Infrared study of the interaction of acrylic bone cement with bone marrow

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Infrared spectroscopy was used for the characterization of some commercial bone cements and investigation of their interaction with bone marrow. The infrared spectra of the cements and their mixtures with bone marrow were recorded after various periods ranging from 1 day to 8 weeks. The quantitative analysis of infrared spectra of the mixtures provided strong evidence that a certain reaction takes place between the acrylic resins and the bone marrow. It was found that the rate of reaction depends on the concentration of the bone marrow and the ageing time. The rate of reaction showed a maximum at 22 and 31 days according to the concentration of the bone marrow and then decreased with ageing up to 8 weeks.

1. Introduction

Acryclic bone cement is used extensively in orthopaedic surgery for the fixation of metallic or polymer endoprostheses, repair of pathological fractures and obtaining immediate stabilization of spinal fixation. Extensive studies on the mechanical properties of bone cement and various factors affecting these properties have been carried out by many investigators [1–6]. In recent years, the material characterization of poly(methyl methacrylate) (PMMA) bone cement and its clinical applications have received considerable attention. Very little is understood, however, about the relationship between these properties and the molecular processes occurring in the cement and its interaction with bone structures. Looney and Park [7] studied the changes in mechanical properties and free radical concentration of curing PMMA bone cement under *in vivo* and *in vitro* conditions. They concluded that the curing of *in vivo* samples takes a much longer time (more than 4 weeks) than *in vitro* curing (less than 2 weeks). The mechanical tests indicated that whether aged *in vivo* or *in vitro*, the strength increased rapidly for the first 1–2 weeks and then slight increases were seen up to 6 months. The modulus of rupture of the *in vitro* specimens showed a maximum at 1 week and then decreased steadily for up to 6 months. Noble and Swarts [8] studied the penetration of commercial acrylic bone cements into cancellous bone. They found that the penetration varied significantly with different cements, was influenced by the coarseness of the cancellous bone, and increased directly with the effective volume of the cells within the osseous matrix. In the present study, infrared spectroscopy was applied for characterization of PMMA bone cements and investigation of their interaction with bone marrow.

2. Experimental procedure

The bone cements used in this study were the commercial brands Surgical Simplex P. Radiopaque, C.M.W.1, and C.M.W.1 new Radiopaque (with premixed barium sulphate). The powder of each cement was thoroughly mixed with its liquid in the ratio suggested by the manufacturer ($2\ g\ ml^{-1}$). Then bone marrow from the humerus of a calf of about 1 month age was added to the dough with various concentrations, namely 13, 38 and 47%. After setting, the samples were ground in a hardened steel vial. The powder was then sieved to the required particle size (80–90 μm). The infrared spectra were recorded on a Beckman 4250 IR spectrophotometer using the KBr disc technique. Also thin films were prepared from the powder of the cements by dissolving it in chloroform and casting on KBr discs.

3. Results and discussion

The i.r. spectra of thin films of Surgical Simplex P. Radiopaque, C.M.W.1 and C.M.W.1 New Radiopaque (with premixed barium sulphate) bone cement powders are shown in Fig. 1. Over the C–H stretching region, the spectra display three-absorption bands at the frequencies 2995, 2940 and 2840 cm^{-1}. The C=O band of the ester group is located at 1728 cm^{-1}. Spevacek *et al.* [9] used the integrated intensity of this band for determination of the content of ordered segments of syndiotactic PMMA (S-PMMA). Havriliak and Roman [10] described the two absorption peaks at 1268 and 1238 cm^{-1} for two different rotational positions of the same ester skeletal vibration. The spectra also show a band of weak intensity at 840 cm^{-1} and a very weak one at 854 cm^{-1} which are associated with C–H bending vibrations. It has been accepted that these bands are sensitive to the conformational structure of the carbon backbone. The band at 854 cm^{-1} corresponds to syndiotactic sequences with backbone conformation. It seems very important to mention that the absorption bands of barium sulphate are absent from the spectra of all

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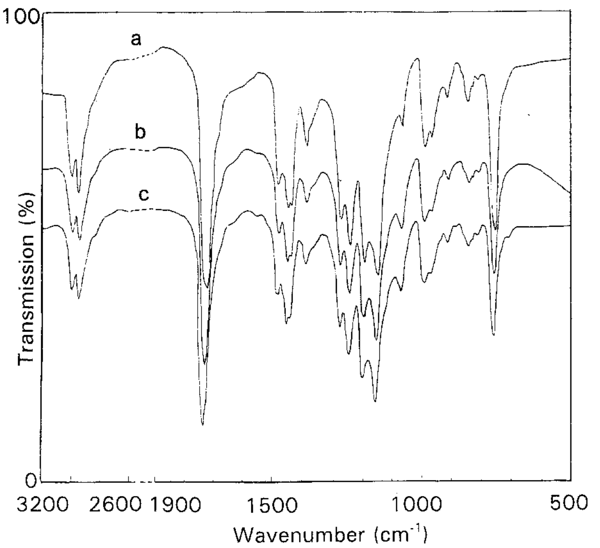

