



## EFFECT OF PROCESSING ON THE PROPERTIES OF POLY(METHYL METHACRYLATE)/SILICA NANOCOMPOSITES.

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### Abstract

The incorporation of nanosilica into thermoplastic matrices by polymer melting compounding is a promising approach for producing nanocomposites. In this work, PMMA nanocomposites were prepared using the commercial PMMA and PMMA/elastomer blend with nanosilica obtained from burned *Equisetum arvense L* and investigated by mechanical, thermal and flammability tests. Torque rheometry was used to optimize the processing conditions of the raw polymeric materials and the nanocomposites with 2wt% of nanosilica. These nanocomposites were blended by melt compounding using a twin screw extruder. The morphology of the nanocomposites was analyzed using cryo-ultramicrotomy and transmission electron microscope (TEM). Addition of silica nanoparticles in PMMA promoted some improvement on the thermal stability and viscosity of the nanocomposites produced. The properties of the nanocomposites PMMA/nanosilica have shown significant dependence on particles morphologies which could be optimized in order to achieve an improvement on composite performance.

### Introduction

In recent years, there have been many attempts to develop polymeric nanocomposites as advanced plastics materials. Nanocomposites are considered a new class of composites constituted by ultra fine inorganic particles with dimensions typically in the range of 1 to 100 nm which are dispersed within the polymer matrix leading to great performance improvement. Various micro or nanofillers have been shown to be efficient additives for also improving the thermal stability and fire retardancy of various polymers [1]. Recently, these kinds of materials have attracted the attention of governments, academic and industrial researchers because their outstanding properties [2].

Poly(methyl methacrylate) (PMMA) is an important amorphous thermoplastic material with excellent transparency, chemical and UV resistance. However, one of its limitations is its thermal instability and dynamic mechanical properties at elevated temperatures which restrict its applications in high temperature environment. In order to delay its degradation, several strategies can be employed, such as incorporation of nanoparticles in the polymer matrix [3, 4]. For instance, numerous works have reported the use of organo-modified clays and silica particles, carbon nanotubes, carbon nanofibers and carbon black [5-6].

In order to improve the thermal stability and the mechanical property of PMMA, synthesized silica nano-particles [4] have been studied in PMMA hybrid composites [7, 8] and also as a function of the adsorbed PMMA on silica [9], showing that some enhancement on the thermal stability of PMMA was achieved. Since the silica particles are hydrophilic, their surfaces need to be modified or pretreated with coupling agents to increase the compatibility between the polymeric matrix and the particles. Previous studies have compared systematically the thermal stability of PMMA-grafted silica with various coupling agents and PMMA/silica composites [10].

*Equisetum arvense L* ("Cavalinha") is a silica-rich plant, member of the Equisetophyta family [11]. This popular Brazilian plant is a vegetal easy to cultivate and it spreads like wildfire.

In this work composites from two types of PMMA and nanosilica from *Equisetum arvense L* were prepared, with and without compatibilizers, and characterized by mechanical, thermal and flammability tests.

## Experimental

### Materials

Two different grades of commercial PMMA resins were used, namely PMMA ODHAF and PMMAelastomer blend SSL/055 (pMMAel) from Resarbras da Bahia. The methyl methacrylate-glycidyl methacrylate copolymer (MMA-GMA) was synthesized according to Ito [12] and used as an interfacial compatibilizer. Silica particles were obtained from burning the organic compounds of the dry *Equisetum arvense L* in controlled conditions, using similar conditions to those used for burned rice hulls described by Sousa et al. [13].

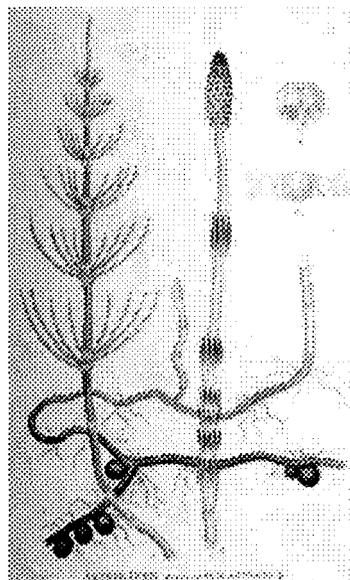


Figure 1 - Plant of *Equisetum arvense L*.

