Synthesis and Study of a Novel Copolymer of Acrylic/Citraconic Acids for Self-cured Dental Glass Ionomer Cement

Mansoor Keyanpour
Materials and Energy Research Center, P. O. Box: 14155-4777, Tehran, I.R.Iran

Received: 28 February 1998; accepted 31 August 1998

ABSTRACT

For comparison of acrylic-itaconic acids copolymers, the acrylic/citraconic acids copolymer is synthesized via emulsion polymerization, and then it is used as aqueous solution along with an ion-leachable glass for formulation of a self-cured glass ionomer dental cement. The presence of the methyl group in citraconic acid, and also less stereoregularity of the copolymer, compared to acrylic/maleic acids copolymer, both maintain hindered hydrogen bonding in the copolymer in aqueous solution over a long period of time and therefore gel formation does not occur. It has been found that the mechanical and physical properties of the formulated self-cured cement are in the range of those obtained for commercial sample and the $S_{42L-21}$ sample which is made from acrylic/itaconic acids copolymer.

Key Words: acrylic/citraconic acids copolymer, hydrogen bonding, gelation, stability, mechanical properties

INTRODUCTION

In making a glass ionomer cement for various dental applications, an aqueous solution of a polymeric material, such as polyacrylic, copolymer of acrylic/itaconic or acrylic/maleic acids in 5% tartaric acid is mixed with a finely grounded ceramic glass. In the pioneer works, the powder and 50% aqueous solution of polyacrylic acid (MW 2300) were mixed together to start the setting reaction [1-3].

Two problems were encountered with this formulation, namely long setting speed and gelation of the liquid [4-6]. To overcome these problems, tartaric acid was added to the high molecular electrolytic solution as a chelating agent, so the setting speed was improved [2, 7-8]. Although the effect of L(+) tartaric acid was known as long as 1972 and reported by Wilson [2], its mode of action remains a subject for speculation [9].

To suppress gelation of the cement liquid, several procedures were designed. Methylation of a portion of the carboxyl radical by adding 5% methanol to the liquid composition gave a weaker cement [6].

Furthermore, to overcome gelation, copolymers of acrylic/itaconic acids, or acrylic/maleic acid were used instead which had less stereoregularity than polyacrylic acid and therefore condensation by hydrogen bonding was hindered [10]. In addition, the stability of these copolymers in solution is thought to
Synthesis and Study of a Novel Copolymer of Acrylic/Citraconic Acids

H—C—COOH
CH₃—C—COOH

(1)
Citraconic acid

CH₃
CH₂—CH—C—CH₂—CH₂—CH—COOH COOH COOH COOH COOH

(2)
(acrylic acid)  (citraconic acid)  (acrylic acid)

Arise from formation of seven-membered intramolecular hydrogen-bonded rings involving both types of pendant acid groups, thus reducing the propensity for intermolecular hydrogen bonds formation [11, 12].

The present article reports the use of citraconic acid (1) as a monomer along with acrylic acid to make the copolymer (2), depicted in Scheme 1, which is not only soluble in water, but also, because of less stereoregularity compared to acrylic-maleic acids copolymer and the presence of the methyl group, it does not gel up over a long period of time. Comparisons are also drawn on some physical and mechanical properties of the formulated cement with those of a commercial sample in this article.

EXPERIMENTAL

Reagents and Materials
Citraconic and acrylic acids were obtained from Fluka Chemical Co., and the latter was vacuum distilled through a column packed with copper gauze and was freshly used prior to the reaction. Ammonium persulphate (the initiator), sodium dodecylbenzene sulphonate (SDBS, the emulsifier), L(+) tartaric acid (the accelerator) and 2-propanol (the chain transfer agent) and the deuterated solvents for NMR spectroscopy were all obtained from Merck Chemical Co.

and used directly in the experiments.

The commercial sample, which is used for comparison, is specified as Fuji ionomer type II (restorative) GC Corporation of Japan.

Instrumentation
FT-IR and ¹H NMR spectra of a freeze dried sample of the copolymer were obtained with Perkin Elmer model 681 and Varian T60 spectrophotometers, respectively. The former spectrum was recorded in DMSO-d₆ at 60 MHz radio frequency, using external TMS.

