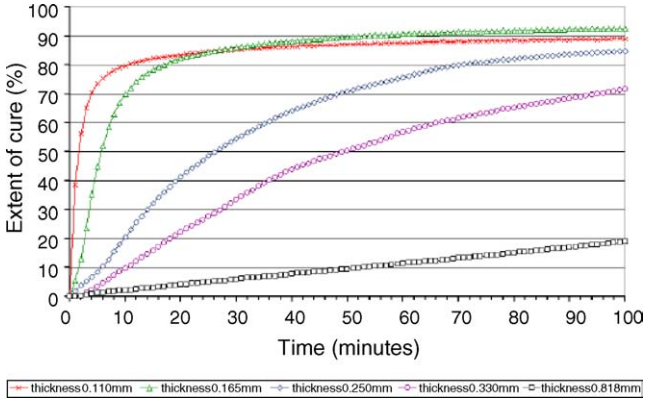

Fig. 12. The extent of cure vs. time curves for cyanoacrylate films of various thicknesses on microscope glass slide (40% relative humidity and room temperature, averaging 22.5 °C).

example, in the case of the KG 23 glass substrate, the 0.3 mm cyanoacrylate film, reached its maximum level of monomer conversion after 100 min. In comparison, for the thinner 0.07 mm film, the bulk of the polymerisation had finished after approximately 20 min as the monomer conversion was levelling to its maximum (see Fig. 11). Similarly, in the case of microscope slide substrate, the 0.11 mm cyanoacrylate film was converging to its maximum level of conversion after 20 min, whereas the 0.33 mm film, after 100 min, attained only 70% conversion (see Fig. 12).

As the curing mechanism is initiated by water, polymerisation is relatively fast both at the surface/adhesive and the adhesive/air interfaces where the adhesive has direct contact with water. A ''waterproof'' layer of polymer chains may be forming at both interfaces. These layers will slow down and possibly, eventually, completely prevent water penetration to the central region of the cyanoacrylate film. Therefore, for thicker films, these impenetrable layers may result in water never reaching the inner region of the cyanoacrylate film, thus leaving it uncured. This might explain why the thicker films levelled to a slightly lower extent of cure even after 100 min in comparison to the thinner film (see Fig. 11).

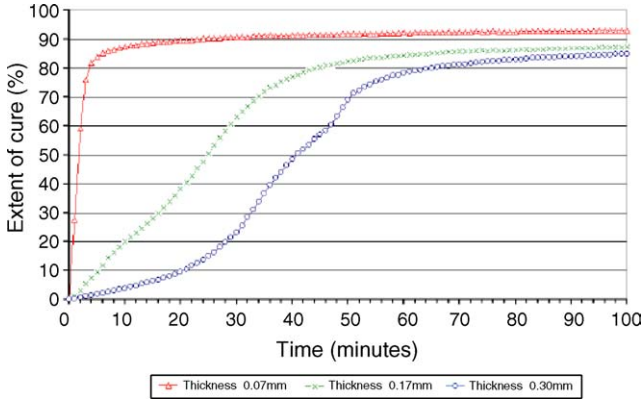

Fig. 11. The extent of cure vs. time curves for cyanoacrylate films of various thicknesses on KG 23 dental glass (40% relative humidity and room temperature, averaging 22.5 °C).

Another factor to consider is that the substrate has a finite amount of water (OH^-) on its surface in comparison to the infinite supply of moisture in the air. Therefore, while the cyanoacrylate can theoretically continuously cure from the upper surface downwards, the cyanoacrylate in contact with the substrate may stop curing after the water on the substrate is consumed. If this is in fact occurring, this will contribute to the lower extent of cure, after a given time, for the thicker films in comparison to the thinner films.

It is important to discuss the fact as the viscosity of the monomer–polymer mixture increases (as a function conversion) the movement of *all* species, not only water, in the mixture will become increasingly hindered. Areas of the adhesive film may be developing, in which ''living'' polymer-chain anions are becoming isolated in the glassy matrix of the polycyanoacrylate [1]. Any further reaction would depend on the slow diffusion of monomer molecules (and water molecules for chain transfer) to the immobile anion chains. This theory might account for some of the remaining monomer (after 100 min) in even the very thin films of cyanoacrylate used in this work [1].

