

# Setting Reaction of Polyacid Modified Composite Resins or Compomers

J.L.R. Arrondo<sup>\*,1</sup>, M.I. Collado<sup>1</sup>, I. Soler<sup>2</sup>, R. Triana<sup>2</sup> and J. Ellacuria<sup>2</sup>

<sup>1</sup>Unidad de Biofísica (Centro Mixto CSIC-UPV/EHU) and Departamento de Bioquímica y Biología Molecular, Universidad del País Vasco, Spain

<sup>2</sup>Departamento de Estomatología, Facultad de Medicina y Odontología, Universidad del País Vasco, Spain

**Abstract:** The hardening of modified polyacid composite resins (compomers) and glass-ionomers have been studied using infrared spectroscopy. The acid-base reaction in Ketac-fil, a glass ionomer, was followed by the ratio between the COOH band located around 1715 cm<sup>-1</sup> and that corresponding to COO<sup>-</sup> located around 1570 cm<sup>-1</sup>. The combination of infrared analysis and band narrowing treatments enable us to propose in the glass-ionomer two maturation steps. First, a very rapid equilibrium acid-base related, and second the cross-linking of polycarboxylate with the metal ions present in the cement. In compomers, a new reaction has been described involving polymerization induced by free radicals besides the two steps associated with the acid-base reaction. Using infrared spectroscopy and band narrowing techniques, it is shown that water is essential to complete the hardening process but no acid-base reaction is produced since the COO<sup>-</sup> band does not appear. The reaction associated with free radicals could be described as a polymerization of methacrylate monomers together with an aqueous dilution of the filling particles releasing different metal cations that would chelate with the polymer molecules to form a macromolecular structure.

## INTRODUCTION

Conventional glass ionomer cements (C-GIC) or glass polyalkenoate cements [1] have been used in odontology since their discovery [2]. One of the major reasons for using them is their prolonged fluoride release and inherent cariostatic effect [3]. Besides the development of these cements, to overcome the clinical problems new materials have appeared via the combination of C-GIC with composite resins [4] without losing the acid-base reaction characteristic which determines its hardening [5] and subsequent fluoride release [6].

Since 1993 new materials known as modified polyacid composite resins or compomers have appeared on the market. Included in their composition are bifunctional monomers which are polymerised via methacrylate and carboxylic groups capable of reacting in the presence of water with the cations released from the filling particles [7]. Whilst there are no doubts as to acrylic polymerisation, the potential existence of an acid-base neutralisation reaction has given rise to great controversy among different authors [8-11].

Among the different methods for determining the transformation of many reactions and the degree of chemical conversion, Fourier-transform infrared spectroscopy (FTIR) has proven to be a powerful technique for detecting the replacement ratio between C=C and C-C in methacrylate groups, as well as the COOH/COO<sup>-</sup> exchange in acid-base reactions [12,13]. In the present work, using mathematical treatments of FTIR spectra we have studied the compomer hardening

reaction looking at the changes in the bands attributed to the methacrylate double bonds and the process of maturation in a conventional ionomer to evaluate the acid-base reaction.

## MATERIALS AND METHODOLOGY

Three commercial materials were used in the present study (Table 1). The Ketac powder was mixed with the liquid according to the manufacturer's instructions. The hardening reaction was stopped by adding ethanol at different time intervals and the specimen was subsequently dried. For Hytac and Compoglass, a small portion of light-cured glass ionomer was exposed to a visible light-curing unit (Visilux 2, 3M Germany) during 40 seconds. The specimens of each light cured glass ionomer were prepared and stored in a glass tube in the presence or absence of distilled water for different measurement time periods; samples were dried before the IR analysis.

## IR SPECTROSCOPY

The samples were measured as KBr disks. IR spectra were obtained using a Nicolet Magna II spectrometer (Thermo Nicolet, Madison, Wisconsin), at a nominal resolution of 2 cm<sup>-1</sup>, averaging 1000 scans. The spectra in the region between 1800 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> were analysed using previously described protocols for data treatment (deconvolution and derivative) and curve-fitting [14,15].

