Effect of cross-linking agents on the molecular properties of denture base resins

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Infrared spectroscopy and dielectric properties were used to investigate the molecular structure and the degree of cross-linking in denture base resins by the determination of the amount of residual monomer. It was found that the addition of triethylene glycol dimethacrylate (TEGDMA) or tetrahydrofurfuryl methacrylate (THFMA) with 12% or 17% by weight of the monomer to the resins reduces the amount of residual monomer in the heat-cured denture base resins. It was found that the dielectric constant and the absorbance of the C–C bond at $1625 \, cm^{-1}$ increased with increasing residual monomer content. The results also indicated that the dielectric constant varies linearly with the absorbance ratio, $A \, (1625 \, cm^{-1})/A \, (1725 \, cm^{-1})$.

1. Introduction

The addition of a cross-linking agent to the monomer on the properties of denture base resins has been the subject of interest in recent years [1]. It is well known that the cross-linking agent improves the crazing resistance, stiffness of resins and water uptake [2, 3]. This is attributed to the changes in molecular structure after addition of the cross-linking agent. The exact effect of cross-linking upon the physical properties varies with the composition and concentration of the cross-linking agent [4]. One important factor generally overlooked is that the efficiency of the various agents in cross-linking is not the same. This may help in producing a cross-linked polymer which contains considerable unpolymerized cross-linking and ordinary monomer.

In the present study, the effect of cross-linking agents TEGDMA and THFMA on molecular structure was investigated by following the changes in their infrared spectra and dielectric properties.

2. Experimental procedure

The materials used in this study were as follows:

1. A commercial brand of non-cross-linked denture base acrylic resin (Supracryle), Spota Dental as provided by the manufacturer.

2. Two commercial brands of cross-linked denture base acrylic resin (Major and Rodex), the cross-linking agent in these brands is polyethylene glycol dimethacrylate.

3. A cross-linking agent and diluent which is triethylene glycol dimethacrylate (TEGDMA) (Ancomer Ltd, Manchester, UK).

4. A cross-linking agent and viscosity reducer which is tetrahydrofurfuryl methacrylate (THFMA) (Ancomer Ltd, Manchester, UK).

Each of these cross-linking agents was added to the liquid of commercially non-cross-linked polymethylmethacrylate by weight to obtain five mixtures with different concentrations, as shown in Table I. The samples containing TEGDMA are represented by symbols A1–A5, while those containing THFMA are represented by symbols B1–B5.

The powder was added to the liquid in proportions according to the manufacturer's instructions for each commercial brand (non-cross-linked and two cross-linked brands). The dough formed was packed into a mould cavity under pressure. Trial packings were conducted with a sheet of polyethylene used as separator and the excess was removed and then heated to

TABLE I The concentration of the cross-linking agents TEGDMA (A) and THFMA (B) in the monomer and cements

Sample	Amount of each of the cross-linking agents (g)	Percentage of each of the cross-linking agents in the liquid	Percentage of each of the cross-linking agents in the total product
1	0.22	7.64	3.00
2	0.37	12.85	5.00
3	0.51	17.71	7.00
4	0.66	22.92	9.00
5	1.44	50.00	19.67

initiate polymerization. The flask was then submerged in a water bath at 73 ± 1 °C for 1.5 h and then immersed in boiling water for 0.5 h; the flask was then allowed to cool to room temperature in the open air.

For dielectric measurements, only control samples and experimentally prepared A1, A2, B1, and B2 were tested, because the infrared measurements showed that they contained different residual monomer contents.

3. Results and discussion
3.1. Infrared measurements
The spectra of PMMA and the commercial powders are shown in Fig. 1. This figure indicates that the
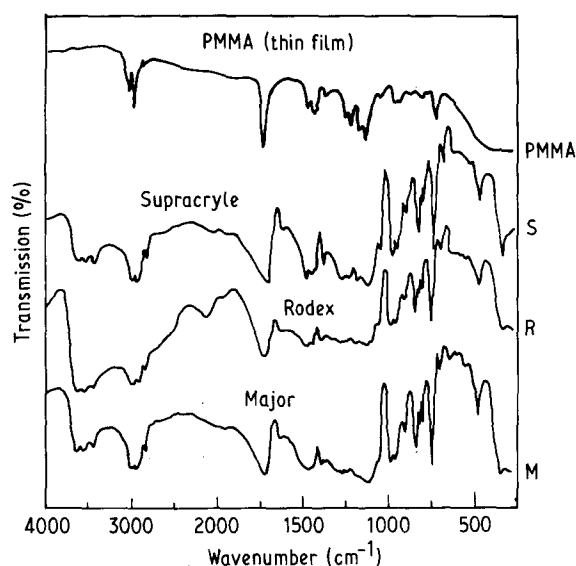

