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Rice husk as bio-source of silica: preparation and characterization of PLA-silica bio-composites

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Abstract

Silica powder has been extracted from rice husk, employing a simple extraction procedure for preparing poly(lactic acid) bio-composites with differ filler contents (namely, 5, 10, 20 and 30 wt.-%). These materials have been obtained through a semi-industrial process of extrusion. The thermal, mechanical and morphological properties have been investigated. In spite of a broad distribution of silica particle size, the prepared bio-composites have exhibited improved storage modulus and reduced oxygen permeabilities. The collected values at 10 and 30 wt.-% have been compared with those of homologous samples prepared using a commercial silica. Two micro-mechanical models (Voigt and Halpin-Tsai) have been used to fit the mechanical data, as well. Finally, an economic analysis of material and energetic costs has been performed on samples containing silica from rice husk in order to establish if the proposed process is sustainable or advantageous.

Keywords: rice husk; PLA; silica; bio-composites; mechanical properties.

1. Introduction

Rice husk (RH) is an agricultural by-product abundantly available: indeed, its accounts is one in five of the annual worldwide rice production. The yearly global paddy production has been estimated in 729 million tons for 2012, which implies more than 150 million tons of RH production, on the basis of the data published by Food and Agriculture Organization (FAO) of the United Nations in “Rice Market Monitor” report [1]. Although RH has been already employed in different fields (namely, as bio-fertilizer, as material for animal husbandry, as absorbent and building material or pest control agent [2]), it is still often considered a waste product of rice milling, and thus often burned in open air or dumped on wasteland.

Furthermore, it is well-known that RH can be also used as a renewable fuel in cogenerating plants, considering its high calorific value (4012 Kcal/kg) [3]. Indeed, during its combustion, about 20-25 wt.-% of rice husk ash (RHA), containing more than 90% silica, with traces of other metal oxides, is produced [4].

In the present scenario, many researchers have focused their efforts on the possible uses of RH and RHA, considering their abundance and cheap cost as industrial wastes. RH main components are cellulose (38.3%), hemicellulose (31.6%), lignin (11.8%) and silica (18.3%) [5], respectively. Due to its high content, different extraction procedures of cellulose from RH [6,7] and rice straw [8] have been explored. On the other hand, also the abundant presence of silica is judged very interesting and useful for a possible industrial exploitation. Several reports on the extraction of silica from RH have been published in the literature [9–11]. As an example, Real et al. [12] found a homogeneous size distribution of nanometric silica particles by burning RH in 873–1073K range in a pure oxygen atmosphere. In addition, Della et al. [13] observed that active silica with a high specific area can be produced from RHA after heat-treating at 973K in air. Alternatively, Kalapathy et al. [14] and Kamath and Proctor [15] proposed a new route for producing silica, suspending RH in sodium hydroxide and then precipitating it with an acid for extracting a silica gel.

For the arising interest in the environmental pollution aspects and necessity to conserve energy and material resources, the use of RHA and derived silica in different applications (namely, fillers in cements, fertilizers, and catalyst carriers) has been encouraged [16-19]. Furthermore, such silica has proven to be a good filler for different polymer matrices, as well [20-29]. As an example, Fuad et al., [25] prepared polypropylene-based composites containing silica from RHA and assessed the resulting properties. Silica from RH has been also employed for preparing high density polyethylene (HDPE)-based composites; indeed, Panthapulakkal et al. [26]; Yao et al. [29] and Ayswarya et al. [21] have shown the twofold advantages of reducing the pollution and modifying the properties of HDPE by a cost effective and reliable method. Main polymers compounded with silica from RH are usually polyolefins or natural rubbers. Only recently, some attempts for poly(lactic acid) - PLA - have been published [30-31] with particular attention to the effect of silica on its thermal and mechanical properties. Indeed, these features together with the high oxygen permeability represent the main drawbacks of PLA, beyond its high price: in comparison with polymers commonly used in packaging, its price strongly limits an industrial exploitation.

Thus, the use of a cheap filler like neat RH or silica (better if derived from RH) may be extremely advantageous, in particular, if an economical and sustainable process if foreseen, notwithstanding the environmental impact. To the best of our knowledge, no one studied and published a scientific paper on the use of silica from RH as filler for poly(lactic acid), PLA, although it represents the most common bio-based and compostable material, currently employed in food packaging.

Therefore, aim of the present manuscript was to prepare composites consisting of PLA and silica derived from RH with enhanced performances through an economical and sustainable process, by using an industrial technology, like extrusion, or easily scaling-up, like water heating. In addition, the mechanical and permeability properties of some of these materials (10 and 30 wt.-%) have been compared with those of other samples containing a commercial silica.

With this purpose, a first exploratory economic analysis of material and energetic costs has been also carried out, and the resulting data are discussed at the end of the manuscript. This raw analysis could be the basis for future fine improvements.

2. Material and methods

2.1 Materials

Poly(lactic acid) (3051D grade, MFI=10-25 g/10min, relative viscosity=3.0-3.5 from manufacturer data sheet) and rise husk as by-products were kindly supplied by NatureWorks LLC and by S.P. S.p.A., respectively. A commercial silica, namely SIDISTAR® T120 purchased from Elkem (especially designed for polymer applications and based on a spherically-shaped amorphous silicon dioxide with an average primary particle size of 150 nm) was used for preparing some samples as comparison.

