Poly(methyl acrylate) plus Mesoporous Silica Nanohybrids: Mechanical and Thermophysical Properties

León D. Pérez,[1, 2] Luis F. Giraldo,[1, 2] Witold Brostow, [2] Betty L. López [1]

[1] Grupo Ciencia de los Materiales, Instituto de Química, Universidad de Antioquia, A.A. 1226, Medellín, Colombia; email: blopez@quimbaya.udea.edu.co.
[2] Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Departament of Materials Science and Engineering, University of North Texas, POBox 305310, Denton, TX 76203-5310, USA; email: brostow@unt.edu; website: http://www.unt.edu/LAPOM/

Abstract: A mesoporous silica MCM-48 is used as a reinforcement agent for poly(methyl acrylate) (PMA). Methyl acrylate is introduced into the mesoporous silica that has an interconnected porous structure, allowing monomer diffusion into the pores before the polymerization reaction. In order to improve the silica plus polymer adhesion and to decrease the silica agglomeration, the silanol groups of the silica are functionalized with methyl groups without decreasing significantly the pore size. The silica is characterized by nitrogen adsorption, scanning electronic microscopy (SEM) and infrared (IR) spectroscopy. The nanohybrids so obtained are analyzed by tensile testing, thermogravimetry (TGA), differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA). The highest improvement of mechanical and thermophysical properties is achieved for nanohybrids containing 5 wt. % mesoporous silica. At 10 % silica, agglomeration of the filler takes place and the dispersed phase is less effective in reinforcing the polymer matrix.

Key words: nanohybrid, mesoporous silica, poly(methyl acrylate), mechanical properties, thermophysical properties.

Introduction

The use of fibers and fillers to improve mechanical and thermophysical properties of polymer-based materials (PBMs) constitutes a rapidly growing field [1 - 12]. Among others silica, titanium oxide, zeolites, or carbon nanotubes are used. The filler is typically a stiff material, thus providing a mechanical reinforcement and enhanced thermal stability at elevated temperatures. The type of the reinforcing agent affects the level of properties that can be achieved and there are certain limitations. Thus, Bismarck and coworkers [12] conclude that in hot water environments carbon-fiber reinforced poly(ether ether ketone) can only be used well below the glass transition temperature of the matrix. Sandler and coworkers [10] note that in fine structures, such as spun fibers or microinjection moldings, conventional chopped fibers cannot be physically accommodated while carbon nanotubes can. Among PBMs with reinforcement, nanohybrids seem interesting where the filler or reinforcing phase of the polymer consists of inorganic particles with dimensions < 100 nm; the resulting PBM escapes the traditional classification of materials into inorganic and organic [13]. Given the growing popularity of nanoscale materials, techniques are being

developed by which structures at the nm level can be evaluated, such as nanoindentation [14, 15].

The reinforcement effectiveness depends on the filler chemical and physical properties such as surface area, porosity, morphology, particle size and the interaction between polymer chains and functional groups on the filler. The affinity between the polymer and the filler can be enhanced by a specific reagent, promoting Van der Waals and covalent interactions between them, or else through reactions with functional groups on the filler surface [16, 17]. Thus, the mechanical properties of the composite will depend on the interface interactions and the contact area. It is believed that interfaces behave as an additional reinforcement; this behavior has been shown for silica-reinforced rubber and numerical simulations validate that observation [18]. The interface region is built up by layers of polymeric molecules strongly attached to the silica so that their mobility is lower [19]. According to Gilman [20], thermal degradation is easier when molecules have higher mobility at the interface. Since fillers lower the mobility, they improve the thermal stability of the composite.

Mesoporous silicas are worthwhile fillers for polymers; the pores can be occupied by polymer chains, especially during melt blending [21, 22]. To realize the polymerization inside the silica pores, the pores should be empty; we cannot use solvents or surfactants, and the most suitable method is bulk polymerization. This technique has been used to prepare PMA plus clay nanocomposites before [23]. Then silica particles reinforce the polymer matrix [24 - 26]. In some cases a supercritical fluid is the solvent, apparently helping the growth of the polymer into the pores [27].

