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Yongqing Huang[a]; Scott R. Schricker[a]; Bill M. Culbertson[a]; Susan V. Olesik[b]
[a] College of Dentistry, The Ohio State University, Columbus, OH, U.S.A. [b] Department of Chemistry, The Ohio State University, Columbus, OH, U.S.A.

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SYNTHESIS OF POLY(ACRYLIC ACID-CO-ITACONIC ACID) IN CARBON DIOXIDE–METHANOL MIXTURES

Yongqing Huang,[1] Scott R. Schricker,[1] Bill M. Culbertson,[1,]* and Susan V. Olesik[2,]*

[1]College of Dentistry, The Ohio State University,
305 W. 12th Street, Columbus, OH 43218-2357
[2]Department of Chemistry, The Ohio State University,
100 West 18th Avenue, Columbus, OH 43210

ABSTRACT

High fluidity solvents, such as supercritical fluids, have several advantages over traditional solvents as polymerization media, such as offering a more environmentally-friendly reaction media, providing increased reaction rates, and simplifying the separation and purification of polymers. In this study, a traditional glass-ionomer polymer, poly(acrylic acid-co-itaconic acid) (PAA/IA) was synthesized by using mixtures of CO_2 and methanol as the reaction solvent and was characterized by ^{1}H-NMR, FT-IR, GPC, and viscometry. The mechanical and working properties of the glass-ionomer cements, prepared by mixing aqueous solutions of the polymers with Fuji II glass powder, were evaluated for compressive strength (CS), diametral tensile strength (DTS) and flexural strength (FS), as well as setting time and working time. The results showed that the polymerization reaction in CO_2/methanol mixtures was faster and had higher conversion than the polymerization reaction in water. The glass-ionomer formulations made from the copolymer prepared under SC conditions showed higher CS, comparable FS and DTS compared with those made from the same polymer prepared in water. Both of the synthesized copolymers had significantly higher CS and FS

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*Corresponding authors.

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than Fuji II. The working properties of PAA/IA made in CO_2/methanol met the requirement of ANSI/ADA No. 96.

Key Words: CO_2; Supercritical fluid; Glass-ionomer; Poly(acrylic acid-co-itaconic acid); Dental restoratives

INTRODUCTION

A supercritical fluid is a substance at temperatures and pressures above its critical temperature (T_c) and pressure (P_c) [1]. Recent work in polymer synthesis has illustrated the utility of supercritical fluids as reaction media for various polymerization reactions [2]. Advantages of supercritical solvents include [3]; increased reaction rates and degrees of polymerization, elevation of ceiling temperatures, decreased viscosities of fluids, more environmentally-friendly media and simplified separation and purification of the polymers. These advantages are also shared with enhanced-fluidity liquid mixtures, which are liquids such as methanol to which high proportions of liquefied gases has been added [4].

Carbon dioxide [5] is the most commonly used supercritical solvent, because it has the following advantages: easily accessible critical condition ($T_c = 31.1°C$ and $P_c = 1084.6$ psi), inexpensive, nonflammable, nontoxic, more environmentally friendly, abundant and easy to obtain. The major problem of supercritical CO_2 as a polymerization solvent is that its polarity is so low that the solubility of a highly polar substance in CO_2 is very low. The addition of polar cosolvents can substantially increase the solubility of polar compounds [1, 6].

