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Synthesis of *N*-vinylpyrrolidone modified acrylic acid copolymer in supercritical fluids and its application in dental glass-ionomer cements

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Abstract Compressed fluids such as supercritical CO_2 offer marvellous opportunities for the synthesis of polymers, particularly in applications in medicine and dentistry. It has several advantages in comparison to conventional polymerisation solvents, such as enhanced kinetics and simplified solvent removal process. In this study, poly (acrylic acid-co-itaconic acid-co-*N*-vinylpyrrolidone) (PAA-IA-NVP), a modified glass-ionomer polymer, was synthesised in supercritical CO_2 (sc-CO_2) and methanol as a co-solvent. The synthesised polymer was characterized by ^{1}H-NMR, Raman and FT-IR spectroscopy and viscometry. The molecular weight of the final product was also measured using static light scattering method. The synthesised polymers were subsequently used in several glass ionomer cement formulations (Fuji II commercial GIC) in which mechanical strength (compressive strength (CS), diametral tensile strength (DTS) and biaxial flexural strength (BFS)) and handling properties (working and setting time) of the resulting cements were evaluated. The polymerisation reaction in sc-CO_2/methanol was significantly faster than the corresponding polymerisation reaction in water and the purification procedures were simpler for the former. Furthermore, glass ionomer cement samples made from the terpolymer prepared in sc-CO_2/methanol exhibited higher CS and DTS and comparable BFS compared to the same polymer synthesised in water. The working properties of glass ionomer formulations made in sc-CO_2/methanol were comparable and in selected cases better than the values of those made from polymers synthesised in water.

1 Introduction

A supercritical fluid (SCF) is any substance, the temperature and pressure of which are higher than its critical values. Below the critical point the fluid can coexist in both gas and liquid phases, but above the critical point, there is only one phase. In the supercritical state the physical properties of the fluids such as density and viscosity can simultaneously become between those of a gas and liquid phase [1–3]. Unlike conventional hydrocarbon liquid solvents, the density of supercritical fluids can be changed by altering the pressure and temperature of the fluid and therefore the dissolution power of a supercritical fluid can vary. SCFs can also possess gas-like diffusivities which have important implications for reaction kinetics while having liquid-like densities which allows solubilisation of many compounds.

In particular, supercritical CO_2 has been used as a promising alternative to conventional organic solvents in a range of reactions to date. It has an easy accessible critical point with a T_c (critical temperature) of 31.1°C and P_c (critical pressure) of 73.8 bar. Furthermore, supercritical CO_2 is chemically inert, inexpensive, non-toxic and non-flammable [1–8]. According to properties of supercritical

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CO_2 it is suitable for extraction of different materials and it can be used as a reaction medium for certain polymerisation reactions [4–7]. Supercritical carbon dioxide is an excellent non-polar solvent for many organic compounds such as, alkenes, alkanes, aromatics, ketones and alcohols, which up to approximate molecular mass of around 400 amu will dissolve in this medium. The main problem of supercritical CO_2 as a solvent is, its poor solubility of many polar substances due to the solvents' own low dielectric constant. Consequently, polar co-solvents are often added in order to overcome this problem.

Glass ionomer cements (GIC) were invented by Wilson and Kent at the Laboratory of the Government Chemist in early 1970. These materials are water based cements, known as polyalkenoate cements. Glass ionomer cements are formed by the reaction of an ion leachable aluminosilicate glass with an aqueous solution of poly acrylic acid (poly alkenoic acid) in concentration of about 50% [9–12].

