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Novel PMMA/$CaCO_3$ Nanocomposites Abrasion Resistant Prepared by an in Situ Polymerization Process

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ABSTRACT

Novel abrasion-resistant nanocomposites based on poly(methyl methacrylate) (PMMA) as matrix and calcium carbonate ($CaCO_3$) nanopowder as filler have been prepared by an in situ polymerization process. The influence of nanopowders on the chemical–physical properties of the polymeric matrix have been investigated by performing thermal, morphological, and mechanical analysis. The abrasion resistance has also been evaluated. The nanocomposites showed an average weight loss about half with respect to that of neat PMMA, by adding only 2% of nanoparticles.

1. Introduction. In the past years, new methodologies to prepare materials containing organic and inorganic as single-phase have rapidly developed to produce new systems called hybrids, ceramers, or nanocomposites.[1−3] They often exhibit properties that are completely different from those of polymeric systems in which an inorganic component is added to a polymeric matrix at micrometer level.[4−6] These unexpected behaviors such as superconductivity,[7] magnetism,[8,9] nonlinear optics,[10,11] thermal stability,[12,13] etc. can be observed due to the enormous interfacial adhesion region characteristic of the nanoparticles.[14−19] Then, the nanocomposite properties are strongly influenced by the nature of the interface, hence a high interface allows having unusual properties.[20]

In the past, several methods to produce polymer nanocomposites such as sol−gel reactions,[21−23] intercalative polymerization,[24−26] via melt-processing[27−29] have been used depending on the nature of nanoparticles and on the synthesis and processing of polymeric matrices. However, more versatile synthetic approaches are needed to prepare polymer-based nanocomposites characterized by controlled composition and microstructures. The key factors for the preparation of enhanced performance nanomaterials are to obtain a uniform distribution of small ceramic particles within the polymer matrix and to promote a strong interface adhesion between the matrix and nanofillers.

Poly(methyl methacrylate), PMMA, is an important commercial plastic that finds application in many sectors such as in aircraft glazing, signs, lighting, architecture, transportation, and merchandising. Moreover, since PMMA is odorless, tasteless, and nontoxic, it can be used in dentures, medicine dispensers, food-handling equipment, throat lamps, and contact lenses.

Unfortunately PMMA is characterized by a poor abrasion resistance with respect to glass, and this is one of the reasons for its limited use in other fields such as for dental applications. Despite considerable efforts, attempts to improve the scratch resistance of this polymer have been accompanied by deterioration in other properties, such as impact strength.

The main goal of this research is to improve PMMA performance by filling with precipitated calcium carbonate nanoparticles. The results of preparation and property characterization of poly(methyl methacrylate)/calcium carbonate nanocomposites are reported in this letter.

The materials were prepared by "in situ polymerization". This preparation strategy consists of polymerization of the polymeric matrix in the presence of the nanofillers. The influence of the nanoparticles on the chemico−physical properties of the polymeric matrix by examining thermal, morphological, and mechanical behavior of the nanocomposites was investigated. The abrasion resistance of the materials has been tested to evaluate if the presence of inorganic nanoparticles such as $CaCO_3$ can improve also the hardness of the neat poly(methyl methacrylate).

Correlations between the morphology of the prepared nanocomposites and the microwear mechanism have been established. The existence of a different behavior between PMMA-based nanocomposites and PMMA homopolymer has been demonstrated. As matter of fact, the small amount of material removed from the nanocomposites surface, by

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the attack of hard abrasive particles, produces only furrows caused by a microploughing and/or microcutting mechanism; on the other hand the brittle PMMA matrix presents an abraded surface characterized by individual cracks due to the larger amount of removed material.

2. Preparation of PMMA/$CaCO_3$ Nanocomposites. The PMMA/$CaCO_3$ nanocomposites were prepared by in situ polymerization. Precipitated $CaCO_3$ nanoparticles covered by stearic acid, commercialized under the trademark SOCAL (Solvay & Cie), with a mean size of about 40 nm as fillers were used. The presence of stearic acid as organic coating on the nanofiller surface permits to confer hydrophobic properties to $CaCO_3$ that can improve its compatibility with the polymeric matrix.

In particular the experimental conditions of the sample preparation were as follows. (Step 1) In a cylindrical reactor equipped with inlets for refrigeration, mechanical stirring, and nitrogen, kept in an oil bath at 90 °C, methyl methacrylate containing 1 wt % of dicumylperoxide, previously dissolved, was added. To this solution 2, 3, 4, and 6 wt % of calcium carbonate nanoparticles were added.

This solution was stirred mechanically at 90 °C until a critical viscosity that corresponds to a prepolymerization of the monomer was reached. It was observed that the time it takes to achieve a critical viscosity value was related to the amount of nanoparticles. (Step 2) The viscous mixture was then inserted into a mold and kept at 100 °C for 24 h to complete the polymerization process. Finally, the nanocomposite so obtained was kept for 4 h at 140 °C to be sure that the entire prepolymer fraction has been converted.