Originally, the glass-ionomer cement liquid was an aqueous solution of polyacrylic acid in a concentration of about 50 per cent by mass [7]. The liquid was quite viscous and tended to gel with time. To decrease the viscosity and reduce the tendency for gelation, a copolymer of acrylic acid and itaconic acid was used [8]. The resulting glass-ionomer cement showed good physical properties, such as good mechanical properties, low viscosity and good working properties [9]. However, there are some problems [10] associated with the copolymerization. First, a long reaction time is needed due to the lower monomer reactivity ratio. Second, a lower conversion rate is experienced. Third, separation and purification of the products are energy consuming because a large volume of water is needed for the polymerization. These problems can be solved by using a supercritical fluid as the polymerization solvent. Based on the previous research on poly(acrylic acid-co-itaconic acid) as a glass-ionomer polymer in our group, the optimal molar ratio of acrylic acid to itaconic acid is about 7:3 for the best physical properties. In this study, poly(acrylic acid-co-itaconic acid) (PAA/IA) with this optimal molar ratio was synthesized using CO_2/methanol mixtures as the solvent; and its properties were compared to that synthesized in water. Due to the insolubility of the itaconic acid in CO_2, the copolymerization of AA and IA cannot be directly performed in CO_2. Methanol was added as a co-solvent to solve this problem. Itaconic acid dissolves in methanol, and mixtures of CO_2 and methanol.

EXPERIMENTAL

Materials

Acrylic acid (99%, inhibited with 200 ppm hydroquinone monomethyl ether), itaconic acid (99%), 2,2′-azobis(isobutyronitrile) (AIBN), and Potassium persulfate ($K_2S_2O_8$) (99%) were obtained from Aldrich Chemical Co. AA was purified by vacuum distillation before use. Carbon dioxide was SFC/SFE grade (99.999% pure, Matheson, Newark, CA). Methanol was Fisher HPLC grade.

Syntheses of Poly(Acrylic Acid-co-Itaconic Acid)

Copolymerization Reaction of AA and IA

The copolymerization reaction of AA and IA is a free-radical polymerization, shown in Fig. 1.

In CO_2/Methanol Mixtures

Preparation of Supercritical Fluid CO_2/MeOH Mixture

Mixtures of CO_2 and methanol were made on a mol% basis. Pressurized liquid CO_2 was transferred from an ISCO (Lincoln, NE) syringe pump (Model 260D) into another ISCO syringe pump that contained deoxygenated methanol. The amount of CO_2 added to the second pump was determined from the density of the liquefied gas and the volume difference before and

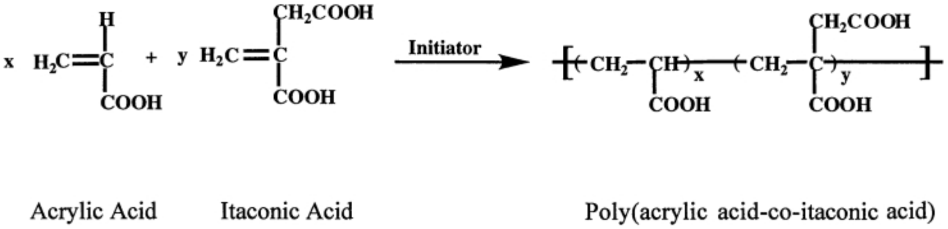

Figure 1. Reaction route of copolymerization.

after the transfer. The molar ratio of CO_2 to methanol used for the polymerization was determined by solubility tests of monomers in supercritical CO_2/methanol mixtures. Prepared mixtures were allowed to equilibrate at least 12 hours before use. The pressure of the mixtures was maintained at 3500 psi (reaction pressure) and the mixture was one phase at room temperature [11].

Solubility of Monomers in CO_2/Methanol Mixtures

The solubility of the monomers in CO_2/methanol mixtures was investigated by using a high-pressure view cell containing a magnetic stir bar. Monomers (10% vol/vol based on the volume of the 5 ml cell) with 7:3 molar ratio of AA and IA, were added into the cell consisting of a 1 cm thick quartz window sealed with a Teflon O-ring on both ends of the cell. Different molar ratios of the CO_2/methanol mixture were pumped into the cell. The solubility of the monomers in the CO_2/methanol mixtures under different temperature and pressure condition was visually monitored. In order to avoid the chain transfer interactions the amount of added methanol should be as low as possible. It was found that at least 3% by mole of methanol was needed to achieve a homogeneous solution before polymerization.

