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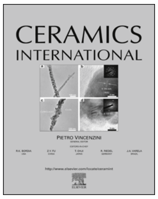

Enhanced thermo-mechanical properties of acrylic resin reinforced with silanized alumina whiskers

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ABSTRACT

The acrylic resin reinforced with silanized alumina whiskers with self-healing (SH) agents was synthesized. The self-healing system consisted of microcapsules with the healing agent dicyclopentadiene (DCPD) and modified Grubbs' catalyst in PS electrospun nanofibers. The content of alumina whiskers was 3% w/w, and the concentration of PS fibers and UF microcapsules in the samples were 1% w/w each. The embedded silanized alumina whiskers achieved higher T_g and absorbed impact energy in relation to unmodified alumina whiskers. The nanoindentation test revealed the reduced modulus increased for about 65% and hardness increased is about 90% for composites with silanized whiskers. Cracks were induced on the composite surface using the low energy impact test machine. The self-healing efficiency of 74% was approved by the repeated impact test after 96 h.

1. Introduction

This paper relates to resin-based composite materials that have high strength and toughness properties, and particularly have self-healing characteristics, or capability to autonomously heal the cracks occurring in the material [1–3]. Resin composites are generally composed of silanized particulate fillers in a polymeric matrix derived from the polymerization of a mixture of methacrylate monomers. Besides ceramic particles [4], chopped glass fibers and porous networks of fibers have also been incorporated as fillers into dental composites and bone cements [5,6]. The advanced composite research is focused on producing a material that has perfect filler–resin interface and improvement in filler packing, optimization in filler levels, and development of hybrid filler phases [7,8]. The transition to nanocomposites yields dramatic changes in physical properties. Nanoscale materials have a large surface area for a given volume. These fillers are classified by their geometries as: particle, fibrous, and layered. Fibrous materials provide reinforcing efficiency because of their high aspect ratios and single crystal nanowhiskers are close to that definition. The ceramic whiskers are single crystals possessing a high degree of structural perfection and, hence, superior strength and toughness values. So, they were described as reinforcement in polymer composites [9,10]. The nano-particles and hence nanowhiskers behaved as functional physical crosslink and thus reduced the overall mobility of the polymer chains, leading to better thermal and mechanical properties. Mostly, in the biomaterials, and particularly in acrylic resin, the silica and nitride whiskers are widely used. Alumina nanowhiskers have good potentials for improvement of thermal and mechanical properties [11–13], and also posses a good osteoblast (bone-forming cell) function [14].

The surface of whisker should be modified with the aim to minimize their agglomeration by facilitating their dispersion and achieve the better matrix–particles interface bonding [15]. The alkoxy groups of silane coupling agent react readily with the hydroxyl groups on the surface of alumina whiskers. Owing to their perfect crystal structure, whiskers typically have very high tensile strengths which approach the binding forces of adjacent atoms. So, with the surface modification the area with very good bonding and mechanical properties uniformity could be obtained. Modification of whiskers surface by 3-mercaptopropyltrimethoxy silane (MPTMS) was made in this paper. Among the other silanes, 3-mercaptopropyltrimethoxy silane have showed the good results with improvement of thermal and mechanical cyclic life of composites [16]. The possible interaction between PMMA and modified whiskers is hydrogen bonding between thiol group of silane and carbonyl groups of the polymer matrix (see Fig. S2 in Supplementary data) [17].

The goal of this work is the synthesis and characterization of advanced nanocomposites with improved mechanical, thermal and self-healing properties. It is extremely important for the

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nanocomposite to exhibit superior properties with the ability to self-heal because of the difficulties faced when repairing a dental material or bone cement. The novelty of this work is reflected in the synergistic effect of nanomodifying acrylates with silanized whiskers and self-healing agents in order to use them as dental materials or bone cements. In our previous studies the focus was on non-modified alumina fillers of different shapes (particles, whiskers or fibers). The effect of the filler content was also studied [11,12]. To the best of our knowledge, this is the first time that 3-mercaptopropyltrimethoxy silane (MPTMS) modified alumina whiskers were used in an acrylate. Typically the inorganic acrylic based composite fillers are modified with 3-methacryloxypropyltrimethoxysilane using conventional or supercritical CO_2 methods [18]. The aim of this work was not only to obtain a composite with modified alumina whiskers, but for the composite to also have the self-healing effects. Also, his is the first time that the modified Grubbs' catalyst was employed as a self-healing agent in PS nanofibers for a thermoplastic nanocomposite.

Although the acrylates have been a subject of many prior studies they are still very appealing materials to work with because of their good mechanical and optical properties, chemical stability and biocompatibility. For these reasons the ongoing research is focusing on the improvement of mechanical and biological properties of fillers and active agents. Acrylate based nanocomposites represent the step further towards improving mechanical and thermal properties in the field of dental materials and bone cements.

