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MICROHARDNESS OF N-VINYLPYRROLIDONE MODIFIED GLASS-IONOMER CEMENTS

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Key Words: N-Vinylpyrrolidone Copolymers, Calcium-Fluoro-Alumino-Silicate Glass Powders, Dental Restoratives, Microhardness, Knoop Hardness

ABSTRACT

The water soluble N-vinylpyrrolidone (NVP) monomer was used to prepare poly(N-vinylpyrrolidone-co-itaconic acid-co-acrylic acid) glass-ionomer copolymers, using a free-radical polymerization process. NVP modified terpolymer was mixed with glass powders from four commercial glass ionomer systems. Microhardness from the set cement was measured and compared to several commercial glass-ionomer systems. The Knoop hardness number (KHN) values were recorded on polished specimens conditioned for 48 hours and 7 days. One-way analysis of variance and Tukey-Kramer tests were used to determine the significant differences among the materials tested in each group. Among the four commercial cements, Ketac-Molar (KM) showed the highest value and α-Silver (AS) showed the lowest value in KHN. Fuji II (F2) and α-Fil (AF) showed much the same values in KHN. At the same P/L ratio, NVP modified glass-ionomers showed higher KHN values than the AS, similar to the AF and F2, and lower than the KM. The effect of P/L ratios was evident and highest KHN values for each group were basically presented by the one with a higher P/L ratio. Higher P/W ratio did not improve the KHN for the AS and KM group, but improved the F2 group.

INTRODUCTION

It is well known that glass-ionomer cements [1-5] are clinically attractive dental restorative materials, comprised of a calcium fluoro-alumino-silicate glass powder and an aqueous solution of an acrylic acid homo- or copolymer (polyelectrolyte). These cements possess certain unique properties that make them useful as restorative and adhesive materials, including adhesion to moist tooth structure and base metals, anticariogenic properties due to release of fluoride, thermal compatibility with tooth enamel because of low coefficients of thermal expansion similar to those of tooth structure, biocompatibility and low cytotoxicity. However, the low mechanical strengths of the existing conventional formulations make the cements unsuitable for use in high-stress sites, such as Class I and II restorations. Efforts for improvement have been made in several aspects, which involved formation of different kinds of self-cured glass-ionomers, such as acrylic acid-co-itaconic acid(AA-IA) copolymers and acrylic acid-co-maleic acid(AA-MA) copolymers [6], formulation of water hardening versions [7], birth of dual setting resin modified glass-ionomers(resionomers) [8-10], and recent formulation of amino acid residue modified glass-ionomers [11, 12]. There exist two ways to improve the performance of glass-ionomer cements from the polymers perspective. One is to introduce tough polymer structures to increase the mechanical strength [8-12]. The other is to enhance the strengths by improving the working properties [7, 13]. Present commercial self-cured glass-ionomer cements extend working time mainly with the help of additives, such as tartaric acid. But, plasticising has a siginificantly negative effect on microhardness of the polymer matrix [14]. Even though the amount of additives are small, plasticising effects from small molecules still need to be considered.

Polymers composed of N-vinylpyrrolidone (NVP) have very unique water retention characteristics and have been widely applied [15] in medicine as a blood plasma substitute, for prolonging the action of drugs, and also for detoxication of the organism; in biomaterial application as contact lens components; as well as in various industrial fields, such as food, textile and pharmaceutical industries, due to their hydrophilicity, non-toxicity and high proclivity to complexation [15]. Considering its special hygroscopic behavior and non-toxicity in the polymer backbone, we chose NVP as a good candidate to improve the working property as well as mechanical properties of glass-ionomer polyelectrolytes. Previous studies confirmed our hypothesis that water soluble NVP copolymers, having a high concentration of carboxylic acid groups, have potential for formulation of glass-ionomers [13]. In our initial study, we looked at commercially available poly(N-vinylpyrrolidone-co-acrylic acid) or poly(NVP-AA), supplied by ISP Corp. The initial study suggested our hypothesis had some merits [16]. In a follow up study, we prepared, characterized, and evaluated poly(N-vinylpyrrolidone-co-itaconic acid-co-acrylic acid) or poly(NVP-IA-AA) (Figure 1) as a copolymer for formulating conventional glass-ionomers [13]. We clearly established that poly(NVP-co-IA-co-AA) could be formulated to fabricate conventional glass-ionomers with improved mechanical properties [13, 17]. In this communication, we look at the microhardness of glass-ionomers formulated with poly(NVP-co-IA-co-AA), compared to the microhardness of several commercially available glass-ionomers.