Figure 1 I.r. spectra of powder films of the three cement brands: (a) C. M. W. 1, (b) C. M. W. 1 New Radiopaque, (c) Surgical Simplex P.

TABLE I The absorbance ratio A_{1725}/A_{2940} for powders and cements of three commercial brands

Cement type	A_{1725}/A_{2940}	
	Powder	Cement
Surgical Simplex P	1.90	1.17
C. M. W. 1	1.55	1.23
C. M. W. 1 New Radiopaque	1.48	1.10

TABLE II The absorbance ratio A_{1240}/A_{1270} for powders and cements of three commercial brands

Cement type	A_{1240}/A_{1270}	
	Powder	Cement
Surgical Simplex P	0.90	0.93
C. M. W. 1	1.06	1.06
C. M. W. 1 New Radiopaque	0.93	0.96

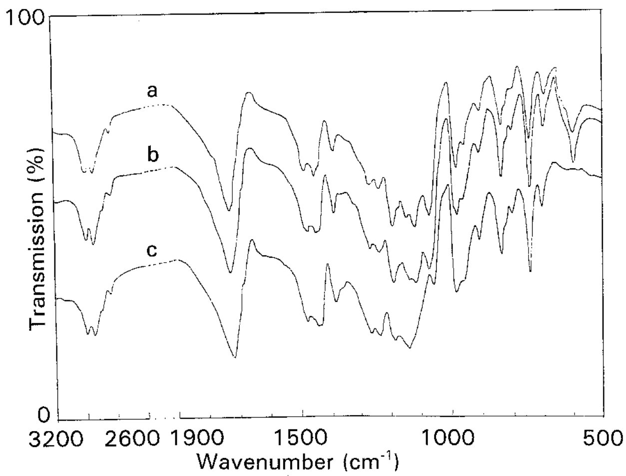

Figure 2 I.r. spectra of powders of the three cement brands: (a) Surgical Simplex P, (b) C. M. W. 1 New Radiopaque, (c) C. M. W. 1.

samples prepared as thin films. This means that the $BaSO_4$ can be separated from the powder, and this provides strong evidence that no reaction takes place between $BaSO_4$ and PMMA powder.

In the present study, the KBr disc technique was also used for measuring the i.r. spectra of powders under investigation. The spectra are shown in Fig. 2. In addition to the characteristic bands of PMMA, the spectra exhibit the diagnostic bands of $BaSO_4$ at the frequencies 600, 1075 and 1115 cm^{-1}. The absorbances of the bands at 2940, 1725, 1270 and 1240 cm^{-1} were determined by using the baseline method. The absorption band at 2940 cm^{-1} was chosen as the standard band. The absorbance ratios A_{1725}/A_{2940} and A_{1240}/A_{1270} for the powder and cement samples are given in Tables I and II, respectively. Table I indicates that the powder of Simplex P shows an absorbance ratio A_{1725}/A_{2940} equal to 1.90, which is significantly greater than the values 1.55 and 1.48 of the others. It may be mentioned that the absorbance ratios for the two types of C. M. W. 1 bone cement appear more or less equal, and the slight difference between the two values is in the range of experimental error and can be neglected. This result leads to the conclusion that the polymer of Simplex P type contains a greater content of ordered segments of S-PMMA than the polymers of the other types.

Each powder was then mixed with its corresponding liquid according to the manufacturer's suggestions (2 g ml^{-1}). The i.r. spectra of these cements are shown in Fig. 3. It is apparent from Fig. 3 that the only observable striking difference between the spectra of the three cements is the presence of the characteristic absorption bands of $BaSO_4$ in the spectra of Simplex P and C.M.W.1. New Radiopaque, and their absence in the spectrum of the C.M.W.1. Table I indicates also that the mixing of the monomer for the formation of bone cement produces a marked decrease in the absorbance ratio A_{1725}/A_{2940}. It is clear from Table I that the magnitude of reduction of the absorbance ratio for the Simplex P type is significantly greater than those of the two types of C.M.W.1. However, it is evident that the difference between the absorbance ratios of the three cements is not large and can be considered as experimental error (standard deviation $\simeq$ 0.05). On the basis of this final result, one can come to the conclusion that the molecular structures of the three commercial acrylic cements behave similarly. The absorbance ratio A_{1240}/A_{1270} for the samples analysed were also determined. The values determined are given in Table II. Comparison of the data listed in Table II reveals that the powders and cements assume the same values. This result confirms the previous finding which states that the molecular structures of the commercial cements are similar.

