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The use of different alumina fillers for improvement of the mechanical properties of hybrid PMMA composites

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ABSTRACT

Alumina fillers having different morphologies were used for reinforcement of PMMA-based composite materials. The employed fillers had the same chemical composition but morphologically were spherical nanoparticles, whiskers and an electrospun product that was composed of micro-sized mostly spherical particles and nanofibers. The electrospun product was obtained from aluminum chloride hydroxide/PVA/water solution. All fillers were added without surface treatment and mechanical characteristics of obtained composites were determined using dynamic mechanical analysis (DMA) and nanoindentation. From the nanoindentation results, the reduced elastic modulus for the obtained specimens using 3 wt.% of electrospun product was 134% of the one obtained with the polymer alone and the hardness was improved to 157.8% compared to the polymer without any additive. DMA shows that the storage modulus at room temperature was twice that of the polymer alone.

1. Introduction

Poly(methyl methacrylate) (PMMA) is a widely used polymer in cases when the transparency is of utmost importance. PMMA has a favorable biocompatibility and has been used as a restorative material in dentistry and medicine [1]. Reinforced polymer composites have been used for nearly 50 years in restorative components utilized in medicine and dentistry [2,3]. The use of this material has recently increased as a result of consumer demands for esthetic restorations, coupled with the public concern of mercury-containing dental amalgam [4]. Composites are now used in over 95% of all anterior direct restoration teeth and in 50% of all posterior direct restoration teeth [5]. In medicine, fiber-reinforced composites have been used in orthopedics as implants, and load bearing surfaces [6]. In addition, hydroxyapatite composite implant materials have become a promising alternative to acrylic cement in stabilizing fractures and cancellous screw fixation in elderly and osteoporotic patients [7,8]. The first use of poly(methyl methacrylate) as a dental device was for the fabrication of complete denture bases [9,10]. Although numerous new alloplastic materials show promise, the versatility and reliability of PMMA cause it to remain a popular and frequently used material [11,12].

The use of PMMA-based composites is based on the need to achieve favorable mechanical properties with appropriate polymer-reinforcement bonding, and benefit from the biocompatibility of PMMA. The even distribution of composite reinforcement particle plays a pivotal role in the durability of a material during long-time service. This is the situation where the properties of the composite are important and when the even distribution of the reinforcement plays a vital role for enabling the material to be used safely and for a long time. The de-agglomeration and distribution of particulate reinforcements in the matrix can be achieved using several techniques of which ultrasonication of the reinforcing particles in the monomer is one of the most efficient techniques for the fabrication of composites with the desired mechanical properties [13].

Electrospinning is a process that enables the production of fine fibrous ceramic structures enabling particles having to obtain shapes with a good capacity for reinforcement to be obtained [14]. Alumina fibers are among the fibers that are easily produced using electrospinning and there are several reported chemical fabrication routes [15,16]. The fibers can be easily produced from precursor chemicals and then transformed into oxides by heat treatment in air [17]. The obtained fibers have promising potentials for use as reinforcements in composite materials. The process can be controlled using different process parameters, such as mass flow of the precursor, the voltage of electric field, chemical composition of the precursor and the distance between the syringe and the collector. By varying the mentioned parameters, the shape and dimensions of the fibers could be adjusted. The products mostly have a fibrous structure, but sometimes it is possible to obtain different shapes

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of the precursor. Appearance of the fiber shapes could be analyzed using image analysis techniques with precise measurement scales [18]. Usually, this technique is coupled with scanning electron microscopy in order to capture the real morphology of the fabricated materials [19].

Elastic modulus and hardness at ambient temperature and under heating cycles are essential for composite characterization. Nanoindentation is a technique that enables the determination of elastic modulus and hardness of a material on submicron scales. In the case of a composite material having nanoparticles as reinforcement, it is essential to elucidate the uniformity of mechanical properties that could be compromised due to uneven particle distribution or weak particle–matrix bonding. Dynamic mechanical analysis (DMA) is a sensitive technique that measures the thermo-mechanical response of materials with respect to temperature and the frequency of the applied sinusoidal stress. This analysis enables the determination of the storage modulus (E'), loss modulus (E''), damping factor (tan δ) and the ratio between loss modulus (E'') and storage modulus (E') (Cole–Cole plot). DMA also enables the determination of the glass transition temperature (T_g) of the composite and an evaluation of the contact between the reinforcement and the matrix. A comparison of the results of these methods gives the possibility to study the mechanical behavior of the composite and to evaluate the influence of the shape and quantity of the reinforcement.

The goal of this research was to examine the feasibility of using electrospun alumina fillers as reinforcement for PMMA-based hybrid composite materials. The influence of the size and shape of electrospun alumina fillers on the mechanical properties of the hybrid composites was studied and compared with those of the two types of composites prepared using industrial alumina fillers: alumina spherical particles and alumina whiskers. All fillers were added without surface modification, which makes the process very simple and lowers the cost of the processing of the materials.