Hardness may be broadly defined as the resistance to permanent surface indentation or penetration and it is a measure of the resistance to plastic deformation [18]. The property of hardness is one of major importance in comparison of restorative dental materials [18]. Some studies dealing with surface coating [19], glazing [20], wear [21], and the influence of some fluids [22, 23] have been published. However, little effort has been devoted to evaluating how the polymer structure influences hardness in cured glass-ionomer cements, including the commercial controls used in this study.

The purpose of this study was to evaluate the hardness properties of newly synthesized water-soluble, poly(NVP-co-IA-co-AA) modified glass-ionomer cements, using the Knoop hardness test and compare the results with the corresponding commercially available conventional systems. In addition, the effects of various powder/liquid (P/L) ratios and polymer/water (P/W) ratios on the hardness of the NVP modified glass-ionomers were investigated.

EXPERIMENTAL

Materials

NVP, AA and IA were used as received from Aldrich, without further purification. ammonium persulfate ($(NH_4)_2S_2O_8$), diazald, methanol and diethyl ether were also used as received from Aldrich.

Synthesis and Characterization

To a three-neck reactor, containing 1.313 g of $(NH_4)_2S_2O_8$, 9.28 g(0.084 mol) of NVP, and 150 ml of water, a mixture of 1.313 g of $(NH_4)_2S_2O_8$, 52.65 g(0.73 mol) of AA, 40.74 g(0.313 mol) of IA, 2.32 g(0.021 mol) of NVP and 210

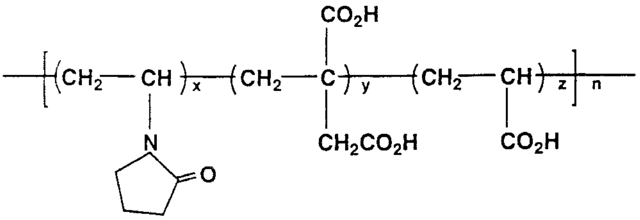

Figure 1. Schematic Structure for poly(NVP-co-IA-co-AA).

ml of water was added dropwise within one hour. Before the reaction was initiated, the system was purged with N_2 for 30 minutes to displace dissolved oxygen and then the temperature was raised to around 100°C. After completion of the additions, the polymerization was run for an additional 6 hours at 100°C. The molar feed ratio for the copolymer was 7:3:1 (AA:IA:NVP).

The crude copolymer was recovered in 94% yield, using freeze drying (Edwards High Vacuum International) techniques. The polymer was purified by dissolving in methanol and precipitation from diethyl ether, followed by drying in a vacuum oven.

The copolymer was identified by Fourier transform-infrared spectroscopy (FT-IR), elemental analysis, nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) (Table 1). The IR spectrum of the copolymer was obtained with a FT-IR Spectrometer(MIDAC Co.), where the sample film was cast on the NaCl crystal. ^{1}H and C NMR spectra of the copolymer were conducted on a Bruker AM 250 MHz NMR analyzer using deuterated methyl sulfoxide as a solvent and trimethylsilane (TMS) as reference. The copolymer was treated with diazomethane, generated from the diazald reaction with potassium hydroxide in the water/ethanol solution at 65°C, to obtain partially esterified products, in order to obtain solubility of the copolymer in THF for molecular weight estimations (Table 1). Molecular weights were estimated by Ashland Chem.Co., using a Waters GPC unit, with standard GPC techniques. Elemental Nitrogen percent for the copolymer was obtained by Desert Analysis (Tucson, AZ).

Specimen Preparation

The commercial glass-ionomer materials (controls) used in this study are listed in Table 2. Variations in the powder/liquid (P/L) ratio was based on different manufacturer's recommendation. The range of P/L ratio was taken randomly.