Polymerization Procedure in CO_2/Methanol Mixtures

In a typical reaction, 1.75 ml (0.023 mols) of deoxygenated AA, 1.423 g (0.011 mols) IA with 1.0 wt% AIBN based on the mass of the monomers were charged into a 25 ml, stainless steel high pressure cell (Thar Designs, Inc., Pittsburgh, PA) containing a magnetic stir bar. CO_2/methanol (7:3 molar ratio) was pumped through the cell by a high-pressure syringe pump (Model 260D, ISCO, Lincoln, NE), and the pressure was maintained at 2000 psi for 5 minutes. Then, the temperature and pressure were increased gradually at the same time to the desired condition. The reaction temperature was held at $75 \pm 1°C$ (using an Omega CN9000 temperature controller and a band heater attached to the cell) and the pressure was maintained at 3500 psi for about two hours. Note: The high proportion of methanol used in the mixture (30 mol%) was chosen to make certain that the product copolymer remains dissolved in solution. This mixture at 3500 psi and 75°C corresponds to subcritical conditions, $T_c = 176.85$ and $P_c = 1235$ psi, (i.e., an enhanced fluidity liquid) which continues to share the advantages of supercritical fluids. After this reaction time, the cell was cooled and vented slowly to atmospheric pressure. The product was collected as a yellow viscous liquid. The products were precipitated out by adding an excess of diethyl ether. The precipitate was collected, washed with diethyl ether and dried in a vacuum oven.

Polymerization in Water

AA 15 g (0.208 mols) and IA 12 g (0.092 mols) monomers were copolymerized in water [9], using 1.0 wt% potassium persulphate as the initiator and 2% isopropanol as a chain transfer agent. The reaction process was monitored by FT-IR using the stretch around 1620 cm^{-1} corresponding to the double bond(s) of the monomers.

The reaction time was about 8 to 10 hours. The product solutions were first isolated using a freeze dryer (Edwards High Vacuum International, Wilmington, MA) to obtain solid products. The solids were purified by using methanol as a solvent and diethyl ether as a precipitant.

Characterization of Poly(Acrylic Acid-co-Itaconic Acid)

IR and ^{1}H-NMR Characterization of PAA/IA

The IR spectra of polymers were obtained with a FT-IR Spectrometer (MIDAC Co., Costa Mesa, CA). The ^{1}H-NMR analyses of the polymers were conducted by using a Bruker AM 500 MHz NMR analyzer (Bruker Analytik GmbH, D-76287 Rheinstetten, Germany), where deuterium oxide was used as a solvent, sample concentration was around 50 ppm, and the temperature was 75°C.

Measurement of Molecular Weight

Molecular weight was determined using two steps:

(1) Methylation of the polymer: the polymer was dissolved in 65°C methanol with sulfuric acid for more than 6 hours to obtain partially esterified product. The products were dissolved in tetrahydrofuran (THF) for molecular weight estimation.
(2) Molecular weights were measured by gel permeation chromatography (GPC, Shimadzu Class VP version 4.2, SHIMADZU Corporation, Kyoto, Japan) using two PL-Gel 5 μm Mixed-D 300 × 7.5 mm columns (Polymer Laboratories Inc., Amherst, MA). The values were relative to the polystyrene standards.

Measurement of Viscosity

The copolymer was dissolved in distilled water with the concentration of the copolymer at 50 wt%. A cone and plate viscometer (BEL CAP 2000 Viscometer, Brookfield Engineering Laboratories, Inc., Stoughton, MA) was used to evaluate the viscosity at 25°C. The Bingham Plastic mathematics model was applied to analyze the data and calculate the plastic viscosity. For each solution, three samples were tested.