The unreacted monomer in the film, apparent from the conversion plots, may be therefore due to a combination of two main factors. Firstly, the ''waterproof'' layer of polymer chains forming at both film interfaces will prevent any more water entering the film. This will prevent initiation by the hydroxyl anions and will prevent the water from producing any further hydroxyl anions by reacting with the ''living'' polymer-chain anions. Secondly, ''living'' polymer-chain anions may be becoming isolated within the glassy matrix of the polycyanoacrylates. This means they will not readily be able to react with unreacted monomer; in time (slow) diffusion may result in further monomer conversion. As the conversion plots are based on the changing peak area of the $H_2C{=}C$ feature, which should only significantly be affected during initiation and propagation, we cannot directly identify what transfer and termination steps are occurring.

An interesting feature to note is that for the samples cured on KG 23 dental glass (Fig. 11), the shapes of the cure curves are different for the various film thicknesses. A change as little as 0.1 mm in film thickness drastically modifies the cyanoacrylate cure curve profile. This indicates that the mechanism of cyanoacrylate curing is changing as a function of thickness. This is not the case for samples cured on microscope glass slides (Fig. 12) where the cure curves for the various film thicknesses are similar in shape. It can therefore be concluded that both the type of substrate and the film thickness significantly effect the curing of cyanoacrylates. Further investigations are required to gain a full understanding of the mechanisms and kinetic models governing the cyanoacrylate curing process for the two substrates.

In the future, this work will be extended to various glass powder/cyanoacrylate cement compositions, for possible use as dental filling materials [10].

4. Conclusions

This study demonstrates the feasibility of monitoring the curing of cyanoacrylates using near-IR reflectance spectroscopy. Near-IR spectroscopy has proved to be a versatile, simple tool for monitoring the curing of cyanoacrylates. The flexibility of the optical fibre probe makes this technique particularly convenient for use with a controlled humidity chamber. Both the type of substrate and thickness of the cyanoacrylate film have been found to have a strong effect on the cure curve profile.