Average molecular weight of a sample of the copolymer was found by gel permeation chromatography (GPC; Waters 150-C). Mechanical properties of the cement, such as tensile, compressive and bending strengths were performed by Instron 1196. Hardness test was obtained by Vickers micro-hardness testing equipment. Working and setting times were performed in accordance of BS 6039 (British standard for glass ionomer cements, 1981). The former was assessed at the time at which a Gilmor needle of 28.3 g, diameter 1.05 mm, just failed to penetrate to a depth of 0.5 mm in 5 s. The latter load was 400 ± 5.0 g with the Gilmor needle of 5 mm length and 1 mm diameter. The solubility test was performed at 37 °C for 24 h. The viscosity of aged liquid was measured by a rotating cylinder Brookfield viscometer model DV-III.

Copolymer Synthesis
A 500 mL 4-neck flange-type round-bottomed flask, fitted with mechanical stirrer, dropping funnel, reflux condenser, gas inlet and a thermometer was charged with a solution of 1.25 g ammonium persulphate in 100 mL de-ionized water. It was then purged thoroughly with N₂ gas and warmed gradually to ca. 95 °C (solution 1). To this solution was added aliquots containing 1/24 of solution 2 + solution 3 and 1/24 of 49.8 g (0.38 mol) citraconic acid (ca. 2.1 g) in every 5 min, while stirring the mixture at ca. 95 °C.

Solution 2: 55.2 g (0.72 mol) acrylic acid, 0.1 g SDBS, 10 mL 2-propanol in 50 mL de-ionized water.
Solution 3: 1.25 ammonium persulphate in 30 mL de-ionized water.
Addition of the aliquots were completed in 2 h. It was then stirred at 100 °C under N₂ gas for additional 2 h, and then concentrated to about half of its volume, using high vacuum distillation technique.

A 1.0 mL portion of this solution was freeze-dried, using about 10⁻³ mm Hg high vacuum, affording ~0.4 g of an off-white polymeric material (the copolymer 2). IR(KBr, cm⁻¹): 3400 (O–H), 2940 (C–H), 1700 (C=O), 1560, 1450, 1400, 1350, 1100, 600.

Formulation of the Liquid
The liquid part of the glass ionomer cement was made by addition of 5% L(+)-tartaric acid to the resulting concentrated solution of the copolymer.

Synthesis of the Powder
The Chemicals of 41.9 g SiO₂, 28.6 g Al₂O₃, 15.7 g CaF₂, 1.6 g AlF₃, 3.8 g AlPO₄ and 9.3 g NaF were mixed and fused at 1250 °C for 2 h. The mixture was then shock-cooled by pouring onto a steel tray. The solidified glass masses, while still hot, were then plunged into water. The glass frits were ground by a vibratory mill and sieved by means of a 45-µm mesh. Only the fraction below 45-µm was used in this study.

RESULTS AND DISCUSSION
A sample of the formulated liquid was stored at 4 °C, which promotes gelation, and inspected from time to time for signs of thickening or gelation. It was found that the liquid at the concentration of 50% is quite stable and does not gel over a long period of time (>30 days). Thus, a shelf life of at least 30 days at 4 °C corresponds to a shelf life of several months at room temperature.

The most important copolymer used in glass ionomer cement is acrylic itaconic acids copolymer [9]. For making this copolymer in the liquid which gives good cement characteristic, the molar ratio of the starting monomers should not exceed 2:1 [13]. We have taken this into account to make the acrylic/citraconic acids copolymer. The viscosity of the copolymer solution is found to be a relatively low value of 58 poses with no changing after aging for 30 days (checked from 3 to 30 days) and, therefore, like itaconic/acrylic acids copolymer it has good mixing characteristics [14, 15]. The low viscosity of the solution encountered with this copolymer, like itaconic/acrylic acids copolymer, derive in part from its relatively low molecular weight (Table 1) and, also, from differences in the modes of hydrogen bonding. Usually, a lowering of the molecular weight of the polyacid results in weakening of the cement derived from it [6]. However with this copolymer, this effect

Table 1. Comparison of physical and mechanical properties between the prepared glass ionomer cement and Fuji Ionomer type.