Figure 1 Infrared spectra of pure PMMA powder and the commercial powder.

spectra of all commercial powders are similar to that of the pure PMMA and show no observable differences. The frequencies of the most evident absorption bands, together with their structural assignments, are given in Table II.

Fig. 2 shows the infrared spectra of the heat-cured commercial denture base resins. Careful examination of the spectra revealed that no appreciable spectral differences are observed, apart from slight changes in the intensities of some absorption bands.

In the present study, the band at $1625 \, cm^{-1}$ which corresponds to the absorption of C–C of the monomer was taken to measure the relative content of the residual monomer in the heat-cured denture base polymeric resin [5, 6]. The band at $1725 \, cm^{-1}$ (C–O) was taken as an internal standard. The absorbances of these two bands were measured by using the baseline method. A baseline was drawn across the first band from $1670 \, cm^{-1}$ to $1590 \, cm^{-1}$ and another baseline was drawn across the second band from $2035 \, cm^{-1}$ to $1670 \, cm^{-1}$. The determined values of absorbances ratio are given in Table III.

It is clear from the table that the Supracryle resin shows the highest value of residual monomer content whereas Major shows the lowest one. This result agrees with the fact that the liquid of Supracryle consists mainly of pure MMA monomer, while the liquids of other commercial samples contain a percentage of cross-linking agent.

The infrared spectra of heat-cured experimentally prepared samples in Figs 3 and 4 indicate that there are no observable differences between their spectral features, apart from slight changes in the intensities of some absorption bands. The absorbances ratio, $A \, (1625 \, cm^{-1})/A \, (1725 \, cm^{-1})$, was determined, and the values are given in Table IV.

It can be seen from Table IV., that the absorbance

Table II The relative intensities and structural assignments of PMMA (s = strong, m = medium, w = weak, v = very, sh = shoulder)

| Frequency (cm^{-1})	Relative intensity	Tentative assignment
2995	m	CCH_3, OCH_3 stretching vibrations
2942	m	CCH_3, OCH_2, CH_2 stretching vibrations
2835	vw	Combination band associated with ester CH_3 group
1730	vs	(C–O)
1483		CCH_3 bending vibration
1465	sh	CH_2 bending, CCH_3 bending, OCH_3 bending
1452	s	CH_2 bending, CCH_3bending, OCH_3 bending
1438	s	OCH_3 bending vibration
1388	m	CCH_3 bending vibration
1270	s	
1240	s	C–C–O stretching vibration
1190	vs	Skeletal stretching coupled with
1150	vs	internal C–H deformation vibration
1063	w	Band arises from intra molecular interaction C–O–C stretching vibration
988	m	coupled with CH_3–O bending vibration
967	m	CH_3 bending vibration
910		
842		
749	w	CH_2 bending vibration coupled with skeletal vibration
710		
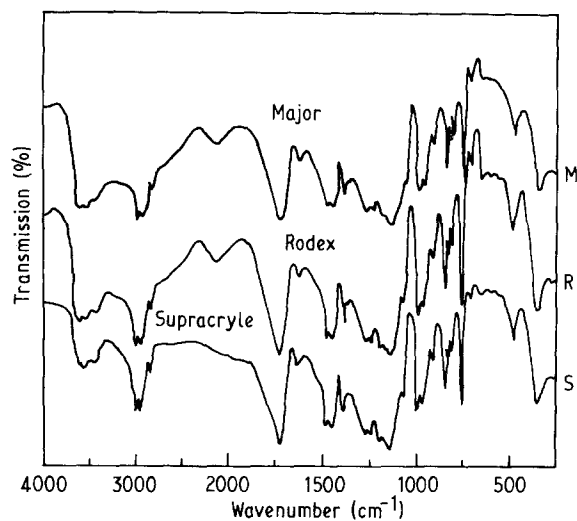
Figure 2 Infrared spectra of commercial heat-cured samples.