The effect of ageing on the molecular structure of C.M.W.1 bone cement was also taken into consideration. The i.r. spectra of the samples were recorded after different periods of up to 8 weeks. Careful investigation of the i.r. spectra showed that ageing has no effect on the spectral features of the cement. The absorbance ratios A_{1240}/A_{1270} and A_{1725}/A_{2940} are given in Table III. This table indicates that over 8 weeks the

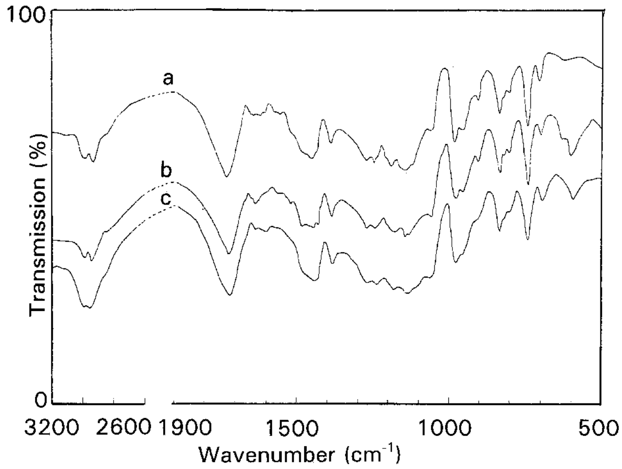

Figure 3 I.r. spectra of bone cements (powder/liquid = 2 g ml^{-1}) (a) C. M. W. 1, (b) C. M. W. 1 New Radiopaque, (c) Surgical Simplex P.

TABLE III Effect of ageing on the absorbance ratios of C. M. W. 1 bone cement

Time (days)	A_{1240}/A_{1270}	A_{1725}/A_{2949}
1	0.99	1.33
14	0.98	1.24
22	0.96	1.32
31	0.96	1.23
41	0.96	1.30
56	0.98	1.29

absorbance ratios remain more or less constant. This result shows that ageing time has no effect on the molecular structure of the cement.

The cement C.M.W.1 was then thoroughly mixed with bone marrow with different ratios, namely 13, 37 and 47%. The i.r. measurements were carried out after different periods of up to 8 weeks. The i.r. spectra of the bone marrow, bone cement and the mixture of them are illustrated in Figs 4 and 5. The spectrum of the bone marrow shows the amide A and B N–H stretching bands at 3300 and 3050 cm^{-1}. The C–H stretching vibrations are located at the frequencies 2900 and 2840 cm^{-1}. The amide I and II N–H bending vibrations are present at 1640 and 1528 cm^{-1}. The characteristic C=O band of the lipids appears at 1725 cm^{-1}. It is clear from Figs 4 and 5 that most of the absorption bands of the bone marrow are incorporated in the absorption bands of the PMMA except the amide bands appearing at 3300, 3050, 1640 and 1528 cm^{-1}. The intensities of these absorption bands increase with increasing concentration of bone marrow in the mixture.

On the other hand, it can be seen from Figs 6 and 7 that the intensity of the amide I band at 1640 cm^{-1} depends on ageing. The most intense well-defined absorption band appears in the spectra recorded after 22 and 31 days for the samples containing 37 and 47% bone marrow, respectively. In order to determine the changes in the intensity of the 1640 and 1725 cm^{-1} bands on a quantitative basis, the absorbances of the two bands were measured by using the baseline method. A baseline was drawn across the bands from 1900 to 1575 cm^{-1}. The absorbance ratio A_{1640}/A_{1725}

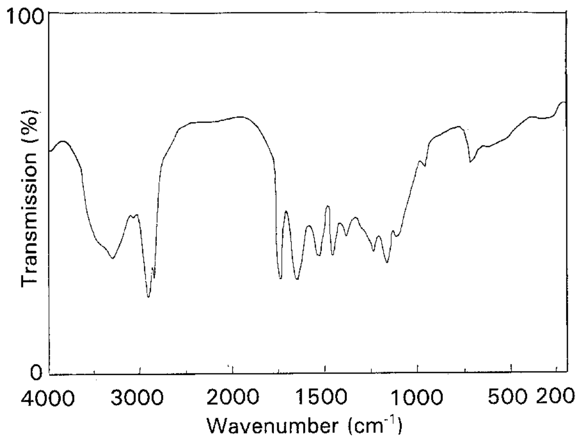

Figure 4 I.r. spectrum of the bone marrow of calf humerus.

