Research Article

Incorporation of Nanohybrid Films of Silica into Recycled Polystyrene Matrix

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An alternative for the reutilization of polystyrene waste containers consisting in creating a hybrid material made of SiO_2 nanoparticles embedded in a matrix of recycled polystyrene (PSR) has been developed. Recycled polystyrene functionalized (PSRF) was used to influence the morphological and antifog properties by the sol-gel synthesis of nanohybrid silica. To this end, silica nanoparticles were produced from alkoxide precursors in the presence of recycled polystyrene. The functionalization of this polymeric matrix was with the purpose of uniting in situ carboxyl and silanol groups during the sol-gel process. In this way, opaque or transparent solid substrates can be obtained, with each of these endowed with optical conditions that depend on the amount of reactants employed to prepare each nanohybrid specimen. The nanohybrids were labelled as SiO_2/PSR (HPSR) and SiO_2/PSRF (HPSRF) and their properties were then compared to those of commercial polystyrene (PS). All the prepared samples were used for coating glass substrates. The hydrophobicity of the resultant coatings was determined through contact angle measurement. The nanohybrid materials were characterized by FT-IR and ^{1}H-NMR techniques. Additionally, TGA and SEM were employed to determine their thermal and textural properties.

1. Introduction

In the recent decades, the development of new plastics has been a great challenge for the scientific and technological community, because of the harmful influence of plastics on the environment and the accumulation of polymeric materials. Additionally, the degradation time of these materials is very long and nonrenewable resources have been declining in tandem with the growth of plastics engineering [1]. This situation has forced society to diminish the use of plastic materials in the immediate future and so, now, these substances must be recycled [2].

Inorganic-organic hybrids [3, 4] are rapidly emerging as alternatives to traditional antifog, self-cleaning, and UV protected materials, since they combine the chemical and mechanical properties of both inorganic and organic components [5–7]. In another sense, human health protection and environmental remediation have been constantly deteriorated. In the following work we propose an application for reusing polystyrene, which is commonly used for transporting fast food disposables, food trays, and beverage containers and as a general packaging product.

Polymers can be reused as intelligent window coatings with water repellent properties, antifogging agents, UV protectors, or self-cleaning products. It is known that polymers such as HDPE, LDPE, PS, or PP are used for these applications; the PS surface can be modified with a hydrophobic group to improve these characteristics [8–10]. Also, nano- or

microsilica particles incorporated into the polymer matrix combine the useful polystyrene features. The incorporation of these SiO_2 particles can be performed via the sol-gel method [11]; this process allows a better control of the hydrophobic coating properties. The initial conditions can be manipulated to improve the mechanical, optical, thermal, antifog, and other properties of new materials [12, 13].

Coatings are used to indicate the deposition of a material on the surface of another one; the purpose is to provide on the covered area some characteristic that the material has not yet attained by itself [14]. Organic coatings are those applied in liquid state form on a surface after drying and usually result in a continuous solid covering layer. The drying processes involve chemical reactions or simple evaporation of the solvent, such as in paints, lacquers, enamels, and varnishes [11]. The effect of the coating is to provide some type of insulation, protection by adding a surface or interfacial property, while keeping the original properties of the covered material [15, 16].

Inorganic-organic hybrid composites are rapidly emerging as alternatives to traditional self-cleaning, antifog, or UV protection materials [17] since coatings alone usually exhibit no sufficient wear protection properties due to their low densities, thickness the wear and stress resistance of lining materials, but they can be improved with the incorporation of new hybrid composites.

There is particular interest in the functionalized polymers from the technological and scientific points of view; therefore, the inclusion of nanoparticles to improve the properties of polymers or resins [17] and even recycled polymers is a highly appreciated alternative.

In this work hybrid materials were prepared by incorporating silica nanoparticles (SiO_2) into recycled polystyrene matrices (PSR). Recycled polystyrene was functionalized (PSRF) by using abietic acid. The functionalization of the recycled polymeric matrix has the purpose of uniting carboxyl with silanol groups in situ during the sol-gel process. Infrared and ^{1}H-NMR spectroscopies were used to verify the functionalization of polystyrene and incorporation into it of silica particles. The prepared nanohybrids were labeled as SiO_2/PSR (HPSR) and SiO_2/PSRF (HPSRF), respectively, and then were compared to commercial crystal polystyrene (PS) and their corresponding hybrids.

