Innovative PMMA/Silica nanocomposites for optical and biomedical applications

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ABSTRACT

PMMA based nanocomposites filled with silica nanoparticles (SiO_2) were prepared and characterized. In order to obtain a good nanoparticles dispersion and to promote the polymer/nanofillers interfacial adhesion, silica surface was modified by grafting a silane coupling agent characterized by unsaturated end-groups, able to react during the polymerization process of the matrix precursor. SEM analysis performed on the fractured surface of nanocomposites revealed homogeneous and fine nanofillers dispersion. Mechanical analysis evidenced that elastic modulus increases at high nanoparticle content while PMMA toughness is clearly influenced by the presence of the nanoparticles. Finally, SiO_2 nanoparticles are responsible for a significant improvement of the abrasion resistance of the prepared materials.

Keywords: interfacial adhesion, mechanical properties, nanocomposites, optical properties, PMMA.

1 INTRODUCTION

Poly(methyl methacrylate), PMMA, is a thermoplastic resin used in many sectors such as aircraft glazing, signs, lighting, architecture, and transportation. Moreover, since PMMA is biocompatible, it is also used in dentures, medicine dispensers, food handling equipments, and lenses. The main drawback of PMMA is the poor abrasion resistance that prevents its usage both in specific biomedical and structural sectors. Moreover, many attempts to improve PMMA abrasion resistance have always induced strong decrease of other mechanical properties. Previous researches focused on the preparation of polymer based nanocomposites [1,2] have shown that properly modified nanoparticles [3,4] are competitive, with respect to unmodified inorganic nanofillers, to impart interesting properties to several thermoplastics.

Moreover, also for biomedical application, there is an even growing attention to polymer based nanocomposites containing mineral nanoparticles. In this way the obtained biomaterials show hybrid properties such as the polymer flexibility and ease of workability with improved strength and resistance [4].

The main goal of this research was to improve PMMA performance by preparing innovative PMMA based nanocomposites filled with silica nanoparticles. It is important to underline that among the very interesting properties of silica, typical of a mineral filler, osteointegration ability represents a key factor to realize a multiphase material that can find application also in biomedicine.

Particular attention was devoted to solve interfacial problems due to the different nature of the organic matrix and the inorganic phase and to the high adsorption nanoparticle surface energy both responsible for agglomeration phenomena.

As a matter of fact, silica nanoparticles were modified by grafting onto surface a proper silane agent characterized by unsaturated end-groups able to react during the polymerization process of the matrix precursor.

To evaluate the effect of the silane agent on the compatibilization between matrix/silica, nanocomposites containing unmodified nanoparticles were also prepared. Structure/properties relationships were deeply investigated by means of morphological, mechanical and thermomechanical analyses as well as by abrasion tests.

Finally, the bio-activity of the prepared nanocomposites is still under evaluation through studies on cytotoxicity and inflammatory properties.

2 EXPERIMENTAL SESSION

2.1 Materials

Methylmethacrylate (MMA) and dibenzoylperoxide (DBPO), vinyltrimethoxysilane (VTMS), KI, ICl, $Na_2S_2O_3$ 0.1 M solution, Aldrich reagent-grade products, were used without further purification.

Unmodified and modified silica were kindly supplied by Degussa GmbH (Hanau, Germany). Unmodified nanoparticles, commercial name Aerosil (SiO_2), are characterized by spherical shape, average diameter ~ 20 nm, BET surface area ~ 90 m^2/g. Modified silica nanoparticles, commercial name Aerosil R7200 (mod-

SiO$_2$), are hydrophobic fumed silica nanoparticles, obtained by treating silica with with 2-Propenoic acid, 2-methyl-, 3-(trimethoxysilyl)propyl ester:
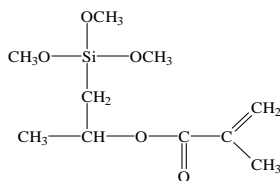
Modified silica nanoparticles have spherical shape, average diameter ~ 12 nm, BET surface area ~ 150 m^2/g.