We have focused on mesoporous silica MCM-48, prepared as described below, because it presents an interconnected porous structure where the monomers can be trapped. When the polymerization takes place, some polymeric chains grow into the silica, and the interaction of polymer with filler should increase. We have determined mechanical and thermal properties of nanohybrids prepared by polymerization of methyl acrylate inside of the MCM-48 mesoporous silica modified with trimethylchlorosilane.

Characterization of Silica

Figure 1 shows the infrared spectra of the trimethylchlorosilane (TMCS)-modified mesoporous silica compared with the unmodified silica. The modified silica shows the band at 2962 cm^{-1} that indicates the silica has CH_3 groups attached. The intensity at 3442 and 1625cm^{-1} bands of silanol groups is lowered by the modification. Thus, the hydrophobicity is partially reduced but residual silanol groups are still present.

Consider now SEM results, see Figure 2a. The mesoporous silica has a particle size close to 200 nm and also presents some agglomerates smaller than 1 µm. Apparently the agglomerates are present due to the incomplete silylation seen in IR spectra; the OH residual groups can build agglomerates through hydrogen bonding. Figure 2b shows the X-ray diffraction results for silylated mesoporous silica MCM-48. The peak position at 2θ = 2.63° and the high intensity corresponds to mesoporous silica.

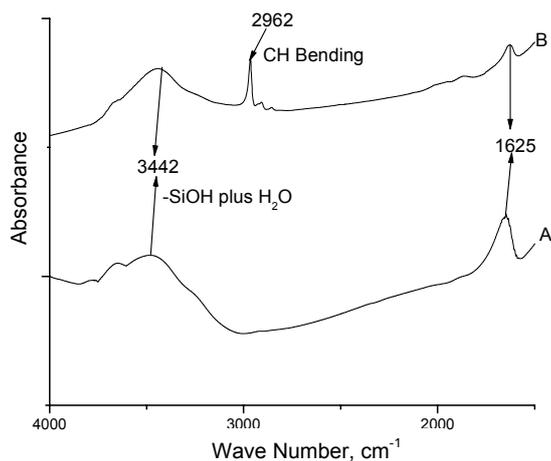**Fig. 1.** Infrared spectra: unmodified mesoporous silica (A); TMCS silylated mesoporous silica (B).
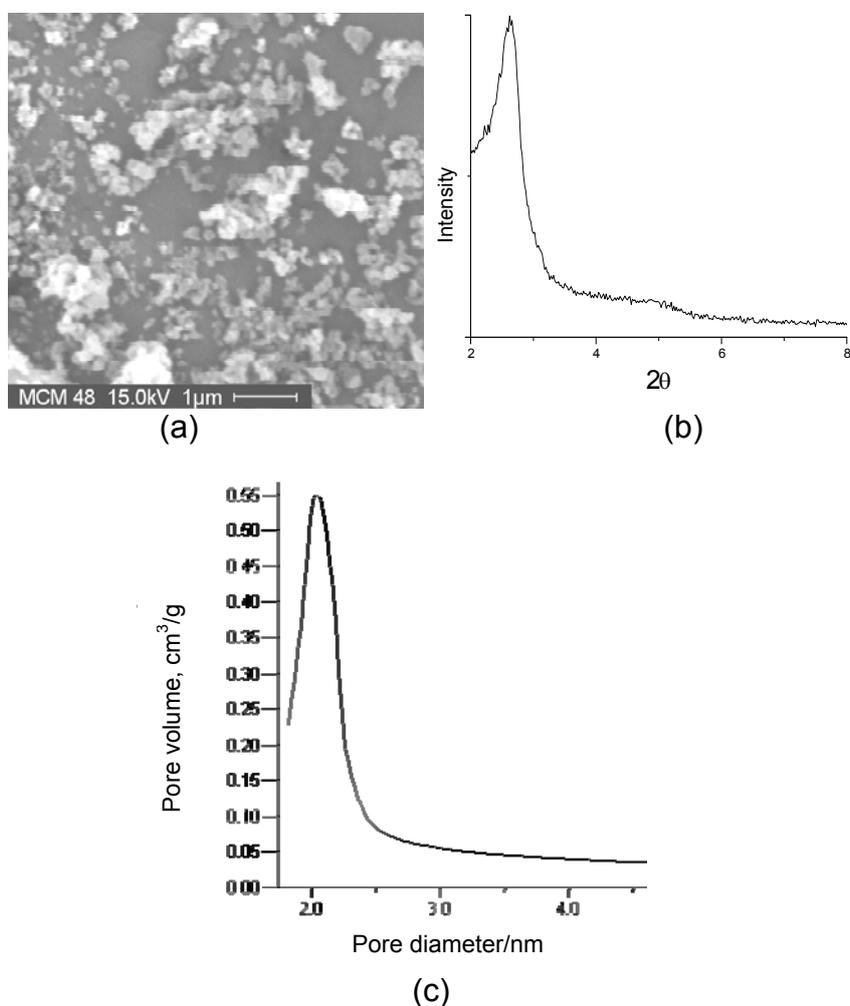