## RESULTS

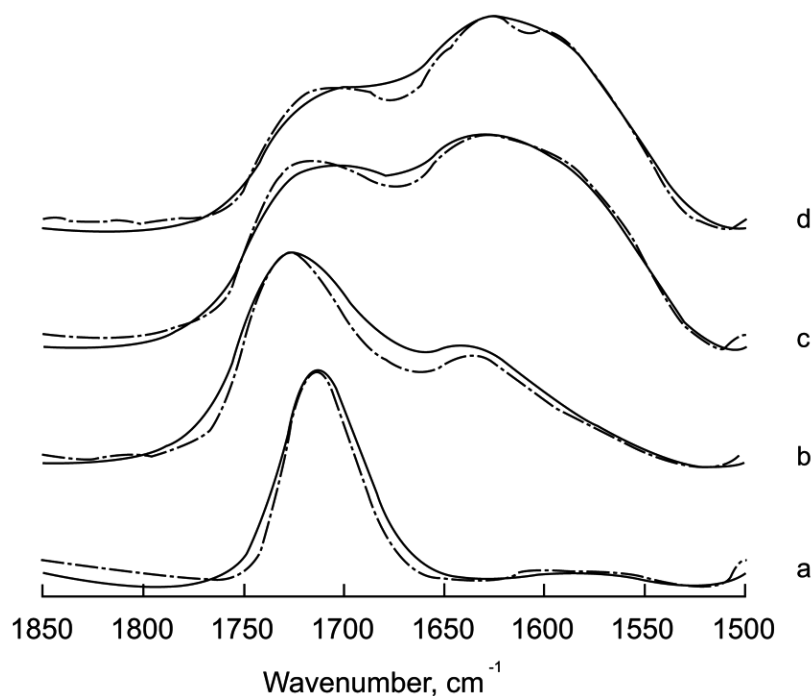
### Ketac-Fil: Glass Ionomer

The acid-base reaction in the hardening and maturation of a glass-ionomer cement was monitored by IR spectroscopy looking at the C=O stretching vibration ratio between the COO<sup>-</sup> (base) and COOH (acid) bands. Fig. (1) shows the

\*Address correspondence to this author at the Unidad de Biofísica (Centro Mixto CSIC-UPV/EHU). B° Sarriena s/n, Leioa, Vizcaya, Spain; Tel: +34 946 012 485; Fax: + 34 946 013 360; E-mail: joseluis.arrondo@ehu.es

**Table 1. Materials Tested**

Product	Type	Manufacturer	Batch
Ketac-Fil	Conventional Glass Ionomer	ESPE, Germany	007
Compoglass	Compomer	VIVADENT, Liechtenstein	902646
Hytac	Compomer	ESPE, Germany	231



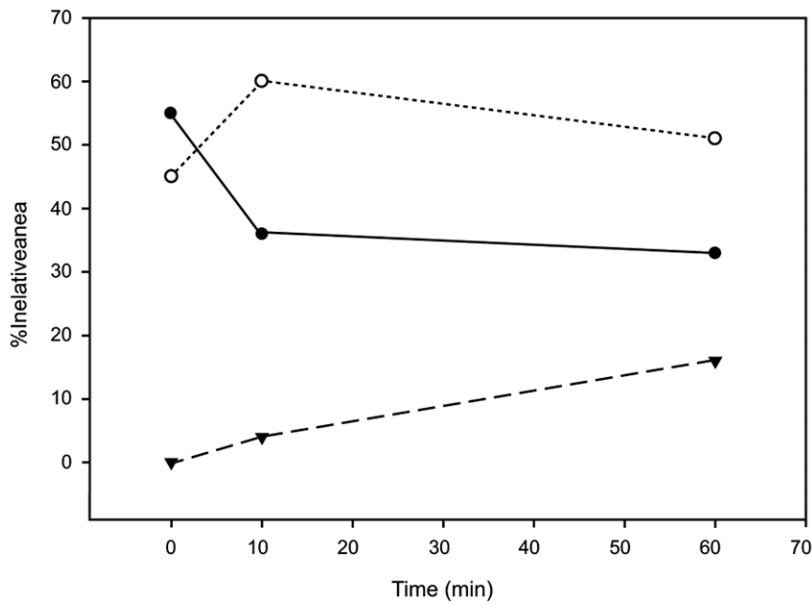
**Fig. (1).** Original and deconvoluted spectra of Ketac Fil in the region 1850-1500  $\text{cm}^{-1}$ . (a: Liquid component of the mixture; b: time zero; c: 10 minutes; d: 1 hour). Deconvolution parameters are FWHH=25 and  $k=1.5$ .