2. Experimental Procedure

2.1. Materials and Methods. The materials used in this work were (a) tetraethyl orthosilicate (TEOS) (Aldrich Chem.), (b) CO_2-free triple distilled water, (c) toluene (reactive grade) (J. T. Baker), (d) polystyrene containers that were used as the recycled polymer, (e) commercial crystal polystyrene (Resirene Co.), (f) benzoyl peroxide (Sigma-Aldrich 99%), and (g) abietic acid (Sigma-Aldrich 70%).

2.2. Functionalization of Polystyrene (Commercial and Recycled). The functionalization of commercial or recycled polystyrene was made from a solution of toluene subjected to mechanical stirring. In order to prepare the PSF or PSRF

substrates, abietic acid (AA) and benzoyl peroxide employed as initiator (i) (i.e., an i/AA molar ratio of 0.376) were added to the PS or PSR materials and refluxed for 1 h under mechanical stirring. The method of synthesis and the preparation conditions for preparing the modified polystyrene (PSF) materials have been described elsewhere [18].

2.3. Hybrid Materials Preparation. The PS-SiO_2, PSR-SiO_2, PSF-SiO_2, and PSRF-SiO_2 hybrid materials were prepared from solutions of nonfunctionalized or functionalized recycled polystyrene (PSR or PSRF, resp.). Previously, the PS or PSF commercial solids were dissolved in toluene. TEOS was dissolved in another glass beaker containing a volume of toluene equal to the quantity employed to prepare the above PS or PSR solutions. Afterward, PS, PSF, PSR, or PSRF solutions were added sequentially to the beaker containing the TEOS/toluene mixture. The reactant mixture was kept under stirring and refluxing conditions for 2 h. The TEOS molar ratios employed in the above preparations corresponded to 2.5 and 6.3×10^{-5} mol of initiator and were added to the PS and PSR polymers.

2.4. Substrates Coating. Clean glass plates of 4×1 in. and $4.8 \times 10^{-2} \pm 0.00005$ in. thickness were coated with PS, PSF, PSR, PSRF, HPS, HPSF, HPSR, and HPSRF films, respectively. The surface of each glass plate was immersed (at a rate of 5 mms^{-1}) inside the polymers solutions under study.

2.5. Characterization Techniques. The characterization of the obtained hybrid materials was carried out by FT-IR spectroscopy. Infrared analysis (FT-IR) was performed on a Bruker Vector 33 spectrometer, by using the transmittance technique. The samples were prepared as thin films.

The ^{1}H-NMR spectra were recorded on a Bruker Avance 400 spectrometer, with a BBI 400 MHz SB 5 mm with z-gradient probe and TOPSPIN 2.1 software; all samples were previously dissolved in $CDCl_3$ at room temperature.

In turn, TGA/DTA analyses were carried out in a DuPont 951 instrument operated in an air atmosphere at a rate of 10 K min^{-1}.

The contact angle was measured on the surface of the coated material that was prepared on the glass surface. One drop of water ($1 \mu L$) was placed on the surface and then a photograph was taken of the solid-liquid interface with a camera Cannon Power Shot Sx30 IS. These images were transformed to gray scale and analyzed with the MatLab 6 program, version 6.0.0.88, and five measurements of each sample were made.

Scanning Electron Microscopy (SEM) observations were carried out in a Jeol JSM-5200 scanning microscope. The samples were coated with carbon by vacuum evaporation.

