Influence of Moisture in Nanofiller on Self-adhesive Cement

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Introduction: Unlike zinc phosphate, polycarboxylate, conventional resin cements, self-adhesive resin cement appeared to offer a promising new approach in indirect restorative procedure of dentistry because of some unique features such as skip of etch-rinse procedure, no post-operative sensitivity, minimum technique sensitivity, and adequate physico-chemical properties. Incorporation of multi-functional monomers with phosphoric acid groups was the proper rationale to employ in this case. In particular, acidic monomer was present as a key component to initially disturb a smear layer and then affect micromechanical retention. However, awareness of moisture sensitive nanofiller was limited to report during the complete setting reaction. As such, the purpose of this study was to investigate the influence of moisture in the nanofiller on setting mechanism of self-adhesive cement.

Methods: Formulation: Aerosil 200 (A200) as a nanofiller was selected. A200 is nonporous hydrophilic fumed silica with a specific surface area of 200 m²/g and an average size of 12nm in diameter. A200 was mixed with St glass(wt. ratio: 5/95). The fillers(65wt%) were mixed with BisGMA/TEGDMA/BPO/BHT(35wt%) resin with organic phosphoric acid(25parts). The control group was the same as above, but without A200. As a counterpart, inorganic silica fillers combined with Bis-GMA/TEGDMA/amine/CQ/BHT were mixed to yield a redox system. Measurement of Water amount: Test was performed in a TGA-50 Shimadzu under N_2 purging ($10ml/min^{-1}$). A200 was dried for 3 hrs at 110°C before TGA measurement. Non-dried and dried A200 (each ≈30mg) were run at the temperature sweep of 10°C/min from 20 to 300°C, respectively. Measurement of Degree of Conversion: ATR-FTIR spectrometer (Nicolet 6700 FT-IR Spectrometer, Thermo Scientific) was used to compare the peak height of aliphatic and aromatic double bond before and after curing. They were then used to calculate the relative degree of conversion (DC) using the baseline technique.

$DC\% = [1 - (H_{alip}/H_{arom})/(Ho_{alip}/Ho_{arom})] \times 100$, where H_{alip} is the height of the peak at 1636 cm^{-1} and H_{arom} the height of the peak at 1607 cm^{-1}. Ho_{alip} and Ho_{arom} standard for those of the uncured sample. Rheological study: Dynamic frequency sweeps were performed using AR2000ex (TA Instruments, New Castle, DE) at certain stress values of 2-5Pa (corresponding to the linear viscoelastic regime) at 25mm disposable parallel pate geometry and a 1.0 mm gap to evaluate the elastic and viscous moduli, determining the complex viscosity to represent the handling property. Working time/setting time (WT/ST) was collected using custom-made Oscillating Rheometer to monitor the autopolymerization process. HPLC Analysis: Samples were analyzed using HPLC(Waters 600, Waters Corp., Milford, MA) to determine the retained amount of BPO (RT: 5.1min) and BHT (RT: 10.2 min). The mobile phase consisting of 90% MeOH(v/v) and 10%(v/v) H_2O was eluted through C-18 RP column(5µm, 15cm×4.0cm, Supelco, Bellefonte, PA). Ten μl of the tested sample were injected and a diode array detector(Waters 996, Waters Corp., Milford, MA) set at 233nm was used. Shear Bond Strength: The gelatin capsule volume was filled with a tested sample and directly bonded perpendicularly to the dentin surface for 20sec. Excess marginal sample was removed. After the bonding, the specimen was temporarily placed into the oven for 15min at 37°C and 50±5%. The specimen was soaked in DI water at 37°C oven for 24hrs. Maximum shear loading force was recorded at a crosshead speed of 0.5 mm/min (Instron 4466, Norwood, MA), and shear bond strength (SBS) (area: $0.1684cm^2$) was calculated.

Results: The water content was measured to 1.52%(w/w) for non-dried A200 and 0.49%(w/w) for dried one, showing about 1% (w/w) difference. Whereas DC by dual-curing mode was comparable (50-55%) for control and sample groups, DC by self-curing mode was significantly lowered by the fact of alteration in a catalyst part including moisture content in A200. BPO initiator was decomposed by a heat under non-dried A200 and further readily aggravated in a presence of acidic monomer, which was supported in HPLC by BPO residual amount against the aging time (101.8, 77.0, 47.4, 33.9, 37.0 & 12.7% at time 0, 5, 9, 13, 17 & 19M). Non-dried A200 was affected to the thickened paste, leading to an oligomeric gel formation. This might be because hydroxyl groups from non-silanated A200 and moisture may react with acidic monomer. A200 itself increased complex viscosity a lot while the addition of hydrophobic Al2O3 and OX50 was attributed to the lower complex viscosity (Figure 1).

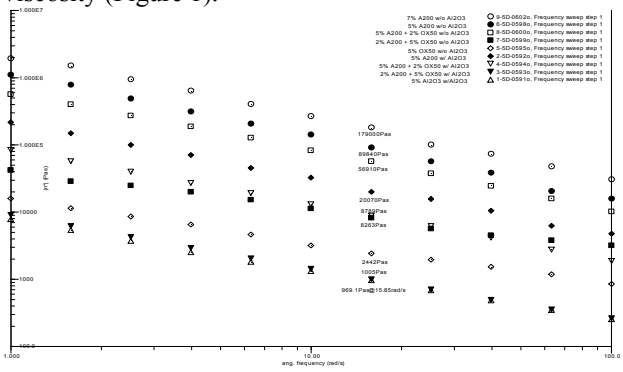

Figure 1. Effect of co-powders (A200 & OX50) with or without Al_2O_3.

As a result of harsh environment, unlike control group(3.9 ±0.8MPa), the sample group with A200 including 1% higher moisture had a significantly lower bonding at 0.15 ±0.07MPa in 9M ($p<0.05$) and was de-bonded after that.

Conclusion: The moisture-contained nanofiller was attributed to thickening behavior when contacted with a acidic monomer, creating a gel and reducing the amount of BPO. The hardened gel prevented a homogeneous mixing, resulting in inconsistent WT/ST and lower SBS.

Reference: Radovic I. (2008) J Adhes Dent 10(4) 251-8.