Monomer polymerization has been promoted by thermal decomposition of the organic peroxide during the blending. Generally, acrylic polymerization is carried out in suspension, and the suspending medium is a salt-water solution. Due to the incompatibility of the nanoparticles with water, in this case methyl methacrylate polymerization has been performed in bulk.

The main parameters that allow one to obtain high-performance nanocomposites are the dispersion of the nanoparticles and the interfacial adhesion between filler and matrix. Moreover, it is known that the nanoparticles often act as catalysts influencing the overall rate of the polymerization process.

For these reasons it was important to optimize some experimental parameters such as the nature of the organic peroxide, temperature, stirrer, and subdivision of the polymerization process in two steps to prepare a material characterized by a fine nanoparticle dispersion.

The selected free-radical initiator was dicumyl peroxide (DCPO) at a concentration of 1 wt % with respect to the acrylic phase. Such a relatively high amount of peroxide is related to the use of the monomer without purification, i.e., in the presence of the *tert*-butylchatechol inhibitor, to provide time for a good dispersion of nanoparticles into the monomer before the acrylic polymerization starts. Therefore, high amounts of DCPO are required to deactivate the inhibitor. The temperature of the polymerization process was around 90 °C, and the decomposition time ($t_{1/2}$) of the dicumyl peroxide at $T = 120$ °C is about 30 min. In this way it was possible to obtain a better control on MMA polymerization rate due to the larger time of the initiator thermal dissociation. These choices permit to control experimental conditions, especially at the beginning of the process, favoring fine dispersion of the nanoparticles in the polymeric matrix. Materials containing the 2, 3, 4, and 6 wt % of the nanoparticles have been prepared and tested.

3. Morphological and Thermal Characterization. To establish the degree of nanoparticle dispersion within the polymeric matrix, nanocomposite samples were cryogenically broken after immersion in liquid nitrogen and the fractured surfaces were observed by scanning electron microscope (SEM). This analysis was carried out with a Philips SEM 501 electron microscope, and the scanning electron micrographs were taken on Au/Pd-coated fractured surfaces of the dumbbell specimens.

In Figure 1a and 1b, the SEM micrographs of the fractured surfaces of the nanocomposites containing 4 and 6 wt % of the calcium carbonate nanoparticles are shown as example. From the figures it can be observed that the nanoparticle size ranges between 40 and 70 nm. A fine nanoparticle dispersion into the polymeric matrix is also evident, and only a few nanopowder agglomeration phenomena have been noted in the case of highest nanoparticles content (6 wt %, see Figure 1b). This result allows to assume that the used preparation methodology permits to obtain a good dispersion of the nanoparticles into the polymeric matrix also at a relatively high content of nanofiller.

Glass transition temperatures (T_g) were analyzed with a differential scanning calorimeter (Mettler TA 3000). The DSC experiments were performed on about 10 mg of neat PMMA and of PMMA-based nanocomposite samples. The samples were heated from 30 to 200 °C at a rate of 20 °C/min. The glass transition temperature was determined at the middle of the peak. This analysis revealed that the presence of the calcium carbonate nanoparticles is responsible for an increase in T_g of about 30 °C with respect to plain PMMA.

The glass transition temperatures, determined for all samples, are reported in Table 1. It can be emphasized that the T_g values increase as a function of the amount of nanoparticles used, up to a plateau of about 125 °C for the sample containing 3−4 wt % of nanoparticles.

These data are correlated to the good nanoparticle dispersion in the polymeric matrix that guarantees a large matrix/filler interface. In this situation, the mobility of PMMA chains is limited, due to a strict interconnection between the two phases. In fact, as shown by the SEM micrographs of Figure 1, the nanoparticles are completely covered by the polymeric matrix and the material appears as a one-phase system.

4. Mechanical Characterization. The effects of $CaCO_3$ nanoparticles on mechanical properties of PMMA/$CaCO_3$ nanocomposites have been analyzed and the data are summarized in Table 2. The testing machine was an Instron model 1122, and it was used for compression tests with different loading noses and supports. The specimens were