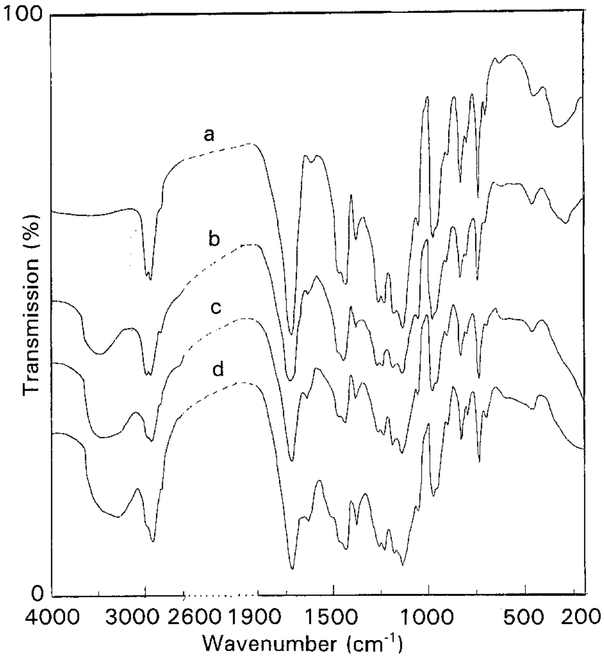

Figure 5 I.r. spectra of C. M. W. 1 bone cement and its mixture with bone marrow: (a) bone cement alone, (b) 13% bone marrow, (c) 37% bone marrow, (d) 47% bone marrow.

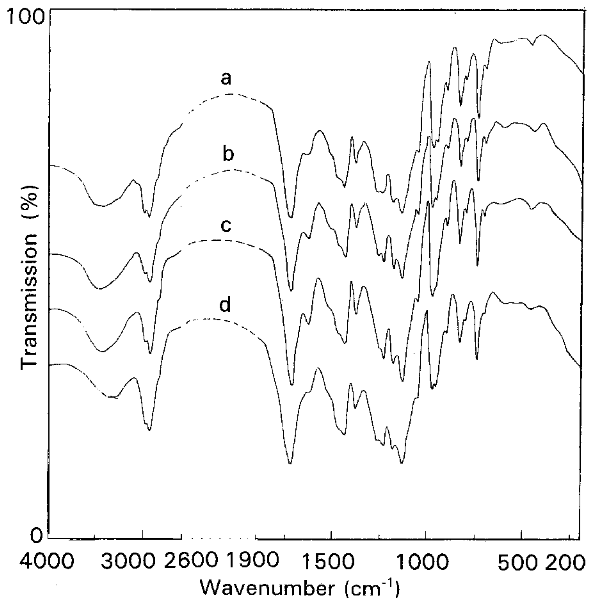

Figure 6 I.r. spectra of C. M. W. 1 bone cement containing 37% bone marrow after (a) 4 days, (b) 14 days, (c) 22 days, (d) 41 days.

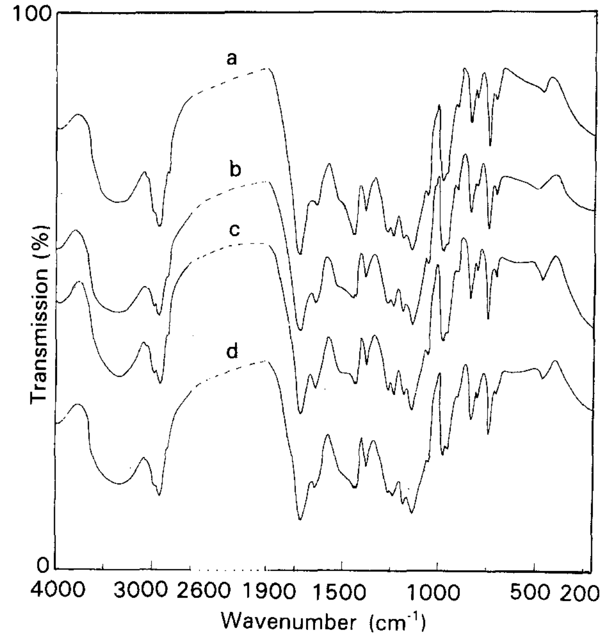

Figure 7 I.r. spectra of C. M. W. 1 bone cement containing 47% bone marrow after (a) 4 days, (b) 22 days, (c) 31 days, (d) 41 days.

