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Photo-polymerisation effects on the carbonyl C=O bands of composite resins measured by micro-Raman spectroscopy

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Abstract

The spectra of photo-polymerised composite resins, measured by the micro-Raman spectroscopy, are analysed in the frequency region of the C=O carbonyl stretching bands. The band intensities at about 1700 and 1715 cm^{-1} (the peak frequencies of the hydrogen bonded and free C=O bands, respectively) decrease with the irradiation time and with the methacrylate monomer conversion. Consequently, a degree of apparent conversion (DAC) can be defined. It is shown that the intensity variations conserve the band-shape and allow the DAC measurements via the single frequency intensity ratio. Both the bands give rise to DAC values which exhibit a one-to-one dependence on the degree of C=C conversion, in partial disagreement with previous results. The microscopic mechanisms, associated to the intensity decrease, are critically revised and discussed on the basis of the experimental findings.

Keywords: Polymer composite materials; Micro-Raman spectroscopy; Photo-polymerisation

1. Introduction

For the relevant rigidity of the resin matrix produced by aromatic rings, the bis-GMA (bis-glycidyl methacrylate) is the basic monomer constituent of many restorative dental materials [1]. The strong monomers viscosity makes the pure bis-GMA difficult to use and the triethylene or polyethylene glycol dimethacrylate are used as diluents [2] for improving the clinical handling. The polymerisation is a key-process since it yields hardness and permanent stability in the composite. In bis-GMA based resins, it consists of the single bond conversion of the carbon–carbon C=C double bond of the methacrylate group of the monomer. It is important to have methods which allow reliable measurements of the degree of conversion (DC) of C=C double bonds. The spectroscopic techniques probe directly the presence of bonds in the samples and, if applicable, are usually preferred. A problem in the measurements consists in the choice of the internal standards. Since, the aromatic ring is unaffected by the polymerisation processes, the use of the aromatic C=C bands as an internal standard is suitable. The modern commercial resins are mostly formed by fillers (usually particles of amorphous silica) whose concentration is kept high (about 80% by weight). They couple to the resin matrix via silane bridges and can contribute to the C=C photo-conversion via a multiple light scattering mechanism [3]. Their presence seems to be responsible for intensity fluctuations of specific Raman bands and for the presence of spurious bands [4].

In this work, we report the results of applying the micro-Raman spectroscopy to the photo-polymerisation measurement of Z100 commercial resin. These kinds of micro-Raman applications are rare and, to our knowledge, are limited to the works of Refs. [4,5]. The present work extends the analysis of Ref. [4] and reports measurements of the degree of apparent conversion (DAC) for the carbonyl C=O bands. The microscopic mechanisms responsible for their intensity variations under sample irradiation are not clear. It is generally recognized that C=O band alterations are due to the rupture of the C=C bonds [6,7] rather than to a direct action on the C=O bond itself; for this indirect effect of the photo-polymerisation reactions we refer to the apparent conversion of C=O double bonds. The DAC measurements are complicated by the strong overlap of the bands at 1700 and 1715 cm^{-1}; this introduces large

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uncertainties in the integrated intensity evaluations and alternative ways become compulsory [4,5]. The aims of this paper are (1) to obtain reliable DAC trends as the polymerisation proceeds and (2) to compare the results of previous findings and to explain the observed differences on the basis of the usually proposed microscopic mechanisms.