Mechanical loading and thermal cycling can result in the formation of micro-cracks in composite materials, and after that it can result in a drastic reduction in mechanical properties. Once implanted in the body, dental materials or bone cements are difficult to monitor and access for repair. So, there is a good opportunity for self-healing principles of these materials. The healing process results in the partial restoration of the material properties, such as mechanical properties, as well as other functions (*e.g.* conductivity, protection, esthetics). The initial self-healing system developed by White et al. [19] involves the incorporation of a healing agent in an epoxy matrix: microencapsulated monomer dicyclopentadiene (DCPD) and wax microspheres containing Grubbs' catalyst, bis(tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride. When the capsules have been broken with initiating crack, the repair agent from capsules released and the ring-opening metathesis polymerization (ROMP) has occurred. The new polymerized poly (DCPD) fills the crack and repairs the material. In this work, the self-healing technique of embedding self-healing agents (SHA) in acrylic resin was applied. The self-healing agents were electrospun PS nanofibers with Grubbs' catalyst and urea-formaldehyde (UF) capsules with DCPD. Polymer protection of Grubbs' catalyst allows the catalyst to be incorporated into a matrix at smaller size scales without deactivation. PS in the catalyst particles also contributes to healing as it is dissolved by the DCPD and redeposit in the crack plane. Advantages of that system of SHA in case of bone cement would be the coverage of dissolved Grubbs' catalyst in PS nanofibers and prevention of direct contact with tissues. The ring-opening metathesis polymerization reaction between dicyclopentadiene and Grubbs' catalyst (see Fig. S1c in Supplementary data) is especially important to self-healing applications and provides a model system that uses both encapsulated liquid and solid healing agents.

The adhesion between the capsules and the polymer of the composite influences whether the capsules will rupture or debone in the presence of an approaching crack. To promote the adhesion between the polymer and capsule wall, various silane coupling agents may be used for modification of capsule surface [20]. The tensile, bending and impact fracture loading before and after healing is required for demonstration of self-healing efficiency [21].

In this work, the fracture healing efficiencies after a low energy impact test were assessed. The impact test allowed the determination of the mode of fracture of the specimen, the peak load, the energy of the peak load and the totally absorbed energy obtained during the fracture test. When subjected to impact loading, energy is absorbed by the creation of new surfaces. This considerably reduces the residual mechanical properties of the material. After impact, the repair agent passes from within any broken capsules to infiltrate the damage zone and heal the crack and so prevent further propagation damage.

The healing efficiency, η, is defined as the ability of a healed sample to recover fracture

$$\eta = E_{healed}/E_{virgin} \tag{1}$$

where E_{virgin} and E_{healed} represent the energies (energy in peak load, or totally absorbed energy) of the virgin and healed samples, respectively [22].

2. Materials and methods

2.1. Materials

A chemically (self)-cured auto polymerizing resin, Simgal-R® (Galenika, Serbia) was used as polymer matrix. It is a two component system, including a powder and a liquid. The powder consists of a PMMA copolymer and the initiator benzoyl peroxide (BPO) in a concentration of 1.1% w/w. The number average molecular weight of the Simgal powder obtained from gel permeation chromatography measurements was 116,000 g mol^{-1}, with a polydispersity of 4.54. Size exclusion chromatography measurements were performed using a Waters HPLC system with an RI detector and a set of four styragel columns. Chloroform was used as the eluent with a sample concentration of 10 mg ml^{-1} and mobile phase flow rate 1 ml min^{-1}. Calibration was performed using polystyrene standards. The liquid consists of methyl methacrylate (calc) 94.15% w/w; acid as methacrylic acid 19.8 ppm w/w; *N*,*N*-dimethyl-*p*-toluidine as accelerator 0.85% w/w; ethylene glycol dimethacrylate as cross linking agent 5.00% w/w; water 27 ppm w/w. The alumina whiskers were commercially available from Sigma-Aldrich, and they were characterized by diameters of 2–4 nm and lengths of 200–400 nm (specified by the producer). 3-mercaptopropyltrimethoxy silane (MPTMS, 95%; Sigma-Aldrich.) was used as a coupling agent. The chemicals that were used in preparing the self-healing system: dicyclopentadiene, (DCPD), 95%, stabilized, ACROS Organics; dimethylformamide, (DMF), 99.8%, Sigma-Aldrich; Grubbs' catalyst 1st generation, bis (tricyclohexylphosphine) benzylidene ruthenium (IV) dichloride Sigma-Aldrich; polystyrene (PS) Empera ®251N, Ineos Nova, urea-formaldehyde resin, Sigma-Aldrich.

2.2. Methods

2.2.1. Modification of alumina whiskers surface

The thiol group grafted samples were prepared as follows: 0.6 ml of MPTMS was mixed with 1.5 g of alumina whiskers in 50 ml of dried toluene. This mixture was stirred under reflux condition for 36 h. Then the solid in the mixture was collected by filtration, rinsed with anhydrous ethanol to remove the non-reacted MPTMS and dried at 80 °C for 24 h [23]. The unmodified whiskers were denoted as W, while modified whiskers as WMPTMS.

2.2.2. Preparation of self-healing agents

The first generation Grubbs' catalyst (Bis (tricyclohexylphosphine) benzylidine ruthenium (IV) dichloride) was embedded in