(a)

(b)

(c)

Fig. 2. (a) SEM picture of mesoporous silica MCM-48. (b) X- ray diffraction spectra for silylated mesoporous silica MCM-48. (c) Pore size distribution for MCM-48 mesoporous silica.

Figure 2c shows the pores size distribution for the silica MCM-48. The silica has a BET area of 679 m²/g, BJH pore diameter of 2.2 nm and the specific volume of 0.94 cm³/g. The sharp and narrow pore size distribution indicates that the material presents an organized porous structure.

Characterization of Nanohybrids

-Scanning electron microscopy

SEM images in Figure 3 show the dispersion of silica for PMA/MCM-48 nanohybrids containing 5 % and 10 % silica. The former has few small agglomerates (smaller than 1 μm). In the latter the silica dispersion is less uniform while the agglomerates are larger than 1 μm.
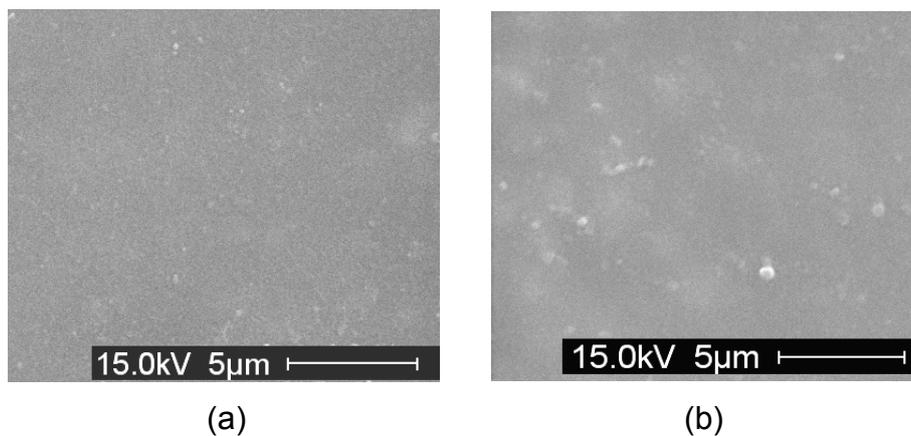

15.0kV 5μm   15.0kV 5μm

(a)   (b)

Fig. 3. Nanohybrid morphology. (a) PMA MCM-48 5, (b) PMA MCM-48 10.