The use of sc-CO_2 mixtures for the preparation of dental polymers was recently applied by Huang et al. [13]. In their study, they synthesised AA/IA copolymers in supercritical CO_2/methanol mixtures and used them in Fuji II glass-ionomer cement (a commercial glass ionomer cement formulation). They investigated the effect of using modified supercritical CO_2 as the polymerisation solvent on the mechanical and working properties of the resulting cements in comparison to the samples prepared with polymers made in water that were mixed with Fuji II glass powder. They reported the PAA/IA samples prepared in the CO_2 mixture showed higher compressive and flexural strength in comparison to both PAA/IA samples prepared in water and Fuji II glass ionomer control group, respectively. They also reported that working properties of the cements made with polymers in CO_2 were generally amongst the best ones [13]. In this regard, the use of supercritical CO_2 enabled them to overcome some of the disadvantages of the traditional polymerisation reactions such as long required reaction time, lower conversion rates and time and energy consuming purification and separation procedures [13].

Various reports by Culbertson et al. and Yamazaki et al. [14–18] and more recently by Moshaverinia et al. [19] have suggested that NVP modified polyacids can significantly enhance the strength of glass ionomer dental cements. These results and the aforementioned work of Huang et al. [13], led to our work reported herein in which the synthesis of poly(acrylic acid-co-itaconic acid-co-*N*-vinylpyrrolidone) (PAA-IA-NVP) polymers were investigated in a supercritical CO_2 mixture. These polymeric products were then used in glass ionomer cement formulations and the effects upon the mechanical and working properties of the glass ionomer cements were investigated and compared to the samples prepared using polymers that were synthesised in water.

2 Experimental

2.1 Materials and equipment

All the chemicals in this study were in analytical grade and applied as received from Sigma Aldrich Chemical Co (Dorset, UK). Acrylic acid (AA), itaconic acid (IA), *N*-vinylpyrrolidone (NVP), 2, 2′-azobis (isobutyronitrile) (AIBN), D (+)-tartaric acid, ammonium persulfate$[(NH_4)_2S_2O_8]$ and methanol (CH_3OH) were used for polymer synthesis. Carbon dioxide 99.95% purity (British Oxygen Company, Crawley, UK) was used as a solvent. The glass powders and all polymeric liquids which were used in the experiments were from Fuji II (GC International, Tokyo, Japan).

2.2 Syntheses of polymers

2.2.1 *Polymerisation reaction in a supercritical CO_2 mixture*

The polymerisation reaction which was used in this experiment was a free-radical polymerisation reaction. In a typical reaction, initially, 27.43 ml (80 mol%) of acrylic acid (density of 1.05 gcm^{-3}) with 5.31 ml of NVP (10 mol%) (density of 1.045 gcm^{-3}) and 6.5 g of itaconic acid (10 mol%) were measured and were added to the 450 ml Paar autoclave. 1 wt% of 2, 2′-azobis (isobutyronitrile) (AIBN) was added as the initiator of the polymerisation reaction. Methanol was used as the cosolvent of the reaction since the itaconic acid is not soluble in CO_2 solution; as in the methods of Huang et al. [13] and Reighard et al. [20], in our case at least 3 mol% methanol was added to the other reagents which formed a homogeneous solution [13, 20]. The autoclave was very slightly purged with CO_2 gas to remove any air before being filled with liquid CO_2 from the cylinder at 4.99 MPa (725 psi). Then, the reactor was pressurized using the ISCO model 260D syringe pump and the autoclave was then held at 20.68 MPa and 80 ± 5°C, under continued stirring (250 rpm) for 4 h. At the end of the experiment, the stirring was switched off and CO_2 was released over a period of 5 min. The product was obtained as a pale yellow coloured viscous liquid. The product was washed and extracted with diethyl ether and dried using a vacuum oven. Yield was 78% overall based on dried mass of final product.