|                     | Prepared cement | Fuji ionomer type II | S₄₂L-21  
|---------------------|-----------------|----------------------|---------
| Powder–liquid ratio (g/g) | 2.7/1.0         | 2.7/1.0              | 2.7/1.0 |
| Working time (min)          | 2.0             | 2.93                 | 2.84    |
| Setting time (min)          | 4.0             | 4.1                  | 4.82    |
| Compressive strength Sq (MPa), | 214             | 143                  | 166     |
| Tensile strength Sq (MPa),  | 16.3            | 13.2                 | 12.44   |
| Bending strength Sq (MPa),  |                | 10.42                | 12.81   |
| Solubility in H₂O (MPa)     | 0.3             | 0.42                 | 0.580   |
| Solubility in lactic acid (%) | 0.33           | 0.53                 | -       |
| Hardness (HV)               | 0.11            | 0.1                  | -       |
| Average molecular weight of the corresponding copolymer | 16400          | 11800               |

(a) 24 h load, (b) 24 h, 37 °C, (c) 24 h, 0.001 N, 37 °C, (d) 24 h, 10 g load.

![Figure 1. IR Spectrum of acrylic/citraconic acids copolymer.](image-url)

* The concentration of the monomers should be kept below 25% otherwise the reaction could proceed with explosive violence [9].
is offset by the greater cross-linking potential provided by citraconic acid groups, each of which contains two pendant carboxyl (COOH) groups.

In the IR spectrum of this copolymer (Figure 1), the presence of the bands at 3400 cm\(^{-1}\) for OH stretching vibration of acid groups, and 1700 cm\(^{-1}\) for \(-C=O\) stretching vibration for the carbonyl of the carboxyl group along with the absence of the bands at 1200 and 900 cm\(^{-1}\) are indication of the formation of the copolymer.

In the \(^1\)H NMR spectrum of the copolymer, (Figure 2), there is an upfield shift of the protons of the -CH\(_3\) group of the citraconic acid from 2.05 ppm for the monomeric state to 1.2 ppm when it is copolymerized with acrylic acid. In addition, disappearance of the peaks at 5.8 ppm and 6.4 ppm, the olefinic protons for citraconic and acrylic acids respectively, and formation of a new multiplet centring at 2.5 ppm confirm the formation of poly(acrylic-co-citraconic acids). The peak at 12.3 ppm could be exchanged with D\(_2\)O, corresponding to the protons of -COOH groups.

In Table 1 some physical and mechanical properties of the prepared self-cured glass ionomer cement are listed and compared with those of Fuji ionomer type (restorative) and the cement made from itaconic/acrylic acids copolymer (S\(_{42}\)L\(_{21}\)). This average molecular weight of the copolymer is greater than that found for S\(_{42}\)L\(_{21}\) sample [17], and therefore the solubility of the cement in pure H\(_2\)O is less than the cement made from the copolymer of itaconic/acrylic acids (Table 1). But, the presence of 2-propanol, as the chain transfer agent, in the reaction helped the formation of a copolymer with average molecular weight of around 16,000, otherwise the adhesion of the cement with high molecular weight copolymer, around 50,000 or more, to dentin would then be difficult [18].

Setting time of the cement is approximately the same as the commercial sample and less than S\(_{42}\)L\(_{21}\) and it is likewise for the tensile (Table 1). On the other hand, the bending strength and working time of the prepared cement have not been improved. Needless to say that in all the physical and mechanical properties determinations, the powder-liquid ratio (g/g) were kept constant.

The results tabulated in Table 1 indicate that the physical and mechanical properties of the formulated sample are more or less in the range of the commercial sample, specified as Fuji II ionomer cement for restorative purposes. Some clinical studies have been undertaken, the results of which will be published in near future.

**CONCLUSION**

From this study, the following important conclusions can be drawn:

- The synthesized novel copolymer, the most important component of the liquid part of the glass ionomer cement, would give a cement with physical and mechanical properties more or less in the range of Fuji No. II restorative commercial sample.
- The solubility of the synthesized copolymer in water and 0.001 N lactic acid is as good as the commercial sample.
- The polymeric solution does not gel over a long period of time.

**REFERENCES**