Measurement of Properties

Preparation of Specimens

A glass-ionomer liquid was made by dissolving the PAA/IA copolymer with 2% by mass D (+)-tartaric acid in distilled water in which the concentration of PAA/IA was 50 wt/wt%. Then each polymer solution, including the GC Fuji II (GC Corporation, Tokyo, Japan) liquid as a control, was mixed with the Fuji II glass powder, with a powder/liquid (P/L) ratio of 2.7/1, at room temperature. For compressive strength (CS) and diametral tensile strength (DTS), glass tubing (4 mm in diameter) was used to hold the mixtures with the help of a pressure fixture (40 psi) to remove air bubbles from the uncured paste. After conditioning at 37°C for an hour, the cylindrical specimens were cut into 6 mm in height for CS and 2 mm in thickness for DTS determinations. For the FS test, the cement paste was packed into a rectangular Teflon mold with dimensions of 2 mm in width, 2 mm in depth and 20 mm in length. The hardened cement was removed after half an hour. All specimens were stored in water at 37°C for 7 days before property tests.

Measurement of Mechanical Properties

Testing of specimens was performed on a screw-driven mechanical testing machine (Model 4202, Instron Corp., Canton, MA) which was properly calibrated in advance to eliminate bias, with a cross-head speed of 0.5 mm/min for the CS, DTS and FS measurements. The FS test was performed in three-point bending, with a span of 20 mm between supports. Before measurement, the order of the testing of the samples was randomized to eliminate bias. For each test, the sample size was 8.

Formulas used for calculation were as follows:

$CS = P/(\pi r^2)$, where P is the load at fracture and r is the radius of the cylinder sample.

$DTS = 2P/(\pi dt)$, where P is the load at fracture, d is the diameter of the cylinder sample and t is the thickness of the cylinder sample.

$FS = 3Pl/(2bd^2)$, where P is the load at fracture, l is the distance between two supports, b is the breadth of the sample and d is the depth of the sample.

Measurement of Working Properties (ANSI/ADA Specification No. 96-1994)

Net Setting Time. The mold with internal dimensions of 8 mm in width, 10 mm in length and 5 mm in thickness was conditioned to room temperature, placed on a glass slide and then filled to a level surface with mixed cement. Sixty seconds after the end of mixing, the mold and glass were placed into a cabinet maintained at a temperature of $37 \pm 1°C$ and a relative humidity of at least 90%. Ninety seconds after the end of mixing, the 400 ± 5 gram indentor (made in our lab) having a flat end of diameter 1 ± 0.1 mm was carefully lowered vertically onto the surface of the cement and remained there for 5 seconds. The indentation was repeated at 30 second intervals until the needle failed to make a complete circular indentation in the cement, when viewed using a $\times 2$ magnification lens. This time point was recorded as the approximate setting time.

The above process was repeated, during which time the indentation was started at 30 seconds before the approximate setting time and continued at 10 seconds intervals. The net setting time was recorded as the time elapsed from the end of mixing to the time when the needle failed to make a complete circular indentation in the cement. The test was repeated three times.

Working Time. A 28 gram indentor (made in our lab) with a flat end of 2.0 mm diameter was lowered vertically onto three flat blocks of specimens of each experimental and commercial material beginning from the start of the mix at 23°C. The indentor was allowed to remain for 5 seconds. This was repeated at 10 second intervals until the needle failed to make a complete circular indentation in the cement, when viewed using a $\times 2$ magnification lens. This time point was recorded as the working time.

Statistical Analysis

Analysis of variance (ANOVA) with the post-hoc Tukey-Kramer multiple comparison test in JMP IN (SAS Institute Inc. Cary, NC, USA) program at a level of $\alpha = 0.05$ was used to analyze the data.

RESULTS AND DISCUSSION

Polymerization Procedure

The FTIR spectra of the purified copolymers showed only one broad peak at about 1714 cm^{-1}, corresponding to the overlapping peaks of the carboxyl groups of AA and IA. No double bond band appeared in both purified copolymers. The reaction conditions and yields are summarized in Table 1, which shows that the polymerization in CO_2/methanol was faster and had a higher yield.