-Thermal Degradation

Figure 4 displays pertinent TGA results. Two degradation temperatures are seen. The first one corresponds to the polymer matrix and the second to the occluded polymer. The hybrid with 5 wt. % silica shows a higher percentage of occluded polymer; this can be due to the better silica dispersion discussed above that allows more polymeric chains to be adsorbed.
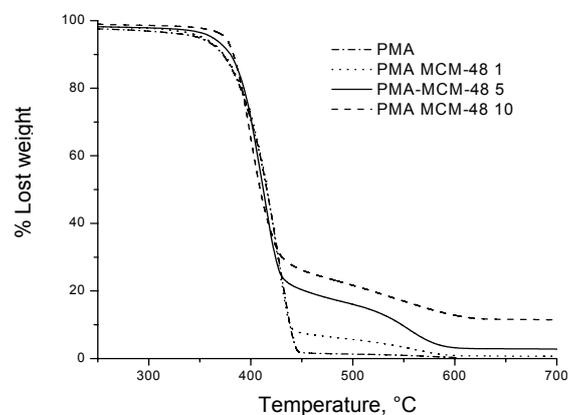

Fig. 4. Thermal degradation of pure PMA and nanohybrids prepared with mesoporous silica.

-DSC characterization

Figure 5 shows DSC thermograms for various silica concentrations. The addition of silica increases the glass transition temperature; apparently silica decreases the overall mobility of the polymeric chains. The largest increase in the glass transition temperature ΔT_g is seen between 0 and 1 % silica. There is a further increase in T_g between 1 and 5 % silica. However, we see a slight decrease of T_g when going from 5 to 10 % silica. We recall the SEM results in Figure 3: there is a better dispersion of the silica phase at 5 %. Thus, agglomeration of silica at 10 % increases slightly the polymer mobility as compared to the nanohybrid with 5 % silica.
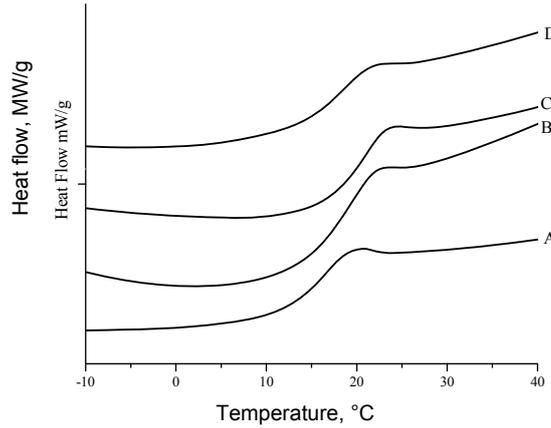

Fig. 5. DSC Thermographs for nanohybrids containing MCM-48: A) pure PMA, B) PMA MCM-48 1, C) PMA MCM-48 5, D) PMA MCM-48 10.

-DMA characterization

For a detailed discussion of the significance of DMA results see Menard [28]. Here we recall that one imposes a sinusoidal stress σ at frequency ν as a function of time t:

$$\sigma(t) = \sigma_0 \sin(2\pi\nu t) \tag{1}$$

This causes the following behavior of the strain ε:

$$\varepsilon(t) = \varepsilon_0 \sin(2\pi\nu t - \delta) \tag{2}$$

Here ∂ represents the lag between elastic and viscous flow response of the material. We have

$$\tan \partial = E''/E' \tag{3}$$

The storage modulus E' represents the solidlike 'face' of viscoelasticity while the loss modulus E'' represents the liquidlike 'face'. Since E'' represents energy dissipation, it is also a measure of the energy converted to heat - important when a mechanical force is applied. Namely, the heat H created is given by

$$H = \pi E'' \varepsilon_0^2 \tag{4}$$

We also recall that brittleness has been defined [29] as

$$B = 1/(\varepsilon_b \cdot E') \tag{5}$$

5

where ε_b is the strain at break in tensile testing. That definition was created since before terms like briitleness were used relying on the intuitive meaning of the word [30 - 32].