TABLE 1. Characterization of the NVP Modified Copolymer

Elemental Analysis (N%)	FT-IR (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)	MW (Mw/Mn)
1.34 (theo:1.39)	1651 (amide group) 1717 (carboxyl group)	8.32 (amide group) 12.10-12.25 (carboxyl group)	172.0 (^{13}CONR$_2$) 176.0 (^{13}COOH)	44200 (Mw) 14300 (Mn)

TABLE 2. Commercial Glass-Ionomers Used in the Study

Material	Code	Manufacturers	P/L ratio (w/w)
a-Silver	AS	DMG Hamburg (Hamburg, Germany)	4.2/1
a-Fil	AF	DMG Hamburg (Hamburg, Germany)	2.7/1
Ketac-Molar	KM	ESPE GmbH (Seefeld, Germany)	3.1/1
Fuji II	F2	GC International (Tokyo, Japan)	2.7/1

Principally, a high P/L ratio should be taken in the range of workable conditions for mixing and for a low P/L ratio enough glass powder would still be available for reaction with the acid to give good properties. The NVP modified copolymer solution was made by mixing with distilled water, with the proportion of copolymer : water = 50/50 and 60/40 (wt/wt). Specimens were fabricated in the molds made of glass tubing (6 mm in diameter x 2 mm in thickness) at room temperature. The mixtures were placed into the molds and then slightly overfilled and compressed with a glass plate. After 5-10 minutes, the hardened samples were removed and stored in distilled water at 37°C for 48 hours and 7 days. Before testing, the specimen surface was ground with a 1200-grit silicon carbide paper, under running water, for removal of its outermost layers at room temperature.

Microhardness Measurement

The hardness of the specimens was determined using a microhardness tester (Model MVK-E, M 400, Leco Co., MI, USA). The Knoop hardness test was achieved with a diamond indenter set at 25 g of force for 30 seconds, and the surfaces of three specimens for each sample were measured. The eight readings taken from those surfaces were averaged to give a hardness value for each sample. Hardness values were taken at 48 hours and 7 days.

Statistical Analysis

One-way analysis of variance (ANOVA) with post-hoc multiple comparison using Tukey-Kramer test, was used to determine the significant differences among the materials tested in each group. A level of 0.05 was considered as not significant.

RESULTS AND DISCUSSION

The characterization data of the synthesized NVP modified copolymer (Figure 1) are presented in Table 1. Elemental analysis shows that the actual percentage of nitrogen in the NVP modified copolymer was a little bit lower than the theoretical value, which may be explained by reasoning that the actual polymerization is different from the ideal prediction. The FT-IR, ^{1}H and ^{13}C NMR spectra confirm that the newly synthesized NVP modified copolymer, consisting of acrylic acid/itaconic acid/N-vinylpyrrolidone, contains the pyrrolidone ring and carboxylic acids. For FT-IR, the band at 1651 cm^{-1} represents the amide on the pyrrolidone ring, while the band at 1717 cm^{-1} belongs to the carboxyl groups. For NMR, the amide group on the pyrrolidone ring shows the chemical shifts at 8.32 and 172.0 ppm in the ^{1}H and ^{13}C NMR spectra, respectively, whereas the carboxyl groups show the chemical shifts at 12.10-12.25 and 176.0 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. The weight average molecular weight (Mw) and the number average molecular weight (Mn) of the copolymer were 44200 and 14300, respectively, as shown in Table 1.

Hardness is measured as a force per unit area of indentation [18, 22]. The indentation produced on the surface of a material from an applied force of a sharp point or an abrasive particle results from the indentation of numerous properties. Among the properties that are related to the hardness of a material are strength, proportional limit, and ductility [24]. The Knoop hardness number (KHN) and Vickers hardness number (VHN) tests are classified as microhardness tests, which are usually used for hardness measurements in composite and glass-ionomer cements [18]. Compared to dental ceramics and composites, glass-ionomer cements in general are softer. For that reason, we chose the Knoop hardness test as a tool to measure the hardness in this study.

Published information on the KHN or VHN values for glass-ionomer cements is very limited. All four commercial dental glass-ionomer cements used in this study, except Fuji II which had been evaluated under different test conditions [19, 20], were studied for the first time. As shown in Figure 2 and Table 3, among