3. Results and Discussion

PS, PSF, HPS, and HPSF FT-IR spectra are shown in Figures 1 and 2, in the ranges of 3300 to 2600 cm^{-1} and 2000 to 400 cm^{-1}, respectively.
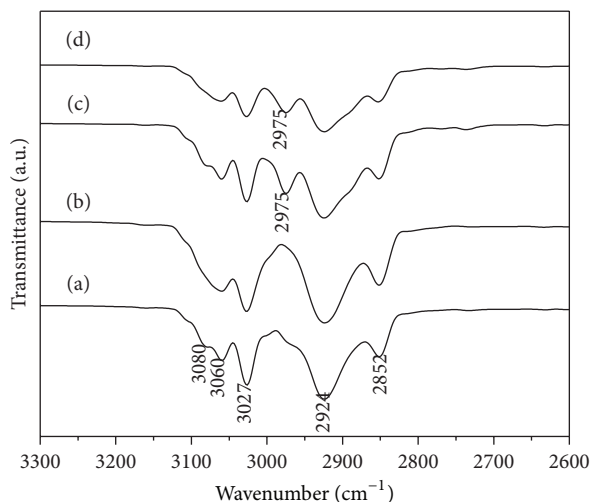
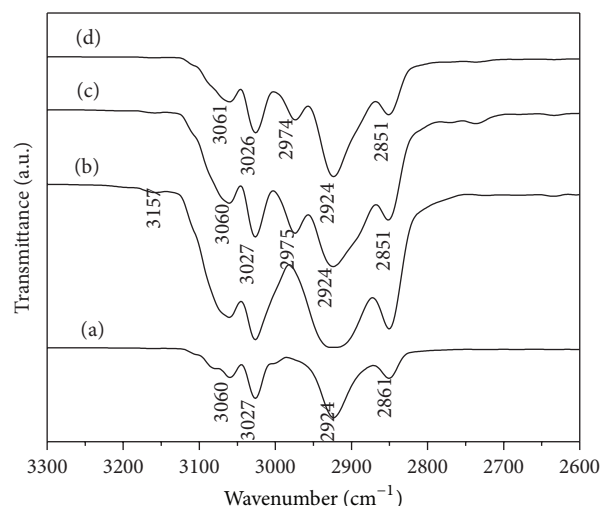FIGURE 1: FT-IR spectra in the range of 3300–2600 cm^{-1} of (a) PS, (b) PS-F, (c) HPS, and (d) HPSF materials.

FIGURE 2: FT-IR spectra in the range of 2000–400 cm^{-1} for (a) PS, (b) PS-F, (c) HPS, and (d) HPSF substrates.

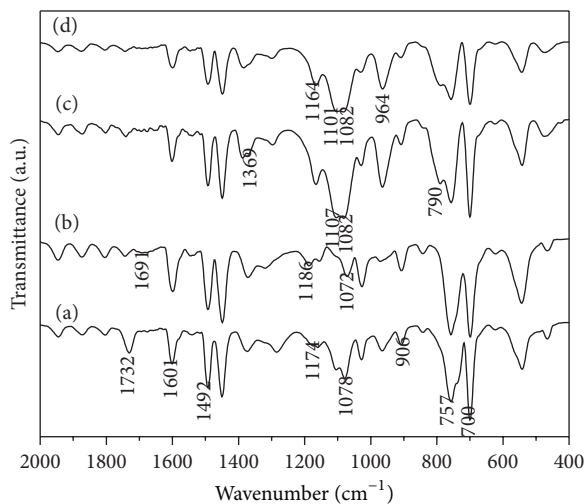FIGURE 3: FT-IR spectra in the range of 3300–2600 cm^{-1} of (a) PSR, (b) PSRF, (c) HPSR, and (d) HPSRF materials.

Polystyrene (PS) presents characteristic absorption bands at 3080, 3060, and 3027 cm^{-1} corresponding to aromatic CH groups; likewise signals from the aromatic hydrogen present in ^{1}H-NMR spectra of polystyrene and recycled polystyrene (PSR) appear between 6 and 7.5 ppm (Figures 5(a) and 6(a)). Polystyrene presents bands at 2924 and 2852 cm^{-1} proceeding from CH$_2$ asymmetric and symmetric vibration, respectively [19] (Figure 1(a)). On the other hand, the signals appearing at 2.4 ppm in Figures 5(a) and 6(a) correspond to aliphatic hydrogen while that of the region between 1 and 2.3 ppm corresponds to methine (CH) and methylene groups (CH$_2$) [20].

Figure 2(a) shows aromatic ring absorption bands at 1601, 1492, and 700 cm^{-1} [19].

The spectrum of the functionalized polystyrene (PSF) containing abietic acid (Figure 1(b)) shows a broadband in the range of 3100 to 3000 cm^{-1} due to the overlapping of bands proceeding from aromatic groups.