2.2   Nanocomposites preparation

In a flask 0.5 g (1.5 g) of silica nanoparticles were added to 49.5 g (48.5 g) of MMA. The dispersion was kept for 20 min in an ultrasonic bath. After this period, 1 % by weight of DBPO (with respect to the acrylic phase) was added to the dispersion and then the flask was put in an oil bath at 80°C. This dispersion was mechanically stirred until a critical viscosity that corresponds to a prepolymerization step of the monomer. The viscous mixture was then poured into a mould and kept at 70°C for 12 h in oven. Finally, the temperature was raised to 140°C for further 12 h to complete the polymerization process.
This preparation procedure was used for both unmodified and modified silica nanoparticles, as well as for neat PMMA.

2.3   Techniques

The content of the double bonds onto modified silica nanoparticles was determined by titration. That is 0.5 g of modified silica, 50 mL of chloroform, and 20 mL of ICl solution in acetic acid (0.1 M) were poured into a 150-mL flask. After stirring for 15 min, a 20 mL of KI solution (15%) was charged. Then the mixture was titrated with 0.1 M Na$_2$S$_2$O$_3$ solution (volume V$_1$). The same experiment was repeated with unmodified nanoparticles, and the necessary volume of the Na$_2$S$_2$O$_3$ solution used for this titration is Vo. Then, the amount of the double bonds (n$_{DB}$) was calculated by the following equation:

$$n_{DB} = 0.5 \times (V_0 - V_1) \times 0.1 \qquad (1)$$

where V$_0$ and V$_1$ are expressed in liters and 0.1 is the Na$_2$S$_2$O$_3$ solution concentration (mol/L).

Thermogravimetric analysis (TGA) was performed on unmodified and modified silica nanoparticles by using a Perkin Elmer Pyris Diamond thermogravimetric Analyzer, by recording the weight loss as a function of temperature. The samples were heated from 40°C to 1100°C at a scanning rate of 10°C/min in air atmosphere. The amount of total organic content of modified silica nanoparticles was evaluated by comparing the corresponding TGA traces with that of unmodified silica.

Morphological analysis was performed by using a scanning electron microscope (SEM), Cambridge Stereoscan microscope model 440, on cryogenically fractured surfaces. Before the observation, samples were metalled with a gold layer.

Glass transition temperatures were evaluated by Dynamic-mechanical analysis (DMA): dynamic-mechanical data were collected at 1 Hz and at a heating rate of 3°C/min from –50°C to 150°C under nitrogen flow with a Perkin Elmer Pyris Diamond Dynamic Mechanical Analyzer. The experiments were performed in bending mode on samples 20 mm long, 14 mm wide and 3.5 mm thick.

Flexural tests were carried out at room temperature by using an Instron mechanical testing instrument (Model 1122). The test span was 48 mm. The cross-head speed was 1 mm/min. The elastic modulus (E) was measured on unnotched samples (60 mm long, 6.0 mm wide, 3.0 mm thick). The critical stress intensity factor (Kc) was calculated according to the concepts of linear elastic fracture mechanics (LEFM) on samples (60 mm long, 10.0 mm wide, 3.0 mm thick) sharply notched as following described: first a blunt notch (about 2 mm deep) was obtained through a machine with a V-shaped tool and then a sharp notch 0.2 mm deep was made by a razor blade. The final value of the notch depth was measured after fracture by an optical microscope [4,5].

Abrasion tests were carried out using a Taber model 5135 rotary platform abraser on neat PMMA, PMMA/SiO$_2$ and PMMA/mod-SiO$_2$ materials. The abrasive wheels were H-18 type and the applied weight of the arms was 1000 g. The dimensions of specimens were 0.5x15x15 cm. Five sessions of 100 cycles were performed on the samples. For each composition three samples were analyzed. The abrasion resistance was evaluated as average weight loss of sample per 100 cycles.

Finally, the bio-activity of the prepared nanocomposites is still under evaluation through studies on cytotoxicity and inflammatory properties performed by measuring the PMMA stimulated expression of surface proteins in humane Jurkat lymphocyte T cells, as well as the production of reactive oxygen species measured by quantification of lipoperoxidation in membranes and genotoxicity by using the comet assay.

3   RESULTS AND DISCUSSION

It is well known that the presence of organic molecules on the surface of nanoparticles promotes polymer/inorganic nanofiller compatibility by increasing the interfacial adhesion between the two nanocomposite components.