Table 1. Comparison of Copolymerization Process of AA and IA in SC-CO_2/Methanol vs. Water

Polymerization	CO_2/Methanol	Water
Solvent	CO_2/methanol	Water
Reaction temperature (°C)	75	100
Reaction pressure (psi)	3500	14.69
Initiator (1 wt%)	AIBN	$K_2S_2O_8$
Reaction time (h)	2 h	8–10 h
Separation time (h)	2 h	6 h
Conversion rate* (%)	75–80	60–70

* Based on the analysis of ^{1}H-NMR; conversion rates were for the polymers after the purification.

Copolymer Composition and Stereostructure of Products

The ^{1}H-NMR spectrum of PAA/IA-SC, PAA/IA-water is shown in Fig. 2 and 3, respectively. The signals appropriate to this discussion are represented in upper-right repeat unit structure of the copolymer as a, b, c, d. The methylene backbone protons (a) of PAA resonated at 2.08, 2.24, and 2.41 ppm. The signals that occurred around $\delta = 3.1-3.3$ ppm were associated with the methylene branch protons (d) of the PIA. The methylene backbone protons (c) of PIA appeared around 2.70 ppm which were overlapped with the signals around 2.90 ppm corresponding to methine backbone protons (b) of PAA. The molar fraction of IA (φ_1) in the copolymer was determined from the following equation in that b and c were overlapped:

$$\varphi_1 = I_d/(I_d + I_a)$$

The φ_1 of PAA/IA-water was 0.3 consistent with the original molar fraction of IA in the starting materials. Although the molar ratio of the monomers was identical for both synthetic ways, the φ_1 of PAA/IA-SC is about 0.4, which is larger than that of PAA/IA-water. In addition, the NMR band structure associated with the d protons for PAA/IA-SC was different from that of PAA/IA-water. To make peak assignments and to determine the microstructure, two-dimensional NMR is needed. Further kinetic studies are also needed to explain this difference in the composition between the copolymers produced in water and in CO_2/methanol. Other peaks at about 4.0 ppm and below 2.0 ppm were found in both products, which might come from by-products of the reaction with chain transfer agent, methanol for the CO_2/methanol reaction conditions and isopropanol for water, or decarboxylation of itaconic acid [11].