### Processing and characterization

Pellets of acrylic resin were reduced to the powder form using a cryogenic mill. The PMMA, PMMAel, MMA-GMA and silica particles were previously dried overnight at 70°C under vacuum prior to their use. Silica particles were diluted in water and dispersed in ultrasound for 5 minutes before the morphological characterization using a transmission electron microscopy (TEM; Philips CM200, operating at 200 kV).

Rheological characterization of the polymer and composites was carried out in a Rheomix 600 mixer connected to a HAAKE torque rheometer at 220°C and 50rpm for 10 minutes.

The composite processing was prepared using a co-rotational twin-screw extrusion (d=19mm and L/D=25) of the B&P Process Equipment and Systems model MP19-TC, using a profile temperature from 200°C in the feed zone and 220°C in the others zones. The samples were molded in a Arburg Allrounder injection molding model 270V using a profile temperature of 210°C in the feed zone and 240°C in the subsequent zones, the molding temperature was 50°C.

The thermal gravimetric analysis (TGA) of the composition, PMMA, PMMA/nanoSi e PMMA/nanoSi/MMA-GMA, was performed with a TA Instruments model TGA Q500, using a nitrogen atmosphere, platinum plates, and approximately 10mg of samples heated from ambient temperature to 800°C at a rate of 10°C/min.

The injection molding samples were conditioned using the ASTM condition and then mechanical, thermo-mechanical, flammability and morphological characterization was performed. Tensile tests (ASTM D638 type I specimens) were carried out using an INSTRON model 5569 equipment. Crosshead displacement rate were of 5 mm min<sup>-1</sup>,

Notched Izod impact testing was conducted according to ASTM D256 using an CEAST model Resil25. HDT (ASTM D648-01) were carried out using a HDTNicat equipment from CEAST model HDT6Vicat.

Rockwell M hardness (ASTM D785 - 98) was carried out using a SOSSEN-WOLPERT durometer type Testor HTI.

Rate of burning in a horizontal position were carried out according to ASTM D635-98 standard.

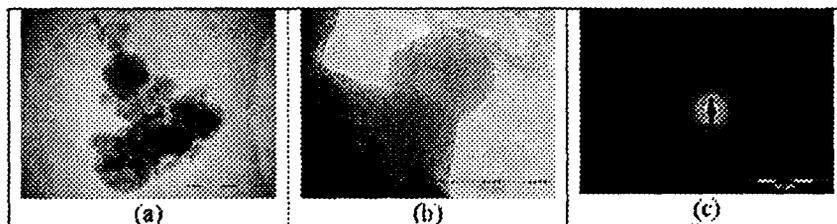
The samples from molded bars were ultra-microtomed into thin films of 30nm thick at -60°C in a RMC ultramicrotome, and then the morphologies of the composites were examined using a PHILIPS CM120 transmission electron microscope at an accelerating voltage of 120kV.

## Results and Discussion

Figure 2a shows silica particles appearing like rigid agglomerates, which were not dispersed even after the ultrasound treatment used to prepare samples for TEM analysis. Particle size presented a broad dispersion, from 20 to 100nm, which must have occurred due to the growing of particles by thermal effect during the obtaining process of silica nanoparticles.

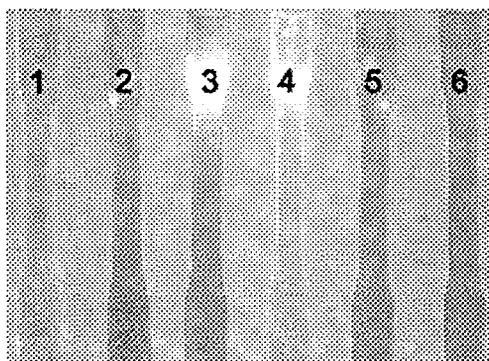
Figure 2b (Figure 2a enlargement), shows particles from 20 to 30 nm during the process of coalescence, indicating that mass transference among particles, a characteristic phenomenon of sinterization process, has occurred.