2.2.2 *Polymerisation reaction in water*

Experimental procedure employed in this study is the method reported by Crisp et al. [18] and Yamazaki et al. [21]. 0.4 mol (27.43 ml) of acrylic acid (density of

$1.05\ \mathrm{gcm^{-3}}$), 0.05 mol (6.5 g) of itaconic acid and 0.05 mol (5.31 ml) of NVP (density of $1.045\ \mathrm{gcm^{-3}}$) were measured and dissolved in distilled water. Ammonium persulfate (2 wt%) was used as an initiator for the polymerisation reaction. The molar ratio was kept at 8:1:1 for the final product AA-IA-NVP polymer [18]. The reaction mixture was heated continuously up to 98°C under flowing nitrogen for 10 h. At the end of this time, the heating was switched off and after cooling for 1 h under nitrogen, the wet polymer was filtered and then freeze-dried. Freeze drying was conducted on a Virtis Wizard 2.0 freeze dryer (SP Industries Co. the Virtis Company, NY, USA) by freeze-drying the polymer at 400 millibars for 22 h. In order to remove any residual monomers, the dried polymers were completely dissolved in anhydrous methanol and then reprecipitated from anhydrous ethyl acetate (3 × 100 ml). Yield of the polymer synthesised in water was 65% overall based on dried mass.

^{1}H-NMR analyses of the polymers were conducted using a Bruker AV 600 MHz ^{1}H-NMR using D_2O as the solvent (Bruker Analytik GmbH, Germany).

Raman spectra of the polymers were obtained using a Nicolet Amelga XR (with 785 nm laser) dispersive Raman spectrophotometer. The samples were placed in quartz tubes and spectra were obtained in the range 4000–400 $\mathrm{cm^{-1}}$ over an average of 128 scans and 2.0 s exposure time.

FTIR spectra of the synthesised polymers were obtained using a Nicolet 8700 FTIR spectrometer (Thermo Electron Corporation, UK) where the polymer sample films were cast on the KBr crystal to obtain spectra. Spectra were recorded in the mid infrared region (4000–400 $\mathrm{cm^{-1}}$) at 4 $\mathrm{cm^{-1}}$ resolution and averaging 128 number of scans.

Molecular weights of the polymers were estimated by using Zetasizer, nanoseries analyzer (ZS, Malvern Instruments Ltd. Worcestershire, UK) at 25°C using static light scattering method according to refractive index of PAA [22]. In order to measure the viscosity of the polymers, 1:1 (wt/wt) mixture of polymer and distilled water were first prepared. The viscosities of polymers were measured by application of a programmable reheometer (DV III V3.0, Brookfield Engineering Laboratories, Inc., Stoughton, MA) at 25°C and spindle rotational speed of 50 RPM.

2.3 Formulation and evaluation of glass-ionomer samples

2.3.1 *Specimen preparation*

All polymers were dissolved in distilled water in a ratio of 1:1 (wt/wt) proportion. D (+)–tartaric acid 2% by mass was added to the polymer solution. The glass powder was Fuji II GIC (GC International, Tokyo, Japan) and the powder to liquid (P/L) ratio of 2.7/1 was used as recommended by the manufacturer. Specimens were mixed and fabricated at room temperature following the manufacturers' instructions. Cylindrical specimens were prepared using PTFE cylindrical shaped moulds with diameter of 4 mm and 6 mm height for compressive strength test and were cut to 2 mm thick cylinders for diametral tensile strength test. For the biaxial flexural strength test, disc shaped moulds with 10 mm diameter and 1 mm thickness were used. The moulds were filled with the uncured cement mixture and covered with PTFE tape and glass slides, flattened and gently pressed by hand in order to remove air bubbles. The specimens were removed from the moulds after 30 min and conditioned in distilled water at 37°C for 23.5 h. Six identical specimens were made for each kind of test.