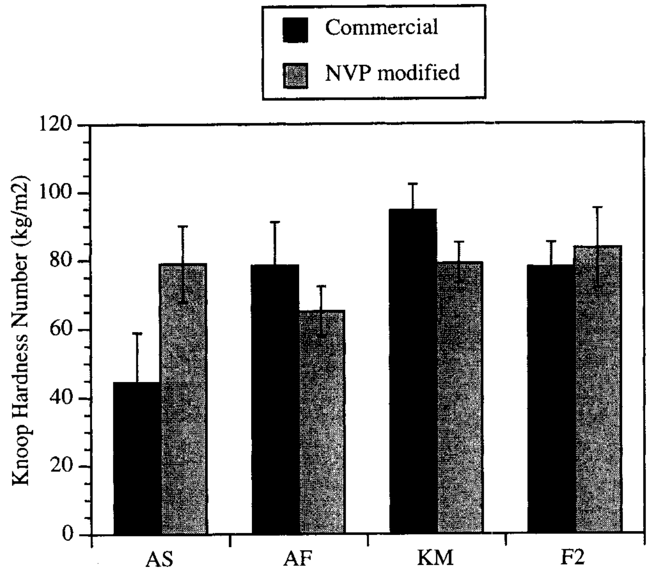

Figure 2. KHN Values of the Commercial Cements and NVP Modified GIs at the Same Corresponding P/L Ratio (Conditioned for 7 days).

TABLE 3. Effect of Powder / Liquid Ratio on the Knoop Hardness Number of NVP Modified GIs

Material	P/L ratio (w/w)	P/W ratio (w/w)	KHN* (SD) [48 h]	KHN (SD) [7 d]
AS	4.2/1	50/50	39.30 (8.71)^{A}	44.04 (14.4)^{G}
NVP/AS**	3.9/1	50/50	45.18 (4.00)^{A}	55.06 (8.00)^{G}
NVP/AS	4.2/1	50/50	60.65 (3.85)^{B}	78.68 (11.3)^{H}
NVP/AS	4.5/1	50/50	55.80 (8.33)^{B}	71.91 (11.4)^{H}
AF	2.7/1	50/50	49.66 (13.1)^{C}	77.98 (13.2)^{I}
NVP/AF	2.4/1	50/50	54.98 (4.66)^{C}	61.63 (9.61)^{J}
NVP/AF	2.7/1	50/50	55.78 (12.2)^{C}	64.98 (7.29)^{I,J}
NVP/AF	3.2/1	50/50	78.51 (17.5)	80.00 (13.9)^{I}
KM	3.1/1	50/50	97.99 (11.0)	94.48 (7.59)
NVP/KM	2.9/1	50/50	58.90 (6.76)^{D}	55.61 (7.65)
NVP/KM	3.1/1	50/50	63.26 (8.55)^{D}	78.89 (5.89)
NVP/KM	3.6/1	50/50	81.44 (14.7)	111.6 (5.40)
F2	2.7/1	50/50	58.91 (7.70)^{E}	77.34 (7.18)^{K}
NVP/F2	2.4/1	50/50	53.21 (6.02)^{E}	46.41 (3.80)
NVP/F2	2.7/1	50/50	84.30 (10.6)^{F}	82.96 (11.6)^{K}
NVP/F2	3.2/1	50/50	84.43 (12.1)^{F}	121.1 (9.00)

*The KHN values with the same superscript letters(A-K) are considered not significantly different at a rejection level of $p = 0.05$.

**NVP/AS, NVP/AF, NVP/KM, and NVP/F2 represent NVP modified copolymers mixed with AS, AF, KM, and F2 glass powders, respectively.

these four commercial products, Ketac-Molar (KM) showed the highest values, a-Silver (AS) showed the lowest values, and Fuji II (F2) and a-Fil (AF) showed much the same values in KHN. All these four commercial materials belong to the filling type of glass-ionomer cements, i.e., cements used for Class III or V restorations, which usually should have higher strengths than other luting or lining cements. According to the results from the study, KM was ranked the hardest glass-ionomer cement, F2 and AF were ranked second in hardness, and the cermet cement AS was ranked the softest among the four cements.

Commercial AS glass-ionomer cements showed the lowest values in KHN (39.30 in a 48 hour test and 44.04 in a 7 day test) in this study. No exact hardness value has been previously reported for the AS material. The only similar reference material available is Ketac-Silver. A rather low Vickers hardness number, which was 39.2 for the 7-day test, was reported by Forss, *et al.* [21]. The reason is still unclear. One possible explanation may be due to the heterogeneous phases in cermet glass-ionomers. Larger silver particles may cause the silver cermet cement to have less abrasion-resistance than other conventional glass-ionomer cements [21]. On the contrary, the finding by McKinney [23] was the opposite of both the Forss's and our results. The comment was made that the incorporation of silver provides a lubricating effect, contributing to better abrasion resistance [23].