TABLE III The values of absorbance ratio of commercial brands

Sample	A (1625 cm^{-1})/A (1725 cm^{-1})
Supracryle	0.150
Rodex	0.144
Major	0.138

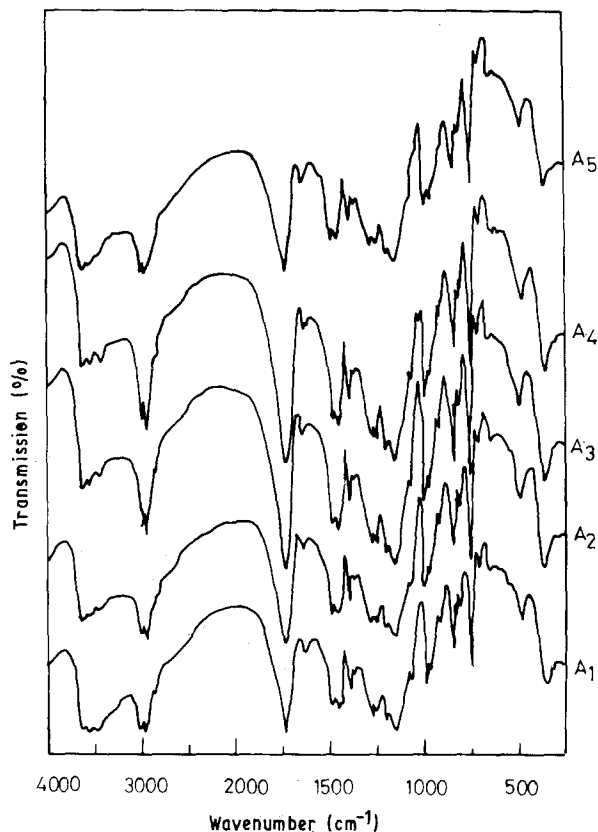
Figure 3 Infrared spectra of heat-cured experimentally prepared samples mixed with TEGDMA.

ratio A (1625 cm^{-1})/A (1725 cm^{-1}) varies from sample to sample according to the concentration and type of cross-linking agent. The samples mixed with triethylene glycol dimethacrylate cross-linking agent, A1 and A5, have the highest value of residual monomer, while
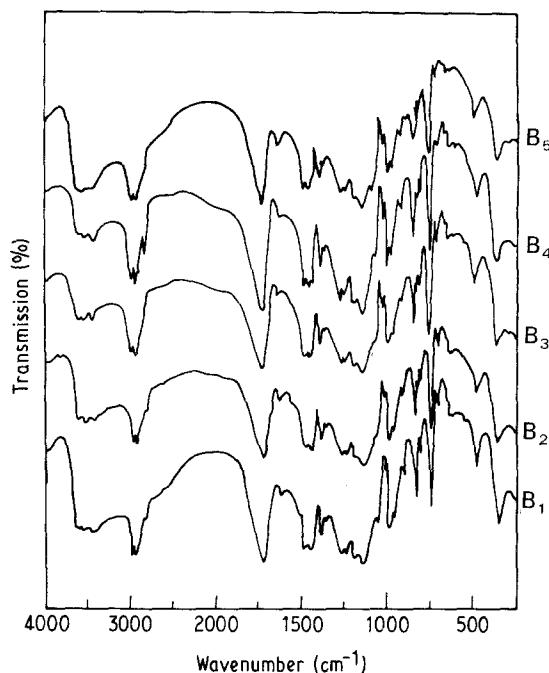

Figure 4 Infrared spectra of heat-cured experimentally prepared samples mixed with THFMA.

the samples mixed with A2 and A3 had the lowest values. Sample A4 showed an intermediate value.

Table IV shows also that the lowest value of absorbance. ratio in the case of experimentally prepared samples mixed with tetrahydrofurfuryl methacrylate, occurs in the sample B1. Samples B2 and B3 suggested more or less the same values while B4 and B5 showed the highest values of absorbance ratio. It seems very important to mention that, except for B1, for any given concentration, the absorbance ratio of THFMA is always higher than those of TEGDMA, i.e. higher residual monomer content. These results provide significant evidence that the residual monomer content is influenced by the type and concentration of the cross-linking agent.