2.3.2 *Mechanical properties measurements*

Mechanical tests were performed on mechanical testing machine (Model 4206, Instron Corp., Canton, MA) with the cross-head speed of 0.5 mm/min. The compressive strength (CS) was calculated from the relationship $CS = 4P/\pi d^2$, where P is the load (N) at the fracture point and d is the diameter of the cylindrical specimen (mm). The diametral tensile strength (DTS) was determined according to the equation $DTS = 2P/\pi dt$, where the P is load (N) at fracture point, d and t are diameter and thickness respectively of the specimen (mm). For biaxial flexural strength (BFS) test, a loading rate of 0.5 mm/min was used on the Universal Testing machine using the same method as described by Kaplan et al. [23]. The minimum number of repeat specimens for each test was 7. Biaxial flexural strengths were calculated from the following equation; $S = P/h^2\ (0.606\ln a/h + 1.13)$, Where P is the load, "h" and "a" are thickness of the sample and diameter of the support ring, respectively. From the previous studies of Akinmade et al. the value of the Poisson's ratio was taken to be 0.27 [24]. One way analysis of variance was used to determine if there is remarkable difference between the strengths of the various experimental cements For statistical significance a level of $\alpha = 0.05$ was used.

2.3.3 *Working time and setting time*

The working and setting time were determined by using a Wilson oscillating rheometer using the method described before by Deb and Nicholson (1999) [25]. A small amount of the cement after 20 s of mixing was placed between the plates of the rheometer and allowed to set. Working and setting times were determined by calculating the time taken to reach 95 and 5% of the initial amplitude of the oscillation. The values reported are the average of five samples.

3 Results and discussion

3.1 Characterisation of synthesised polymers

The reaction time and reaction conditions of both polymerisation reactions are given in Table 1 (below). In comparison to traditional polymerisation reactions in aqueous mediums, polymerisation in methanol and supercritical CO_2 appears more efficient, faster and has higher yield for final products. The purification procedures for the final product are easier and less time and energy consuming.

^{1}H-NMR spectra (Fig. 1a, b) of the synthesised polymers revealed signals at $\delta = 1.65$ (CH_2 from acrylic acid and NVP, respectively), $\delta = 4.3$ (CH from NVP backbone), $\delta = 3.3$ (CH_2 on NVP ring), $\delta = 2.3$ (CH from acrylic acid) and $\delta = 3.1$ (CH_2 of itaconic acid). The molar fractions of all the three components (AA, IA and NVP) of the final terpolymers were calculated after accounting for the overlapped signals of methylene and methine groups in each monomer. The molar yield for each monomer fraction (IA and NVP) was calculated by characterisation of residual solvents which were used for final purification of the polymers [13]. Molar fraction determination of both polymeric products showed that the molar ratios of monomers were AA: IA: NVP 8:1:1 for both of the polymers and (IA/PAA and NVP/PAA) ratios were greater for PAA-IA-NVP in sc-CO_2 in comparison to the PAA-IA-NVP polymer which was prepared in water. There are some other peaks in areas above 4.5 and less than 1.5 ppm, which might be related to by-products of the reaction with methanol in sc-CO_2. Further studies are required to explain the differences in the composition between the terpolymers produced in sc-CO_2 and the water [13, 20].

Both Raman and FTIR spectra confirmed the disappearance of peaks due to C=C stretching (of monomer) which suggests a high purity of the final products. The results were in correlation with the former studies and showed that the synthesised polymers had desired structures and molar ratios [26, 27].

Table 1 Comparison of polymerisation reaction of AA, IA and NVP in supercritical CO_2 and water

Polymerisation reaction medium	Supercritical CO_2/MetOH	Water
Reaction time (h)	4	10
Reaction temperature (°C)	80	100
Reaction pressure (MPa)	20.68	0.103
Conversion rate (%)	78 ± 3	67 ± 3
Purification time (h)	4	28