Figure 6-1 shows the storage modulus E' versus temperature T obtained by DMA for the hybrids prepared with different compositions of mesoporous silica MCM-48. The interactions of filler plus filler and polymer plus filler are competitive; when strong filler plus filler interactions are present, tight agglomerates are formed and the dispersion is low. The storage modulus values for all nanohybrids are higher than for the PMA. E' for 5 wt. % silica is higher than for 10 wt. % silica. This corroborates the explanation provided above: at 10 % the silica agglomeration occurs, this weakens polymer plus filler interactions; at 5 % better silica dispersion favors the polymer plus filler interactions. The filler dispersion seems the most important parameter affecting the storage modulus in the glassy region.

Table 1 and Figure 6a show E' for the rubbery region. Here the situation is different. E' increases with the silica content up to the highest concentration we have created, the nanohybrid with 10 % silica. However, the E' increase from 5 % to 10 % silica is insignificant, hence 5 % is sufficient for reinforcement purposes.

Figure 6b and Table 1 show also tan ∂ vs. temperature. T_g values in the third column of the Table correspond to the maximum of tan ∂. The highest T_g is seen for 5 % silica; thus the DMA results support those from DSC, and we have already explained above the reason for this behavior. For perspicuity the values of T_g from DSC are listed in the last column of the Table 1.

Tab. 1. DMA and DSC characterization of the nanohybrids.

Sample	T_g/$^{\circ}$C from tan ∂	Max tan ∂	E'/Pa Glassy at -10 $^{\circ}$C	E'/Pa Rubbery at + 25 $^{\circ}$C	T_g/$^{\circ}$C from DSC
PMA	14.6	2.90	$1.93 \cdot 10^9$	$1.7 \cdot 10^6$	14.7
PMA MCM 48 1	16.9	2.83	$2.01 \cdot 10^9$	$3.45 \cdot 10^6$	17.6
PMA MCM 48 5	18.9	2.40	$2.25 \cdot 10^9$	$5.84 \cdot 10^6$	19.4
PMA MCM 48 10	18.5	2.15	$2.15 \cdot 10^9$	$6.2 \cdot 10^6$	17.9

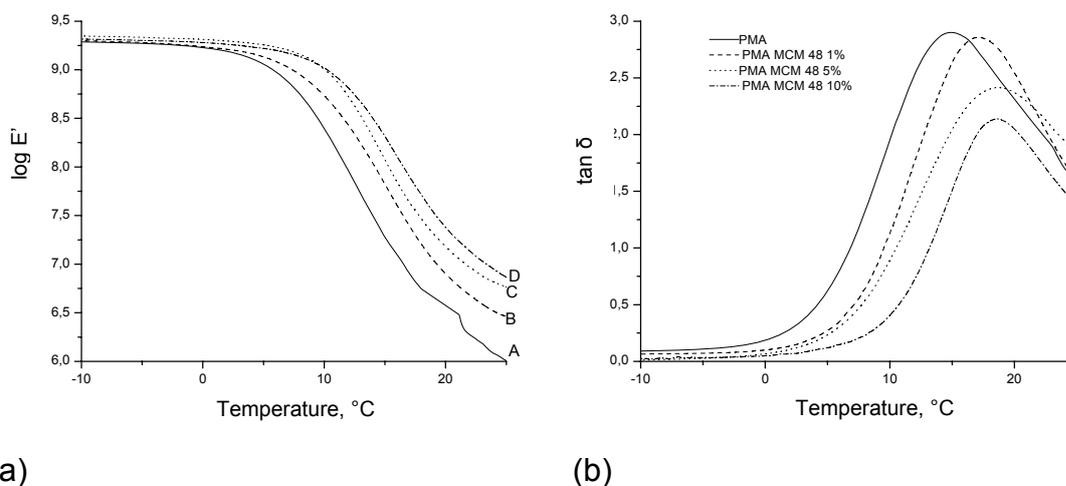(a)   (b)

Fig. 6. (a) DMA results; A) log E' vs. temperature; (b) tan ∂ vs. temperature. Silica contents: A) PMA, B) PMA MCM-48 1, C) PMA MCM-48 5, D) PMA MCM-48 10.