The presence of abietic acid was identified in Figure 2(b) through the signal of carboxyl group (C=O) in 1691 cm^{-1}, aromatic rings at 1186 cm^{-1}, and CH bonds at 842 cm^{-1}. The spectrum also shows overlapping bands of PS aliphatic groups and of the initiator in the range of 720 to 800 cm^{-1} (Figure 2(b)).

Figure 1(c) shows the hybrid polystyrene (HPS) FT-IR spectrum. Vibration of the asymmetric methyl groups (CH$_3$) was identified at 2975 cm^{-1} and symmetric vibration of the CH$_3$ groups appeared in the range of 2960 to 2860 cm^{-1}. Absorption bands at 1107 and 790 cm^{-1} (Figure 2(c)) correspond to Si-O-Si asymmetric and symmetric vibrations, respectively [21, 22].

The hybrid materials prepared from the recycled polystyrene (HPSR) present the same absorption bands (Figures 3(c) and 4(c)).

The FT-IR spectrum of functionalized hybrid polystyrene (HPSF) shows a broadband at the range of 3200 to 2800 cm^{-1} (Figure 1(d)) which is associated with the overlapping of the bands due to the aromatic ring present in PS and abietic acid, as well as by the absorption bands of CH$_2$ group at 2925 and 2852 cm^{-1} [19].

The presence of the Si-O-Si group was identified at 1101 and 964 cm^{-1} (Figure 2(d)), while the absorption band of the C=O group of abietic acid disappears; this same behavior was observed for the functionalized hybrid of recycled polystyrene (HPSRF) in Figures 3(c) and 4(c) [21].

Figures 3 and 4 show the PSR, PSFR, HPSR, and HPSRF spectra in a range of 3300 to 2600 cm^{-1} and 2000 to 400 cm^{-1}, respectively. Recycled polystyrene (PSR) presents the same characteristic bands of polystyrene (Figures 3(a) and 4(a)). In the respective ^{1}H-NMR spectrum, a band appears at 5.4 ppm, which is associated with other compounds that are present in the recycled material (Figure 6(a)).
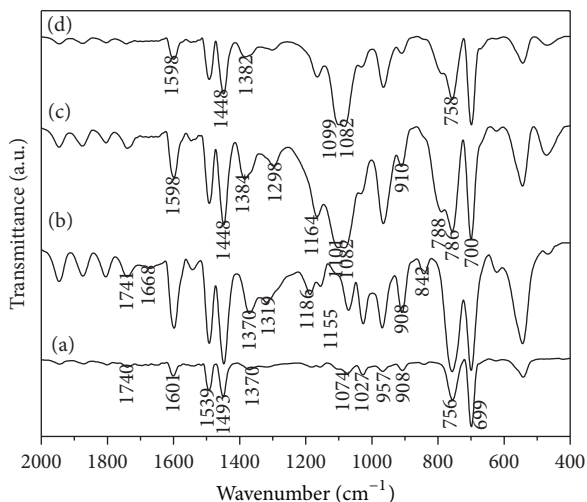
FIGURE 4: FT-IR spectra in the range of 2000–400 cm^{-1} of (a) PSR, (b) PSRF, (c) HPSR, and (d) HPSRF samples.
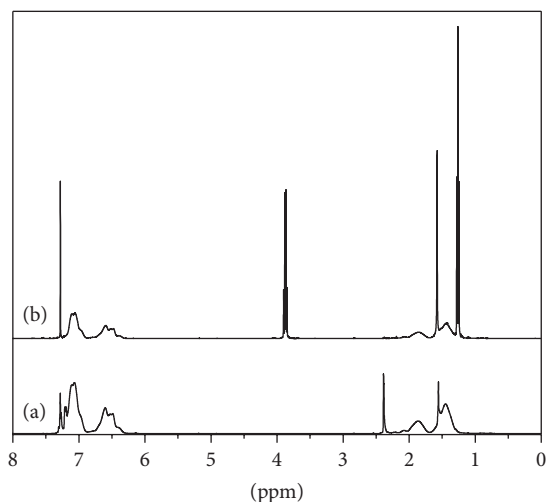
TABLE 1: Degradation and glass transition temperatures and contact angle measurements of the studied materials.