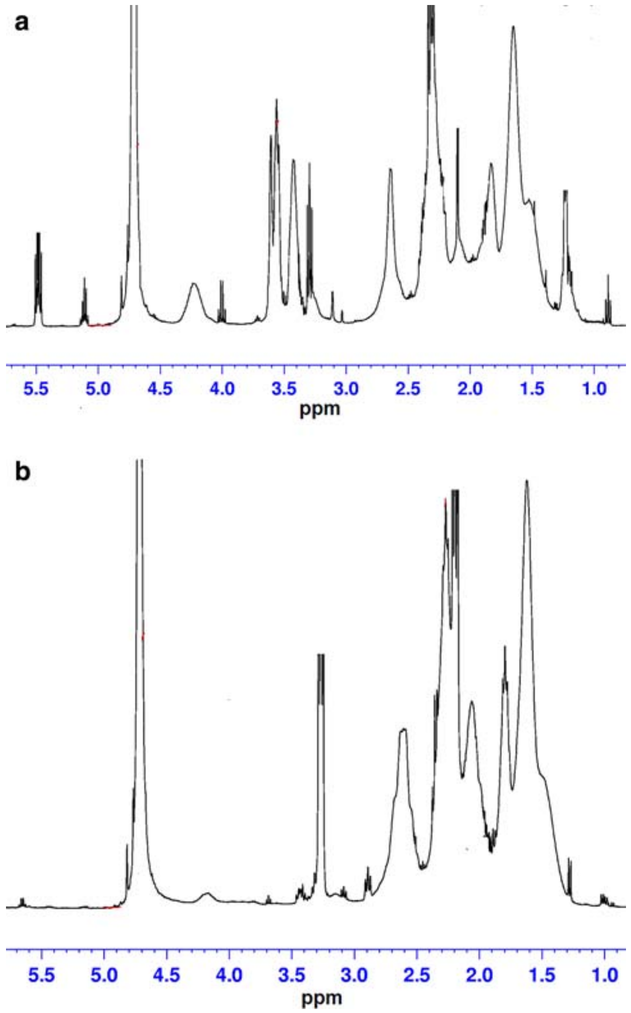

Fig. 1 ^{1}H-NMR spectra of synthesised polymers in modified supercritical CO_2 (**a**) and in aqueous medium (**b**)

Raman spectra (Fig. 2) of the synthesised polymers showed the disappearance of the C=C bonds in comparison to spectra of the starting reactants, which indicated the occurrence of the polymerisation reaction. Raman spectra (Fig. 2) of the terpolymer prepared in supercritical CO_2 (PS) and in water (PW) showed peaks at 2930, 1720, 1630 and 1308 cm^{-1} which were assigned as C–H stretch, carbonyl group amide groups and C–N stretches of amide group, respectively (Fig. 2). The disappearance of peaks at 1620 and 1410 cm^{-1} which ascribe to C=C and =CH_2, respectively, confirmed that the polymerisation reaction was successful. In Raman spectra, the peak at 2930 cm^{-1} belongs to CH_2 asymmetric stretch. Since this peak is in the area less than 3000 cm^{-1} and there are two other peaks at 1448 and 744 cm^{-1}, the final product does not have any C=C bond in its structure and the polymerisation has been successful and all the monomers with C=C groups have been converted to C–C simple bonds, and these peaks belong to a C–H bond of an aliphatic hydrocarbon with a long chain. The peaks at 1077 cm^{-1} related to C–C backbone (skeletal vibration) while the one at 978 cm^{-1} is related to C–C bonds on the NVP cyclic structure. The products also showed a broad peak ranging from 3500 to 2400 cm^{-1} which are related to hydroxyl groups of carboxylic acid groups and C–H stretchings [26, 27].

FTIR spectra (Fig. 3) of the synthesised polymers showed peaks at 1730, 1715, 1650, 1490, 1176 and 1291 cm^{-1} which are associated with carbonyl group, amide, CH_2 bending and C–N stretch, respectively. The peaks at1730 and 1715 cm^{-1} belong to Carbonyl (C=O) group of carboxylic acid and amide structures. The peaks at 1650, 1490, 1291 and 1176 cm^{-1} belong to carbonyl group (amide I) of NVP, C–H stretch (or (–CH_2–) C–H twist), C–N stretch and CH_2 rocking, respectively (see Fig. 3, below).