Figure 2c presents X-ray pattern of silica nanoparticles, with a very diffuse central halo, characteristic of amorphous silica with short-range order, which is related with cristobalite order, known to general amorphous silica.



**Figure 2** - TEM photomicrographs of the powder of the silica.

Injection molded samples were presented in Figure 3, with different tonalities associated with the silica particles addition. As it can be seen a transparency reduction is noticed, with some materials becoming semi transparent.



**Figure 3** - Injection molded samples (1) PMMA; (2) PMMNanoSi; (3) PMMNanoSi/MMA-GMA; (4) PMMAel; (5) PMMAel/nanoSi; (6) PMMAel/nanoSi/MMA-GMA.

Torque rheometry results are presented in Figure 4, in which an improvement of torque at 10 minutes after addition of silica nanoparticles can be observed. These results indicate an improvement on the viscosity of the composite as compared with that of the neat polymer.

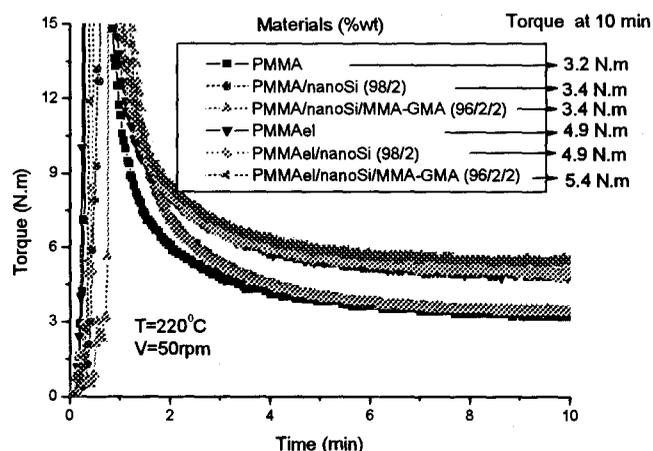


Figure 4 - Torque curves in function of time.

Onset of degradation temperatures in nitrogen atmosphere are presented in Table 1. Addition of silica nanoparticles in PNFMA improved in 7°C the thermal stability of the nanocomposites. This result is highly desirable since the thermal stability of PNFMA can limit its application and it is in agreement with the literature which reported a similar behaviour for PNFMA/silica hybrid materials [7].

Table 1 - Degradation onset temperature

Composition	T <sub>onset</sub> (°C)
PMMA	334.3
PMMA/nanoSi (98/2)	341.6
PMMA/nanoSi/MMA-GMA (96/2/2)	341.6

Table 2 - Tensile tests results

Materials (%wt)	Tensile Strength (MPa)	Elastic modulus (GPa)	Elongation at rupture (%)
PMMA (100)	58.1 ± 1.6	3.0 ± 0.3	3.3 ± 0.7
PMMA/nanoSi (98/2)	56.2 ± 2.7	3.0 ± 0.2	2.7 ± 0.3
PMMA/nanoSi/MMA-GMA (96/2/2)	53.6 ± 3.4	3.1 ± 0.2	2.4 ± 0.3
PMMAel (100)	49.2 ± 0.8	2.4 ± 0.2	22.6 ± 3.7
PMMAel/nanoSi (98/2)	49.0 ± 0.3	2.5 ± 0.2	22.7 ± 3.2
PMMAel/nanoSi/MMA-GMA (96/2/2)	48.8 ± 0.5	2.5 ± 0.2	24.4 ± 4.9

Mechanical properties of the composites showed small variation namely, an increase in Rockwell hardness, a slight reduction in tensile strength, elongation at rupture and IZOD impact and no significant variation on elastic modulus, and HDT, when compared with neat polymer, (Tables 2 and 3). Methyl methacrylate-glycidyl methacrylate copolymer, MMA-GMA, an interfacial compatibilizer, was added in the PMMA/nanosilica and PMMAel/elastomer/nanosilica composites due to the epoxide group from GMA, responsible for the stronger interfacial interaction between the PMMA (or PMMAel) and silica particles. No improvement on the flammability tests were observed which might be due to the low content, only 2% by mass, of silica particles used in the present work. Kashiwagi et al. [5] investigated PMMA/silica nanocomposites and concluded that the addition of 13% by mass of nanosilica is adequate to obtain a good flame-retardant effectiveness. On-going work is being done in our laboratories to increase this content, as well as to test other compatibilizing agent.