original and deconvoluted spectra of Ketac-Fil in the 1850-1500  $\text{cm}^{-1}$  region measured at different incubation times up to 1 h after activation. Longer incubation periods did not produce any further changes. The use of deconvolution enables visualization of overlapping bands in the spectrum and clearly shows the maturation course. Before mixing the components, the spectrum of the liquid is dominated in both cases by a band at 1715  $\text{cm}^{-1}$ , characteristic of the vibration corresponding to the carboxylic acid. Immediately after mixing with the ionomer, a clear decrease in the band at 1715  $\text{cm}^{-1}$ , concomitant with an increase in the band at 1637  $\text{cm}^{-1}$  and the appearance of a new component around 1598  $\text{cm}^{-1}$ , corresponding to different  $\text{COO}^-$  species occurs. It must be noted that discrimination between these bands can be made only after the use of band narrowing techniques, such as Fourier deconvolution, since they cannot be distinguished in the original spectra. The band at 1598  $\text{cm}^{-1}$  can be assigned to a carboxyl stretching vibration arising from  $\text{COO}^-$  conjugated with cations from the cement. Polycarboxylate cross-linking with ions would decrease the frequency of the band in a similar way to the effect of hydrogen bridges in  $\text{C}=\text{O}$  band absorption in biological molecules; *i.e.*, the stronger the interaction, the larger the decrease in band wavenumber.

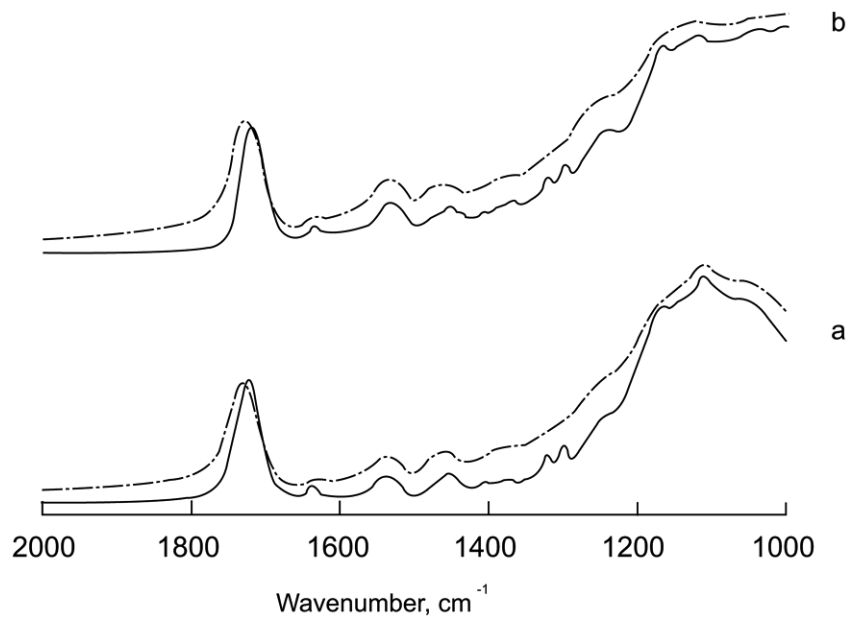
The degree of reaction can be followed by curve-fitting the region 1800-1500  $\text{cm}^{-1}$  and obtaining the percentages of the components corresponding to the  $\text{COOH}$  band and the two  $\text{COO}^-$  bands (Fig. 2). The decrease in polycarboxylic acid is very rapid and in 10 minutes reaches 35% of the percentage in equilibrium. In the bands corresponding to the  $\text{COO}^-$  components, the maximum for the 1630  $\text{cm}^{-1}$  band it is also at 10 min, where it can also be observed an increase in the 1590  $\text{cm}^{-1}$  band at the expense of the other component. This response would be compatible with a rapid acid-base reaction, corresponding to a  $\text{COOH} \rightarrow \text{COO}^-$  transition and a slower process of cross-linking of the base components conjugated with the cations present in the cement.