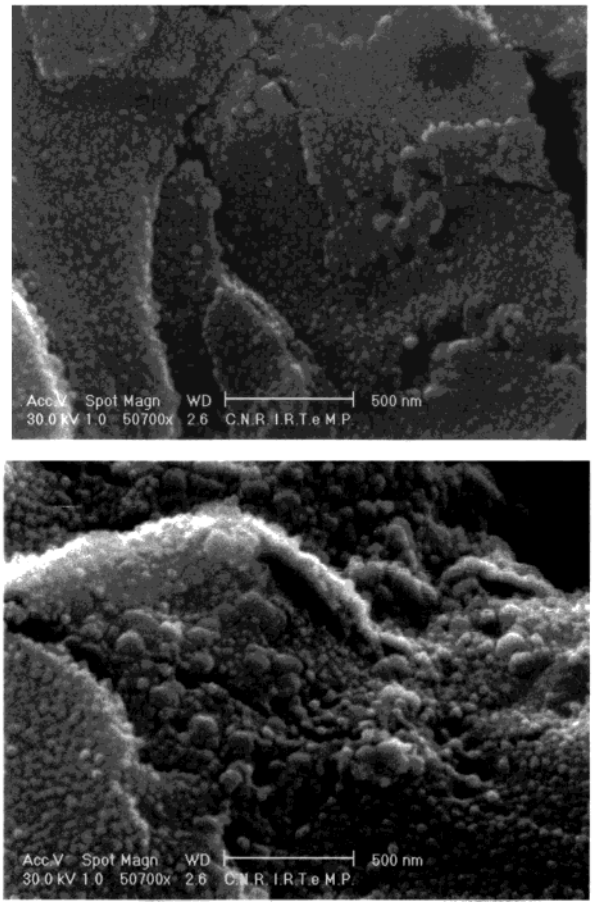

Figure 1. (a) SEM micrograph of fractured surface of PMMA based nanocomposite containing 4% of $CaCO_3$ nanoparticles. (b) SEM micrograph of fractured surface of PMMA based nanocomposite containing 6% of $CaCO_3$ nanoparticles.

Table 1: Glass Transition Temperature of Neat PMMA and of PMMA Based Nanocomposites

$CaCO_3$ content (%)	T_g (°C)
0	90
2	120
3	124
4	127
6	125

beam-sized 6 × 3.5 × 48 mm. The rate of loading was 1 mm/min.

From Figure 2 a strong increase of flexural modulus with the nanoparticle content can be observed: in fact, a nanoparticle content of only 3% produces a modulus increase of about 50%, up to around 67% when 6 wt % of nanopowder is added. The increase of modulus is obviously related to the large glass transition increase previously described. This result is obtained without a significant decrease of the ultimate strength and strain values.

5. Abrasion Resistance. The abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of material from its surface as a result of mechanical action of a rubbing, scraping, or erosion.[30] Abrasion resistance is the most important factor in the wear process of a material. Usually, abrasion reduces the serviceability of the

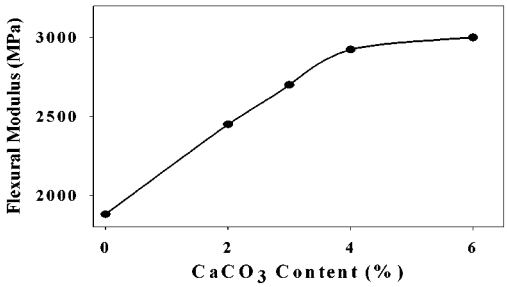

Figure 2. Flexural modulus of PMMA/$CaCO_3$ nanocomposites.

Table 2: Flexural Properties of Neat PMMA and PMMA Based Nanocomposites

$CaCO_3$ content (%)	flexural modulus (MPa)	ultimate strength (MPa)	ultimate strain
0	1880	19	0.0137
2	2450	18	0.0102
3	2700	17	0.0096
4	2920	17	0.0097
6	3000	16	0.0093

affected body and hence low abrasion resistance is a very important drawback that modern products must overcome.

Abrasion occurs in contact situations in which direct physical contact occurs between two surfaces, and one of the surfaces is considerably harder than the other. The asperities of the harder surface press into the softer surface, with plastic flow of the softer surface occurring around the asperities from the harder surface, which removes the softer material by the combined effect of "microploughing", "microcutting" and "microcracking".[31]

On all prepared samples the following experimental procedure was performed in order to evaluate the abrasion resistance of the materials. The abrasion tests were carried out using a Taber model 5130 abrader. The dimensions of the sample specimens were 5 × 10 × 10 cm. The abrasive paper, 80 grain, was applied on the Teflon rollers of the machine. The applied weight of the arms was 1000 g. Three sessions of 500 cycles were performed on the samples. The abrasion resistance was evaluated as the loss of sample weight.

PMMA, together with other glassy polymers such as polystyrene, presents a relatively low resistance to abrasion (e.g., lower than glass). In particular, its wear is initiated by formation of surface cracks parallel to the sliding direction as a result of a high frictional coefficient. This latter is probably due to the presence of polar groups along the backbone chains, which result in high molecular cohesion. These cracks can propagate until wear particles break completely out the surface without notable plastic deformation. This situation is clearly shown in Figure 3 where the fracture surface of PMMA homopolymer sample is reported.