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References

[1] G.H. Millet, in: S.R. Hartshorn (Ed.), Cyanoacrylate Adhesives in Structural Adhesives: Chemistry and Technology, Plenum, London, 1986 (Chapter 6).
[2] E.R. Menzel, J.A. Burt, T.W. Sinor, W.B. Tubach-Ley, K.J. Jordan, J. Forensic Sci. 28 (1983) 307.
[3] D.L. Exline, C. Wallace, C. Roux, C. Lennard, M.P. Nelson, P.J. Treado, J. Forensic Sci. 48 (2003) 1047.
[4] H.G.M. Edwards, J.S. Day, J. Raman Spectrosc. 35 (2004) 555.
[5] J. Grisdale, J. Can. Dent. Assoc. 64 (1998) 623.
[6] D.M. Toriumi, K. O'Grady, D. Desai, A. Bagal, Plast. Reconstr. Surg. 102 (1998) 2209.
[7] M. Kutcher, J.B. Ludlow, A.D. Samuelson, T. Campbell, S.N. Pusek, J. Am. Dent. Assoc. 132 (2001) 368.
[8] B.J.T. Vote, M.J. Elder, Clin. Exp. Opthalmol. 28 (2000) 437.
[9] G.G. Hallock, Ann. Plast. Surg. 46 (2001) 185.
[10] A.J. Bennetts, C.G Wilde, A.D. Wilson, UK Patent No. GB 2386121 (2003).
[11] E.J. Swift Jr., M.A. Pawlus, M.A. Vargas, D. Fortin, Dent. Mater. 11 (1995) 196.
[12] G.J. Mount, C. Patel, O.F. Makinson, Aust. Dent. J. 47 (4) (2002) 339.
[13] J.I. Park, Cyanoacrylate Resins, The Instant Adhesives Pasadena Technology Press, Los Angeles, CA, 1981.
[14] J. Comyn, Int. J. Adhesion Adhesives 18 (1998) 247.
[15] D. Katti, N. Krishnamurti, J. Appl. Polym. Sci. 74 (1999) 336.
[16] C. Vauthier, C. Dubernet, E. Fattal, H. Pinto-Alphandary, P. Couvreur, Adv. Drug Deliv. Rev. 55 (2003) 519.
[17] I.C. Eromosele, D.C. Pepper, B. Ryan, Makromol. Chem. 190 (1989) 1613.
[18] N. Behan, C. Birkinshaw, N. Clarke, Biomaterials 22 (2001) 1335.
[19] G. Costa, J.P. Cronin, D.C. Pepper, (in part) C.P. Loonan, Eur. Polym. J. 19 (1983) 939.
[20] A. Brookes, D. Craston, Internet J. Vibr. Spectrosc. 3 (1999) 4.
[21] I. Kusako, W. Suëtaka, Spectrochim. Acta Part A 36 (1980) 647.
[22] S. Reynolds, D.P. Oxley, R.G. Pritchard, Spectrochim. Acta Part A 38 (1982) 103.
[23] Cambridge Polymer Group Inc., Application Notes, 2004, #001.
[24] F.A. de Alencar Miranda, R.R. Passos, J.A.D. Lopes, J.M.M. Neto, Polym. Sci. Tech. São Carlos 7 (1998) 41.
[25] P.F. McDonnell, R.J. Lambert, E.P. Scott, G.M. Wren, M. McGuinness, US Patent No. 6607632 (2003).
[26] H. Büning-Pfaue, Food Chem. 82 (2003) 107.
[27] C.C. Fertig, F. Podczeck, R.D. Jee, M.R. Smith, Eur. J. Pharm. Sci. 21 (2004) 155.
[28] J.W. Stansbury, S.H. Dickens, Dent. Mater. 17 (2001) 71.
[29] J.H. Fu, J.R. Schlup, J. Appl. Polym. Sci. 49 (1993) 219.
[30] L.G. Weyer, Appl. Spectrosc. Rev. 21 (1985) 1.
[31] L.G. Lovell, S.M. Newman, M.M. Donaldson, C.N. Bowman, Dent. Mater. 19 (2003) 458.
[32] L.A. Hussain, S.H. Dickens, R.L. Bowen, Dent. Mater. 21 (2005) 210.
[33] S.H. Dickens, B.H. Cho, Dent. Mater. 21 (2005) 354.
[34] H. Lu, J.W. Stansbury, S.H. Dickens, F.C. Eichmiller, C.N. Bowman, J. Biomed. Mater. Res. 15 (2004) 206.
[35] H. Fong, S.H. Dickens, G.M. Flaim, Dent. Mater. 21 (2005) 520.
[36] M. Trujillo, S.M. Newman, J.W. Stansbury, Dent. Mater. 20 (2004) 766.
[37] H. Lu, J.W. Stansbury, C.N. Bowman, Dent. Mater. 20 (2004) 979.
[38] J.W. Stansbury, M. Trujillo-Lemon, H. Lu, X. Ding, Y. Lin, J. Ge, Dent. Mater. 21 (2005) 56.
[39] C. Conti, E. Giorgini, L. Landi, A. Putignano, G. Tosi, J. Mol. Struct. 744–747 (2005) 417.
[40] M. Blanco, M.A. Romero, J. Pharm. Biomed. Anal. 30 (2002) 467.
[41] Henkel Consumer Adhesives, Winsford, Cheshire CW7 3QY.
[42] http://www.brukeroptics.com/UK/.
[43] http://www.brukeroptics.com/accessories/catalog/NIR/nir_probes.html.
[44] O.R. Eden, Factors influencing the strength of dental cements, Ph.D. Thesis, The School of Engineering, Computer Science and Mathematics, University of Exeter, 2003.
[45] Chance Propper Ltd., PO Box 53, Spon Lane South, Smethwick, West Midlands B66 1NZ.
[46] G.M. Foster, S. Ritchie, K.E. Evans, C. Lowe, Prog. Org. Coat. 51 (2004) 244.