Table 3 -IZOD Impact, HDT, Rockwell M Hardness and Rate of burning.

Materials (%wt)	IZOD Impact (J/m)	HDT (°C)	Rockwell Hardness (HR)	Rate of burning (mm/min)
PMMA (100)	31.1 ± 1.7	66.1 ± 0.4	50 ± 2	23.8 ± 1.1
PMMA/nanoSi (98/2)	25.0 ± 1.2	66.7 ± 0.6	57 ± 4	26.1 ± 1.0
PMMA/nanoSi/MMA-GMA (96/2/2)	24.5 ± 1.0	66.8 ± 0.8	57 ± 4	27.3 ± 0.6
PMMA elastomérico (100)	41.8 ± 4.0	65.0 ± 0.2	123 ± 3	26.6 ± 0.7
PMMAel/nanoSi (98/2)	35.2 ± 1.1	66.2 ± 0.6	123 ± 4	26.1 ± 0.5
PMMAel/nanoSi/MMA-GMA (96/2/2)	36.6 ± 1.0	66.1 ± 0.8	124 ± 3	27.5 ± 1.0

Transmission electron microscopy analysis shows the presence of large agglomerates (Figure 5) which might be contributing negatively to the improvement on the PMMA/Si nanocomposites performance.

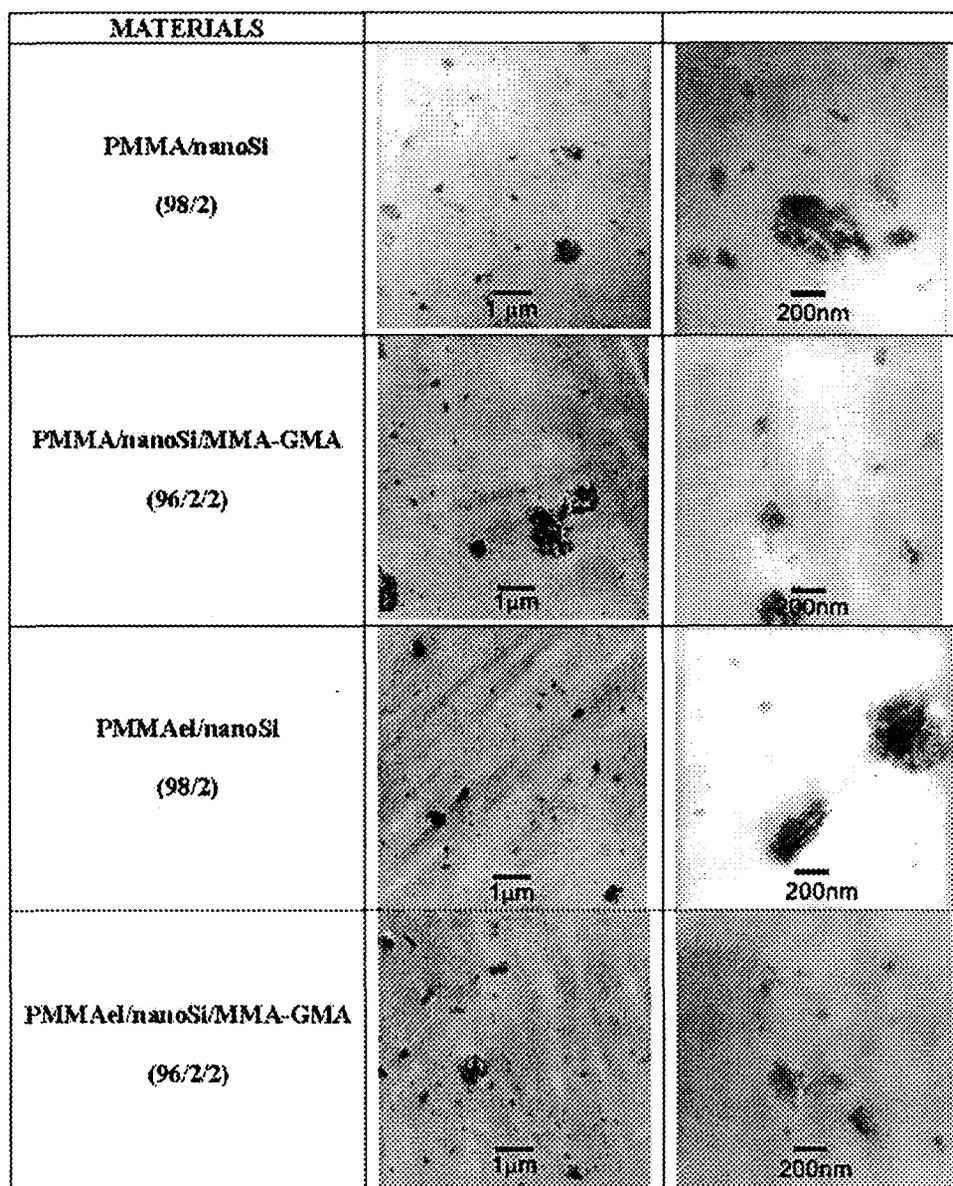


Figure 5 - TEM photomicrographs of the PMMA/nanoSi composites.

## Conclusions

Processing of the PMMA/Si nanocomposites using silica obtained from natural source is practicable to obtain new materials with promising properties, although some improvement on the techniques used should be further investigated. Addition of silica nanoparticles in P:M:MA promoted some improvement on the thermal stability and viscosity of the nanocomposites produced. Mechanical properties of the composites, however, showed small changes, when compared with neat polymer, probably due to the presence of large agglomerates, which might be contributing negatively to the improvement on the PMMA/Si nanocomposites performance.