Obviously, to obtain PMMA with a good abrasion resistance can allow this material to be used for many applications with a longer duration. As can be easily observed, the presence of nanoparticles strongly improves

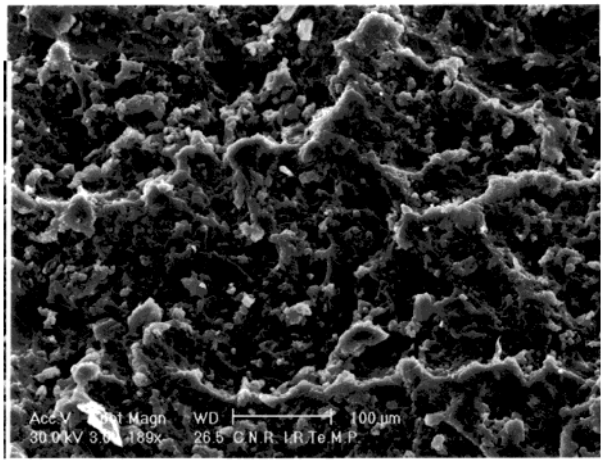

Figure 3. SEM micrograph of PMMA fracture surface after abrasion test.

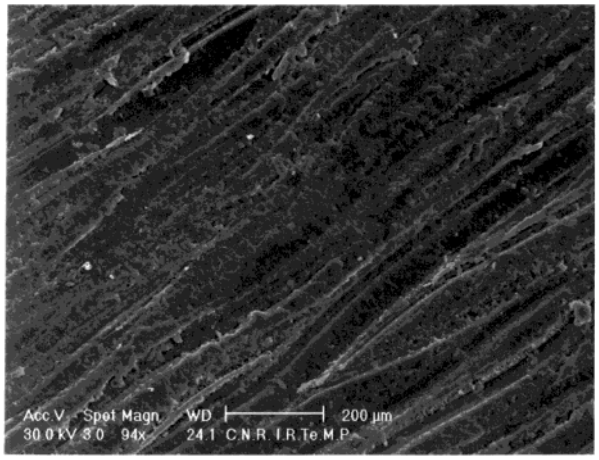

Figure 4. SEM micrograph of PMMA/$CaCO_3$ (3 wt %) fracture surface after abrasion test.

Table 3: Abrasion Test Results Measured as Weight Loss Material

$CaCO_3$ content (%)	weight loss (%)
0	5
2	3
3	2.5
4	2.4
6	2.4

the abrasion resistance, as well as the wear of PMMA (2.5% against 5% of removal material), even when only 2 wt % of $CaCO_3$ are added. This finding can be attributed to the fact that the nanoparticles support part of the applied load; thus, the penetration into the polymer surface is reduced and only microploughing and/or microcutting phenomena can be generated, as can be seen in Figures 4 and 5, where the fracture surfaces of PMMA/$CaCO_3$ nanocomposite samples filled with 3 and 6% of nanoparticles are shown, respectively. Under the attack of the rough abrasive paper, the grains penetrated deeply into the surface of the polymer, removing material from the surface by an extensive microploughing process. During this phase, the polymer is highly plastically

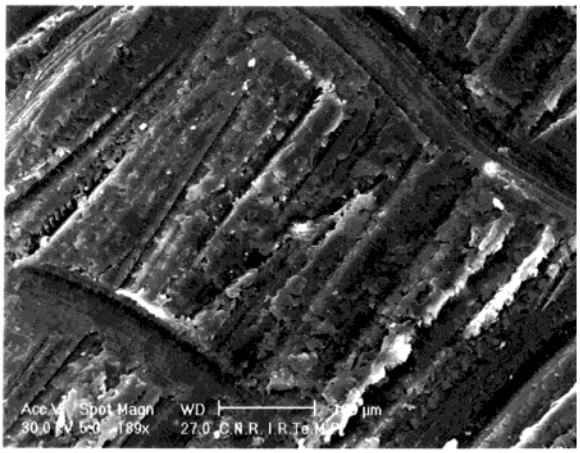

Figure 5. SEM micrograph of PMMA/$CaCO_3$ (6 wt %) fracture surface after abrasion test.

deformed before being separated, due to additional microcutting so that wear debris is formed.

The fact that PMMA/$CaCO_3$ nanocomposites present higher abrasion resistance values than does PMMA demonstrates that a very fine dispersion of nanoparticles, together a good interfacial adhesion between the two phases, was reached. In fact it is well known that wear mechanisms are functions of particle dimensions: if they are bigger than the abrasive grain size, *D*, only a small amount of particles are destroyed by the harder abrasive grits, whereas the main part remains in the work surface, contributing to the wear resistance of the material; conversely, if they are smaller than *D*, they are normally dug out of the polymer matrix. The latter should be our case, but this does not occur because the differernt performances of the nanocomposites, as known, are quite different from the conventional micro-composites, showing a behavior similar to that of one phase system.

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