#### **Hytac and Compoglass: Compomers**

The hardening of these two compomers was followed in the same way as the aforementioned ionomer. The spectral region 2000-1000  $\text{cm}^{-1}$ , (Fig. 3) shows the original spectra for Compoglass and Hytac after 5 days incubation in the presence or absence of added water. The spectra in the absence of water after 5 days is identical to the one before the reaction started thereby demonstrating that water is essential for the reaction to proceed. A prominent band at around



**Fig. (2).** Relative areas of the C=O stretching band components for Ketac Fil. The polycarboxylic acid component (●) is represented together with the two polycarboxylate bands corresponding to the free (○) and conjugated species (▼).



**Fig. (3).** Original spectra for Compoglass (a) and Hytac (b) in the region 2000-1000  $\text{cm}^{-1}$  after incubation in water for 5 days. Solid line: Same time without water incubation.

1720  $\text{cm}^{-1}$  is indicative of the C=O stretching of the COOH species. The band corresponding to COO<sup>-</sup> is located around 1535  $\text{cm}^{-1}$ . Several bands can be attributed to the methacrylate component such as those located around 1700, 1633, 1300 and 1150  $\text{cm}^{-1}$  that decrease after incubation. Curing of the cement by visible light under different water conditions in the region corresponding to the acid-base reaction is shown in Fig. (4). Unlike the glass ionomer, the ratio between the bands at 1720 and 1535  $\text{cm}^{-1}$  in this case does not change during the reaction. However, a clear decrease in the C=C band at 1638  $\text{cm}^{-1}$  from the methacrylate can be clearly seen together with the disappearance of other methacrylate bands around 1300 and 1150  $\text{cm}^{-1}$ . This change in the spec-

trum points to a non-involvement of an acid-base process in the hardening reaction, but to a polymerization of the methacrylate present in the cement. The change in shape and position observed in the band at 1720  $\text{cm}^{-1}$  would imply involvement of the carboxylic acid in the cross-linked organization obtained after the polymerization reaction. It has to be mentioned, that the polymerization reaction observed as the reduction of the 1637  $\text{cm}^{-1}$  band is very fast, with completion during the first minute. There are no subsequent decreases in the methacrylate bands, but the change in shape and position of the band at 1720  $\text{cm}^{-1}$  indicates that compound rearrangement still takes place at longer times after cross-linking of the monomers.



peak position, indicating different –COOH populations until an equilibrium is reached with the band maximum similar in position to before irradiation but broader, being these changes in bandwidth indicative of a more complex rearrangement of the COOH groups. The broadening could be due to an aqueous dilution of the filling particles releasing different metal cations that could chelate with the polymer molecules [20]. This explanation would agree with the need for water to complete the reaction.

## CONCLUSIONS

The use of infrared spectroscopy together with resolution enhancement techniques has been used to follow the hardening of two different materials used in dentistry, glass-ionomers and compomers.

From the results, it can be concluded that no acid-base reaction was observed as a hardening mechanism in the Hytac and Compoglass compomers. Furthermore, they may be lacking in the fluoride release inherent in such a reaction system. The short-term fluoride release process described for the modified polyacid composite resins can be ascribed to an initial leaching of fluoride from the glass particles in the material surface layer [21]. The observed photo-activated polymerization mechanism indicates that this kind of material behaves more like a composite resin as previously noted by other authors [22].

On the other hand, the use of deconvolution allows the differentiation of two components in the carboxylate produced after the acid-base reaction corresponding to different polycarboxylate interactions.

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