Yields of the polymerisation reactions are tabulated in Table 2 alongside the molecular weights and viscosities of the final polymeric products. It is apparent that polyacid synthesised in sc-CO_2 has higher Mw and viscosity compared to the polymer in water, which suggests that the polymerisation reaction is more effective for the former case. It is clear that the yield for polymerisation reaction in supercritical CO_2 was higher than reaction which was done in water.

3.2 Evaluation of cements

Studies elsewhere have suggested that the incorporation of *N*-vinylpyrrolidone in the formulations of polyacid of the glass ionomer cements has the ability to increase the mechanical and working properties of the conventional glass ionomer cements [15, 17, 20]. The results of our study were in broad agreement with previous findings. Mechanical properties of the cements are shown in Fig. 4 and can be compared to the values for Fuji II commercial glass ionomer cement. The results are recorded after 24 h of immersion in distilled water at 37°C. For all the mechanical tests, the cements which were a mixture of Fuji II glass powder with the polyacid synthesised in sc-CO_2 (PS), showed higher values (compressive strength = 178 ± 9.1 MPa; diametral tensile strength = 19 ± 5.7 MPa and biaxial flexural strength = 29.6 ± 3.8 MPa) in comparison to the cement samples which were the mixture of PW (synthesised in water solvent) polyacid (compressive strength = 166.2 ± 10.4 MPa; diametral tensile strength = 17.1 ± 7.9 MPa and biaxial flexural strength = 28.2 ± 5.4 MPa) and Fuji II glass ionomer cement samples as the control group (CS = 161.1 ± 5.3 MPa; DTS = 12 ± 6.1 MPa and BFS = 13.8 ± 4.3 MPa). The compressive, diamteral tensile and biaxial flexural strength of the glass ionomer samples which used polyacid prepared in supercritical situation were higher than values of Fuji II commercial glass ionomer cement. Statistical analyses