Material	Degradation temperature (°C)	Glass transition temperature Tg (°C)	Contact angle on glass
PS	299.19	54.36	85.9623°
PSR	346.55	59.17	82.0304°
PSF	308.04	62.07	77.4712°
PSRF	339.24	59.72	77.4712°
HPS	221.45	56.08	81.5966°
HPSR	318.59	57.60	87.6863°
HPSF	338.05	76.99	88.1720°
HPSRF	325.26	65.24	89.2098°
Substrate			37.6262°

FIGURE 5: ^{1}H-NMR spectra of (a) PS and (b) HPSF materials.
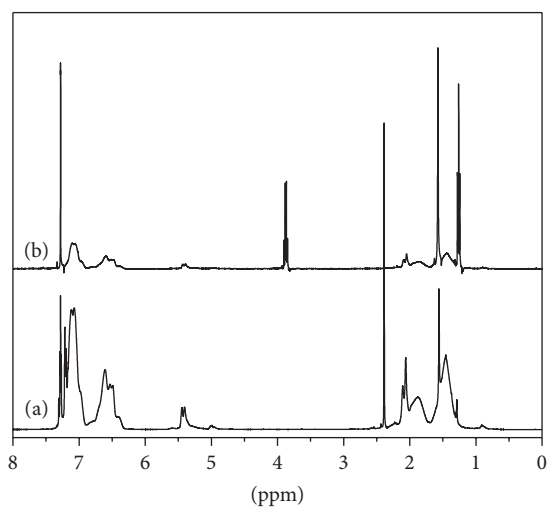
FIGURE 6: ^{1}H-NMR spectra of (a) PSR and (b) HPSRF materials.

Deformations in the ranges of 2850 to 2980 cm^{-1} and 2850 to 2980 cm^{-1} in the FT-IR spectrum of functionalized recycled polystyrene (PSRF) were found (Figure 3(b)). These deformation bands can be associated with the presence of abietic acid. The signals located at 1688 and 1319 cm^{-1} correspond to carboxyl group (Figure 4(b)).

Figures 5(b) and 6(b) show the ^{1}H-NMR spectra of HPSF and HPSRF, respectively. TEOS signals appear at 3.8 ppm and 1.25 ppm for methylene and methyl groups, respectively [CH$_2$(q) and CH$_3$(t)] [20].

In both spectra, it is not possible to distinguish abietic acid signals due to the overlap between the aliphatic signals of polystyrenes (PS and PSR). On the other hand, the signals originally located at 2.4 ppm in PS and PSR spectra disappear altogether, thus suggesting an interaction between the functionalized polymers and TEOS.

The TGA and DSC results of these materials show an increase in the amount of silica and functionalization of the surface improve the thermal stability of these hybrid materials. The glass transition temperature (Tg) of the hybrid materials increases slightly with the functionalization and amount of silica particles; see Table 1.

The hydrophobicity of the coatings was evaluated by measurement of the contact angle, while establishing the following criteria for having a hydrophilic surface <40° and for an acceptable hydrophobic surface >70° [14].