In this research silica nanoparticles were modified by grafting onto surface a proper silane agent characterized by unsaturated end-groups, able to react during the polymerization process of the matrix precursor.

The amount of grafted silane in mod-SiO$_2$, determined by titration, was about 4.3% by weight with respect to the weight of dried nanoparticles. This result was also confirmed by TGA measurements, performed in comparison also on unmodified nanoparticles.

Therefore, MMA based nanocomposites filled with 1 and 3% by weight of both unmodified and modified nanoparticles were prepared by in situ polymerisation [6]. Nanoparticles were dispersed into MMA phase and the polymerisation was induced by thermal decomposition of DBPO (1 wt % with respect to MMA). As detailed described into the experimental session, the in situ polymerisation process was carried out in two steps. During the first step, carried out under mechanical stirring, the low mixture viscosity allowed the fine nanoparticle dispersion. During the polymerisation, the growing PMMA chains contribute to increase the viscosity of the medium thus assuring the *freezing* of the obtained nanofiller dispersion. In the last step, performed in the oven, the PMMA polymerisation was completed. The same experimental conditions were used to prepare neat PMMA.

In order to evaluate nanofiller dispersion into PMMA and the interfacial adhesion between the two components, morphological analysis was performed on cryogenically fractured surface of nanocomposites. This analysis revealed that in situ polymerization methodology of MMA in presence of silica nanoparticles modified with a silane agent characterized by unsaturated end-groups can provide a useful method of nanocomposite preparation with the achievement of good nanoparticle dispersion. In Figure 1, a SEM micrograph of PMMA based nanocomposites filled with the highest amount (3 wt%) of modified silica nanoparticles are reported.
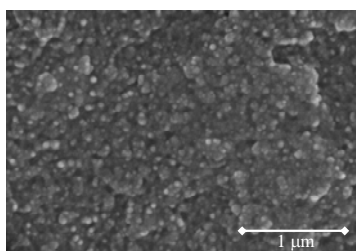

Figure 1: SEM micrograph of PMMA based nanocomposites filled with 3 wt% of modified SiO_2 nanoparticles

From this figure it can be observed that silica particles homogeneously dispersed into the PMMA matrix, whereas agglomeration phenomena have been evidenced in the case of unmodified nanoparticles. Moreover, only in presence of modified nanofillers the cryogenically fractured nanocomposites surface appears completely filled by the nanoparticles and no pull out phenomena are evidenced (absence of voids), thus suggesting a strong interconnection between the polymer phase and the modified nanofillers [7].

In Figure 2 the results of tan δ values are graphed vs. temperature for neat PMMA, and PMMA based nanocomposites filled with 3 wt% of both unmodified and modified silica nanoparticles. T_g values of all the prepared samples, determined from tan δ curves, are reported in Table 1.
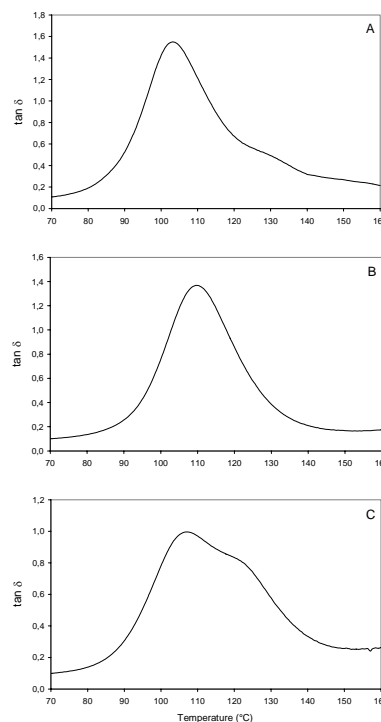

Figure 2: tan δ curves of: A) neat PMMA; B) PMMA/3% unmod SiO_2; C) PMMA/3% mod SiO_2.

Table 1: Glass transition (T_g) temperature values of neat PMMA and PMMA-based nanocomposites.

Samples	T_g (°C)
Neat PMMA	103
PMMA / 1% unmod SiO_2	105
PMMA / 3% unmod SiO_2	109
PMMA / 1% mod SiO_2	105
PMMA / 3% mod SiO_2	108-119

The strong interconnection between the modified silica nanoparticles and the acrylic phase was also confirmed by the results obtained by DMA analysis performed on compression moulded nanocomposite samples.