3.2. Dielectric investigations

In the present investigations, the permittivity, ε', and dielectric loss, ε'', for the commercial non-cross-linked denture base resin (Supracryle) as well as those of the commercial cross-linked resins, were measured at frequencies ranging from 100 Hz to 50 kHz and at temperatures of 30, 50 and 70 °C. The measured values are illustrated graphically in Fig. 5. From this figure it is found that ε' decreases with increasing frequency which shows anomalous dispersion.

On the other hand, it is noticed that ε'' for the commercially cross-linked materials (Rodex and Major) over the whole range of frequencies, are less than that for the commercially non-cross-linked material (Supracryle). This could be attributed to the presence of the cross-linking agent in Rodex and Major (which decreases the permittivity values).

From Fig. 5 it is also clear that the data of ε''–log f are represented by one absorption region with a maximum lying around 1 kHz. This maximum is found to be independent either of temperature or of the material used, which leads to the Maxwell–Wagner effect

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Sample	A (1625 cm^{-1})/A (1725 cm^{-1})	Sample	A (1625 cm^{-1})/A (1725 cm^{-1})
A1	0.137	B1	0.093
A2	0.102	B2	0.113
A3	0.105	B3	0.117
A4	0.110	B4	0.141
A5	0.135	B5	0.157
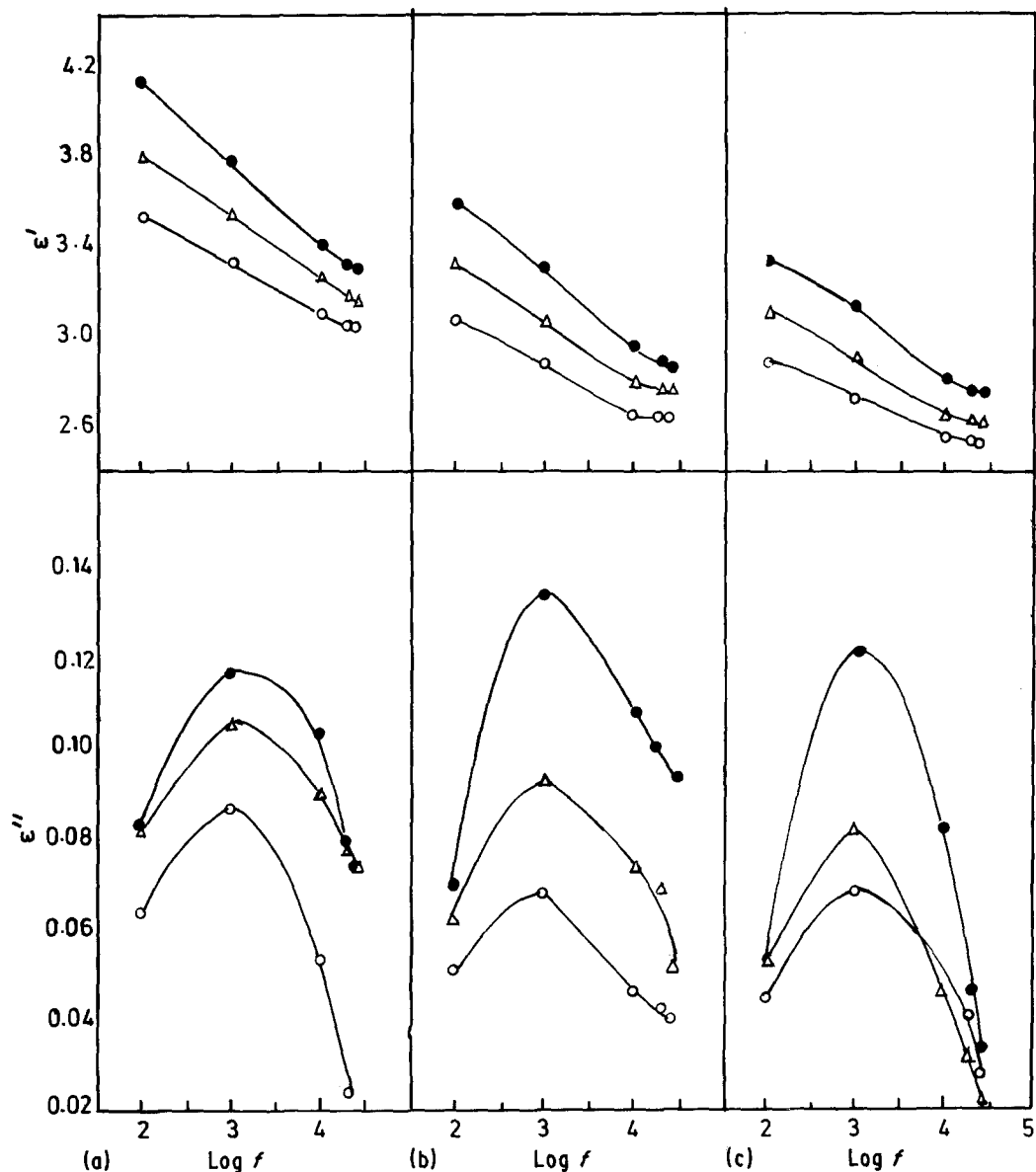
Figure 5 Frequency dependence of ε' and ε'' at (○) 30 °C, (△) 50 °C and (●) 70 °C for (a) Supracryle, (b) Rodex, and (c) Major.