The silica nanoparticles incorporated into the polystyrene matrix and combined with the features of the abietic acid allowed obtaining better hydrophobic properties. One manifestation of this hydrophobic surface is the contact angle, which was rather similar in value for the functionalized hybrid materials. All the obtained hybrid materials have a contact angle >80°. The hybrids of functionalized polystyrene films present an increased contact angle if compared to PS and PSR. This is possible due to the presence of abietic acid, which is an amphiphilic, that is, hydrophobic and hydrophilic, compound and due to the presence of silica particles in the hybrid materials. However, no significant changes in contact angle were observed (Table 1).
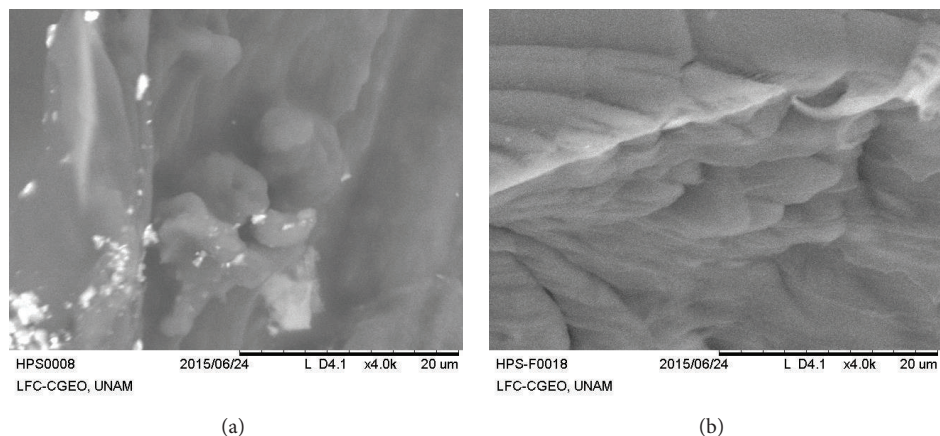
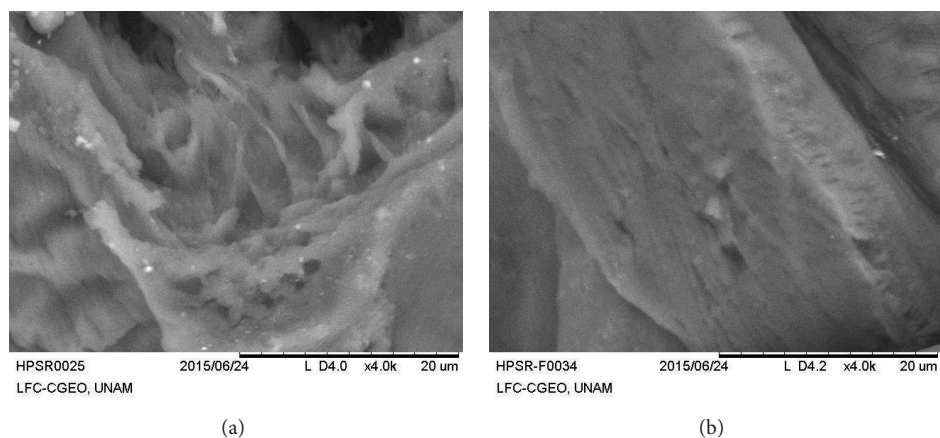FIGURE 7: SEM photographs of (a) HPS and (b) HPSF.

FIGURE 8: SEM photographs of (a) HPSR and (b) HPSRF.

In order to know the homogeneity related to the distribution of silica particles on the surface of the hybrid materials, SEM photographs were taken. Figure 7(a) shows aggregates of silica particles on HPS, which indicates that the sample is not homogenous; in the case of HPSF (Figure 7(b)), this sample presents a homogenous surface, thus suggesting an interaction existing between TEOS and functionalized polystyrene.

Hybrid materials micrographs of recycled polystyrene (Figure 8(b)) present a better homogeneity between silica particles and PSR. This suggests that the presence of abietic acid allows silica particles to be dispersed in the polymer matrix, then forming a free surface of aggregates. HPSR depicts smaller aggregates than HPS (Figures 7(a) and 8(a)).

The homogeneous repartition of silica particles is important since it determines the visual transparency or opacity of the final films to finally apply these hybrids as coatings [7].

4. Conclusions

Hybrid materials were successfully prepared from recycled polystyrene matrices by introducing silica particles to the polymer matrix by the sol-gel method. Carboxyl groups were identified in the functionalized materials (PSF and PSRF), although this species is absent in the functionalized hybrids (HPSF and HPSRF), thus suggesting that there exists an interaction between carboxyl group and SiO_2. ^{1}H-NMR analysis shows the presence of other compounds in PSR, which is attributed to recycled material; however, this did not affect the preparation process and neither the hydrophobicity nor the homogeneity properties of functionalized hybrids.

Hybrids of PS and PSR presented segregation of the silica particles on the material surface, while the functionalized hybrids (HPSF and HPSRF) showed a homogeneous surface, thus improving the visual transparency of the coatings. Also, vitreous temperature (Tg) was increased in these materials and the contact angles on the surface of recycled polystyrene were very similar to those found in commercial polystyrene samples.

The properties of recycled polystyrene analyzed in this work are comparable to those ascribed to commercial polystyrene with the possibility that these materials can be used as hydrophobic coatings. Therefore, this study proposes

a new alternative to the use of recycled polystyrene matrices based on the approach presented.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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