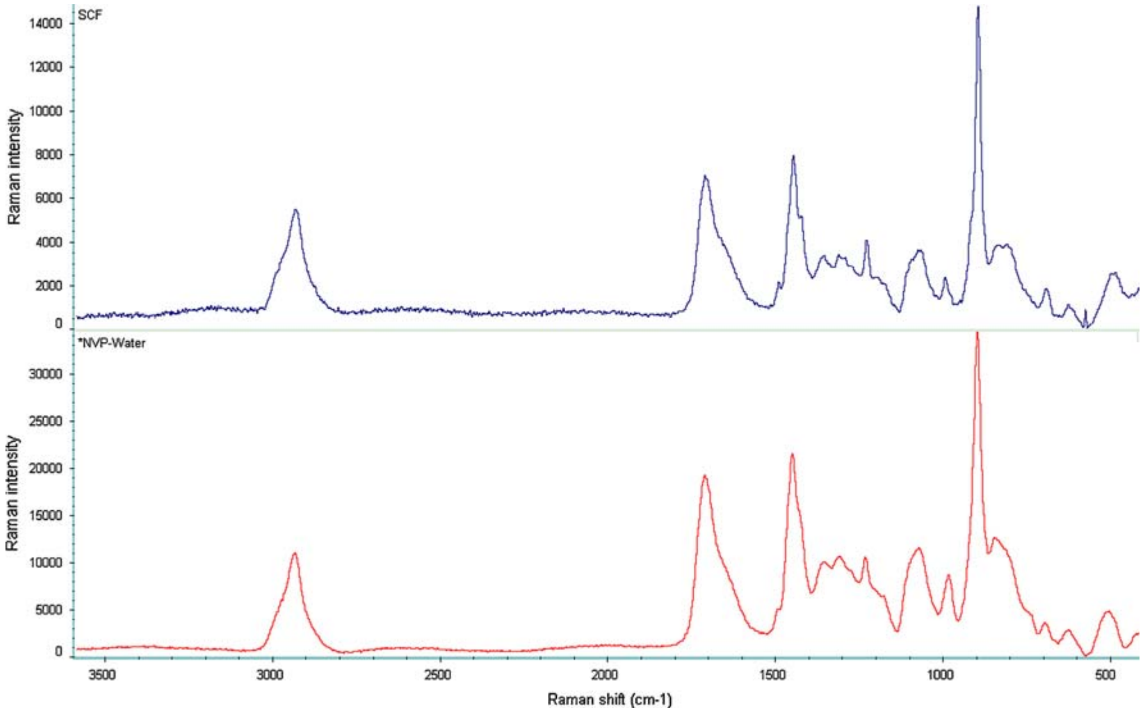

Fig. 2 Raman spectra of synthesised polymers in modified supercritical CO_2 (top), and in aqueous medium (bottom)

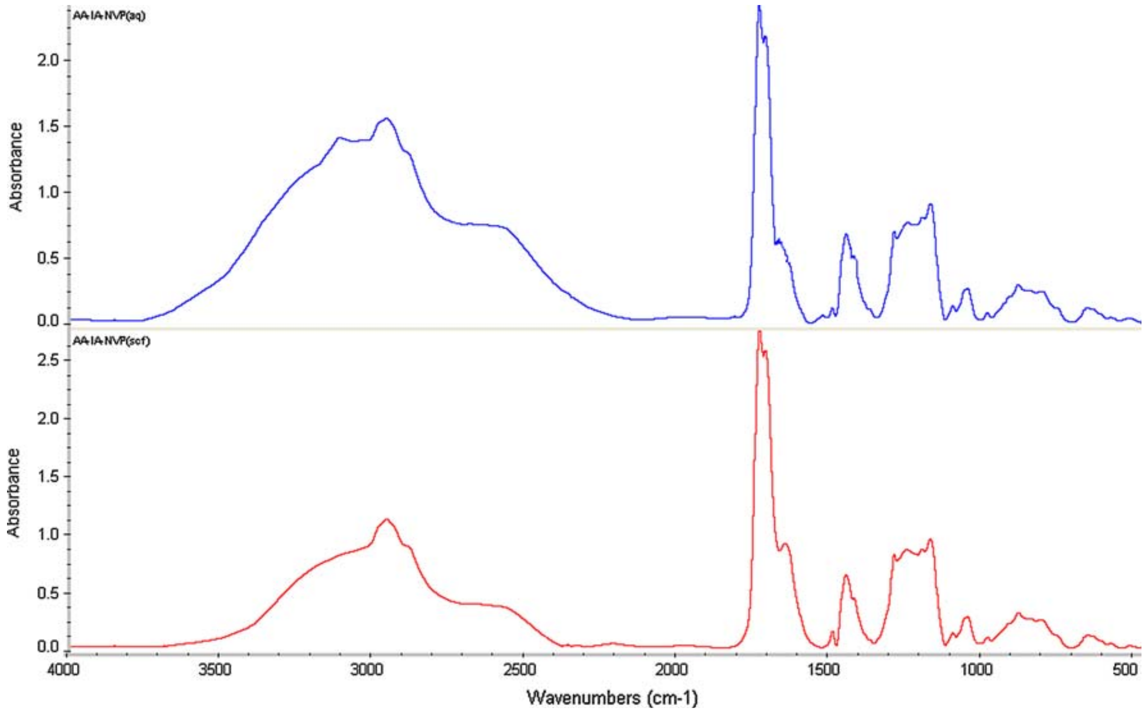

Fig. 3 FTIR spectra of synthesised polymers in modified supercritical CO_2 (bottom), and in aqueous medium (top)

Table 2 Yields, viscosities and molecular weights of synthesised polymers in supercritical Co_2 and water