Hotta, *et al.* [19] reported that the noncoated and nonpolished commercial F2 in KHN value were 18.2, 25.7, and 28.7 at 24 hours, 48 hours and 1 week, respectively and found that 48-hour hardness tests showed more mature KHN value than the 24-hour tests. According to their experience, we chose 48-hours and 7-days as our evaluation times. As a control in our study, F2 showed a higher KHN value, which were 58.91 in the 48-hour test and 77.34 in the 7-day test. This is not surprising, since the specimens in this study were polished and exhibited a better surface for characterization. The purpose of our study was to compare our NVP modified glass-ionomers (NVP MGIs) with commercial systems. Not only the surfaces of the commercial materials but also the surfaces of the NVP MGIs were polished before testing. Therefore, our comparisons were made under comparable conditions.

Table 3 gives the KHN values for NVP MGIs and the corresponding commercial products we evaluated in this study. All comparisons were made by using one-way ANOVA with post-hoc multiple comparison using the Tukey-Kramer test. P/L ratios of 4.2/1, 2.7/1, 2.7/1 and 3.1/1 were used as references in AS, AF, F2, and KM systems, respectively.

The data in Figure 2 showed that at the same P/L ratio NVP MGIs exhibited significantly higher KHN values than the corresponding AS, statistically not different values than the AF and lower values than the KM.

It is not surprising that some of our NVP MGIs exhibited higher KHN values than the corresponding commercial systems. Our NVP modified terpolymer is different than the four copolymers utilized in the AS, AF, KM and F2 systems. Commenting only on the Fuji II system, the copolymer utilized is composed of AA and IA. As our previous studies [11-13, 17] mentioned, the major problem associated with the F2 type glass-ionomer formulation is that the AA homo- or copolymers have COOH groups directly attached to the backbone, along with close orientation to each other. Not all the carboxyl groups on polyacids of this type are converted to carboxylate groups during the course of the reaction. Some free COOH groups remain unreacted because they are inaccessible for steric reasons. Also, as COOH groups on the polyacrylate chain become ionized, the remaining or nearby hydrogen becomes firmly bound by electrostatic forces; as a result, the metal ions are increasingly hindered in their movements to react at carboxyl sites. Further, vitrification significantly reduces diffusion of the Ca^{++} or Al^{+++} to available COO^- moieties. Incorporation of the pyrrolidone ring, first, destroys the regularity of the AA-IA chain, providing more opportunity for conformational transition and rotation of the macromolecules; second, the NVP moiety enhances the hydrophilicity due to its water retention, thus facilitating diffusion related processes in the matrix, even though less COOH groups are present in the NVP matrix. As a result, unreacted COOH groups have a greater chance of interacting with Ca^{++} or Al^{+++} cations, leading to an increase in salt-bridge formation and higher toughness of the cured material. The increase and decrease in mcrohardness depend on crosslinking and scissioning in the polymer matrix [25].

It is significant to point out that the KM system is the strongest system among the four commercial glass-ionomer cements we evaluated. This may be attributed to the reason that the KM system uses very high molecular weight of polymers in its formulation (specified by its manufacturer).

Effect of a P/L Ratio on the KHN of the NVP Modified Glass-Ionomers

The order for KHN in the AS group at different P/L ratios was shown as follows: 4.2/1 > 4.5/1 > 3.9/1, in both 48-hour and 7-day tests. The magnitude of KHN for the AF group was 3.2/1 > 2.7/1 ≅ 2.4/1 in order for the 48-hour test, and 3.2/1 > 2.7/1 ≅ 2.4/1 in order for the 7-day test. In the F2 group, the magnitude was in the order of 3.2/1 ≅ 2.7/1 > 2.4/1 for the 48-hour test, and in the order of 3.2/1 >

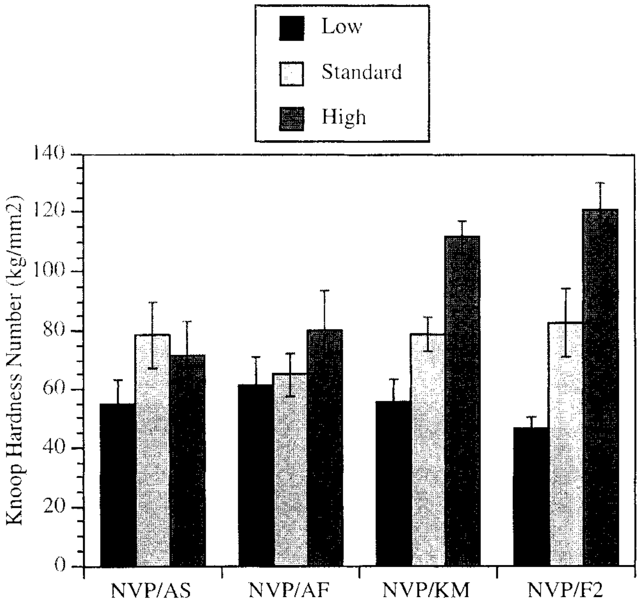

Figure 3. Effect of a P/L Ratio on the KHN of the NVP Modified GIs (Conditioned for 7 days).