2. Materials and methods

2.1. Materials

Aluminum chloride hydroxide (Locron L) was purchased from the Clariant Company in the crystallized state of $Al_2Cl(OH)_5 \cdot 2.5 \cdot H_2O$. The PVA used had a weight average molecular weight ($\overline{M}_w$) of $\approx$130,000 g mol^{-1} and degree of hydrolysis of 86.7–88.7 mol%, and was purchased under the label Mowiol 18-88 (Aldrich). Mecaprex KM, PRESI (Grenoble, France) autopolymerizing acrylic resins consisted of KM powder (PMMA powder containing dibenzoyl peroxide (DBPO) initiator) and of KM liquid monomer (methyl methacrylate monomer — MMA with *N*,*N*-dimethyl-*p*-toluidine as an activator). The spherical aluminum oxide nanoparticles and alumina whiskers were commercially available from Aldrich.

2.2. Methods

2.2.1. Fast preparation of electrospun alumina fibers

For the preparation of alumina ceramic fibers, a fast electrospinning procedure was used. The precursor was based on alumina chloride hydroxide and poly(vinyl alcohol), which served to enable the good spinnability of the solution and to ease the handling of the precursor fibers. The procedure for precursor preparation was selected so as to enable the preparation of mixtures having a desired ratio of aluminum oxide to the polymer in the solution. A 5 wt.% aqueous solution of polymer was used and the aluminum chloride hydroxide was added into the solution. The desired mass ratio of aluminum chloride hydroxide to polymer in the mixture was 5 to 1. The solution was then stirred using a laboratory mixer for 1 h at 30 °C to obtain a homogeneous solution. The resulting solution contained air bubbles that disappeared after 24 h.

An Electrospinner CH-01 electrospinning apparatus (Linari Engineering, Italy) was used for the fiber preparation. A high-voltage supply (SPELMANN PCM50P120, USA) capable of producing 30 kV was used in the experiments. The polymer solutions were supplied to the nozzles using R100E type syringe pumps (Razel Scientific Instruments, USA). The solution was placed into the 20 ml plastic syringe having a needle of 0.8 mm orifice. The voltage used to have a stable process was of 28 kV and the mass flow rate was 20 ml/h. The process was conducted in air at an ambient temperature of 21 °C. The distance between the needle and the collector was fixed at 15 cm. Aluminum foil was placed at the bottom of the installation. After completion of the electrospinning, the electrospun fibers were calcined at 1100 °C for 1 h in order to obtain electrospun alumina fillers [20]. The XRD pattern of the sample calcined at 1100 °C indicated that the α-alumina phase was formed (Fig. 1a). Two industrially available fillers were selected in order to compare the prepared electrospun alumina fillers. These were spherical aluminum oxide nanoparticles, declared to have diameters of less than 50 nm, and alumina whiskers characterized with diameters of 2–4 nm and lengths of 200–400 nm. Thus very different alumina fillers were examined, spherical alumina nanoparticles, with the length to diameter ratio of 1, and alumina whiskers having a length to diameter ratio of approximately 100.

2.2.2. Preparation of hybrid PMMA composites

Alumina spherical nanoparticles, alumina whiskers or electrospun alumina fillers were added to KM liquid. The mixture was sonicated for 60 min and KM powder was dispersed in the mixture. The mixing was performed by hand for 2 min and the mixture was poured out in a cast form having dimensions suitable for DMA and nanoindentation testing. The form was covered using a glass cover to ensure that the surface of the specimen remained smooth. A PMMA/MMA mass ratio of 0.75 was used as this ratio enables minimization of shrinkage as suggested by the manufacturer (PRESI) and as previously reported in the literature [21]. The polymerization of the monomer was realized at a temperature of 25 °C. The manufacturer's suggestion states that the polymerization is considered to be completed in 20 min at a temperature between 20 and 23 °C. The obtained composites were then exposed to a temperature of 37 °C for 30 days before they were mechanically tested in order to obtain the stable composition of the polymer matrix of the composite [22]. The compositions of the composites PMMA/alumina whiskers and PMMA/alumina spherical nanoparticles prepared for analysis in this study are summarized in Table 1. The samples prepared using the alumina spherical nanoparticles as the filler were denoted P1, P3 and P5 for the addition of 1 wt.%, 3 wt.% and 5 wt.% of the filler, respectively. The samples using alumina whiskers as fillers were denoted W1, W3 and W5 for the addition of 1 wt.%, 3 wt.% and 5 wt.% alumina whiskers, respectively. The samples using the electrospun bimodal alumina product having the same contents of fillers as those having industrially produced alumina fillers are annotated as F1, F3 and F5 for the respective contents of 1 wt.%, 3 wt.% and 5 wt.% alumina electrospun fillers, respectively.

2.3. Characterization

2.3.1. DMA analysis

Dynamic mechanical analysis was used to examine the performance of the PMMA matrix composite reinforced with alumina spherical nanoparticles, alumina whiskers and electrospun alumina fillers in order to analyze the influence of the size and shape of the alumina filler on the behavior of the fabricated composites. The storage modulus revealed the ability of the composites to store elastic energy associated with recoverable elastic deformation. Together with tangent delta, the storage modulus describes the behavior of the composite under stress in a defined temperature range. The effect of the structural changes of neat polymer matrix was also confirmed by a Cole–Cole plot where the loss modulus data are plotted as a function of the storage modulus. Dynamic mechanical analysis was performed (DMA Q800, TA Instruments) under a nitrogen atmosphere and the single cantilever mode. Storage modulus