2. Experiments and vibrational lines assignments

The Z100 resin sample was placed in a holder ring of internal diameter of about 0.5 cm and thickness of 2 mm and the top surface was exposed to the irradiation. The laser line at the wavelength of 632.8 nm, provided by the He–Ne laser, was chosen as the probe for exciting the Raman scattering. A counting time of 60 s was in general sufficient to ensure good statistics. Other details concerning the experimental apparatus and the experimental procedure are reported elsewhere [4]. Fig. 1 shows some measured spectra and the main bands of the Z100 composite. From the literature, the vibrational lines assignments for the basic components of commercial resins [6–9] are known. The bands at 1608 and 1583 cm^{-1} are associated to the aromatic C=C stretching vibrations and can be used as internal standards. The band at 1638 cm^{-1} is due to the aliphatic C=C stretching vibrations and its intensity decreases as the polymer matrix grows. Usually, the 1608 and 1638 cm^{-1} bands are used to evaluate DC values (Section 3). The bands around 1700 cm^{-1} are due to the C=O stretching [6,7] and are the object of the present study. The first band at about 1700 cm^{-1} is assigned to hydrogen bonded carbonyl groups; the second one, at about 1715 cm^{-1}, to free vibrations of carbonyl groups. The same assignments have been recently performed for the C=O bands of liquid cyclohexanone [10]. For the Z100 resin, it was found [6] that, during the polymerisation, the intensity of the band at 1700 cm^{-1} decreases linearly with the monomer conversion, while that of the band at 1715 cm^{-1} is practically constant. These effects were explained in terms of strength alterations of hydrogen bonds. The breaking of C=C double bonds, due to the polymerisation, diminishes the delocalisation of π-electrons of the carbonyl group; consequently, the amount of hydrogen bonds diminishes too and the intensity of the band at 1700 cm^{-1} decreases.

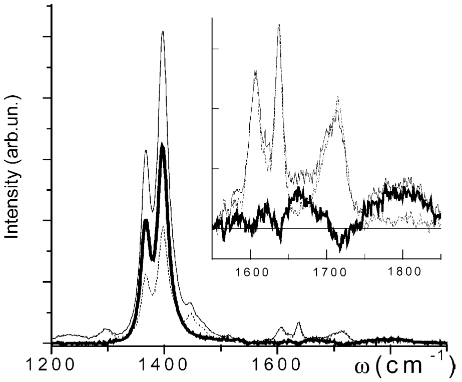

Fig. 1. Examples of micro-Raman spectra obtained from two different surface points (thin and dotted lines) of the same sample recorded after irradiation. The thick solid line represents the difference spectrum. The inset shows the magnification of the main picture, around the C=C and C=O bands. The plotted spectra are those used in Fig. 3 of Ref. [4].

Fig. 1 shows that other weak bands affect the spectra. Their intensity and shape can vary from a surface point to another. The elevated spatial resolution of the micro-Raman allows revealing such surface non-homogeneity. The difference between the spectral shapes measured at two surface points (bold curves of Fig. 1) clearly shows the presence of bands at about 1800 cm^{-1} and of other weak bands just around the C=C and C=O stretching frequencies. Together with the bands at 1370 and 1400 cm^{-1}, they are attributable to the sample surface non-homogeneity and likely due to the fillers [4]. These spurious bands and/or non-correct background subtractions can cause fluctuations in the band area evaluations. In these cases, the recourse to other methods for evaluating the degree of conversion is preferable [4,5].

3. Data treatment and results

The C=O stretching frequency zone is indirectly influenced by the polymerisation process. Fig. 2 shows the comparison between the spectra of polymerized and non-polymerized samples. The two C=O bands, at about 1700 and 1715 cm^{-1}, are unresolved and appear an only broad band (see also the inset of Fig. 2). As in the case of the C=C double bonds, one can define a degree of apparent conversion, DAC, as

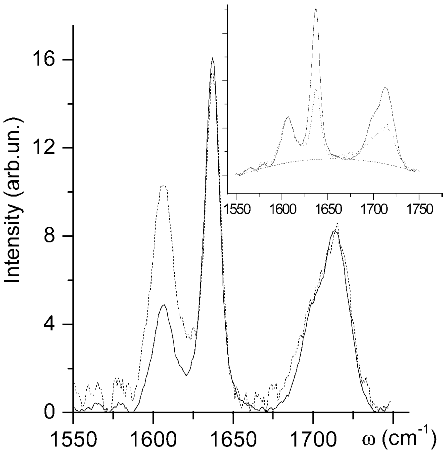

Fig. 2. Comparison between polymerised (solid line) and non-polymerised (dashed line) spectra after the background subtraction (see the inset) and the multiplication of the non-polymerised spectrum by a suitable scale factor. The inset shows the non-polymerised (solid line) and polymerised (dotted line) spectra and the subtracted background (dashed line).