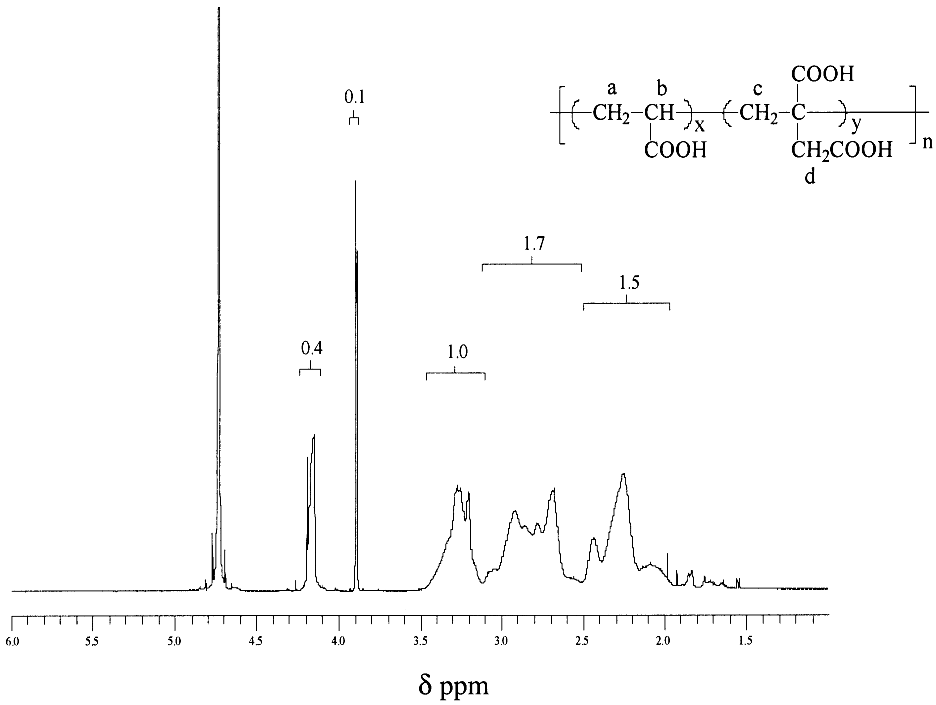

Figure 2. ^{1}H-NMR spectrum of PAA/IA-SC.

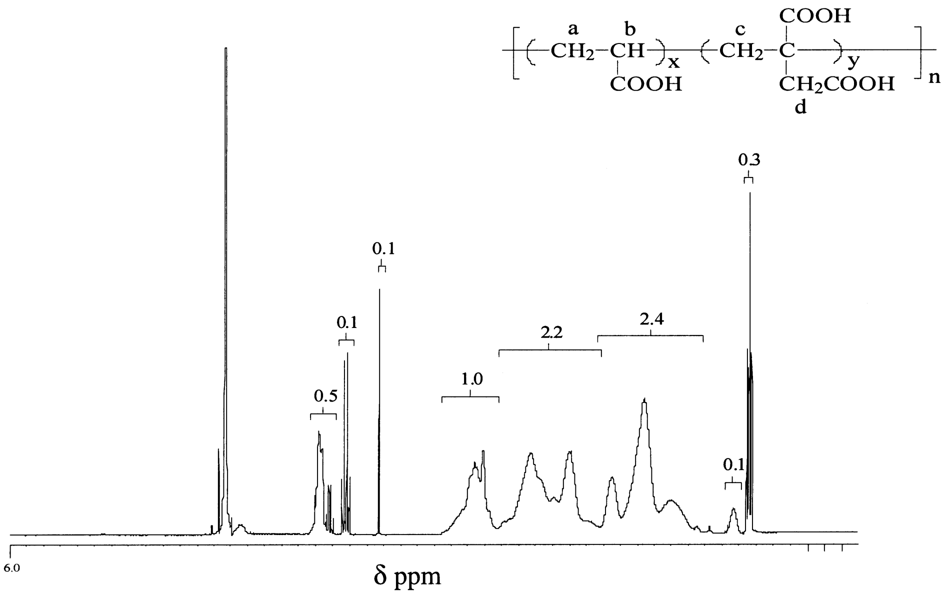

Figure 3. ^{1}H-NMR spectrum of PAA/IA-water.

Molecular Weight and Viscosity of PAA/IA

Table 2 shows the weight average molecular weight M_w, number average molecular weight M_n, polydispersity index M_w/M_n and viscosity of PAA/IA-SC, PAA/IA-water and Fuji II. The liquid Fuji II had the lowest viscosity and lowest molecular weight. PAA/IA produced in CO_2/methanol showed the highest molecular weight and viscosity. In general, higher molecular weight causes higher solution viscosity for a substance. There was no appreciable difference in polydispersity. Since higher molecular weights usually result in higher mechanical properties, the mechanical properties of PAA/IA-CO_2/methanol were expected to be somewhat better than PAA/IA produced in water.

Mechanical Properties of PAA/IA

For the CS, DTS and FS, the numerical mean values and the standard deviations are reported in Table 3. The post-hoc Tukey-Kramer multiple comparison statistical analysis was used to determine whether there was significant difference between each material at a level of $p < 0.05$. PAA/IA-CO_2/methanol had the highest compressive strength, diametral tensile strength and flexural strength. However, the difference in the values was not statistically significant for DTS and FS.