The maximum value of tan ∂ is related to the number of polymeric chains that undergo the transition. In general, the tan ∂ height decreases with increasing silica content - as seen in Figure 6b. The decreasing PMA concentration is reflected in the lower tan ∂ heights.

-Tensile Properties

Table 2 displays the mechanical results for the nanohybrids while Figure 7 shows some of the respective graphs. The incorporation of MCM-48 significantly changes the mechanical performance. We see in Table 2 that an increase in the silica concentration lowers the strain at break – an expected effect since the filler addition increases the stiffness. At the same time and as expected, the stress at break increases upon the stiff filler addition.

Tab. 2. Tensile properties of pure PMA and the nanohybrids.

	Strain/% at break	Stress/MPa at break	Energy/J at break	Stress/MPa at 10 % strain	Stress/MPa at 150 % strain
PMA	269.10	4.1	2.31	0.89	2.30
PMA MCM 48 1%	265.95	6.2	3.00	1.2	3.4
PMA MCM 48 5%	217.36	7.7	5.41	1.7	7.0
PMA MCM48 10%	212.93	7.1	3.85	2.3	5.6

As suggested by Kohls and Beaucage [33], we have determined the stress at a low (10 %) and a high (150 %) deformation. In the former case the stress increases with the filler concentration as seen in Figure 7, first more rapidly and then somewhat more slowly. Thus, the silica filler is doing its job as the reinforcement. At 150 % deformation we observe a maximum in the stress vs. silica concentration curve. Once again, silica better dispersed at 5 % provides more reinforcement than the agglomerated silica at 10 %.
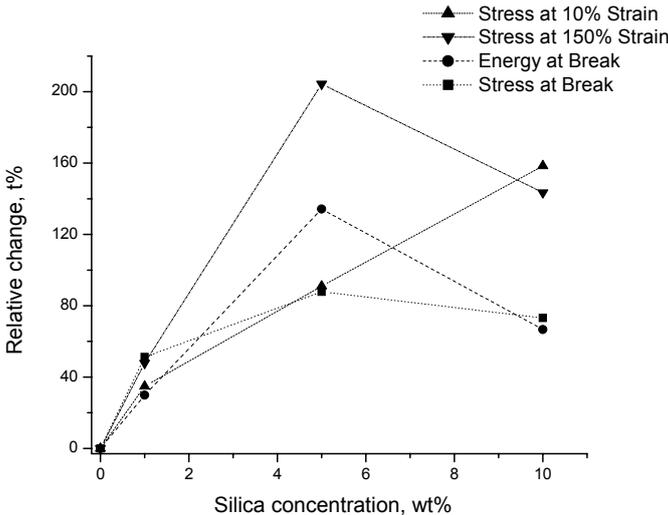

Fig. 7. Relative changes in the tensile properties at different silica concentrations.

The energy at break or toughness, calculated as the area under the stress vs. strain curve, is predicted to be reduced by the addition of filler [24]. This is clearly *not* the

case for our nanohybrids with interconnected porous structure of the inorganic phase. Also for the energy at break, a maximum is observed at 5 % silica, this for the same reason as for other properties we have investigated.

Concluding remarks

In the present work we have found repeatedly how the uniformity of spatial distribution of the dispersed phase and avoidance of agglomeration of the filler helps to provide the reinforcement. In future work we expect to report also on fillers for polymers other than mesoporous silica.

Creation of hybrids by incorporating inorganic fillers into polymers is one of the options in creation of PBMs with improved thermophysical, mechanical or tribological properties. Tribological properties deserve more attention [34], given the gradual replacement of metallic components by polymeric ones. The present approach has been applied to PMA; applying it to thermosets might be worthwhile – also given the large and still increasing range of application of epoxies [35 - 37]. We recall that introduction of a fluoropolymer by blending before curing is a worthwhile option in improving tribological properties of a commercial epoxy [38]. Polymer irradiation is another such option [39 - 42].