$$\mathrm{DAC} = 1 - \mathrm{BF} = 1 - \frac{(I^{\mathrm{i}}_{1715}/I^{\mathrm{i}}_{1608})}{(I^{\mathrm{n}}_{1715}/I^{\mathrm{n}}_{1608})} \qquad (1)$$

where BF is a quantity proportional to the fraction of double bonds. A similar equation can be written for the band at 1700 cm^{-1} and the aliphatic C=C stretching band at 1637 cm^{-1} (in such a case one has the real degree of conversion, DC [4]). In Eq. (1), I^{i} and I^{n} stand for the band intensities of the irradiated and non-irradiated samples, respectively. To evaluate Eq. (1), the knowledge of the band areas is necessary. This implies the separation between the 1715 and 1700 cm^{-1} bands. If one supposes that the band-shape remains nearly unchanged after the irradiation, a frequency dependent DAC(ω) can be used and no band separation is necessary [4]. The best estimate of the DAC is obtained by the ω dependent expression evaluated at the peak frequency ω_{p}, namely:

$$\mathrm{DAC} = \mathrm{DAC}(\omega_{\mathrm{p}}) = 1 - BF(\omega_{\mathrm{p}}) = 1 - \frac{I^{\mathrm{s}}_{1715}(\omega_{\mathrm{p}})}{I^{\mathrm{n}}_{1715}(\omega_{\mathrm{p}})} \qquad (2)$$

where I^{s} stands for the spectral intensity of the irradiated sample scaled for matching the internal standard intensity to that of the non-irradiated one. This way of evaluating the degree of conversion was referred to as the SFIR (single frequency intensity ratio) method [4]. Eq. (2) holds for other bands too, since the scaling procedure of the standard intensity automatically adjusts all the other spectral intensities. An example of scaled spectral intensities is shown in the inset of Fig. 2. The validity of Eq. (2) implies a flat DAC(ω) trend around a given band, which indicates the band shape conservation [4]. Here, the effective conservation of the carbonyl band shape and the validity of the SFIR procedure are tested as follows. As is seen in the inset and in the main picture of Fig. 1, even after the background subtraction, there are other bands around 1780 cm^{-1} and a non-vanishing Raman intensity is present at about 1670 cm^{-1} in both the polymerised and non-polymerised spectra. This signal was attributed to spurious contributions, such as those associated with the surface non-homogeneity and probably related to the strong intensity variations of the 1400 cm^{-1} band. This authorized the further subtraction, shown in the inset of Fig. 2, which sets to zero the Raman intensity at about 1670 cm^{-1}. The conservation of the band shape was then verified by multiplying the irradiated sample spectrum by a suitable scale factor. The result is shown in the main picture of Fig. 2. The line shape of the overall carbonyl band is reproduced with an accuracy comparable to that of the aliphatic C=C stretching band. This validates the use of DAC(ω) for evaluating the apparent conversion, DAC, or the bond fraction, BF, without any procedure of band separation. For practical purposes, the DAC can be evaluated at the peak frequency without setting to zero the spectral intensity around 1670 cm^{-1}. This agrees with the methodology and the data treatment of Ref. [5], where the DC values are determined by peak ratios rather than by band ratios.

4. Discussions and conclusions

In Fig. 3, the time evolutions of the degree of apparent C=O conversion, DAC, are shown. The behaviour is very similar to that of the aliphatic C=C double bonds of Ref. [4]. In order to probe the one-to-one relation between the C=O and C=C conversions and compare with previous results [6], it is worth plotting the intensity ratio BF (Eqs. (1) and (2)) versus the aliphatic C=C double bonds conversion. The main picture and the inset of Fig. 4 show the BF and the DAC trends, respectively. The DAC increases linearly with the conversion DC of C=C double bonds and a one-to-one relationship holds since the slopes of both the plots are nearly 1. Linear fits were performed in the case of the BF trends and are shown in Fig. 4; the straight lines are nearly parallel with a slope of about −1. The differences in the intercepts are related to the different values reached by the DAC in Fig. 3 and are likely due to spurious bands and/or to residual background; both the causes influence weakly the more intense band at 1715 cm^{-1}. The results of Fig. 4 are in contrast with those of Ref. [6] since, in our case, both the carbonyl bands decrease of intensity but no evidence is found for the independence of the 1715 cm^{-1} band on the monomers conversion. This suggests revising the microscopic mechanisms that control the C=O bands modifications, at least in the case of the Z100 composite. The different behaviour of the two carbonyl bands is usually explained by the following microscopic mechanisms: (a) the breaking of the C=C bonds should provide the delocalization of π-electrons of the C=O bonds; (b) less negative charge is distributed around the oxygen; consequently, the hydrogen bond with the hydroxyl group is weaker and can break; (c) the 1700 cm^{-1} band shifts towards the 1715 cm^{-1} band so that the intensity of the first band decreases while