Table 2. Viscosity and Molecular Weight of Copolymers

Copolymers	Viscosity (cP), 25°C	M_w	M_n	M_w/M_n
PAA/IA-CO_2/methanol	950 (10.2)	3.18×10^4	1.57×10^4	2.03
PAA/IA-water	850 (15.6)	2.88×10^4	1.44×10^4	2.00
Fuji II	564 (9.1)	1.66×10^4	7.45×10^4	2.23

* For viscosities: entries are mean values for three times with standard deviations in parentheses.

Table 3. Comparison of Mechanical Properties of Various Cements

Glass-Ionomer	P/L Ratio	CS (SD) Mpa	DTS (SD) Mpa	FS (SD) MPa
PAA/IA-SC	2.7:1	278.47 (6.88)	12.96 (1.62)^a	25.93 (2.20)^b
PAA/IA-water	2.7:1	269.31 (7.95)	11.77 (0.76)^a	20.19 (5.77)^b
Fuji II	2.7:1	220.91 (9.73)	12.05 (1.15)^a	16.09 (3.51)

* Sample size is 8; the strength values with the same superscript letter were not significantly different ($p > 0.05$).

This result is consistent with the above molecular weight data, higher molecular weight of the polymer matrix is favorable to better mechanical properties of the glass-ionomer cement [12]. Another possible factor for higher CS is that the slightly higher fraction of itaconic acid in PAA/IA-CO_2/methanol, causes higher chain stiffness of the copolymer backbone.

The microstructure of the copolymers prepared by water and high fluidity solvents do no appear to be significantly different according to the ^{1}H NMR data. While we had anticipated some microstructure difference between the two methods, this was not seen in the data.

The CS and FS of both PAA/IA-CO_2/methanol and PAA/IA-water were significantly higher than those of Fuji II. It is believed that the markedly higher molecular weight of PAA/IA-CO_2/methanol and PAA/IA-water is a major reason.

Working Properties

The working time and net setting time of PAA/IA-SC, PAA/IA-water and Fuji II are given in Table 4. Fuji II had the shortest working time and net setting time. Compared with PAA/IA-water, PAA/IA-CO_2/methanol showed shorter working time and net setting time which were closer to those of Fuji II, due to its more available $-$COOH groups and higher viscosity. The net setting time of PAA/IA-CO_2/methanol and PAA/IA-water are both within the range of requirement of ANSI/ADA Specification No. 96 [7]. The net setting time can be shortened by adding more D (+)-tartaric acid while lengthening the working time [13]. The D (+)-tartaric acid concentration used in this study was only 2 wt% lower than commonly used 5 wt% [6]. Thus, the working properties of PAA/IA can be adjusted to satisfy various applications.

CONCLUSION

We were able to use a high fluidity solvent system of supercritical CO_2 and methanol to efficiently prepare poly(acrylic acid-co-itaconic acid)

Table 4. Working Characteristics of Various Cements

Cements	Working Time (min)	Net setting Time (min)
PAA/IA-CO_2/methanol	3.0 (0.0)	5.0 (0.2)
PAA/IA-water	3.5 (0.2)	5.5 (0.2)
Fuji II	2.5 (0.0)	4.0 (0.2)

* Sample size is 3; entries are mean values with standard deviations in parentheses.

copolymers for use in glass ionomer restorative materials. Compared to the synthesis of the copolymer in water, the synthesis and isolation in CO_2/methanol took less time and energy. The PAA/IA-CO_2/methanol has higher molecular weight, viscosity and mole fraction of itaconic acid. Compared to the control (Fuji II) and PAA/IA-water, the glass-ionomer restoratives formulated from the PAA/IA-CO_2/methanol had superior mechanical properties as measured by compressive and flexural strength. However, the working properties of PAA/IA-CO_2/methanol are better or comparable with those of PAA/IA-water. Both the mechanical properties and working properties of PAA/IA-CO_2/methanol and PAA/IA-water satisfy the requirement of ANSI/ADA Specification No. 96.

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