Experimental

Reagents

Tetraethyl orthosilicate (TEOS), hydrochloric acid (HCl), sodium hydroxide (NaOH), cethyl trimethylamonium bromide (CTMABr), methyl acrylate (MA), trimethylchlorosilane (TMCS), heptane and α,α'-azoisobutyronitrile (AIBN) were all supplied by Aldrich.

Synthesis and modification of mesoporous silica

Mesoporous silica MCM-48 was prepared according to the procedure described by He [24]: 1 part TEOS, 0.48 NaOH, 0.48 CTAMBr, 55 H_2O. CTMABr was dissolved in the alkali solution; when a clear solution was obtained, TEOS was added, the mixture stirred until a clear and homogeneous solution was obtained again. The solution was put into a autoclave and kept at 100ºC for 3 days, then the material cooled and the pH adjusted to 7 by adding concentrated HCl. The gel was kept at the same temperature for two more days, then the silica filtered, air-dried at room temperature and calcined at 540 ºC for 3 hours.

Silica surface modification: The calcined material was activated at 150°C under vacuum for 2 hours, then the hot material suspended in heptane; the ratio heptane/silica was 8:1. Then TMCS and pyridine were added, with the ratio TMCS/silica = 2, and TMCS/pyridine = 2. The mixture was kept under stirring at 60 ºC for 12 hours, then the solid collected, washed with heptane and then with ethanol and dried at 60 ºC for 24 hours.

Polymer preparation

Methyl acrylate was extracted four times with an alkali solution, washed thoroughly with distilled water, and dried with sodium sulfate.

Bulk polymerization of methyl acrylate: 10.53 mL of methyl acrylate (10 g) were placed into a three-neck flask with 0.025 g AIBN, the flask put into bath at room temperature for 2 hours. Then the temperature was increased up to 70ºC under stirring until a viscous polymer was obtained; then the temperature increased up to 100 ºC and maintained for 14 hours.

Bulk polymerization of methyl acrylate inside of mesoporous silica: nanohybrids were prepared, with 1, 5 and 10 wt % of silica. The amount of silica required for the specified composition was kept in it for 2 hours under vacuum at 150ºC; after cooling the mixture of monomer and initiator was added and the same procedure described above was applied. The samples are represented by symbols showing the silica concentration; thus PMA plus MCM-48 5 means 5 wt. % of silica.

Materials characterization

Nitrogen adsorption**:** The pore size distribution, surface area and pore volume were determined by nitrogen adsorption/desorption isotherms by using a ASAP 2010 Micromeritis equipment.

X-ray diffractometry**:** results were obtained with a Rigaku Miniflex X-ray spectrometer.

Infrared (IR) spectroscopy: The materials before and after the modification were analyzed with a PerkinElmer Spectrum One machine.

Scanning Electron microscopy (SEM): The powder and the polymer films were directly analyzed in a JEOL JSM 5800 using the secondary electron mode.

Thermogravimetric Analysis (TGA): a PerkinElmer TGA-7 was used from 50 to 900 ˚C at the rate of 10 K/min.

Differential Scanning Calorimetry (DSC): a Perkin Elmer Diamond DSC was used; the samples were heated from - 50 to 150 ^{o}C at 20 K/min, kept for 5 minutes at 150 ^{o}C, then cooled to – 50ºC at 100 K/min, then heated again up to 150ºC at 20 K/min. Results from the second heat have been used.

Dynamic mechanical analysis (DMA) characterization: a PerkinElmer DMA-7 machine was used from − 30 to +30 °C, at 5 K/min. The selected mode was film extension, the frequency 1.0 Hz.

Tensile Testing: Type V test probes were prepared by compression molding and analyzed in a tensile machine MTS TEST/5, according to the ASTM D638 standard at 1000 psi, strain speed 50 mm/min, at room temperature (25ºC).

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