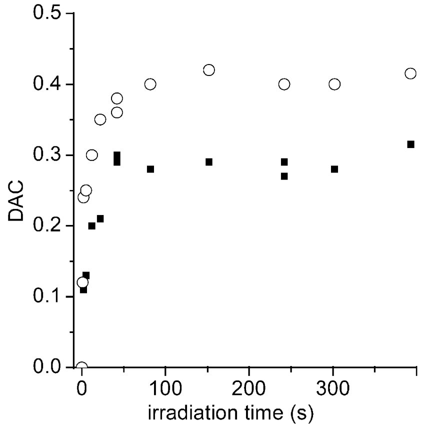

Fig. 3. The degree of apparent conversion DAC for the C=O carbonyl bands computed via the SFIR method: 1715 cm^{-1} band (open circle); 1700 cm^{-1} band (full square).

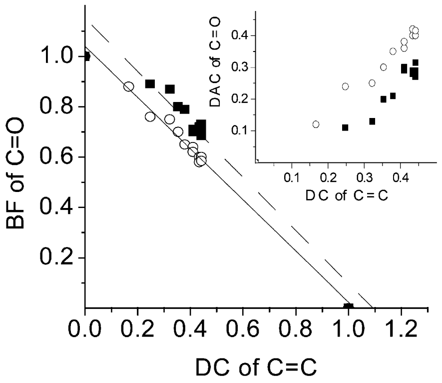

Fig. 4. The intensity ratio BF (Eq. (2)) representing the fraction of double bonds of the two C=O band (1715 cm^{-1} (open circle) and 1700 cm^{-1} (full square)) versus the degree of the C=C conversion, DC. The C=O apparent conversion, DAC, is shown in the inset.

that of the second one could be constant or increase. So, the rupture of the hydrogen bonds is the key process for explaining the indirect effects caused by polymerization to the carbonyl bands.

For better understanding, it is worth to schematise the microscopic mechanisms, probed by the Raman scattering, by the following independent processes: (I) the polarizability derivative decreases for the electronic rearrangement around the C=O bond; this yields intensity decrease without frequency shift. (II) The electronic rearrangement could determine a variation of the bond strength; this implies frequency shifts of the bands. (III) The charges involved in the hydrogen bonds are shielded by the electronic redistribution. This should cause hydrogen bond rupture and the strong spectral effect mentioned above, i.e. the intensity transfer from 1700 to 1715 cm^{-1}. The present analysis indicates that only the first mechanism is necessary for explaining the intensity decrease of the carbonyl bands since the band-shape is conserved. The Raman intensity loss, due to the C=C breaking, could be determined by the increase of the total symmetric character of the C=O vibration which in turn determines the decrease of the polarizability derivative. The other effects, which involve the frequency shifts, appear of minor importance, at least in the case of the Z100 composite. In conclusion, it is found that the polymerisation reaction determines the decrease of the overall C=O Raman bands intensity in agreement with previous findings [5,6]. As concerns the two bands separately, the results of the present work disagree with the band intensity evolutions of Ref. [6] since the intensities of both the bands decrease as that of the C=C band does. No evidence of the constancy of the 1715 cm^{-1} band is obtained.

5. Summary

In summary, the micro-Raman technique allows to detect differences in the Raman spectra obtained from distinct surface points owing to its high spatial resolution. In the C=O stretching zone, such differences are given by spurious bands. If the spectra are carefully analysed and processed, the C=O bands result to conserve the shape under the polymerization effects of the irradiation. Consequently, the conversion degree can be calculated by the SFIR method and the difficulties due to the band areas ratios can be removed. A one-to-one relationship between C=O and C=C double bonds conversion is obtained for both the carbonyl bands at 1700 and 1715 cm^{-1}. A phenomenological interpretation in terms of polarizability derivative change, due to the electronic rearrangement induced by the rupture of the aliphatic C=C double bond, is suggested.

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