In fact, whereas unmodified silica nanoparticles induce only a slight increase of T_g values of PMMA, the presence of modified nanoparticles induce the insurgence of a second T_g at higher temperature, as it can be observed from Figure 2C. This transition can be attributed to the PMMA phase grafted to modified silica nanoparticles during the in situ polymerization reaction through the unsaturated end-groups of the silane agent, able to react during the polymerization process of the matrix precursor.

Results of mechanical analysis are resumed in Table 2 and can be summarized as follows: the elastic modulus increases up to 25% with respect to neat PMMA value as concerning nanocomposite containing both unmodified and modified silica nanoparticles. This result can be well explained taking into account the rigid nature of the filler and its good dispersion into the polymer matrix.

The toughness of nanocomposites was evaluated at low deformation rate through the determination of the critical stress intensity factor, Kc. It can be observed that the presence of nanoparticles deteriorates the toughness of the material matrix. In order to mitigate this negative effect, work is still in progress to perform a further modification of silica nanoparticles by grafting onto their surface a rubbery interphase layer. In fact, it is well known that a rubbery phase is able to significantly improve the toughness of a brittle material [8]. The grafting of a rubbery interphase layer onto silica nanoparticles will allow to transfer the elastic property of the surface modifier to nanocomposites through the interfacial region, by exploiting the high specific surface area of nanofillers [9].

Table 2: Young's Modulus, E, and critical stress intensity factor, Kc, of neat PMMA and PMMA-based nanocomposites.

Samples	E (MPa)	Kc (MN/m$^{3/2}$)
Neat PMMA	2210	1.06
PMMA / 1% unmod SiO$_2$	2520	0.85
PMMA / 3% unmod SiO$_2$	2760	0.74
PMMA / 1% mod SiO$_2$	2500	0.86
PMMA / 3% mod SiO$_2$	2775	0.68

Abrasion resistance is one of the key factors in the wear process of a material [10]. Abrasion occurs in contact situations in which direct physical contact occurs between two surfaces with different hardness by the combined effect of *microploughing*, *microcutting* and *microcracking* [11]. PMMA is characterized by a low abrasion resistance. In particular, its wear is initiated by formation of surface cracks parallel to the sliding direction as a result of a high frictional coefficient.

In Table 3 results of abrasion tests are summarized. The presence of silica nanoparticles strongly improves abrasion resistance of PMMA, up to 35%, even at low nanoparticle content. This result can be explained considering that nanoparticles, homogeneously dispersed into PMMA, support part of the applied load and, in this way, the penetration into the polymer is reduced. Moreover, this improvement is not a function of the coating agent.

Table 3: Abrasion test results of neat PMMA and PMMA-based nanocomposites, measured as weight loss/100 abrasion cycles.

Samples	Weight loss (mg/100 cycles)
Neat PMMA	57.7
PMMA / 1% unmod SiO$_2$	39.3
PMMA / 3% unmod SiO$_2$	39.0
PMMA / 1% mod SiO$_2$	40.3
PMMA / 3% mod SiO$_2$	38.4

Finally, we have investigated the possible induction of cytotoxicity and the regulation of the transcriptional levels of pro-inflammatory cytokine genes. Experiments performed with an Agilent 2100 Bioanalyzer on human Jurkat lymphocyte T cells, have evidenced no effect due to PMMA interaction. Further investigations to screening other inflammatory and cytotoxic compounds by quantitative RT- PCR and to measuring genotoxicity by the comet assay, are in progress.

4 CONCLUSIONS

PMMA based nanocomposites filled with modified silica nanoparticles were prepared by in situ polymerization methodology. Morphological analysis allowed to assess that this preparation procedure is a useful method to achieve a good nanoparticle dispersion. The presence of modified silica nanoparticles induces a homogrnrous and fine dispersion of the nanofillers and a strong interconnection between the phases. Mechanical analysis revealed that the presence of the rigid filler significantly influences both the Young's Modulus and the toughness of PMMA. Finally, silica nanoparticles significantly improves the abrasion resistance of PMMA, independently from the presence of the nanoparticle coating agent.

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