[7]. This effect could be attributed to an a.c. current which is in phase with the applied potential. This current results from the difference in the conductivities and the permittivities of the different constituents of the sample. It was felt to be worth checking whether or not these losses in that range of frequency may be attributed to d.c. conductivity. Ohm's law was applied to direct current flow through the samples at voltages ranging from 0–190 V. No detectable current was seen to flow through the samples, indicating that they had no d.c. conductivity.

From Fig. 5 it is also noticed that ε' and ε'' at the different frequencies increase with increasing temperature. This trend is similar to that found before in the case of some polymers [8]. This result is in good agreement with the results obtained by measuring the residual monomer by infrared spectroscopy. The relationship is drawn in Fig. 6 between the absorbances ratio A (1625 cm^{-1})/A (1725 cm^{-1}) and ε'. The relationship indicates that ε' increases linearly with increasing residual monomer content.
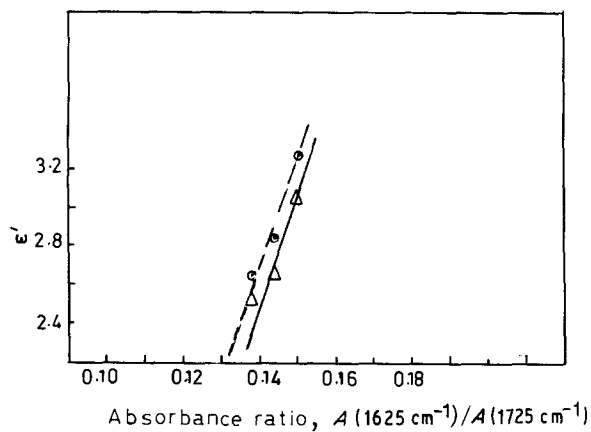
As the Supracryle was free from cross-linking agent,

Absorbance ratio, A (1625 cm^{-1})/A (1725 cm^{-1})

Fig.(6)

Figure 6 Relation between the absorbances ratio A (1625 cm^{-1})/A (1725 cm^{-1}) and ε' at (O) 100 Hz and (△) 25 kHz for commercial brands.
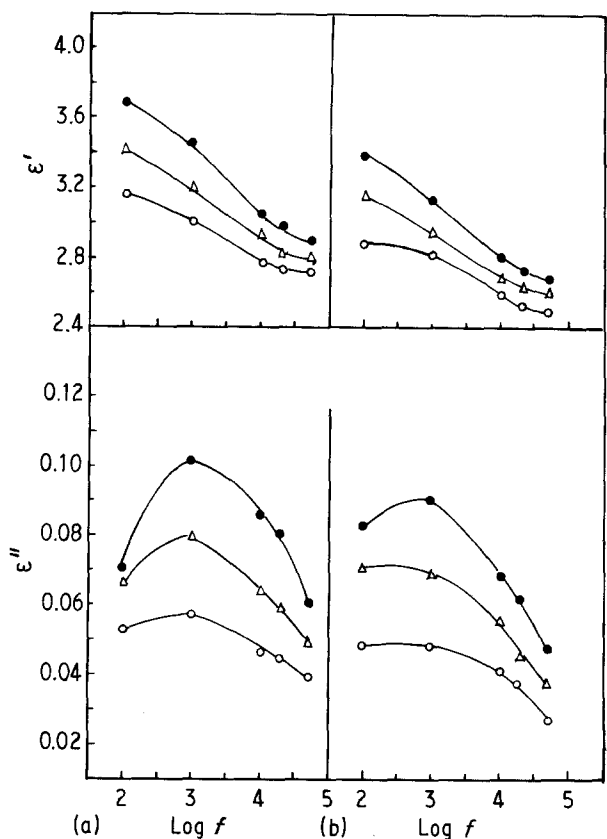
Figure 7 Frequency dependence of ε' and ε'' at (O) 30 °C, (△) 50 °C and (●) 70 °C for (a) A1 and (b) A2.