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## References

1. M. Laachachi, E. Cochez, M. Leroy, JM. Ferriol, Lopez-Cuesta *Polymer Degradation and Stability*, 2007, 92, 61.
2. M. Alexandre; P. Dubois *Materials Sci. & Eng.* 2000, 28, 1.
3. S. Etienne, C. Becker, D. Ruch, B. Grignard, G. Cartigny, C. Detrembleur, C. Calberg, R Jerome *Journal of thermal analysis and calorimetry*, 2007, 87, 101.
4. H. Yang, C-Y. Huang and M. Xanthos ANTEC 2006, 526.
5. T. Kashiwagi; AB. Morgan; J.M. Antonucci; M.R Vanlandingham; RH. Harris Jr.; W. H. Awad; JR. Shields *J. Appl. Polym. Sci.* 2003,89,2072.
6. T. Kashiwagi, F. Du, J.F. Douglas, K.I. Winey, Richard H. Harris Jr, JR Shields *Nature Materials*, 2005, 4, 928.
7. H. Sugimoto, K. Daimatsu, E. Nakanishi, Y. Ogasawara, T. Yasumura, K. Inomata *Polymer*, 2006, 47,3754.
8. S. Gross, D. Camozzo, V. D. Noto, L. Armelao, E. Tondello *European Polymer Journal*, 2007,43,673.
9. F.D. Blum, E.N. Young, G. Smith, and O. C. Sitton *Langmuir*, 2006,22,4741.
10. Z.H. Huang and K.Y. Qiu, *Polymer*, 1997, 38, 521.
11. E.M.Z. Michielin; L. Danielski, S.R.S. Ferreira, H. Hense *Anais do XVIII Congresso Brasileiro de Ciencia e Tecnologia de Alimentos*, 2002,1,3577.
12. E.N. Ito, PhD Thesis, Federal University of Sao Carlos, 2006.
13. M.F. de Souza, W.L.E. Magalhaes, M.C. Persegil *Materials Research*, 2002, 5,467.