TABLE IV The effect of ageing on the absorbance ratio A_{1640}/A_{1725} of C. M. W. 1 bone cement containing 37 and 47% bone marrow

Time (days)	$A_{1640}/A_{1725}{}^{-1}$	
	37%	47%
1	0.26	0.37
4	0.30	0.41
14	0.36	0.46
22	0.38	0.52
31	0.30	0.57
41	0.26	0.54
56	0.21	0.49

was determined for the samples containing 37 and 47% bone marrow. The values determined are listed in Table IV.

The relationship between this absorbance ratio for the samples containing 37 and 47% of bone marrow and the time of ageing is illustrated graphically in Fig. 8. This figure indicates that the absorbances ratio A_{1640}/A_{1725} depends on the ageing time; it increases as the time increases to 22 days for the samples containing 37% bone marrow and to 31 days for the samples containing 47% bone marrow, and then decreases with increasing the time to 8 weeks. It is evident that, at any given time, the absorbance ratio A_{1640}/A_{1725} for the sample containing 47% bone marrow is always higher than that for the sample containing 37% bone marrow. This result suggests that a certain reaction takes place between the cement and the bone marrow, and that the rate of this reaction depends on the time. The rate of reaction is also enhanced with an increase in the concentration of bone marrow.

The absorbance ratio of the protein band at 1640 cm^{-1} and the polymer C–H bending band at 840 cm^{-1} was determined and is given in Table V.

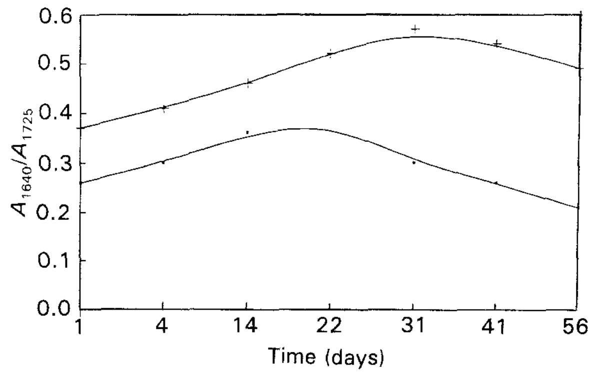

Figure 8 Relationship between absorbance ratio A_{1640}/A_{1725} and ageing time for (■) 37% bone marrow, (+) 47% bone marrow.

TABLE V Effect of ageing on the absorbance ratio A_{1640}/A_{840} of C. M. W. 1 bone cement containing 37 and 47% bone marrow

Time (days)	A_{1640}/A_{840}	
	37%	47%
1	0.45	0.90
4	0.65	1.05
14	0.92	1.18
22	0.95	1.26
31	0.74	1.33
41	0.69	1.29
56	0.65	1.07

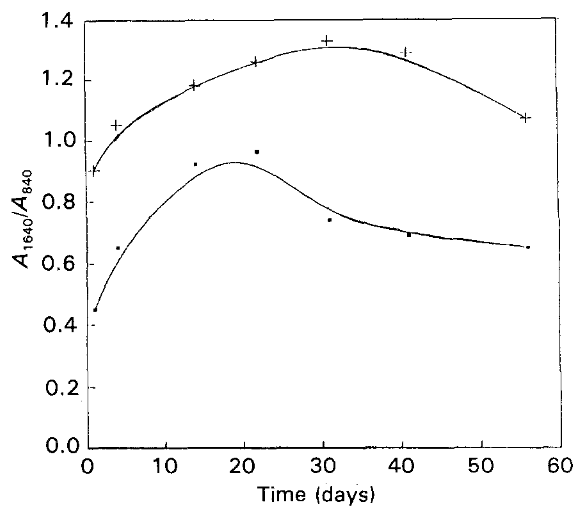

Figure 9 Relationship between absorbance ratio A_{1640}/A_{840} and ageing time for (■) 37% bone marrow, (+) 47% bone marrow.

The variation of this ratio with time is represented graphically in Fig. 9. As can be seen from this figure, the time dependence of this ratio resembles that of the ratio A_{1640}/A_{1725}.

4. Conclusion

Based on the foregoing considerations, one can come to the conclusion that ageing has no considerable effect on the molecular structure of acrylic bone cement. On the other hand, a certain reaction may take place between the cement and the bone marrow. The rate of this reaction depends on the time and concentration of the bone marrow.

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