2.7/1 > 2.4/1 for the 7-day test. In the KM group, the order for the magnitude was 3.6/1 > 3.1/1 > 2.9/1 in both 48-hour and 7-day tests. Results are shown in Table 3 and Figure 3 (7 day data).

First, let's take a look at the AS group. In this group, we used three P/L ratios and compared them with the commercial AS. We found that the highest KHN value fell to the NVP MGI with a P/L ratio of 4.2/1, which was exactly the P/L ratio for AS. This means that our NVP modified terpolymer offers the best hardness at or around the same P/L ratio as AS. The higher KHN values presented by three P/L ratios may be attributed to inherent hardness or toughness of the NVP modified cements. After 7 days, there was no significant difference between 4.2/1 and 4.5/1. This suggests that a higher P/L ratio is not necessary in the NVP modified copolymer with use of the AS glass-powder.

Considering the KM system, 3.1/1 is the P/L ratio recommended by ESPE. The highest value for the commercial system was at the 48-hour test. In contrast, the highest value observed for the NVP MGI system, with a ratio of 3.6/1, was after 7 days. In this group a P/L ratio of 3.6/1 happens to be the best ratio for the NVP modified glass-ionomers using the commercial KM glass powder.

The AF system also belongs to the filling type of glass-ionomer cements, which is produced by DMG. Its P/L ratio of 2.7/1 is utilized for the filling application of dental restorations. As found in KM, the best ratio for the NVP modified glass-ionomer cements in this group was 3.2/1(highest P/L ratio used in this study), even though no significant difference was found between AF and the NVP MGI with a ratio of 3.2/1 after 7 days.

Finally, we look at the system called F2. Like AF, F2 uses 2.7/1 as its optimal P/L ratio in filling restorations. We also compared three different P/L ratios in this group. The interesting thing is that the best P/L ratio is still 3.2/1 for the NVP MGIs with the F2 glass powder, although the ratio of 2.7/1 is very acceptable.

It is to be expected that different P/L ratios can lead to different KHN results and some optimum ratio can be found for producing the highest KHN value. As we know, each commercial system has its own optimized polymer solution, along with a corresponding or optimized glass powder. The P/L ratios for four commercial systems used in this study are the optimal ratios for them. Therefore it is unnecessary to adjust the P/L ratios for these systems. Setting reactions in glass-ionomer cements actually belong to an acid-base reaction. Usually, an equilibrium happens in the setting reaction. Any excessive amount of glass powder or polyacid will cause the property to change (better or worse). Whether our NVP modified copolymers match the powder used or not depends on the P/L ratio used. Below the optimal ratio, an excessive amount of polyacid exists in the system, which may cause the material to be more plastic in nature. Above the best ratio, an excessive amount of glass powder exists in the system, which will increase manipulation viscosity and lead to poor properties. In addition, the glass powder used in one system may not be the same as that used in another, which makes the degree of an acid-base reaction different. Therefore, It is necessary to find or develop an optimum glass powder system for our own NVP modified glass-ionomer formulation, which will be part of our future research direction.

Effect of a P/W Ratio on the KHN of the NVP Modified Glass-Ionomers

It has been reported that excessive water can play a crucially negative role in the setting reaction for glass-ionomer cements [19, 22, 26]. On the one hand, water is an necessary component in an acid-base setting reaction, which acts as a medium. On the other hand, water works as a plasticizer in the cement matrix [26], which may contribute to decreased strength and reduction in other physical properties. In the modified terpolymer we have prepared and studied, the pyrrolidone ring; from the NVP use, offers a very good water sorption site. The existence of the ring is

TABLE 4. Effect of Polymer / Water Ratio on the Knoop Hardness Number of NVP Modified GIs