Copolymers	Yield %	Molecular weight (KDa)	Viscosity (cP), 25°C
Poly(AA-IA-NVP)-CO_2	78	476	2290 ± 19.8
Poly(AA-IA-NVP)-water	65	404	1965 ± 17.3

showed that all the mechanical test (CS, DTS and BFS) values were significantly higher in comparison to control group values ($\alpha < 0.05$). Although the mechanical test values of methanol/sc-CO_2 prepared polyacid formulated glass ionomer samples were higher than those of glass ionomer samples which used polyacid prepared in water, the values were not significantly higher regarding the statistical analysis of mechanical strength data except for CS values. This could be the result of a more complete polymerisation reaction that took place in the CO_2 mixture (due to possibly faster diffusion kinetics of reaction or lower viscosity allowing better mixing) in comparison to the aqueous medium, which lead to higher molecular weight and viscosity of the final polymer in the latter case.

The working and setting time of the three different glass ionomer cement are given in Table 3. It is apparent from these results that addition of NVP in the structure of polyacrylic acid increased the working time of the resulting cement. This effect is more noticeable for the cement which is mixed with polyacid synthesised in the supercritical fluid. From the data contained in Table 3, it is obvious that the working and setting time of experimental glass ionomer cement samples have been lengthened in comparison to working and setting time of Fuji II glass ionomer. This effect could be the result of adding 2% w of D−(+)-tartaric acid and the presence of NVP molecules in the structure of the polyacid. In comparison to terpolymer which was synthesised in water solvent; the AA-IA-NVP (CO_2) polymer

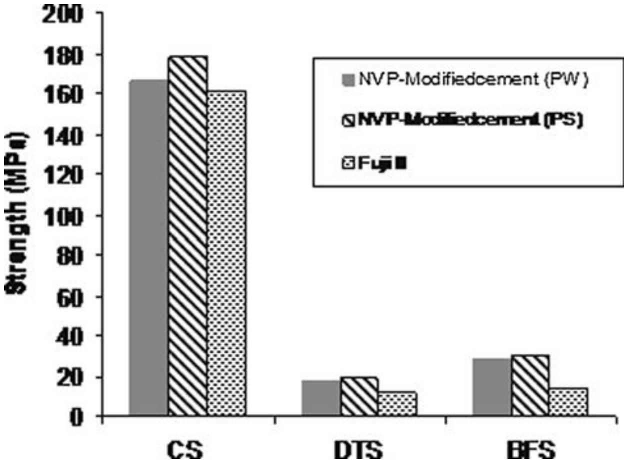

Fig. 4 Compressive, diametral tensile and biaxial flexural strength of experimental glass inomers after 24 h of immersion in distilled water at 37°C

Table 3 Working and setting time characteristics of experimental cements in comparison to Fuji II commercial control group

GIC sample	Working time (min) at 25°C	Setting time (min) at 25°C
AA-IA-NVP (PW)	3 ± 0.1	6.5 ± 0.1
AA-IA-NVP (PS)	3.5 ± 0.1	6 ± 0.1
Fuji II GC	2.1 ± 0.1	5 ± 0.1

has increased working time probably because of more availability of NVP molecules in the structure of the terpolymer due to better polymerisation reaction in SC medium. This enlarged effect of NVP is due to high electronegative nature of nitrogen atoms (in amide group) in the chemical structure of the polymers which act as hydrophilic domains and as a result the polymer has better mixing properties (which may be related to higher degrees of hydrophilic nature of the polyacids) with glass powder in comparison to other experimental glasses which were used in this study. The decreased setting time of AA-IA-NVP (methanol/sc-CO_2) polymer modified cements in comparison to cement prepared from polymers made in water is due to more availability of carboxylic groups (faster acid/base reaction within the cement) and higher viscosities of the synthesised polymers in the former case.

4 Conclusion

It has been found that modified supercritical fluid processing route can be employed successfully for the synthesis of polyelectolytes for dental glass ionomers and it improves the reaction kinetics of polymerisation of a NVP containing polyacid. Both the mechanical and working (working and setting time) properties of glass ionomer cement samples formulated using polymers prepared in supercritical solutions were comparable and higher than those of samples formulated using polymers prepared in water.

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