Interface structure and strength in model dental resin composites

Most composites for dental restoration are based on a methacrylate polymer matrix and a ceramic filler, often silanized silica or silicate glasses. A problem with these composites is the polymerization shrinkage, which causes the filling to loosen from the tooth under formation of a crack. This will facilitate discoloration from e.g. coffee and red wine entering the crack, or even worse lead to secondary caries and infection of dental pulp due to bacteria. The aim of this study was to develop a low shrinkage dental composite based on an expandable metastable zirconia filler. A metastable zirconia filler has been developed, which is able to expand in the cured polymer matrix upon water diffusion from saliva and dentin to the filler particles. The tetragonal zirconia will upon exposure to water transform to the monoclinic phase, which has a larger specific volume. This expansion counteracts the polymer shrinkage and reduces the overall shrinkage of the composite. In this thesis the zirconia filler is characterized and tested for the potential as a filler for use in dental composites. The zirconia powder is composed of highly agglomerated particles of nanosized crystals. The average particle size is 1.5-2 μm and the crystal size is ~6 nm. These crystals are so water sensitive that 65 vol% phase transforms to the monoclinic phase as a result of exposure to the humidity in the air and 84 vol% transforms upon exposure to water. This transformation is very fast and it is impossible to measure the transformation rate with x-ray diffraction. Other molecules are also able to initiate the phase transformation; these are HCl, NH₃, HF, and HBr. Photoacid generators releasing HCl, was tested for their ability to initiate the phase transformation in zirconia crystals imbedded in a dimethacrylate polymer matrix upon radiation with blue light. After 30 min light exposure a monoclinic volume fraction of 0.6 was observed, when using 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine as the photoacid generator. Surface modification is very important in order to obtain a dental composite with good mechanical properties and high resistance towards hydrolysis. Due to their stabilizing effect on the tetragonal phase, it was, however, not possible to modify the filler surface with silanes or phosphate, which are the most commonly used surfactants in dentistry, and simultaneously preserve the ability to phase transform. Instead it was found possible to bind 3-(acryloyloxy)-2-hydroxy-propyl methacrylate to the surface by reaction with surface carbonates. In this way it might be possible to increase the wetability of the surface and hence increase the mechanical adhesion between polymer matrix and the filler. Reaction between the OH-group of the surfactant and the carbonate furthermore increases the reactivity of the zirconia. This increased reactivity originates from an inhibition of the competing reaction between the surface bound carbonates and water molecules. As zirconia has a higher refractive index than the polymer matrix, a large particle size will result in a very opaque material. To improve the esthetics of the composite a low particle size of the filler is necessary in order prevent the particles from scattering light. For this reason a particle size below 40-60 nm is desirable. Different deagglomeration methods were tested and it was found possible to deagglomerate almost to the primary crystals with ball milling, but this method causes the zirconia to undergo phase transformation initiated by shear stresses. Instead ultrasonication was tested and it was found possible to deagglomerate the particles to 300-400 nm without any phase transformation. Finally the ability of the filler to counteract the polymerization shrinkage was investigated. In this test the phase transformation was initiated by water diffusing in to the composite during water storage at 40˚C. The composite was found to have a monoclinic volume fraction, vm, of 0.5 after 8 h of water storage. The overall shrinkage of the composites was found to reduce from 3.2 % (initially) to 1.7% (14 days in water).