Figure 8 Frequency dependence of ε' and ε'' at (O) 30 °C, (△) 50 °C and (●) 70 °C for (a) B1, and (b) B2.

it seems interesting to investigate its dielectric behaviour after addition of either TEGDMA or THFMA in different concentrations.

The values of ε' and ε'' for Supracryle with concentration A1 and A2 of TEGDMA and B1 and B2 of THFMA at frequencies extending from 100 Hz to 50 kHz and temperatures 30, 50 and 70 °C are illustrated graphically in Figs 7 and 8, respectively. From these figures it is seen that ε' decreases with increasing frequency, while it increases with increasing temperature, which shows anomalous dispersion. On the other hand, ε'' is also found to increase with increasing temperature and shows a peak at frequency 1 kHz. Because the frequency at maximum loss for these

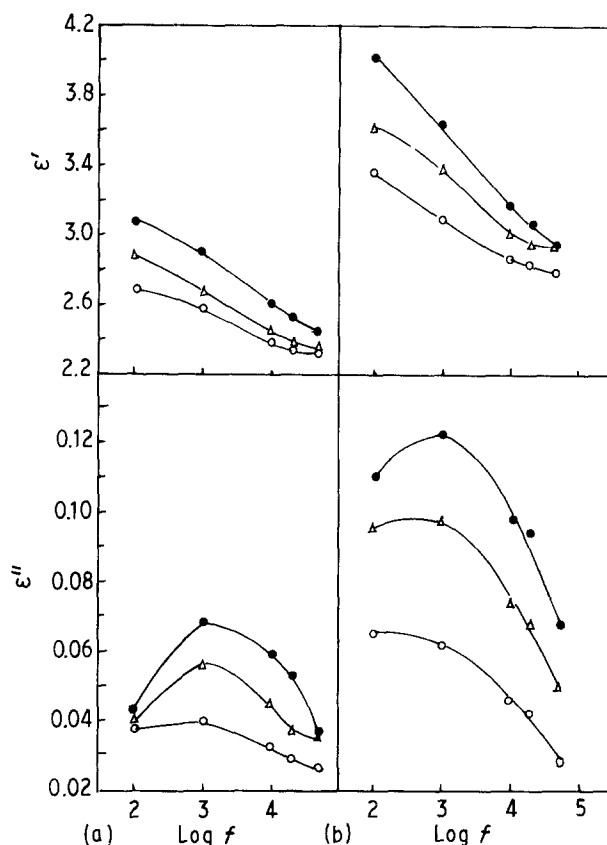peaks is found to be independent either of temperature or the concentration of the agent added, the peaks are mostly due to the Maxwell–Wagner effect as mentioned before, in the case of the commercial brands given in the text.

Comparing the results of ε' and ε'' for the commercial cross-linked resins (Rodex and Major, Fig. 5) with those of the commercial non-cross-linked denture base resin (Supracryle) after the addition of either TEGDMA or THFMA with different concentrations (Figs 7 and 8), it could be concluded that the addition of TEGDMA reduces both ε' and ε'', whereas the addition of THFMA increases them. So, it is interesting to conclude that the values of ε' and ε'' resulting from the addition of A2 are nearly the same as those of Major resin.

Based on the data obtained from the infrared and dielectric properties, one can conclude that the addition of 12% or 17% TEGDMA and THFMA to the non-cross-linked acrylic resin causes considerable reduction in the amount of the residual monomer. The decrease in the residual monomer content results in an increase in the absorbance of the C–C bond at 1625 cm^{-1} (which may be taken as a measure of the residual monomer content) and the dielectric constant of the acrylic resins. The results also indicated that the dielectric constant varies linearly with the absorbance ratio A (1625 cm^{-1})/A (1725 cm^{-1}).

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