Material	P/L ratio(w/w)	P/W ratio(w/w)	KHN* (SD) [48 h]	KHN (SD) [7 d]
NVP/AS	4.2/1	50/50	60.65 (3.85)	78.68 (11.3)
NVP/AS	4.2/1	60/40	47.11 (7.14)	59.20 (2.40)
NVP/KM	3.6/1	50/50	81.44 (14.7)^{L}	111.6 (5.40)
NVP/KM	3.6/1	60/40	69.13 (8.19)^{L}	82.33 (7.65)
NVP/F2	2.7/1	50/50	84.30 (10.6)^{M}	82.96 (11.6)
NVP/F2	2.7/1	60/40	78.05 (9.04)^{M}	108.3 (6.23)^{N}

*The KHN values with the same superscript letters(L-N) are considered not significantly different at a rejection level of $p = 0.05$.

responsible for the accessibility of the peptide bonds to water molecules on sorption [27]. The peptide bonds are believed to be the sorption centers [15]. This NVP induced water retention brings about the result that working time for the experimental glass-ionomers is extended and the manipulation process is more consistent, which may require less water or avoid unnecessary water in the system. In order to investigate the effect of polymer/water (P/W) ratio on the KHN, we used two polymer/water (P/W) ratios (i.e., 50/50, which is normally used in most commercial systems and 60/40, which contains more polyacids than normal systems) to evaluate its effect on the KHN at a constant P/L ratio. Results are shown in Table 4 and Figure 4. In the case of AS, the higher KHN value was found in the P/W ratio of 50/50. This means that an excessive amount of polymer is unnecessary. Similar to the AS situation, the NVP MGI with a P/W ratio of 50/50 in the KM group showed a higher KHN value than the cement with 60/40. In an investigation of the F2 group, it was found that at a P/L ratio of 2.7/1, a significant difference was found between 50/50 and 60/40 after 7 days. The NVP modified cement with 60/40 showed a higher KHN value than the cement with 50/50, which means that a little excessive amount of polymer is beneficial to the NVP MGI in the F2 system.

CONCLUSIONS

Among the four commercial, conventional glass-ionomer cements, KM showed the highest KHN value and AS showed the lowest KHN value. F2 and AF showed much the same KHN values.

The highest KHN value was presented by the NVP modified cements with a ratio of 3.6/1, and the lowest by the AS in this study.

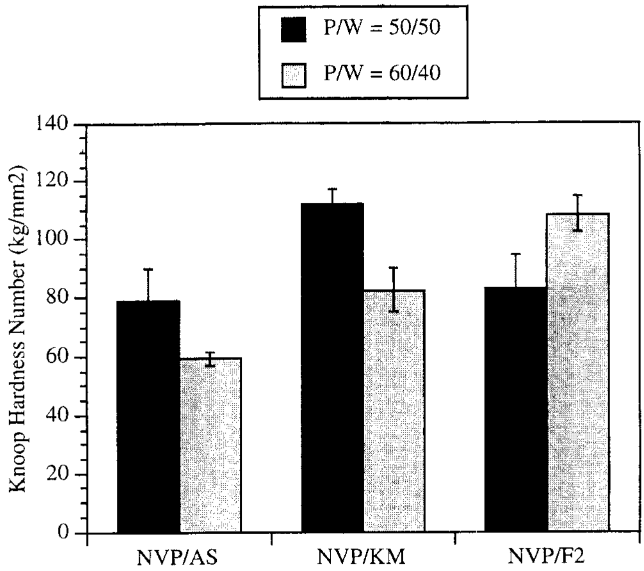

Figure 4. Effect of a P/W Ratio on the KHN of the NVP Modified GIs (Conditioned for 7 days).

At the same P/L ratio, NVP modified glass-ionomers showed higher KHN values than the AS, similar to the AF and F2, and lower than the KM.

Considering the effects of P/L ratio, the NVP modified glass-ionomers with a P/L ratio of 4.2/1 showed the highest KHN values for both 48-hour and 7-day tests in the AS group. In both AF and F2 groups, the NVP modified cements with a P/L ratio of 3.2/1 exhibited the highest KHN values in both the 48-hour and 7-day tests. In the KM system, the NVP modified cements with a ratio of 3.6/1 presented the highest KHN value after 7 days.

In the case of the polymer/water ratio(P/W), the NVP modified glass-ionomers with a P/W ratio of 50/50 showed higher KHN values than ones with the 60/40 ratio for the AS and KM groups, whereas the NVP modified glass-ionomers with a ratio of 60/40 showed a higher value in KHN than ones with a 50/50 ratio for the F2 group.

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