2.2 Silica extraction from RH

In a typical experiment, 40 g of milled RH were placed in a becher containing 386 g of distilled water and 14 g of sulfuric acid under stirring for 3 h at 80°C. Such operation was used as previous step to a further calcination in order to prevent the formation of black particles due to the presence of impurities, such as potassium as reported by Krishnarao et al. [32]. The solid residue was separated by filtration, purified in deionized water and dried. Subsequently, the residue was calcined in a muffle furnace at 800°C for 1 h to obtain 15% of the original material weight as silica.

Figure 1 shows a picture of the original material (namely, RH), silica with and without previous treatment in sulfuric acid (**Figures 1a, 1b** and **1c**, respectively).

2.3 PLA-silica-based bio-composite preparation

PLA was dried at 80°C for 6 h in a vacuum convection oven before extrusion, reaching <200 ppm of water content, assessed by Karl-Fisher titration. Analogously, both extracted and commercial silica were dried before the extrusion in an oven at 200°C for 3 h, as well.

PLA-based silica composites with different filler content (namely, 5, 10, 20 and 30 wt.-% for extracted and 10 and 30 wt.-% for commercial one, respectively) were melt blended using a co-rotating twin screw extruder LEISTRITZ ZSE 18 / 40 D (diameters). The screw speed was fixed at 100 rpm. The heating temperature was set from 175 to 165°C into the eight thermo-stated barrel blocks (as reported in **Figure 2**) and the melt temperature was measured to be 195°C. Two gravimetric feeders were used: namely, the main hopper for the polymer was placed at the beginning of the screw and the second one (side feeder) for the filler after 17-18 D. Close to screw end, corresponding to 32-33 D, a degassing hole in the barrel connected to a vacuum pump was present. The total extrusion flow rate was fixed at 2 kg/h. The used screw profile is reported to **Figure 2**.

Hereafter, the samples will be coded on the basis of their nominal compositions and filler origin: as two examples, PLA10S and PLA10SIDI refer to the bio-composite nominally loaded with 10 wt.-% of extracted or commercial silica, respectively.

Pellets obtained by extrusion were dried at 80°C for 6 h in a vacuum convection oven before the preparation of suitable specimens for dynamic-mechanical thermal (DMTA) and stress-strain analyses, and oxygen permeability tests (OP).

The samples for DMT and OP tests (60x60x1 mm^3 and 100x100x0.2 mm^3 specimens, respectively) were prepared by using a hot compression molding press at 180°C for 3 min (pressure of 5 MPa).

The samples for stress-strain analyses (5B type specimens according to the standard ISO527) were prepared by injection molding using a Babyplast 6/10P machine (200°C of barrel temperature and 130 bar of injection pressure).

2.4 Characterization techniques

The chemical structure of RH and silica was evaluated by Attenuated Total Reflectance (ATR)-infrared spectroscopy (FTIR). ATR spectra were recorded at room temperature in 4000-600 cm^{-1} range (16 scans and 4 cm^{-1} resolution), using a Frontier FT-IR/FIR spectrophotometer, equipped with a diamond crystal.

The surface morphology of the fillers and bio-composites was studied using a LEO-1450VP Scanning Electron Microscope (beam voltage: 20 kV); a X-ray probe (INCA Energy Oxford, Cu-Kα X-ray source, k=1.540562 Å) was used to perform elemental analysis. The samples were obtained fracturing 1 mm thick films in liquid nitrogen (5x1 mm^2). These pieces were pinned up to conductive adhesive tapes and gold-metallized. Powders of RH and extracted silica (5x5 mm^2) were metallized with gold, as well.

A measurement of silica particle sizes (at 90 degree scattering angle) was performed using a Dynamic Light Scattering apparatus (Malvern Zetasiser Nano-S90 model).

Thermogravimetric Analysis (TGA) was performed placing samples (ca. 10 mg) in open alumina pans, by using a Q500 TA Instruments analyser, from 50 to 800°C at 10°C/min with an air flow of 60 ml/min. The data collected were T_{max} (temperature at maximum rate of weight loss) and final residue at 800°C.

Dynamic-mechanical thermal experiments (DMTA) were performed using a DMA Q800 TA Instruments with tension film clamp. The experimental conditions were: temperature range from 30 to 120 ºC, heating rate of 3 ºC/min, 1 Hz of frequency and 0.05% of oscillation amplitude in strain-controlled mode. In addition, measurements in isothermal conditions at 30°C were carried out.

Tensile tests were performed at room temperature (23±1°C) by using a Zwick Roell Z100 machine, following the ISO 527 standard, under a loading cell of 5 kN and a rate of 1 mm/min. By this first step, the tensile modulus was calculated; subsequently, the rate was increased up to 5mm/min till the specimen breaking.

Six specimens were used for each formulation and the average values and corresponding standard deviations were calculated. These tests provided the Young's modulus values (E), elongation at break (ε) and maximum tensile strength (σ) of the bio-composites.

Prior to mechanical tests, all specimens were conditioned at 23±1°C and 50% relative humidity in a climatic chamber for 48 h.

Oxygen permeability (OP) was measured by using a Multiperm ExtraSolution instrument. The experimental conditions were set at 23°C and 65% relative humidity, with an initial conditioning time of 4 h. The end of the test was established when the collected data reached an oxygen transmission rate (OTR) accuracy of 0.5%. OTR value was automatically given by instrument on the basis of the atmospheric pressure depending on weather conditions. OP was calculated following the **Equation (1)**, after measuring film thickness by a micrometer device.

$$OTR = \frac{volume\ O_2}{area * day * pressure}$$

$$OP = OTR * film \text{ thickness}$$

Equation (1)

2.5 Mechanical data analysis

DMT and stress-strain analyses were employed to mechanically characterize the samples containing both extracted and commercial silica in order to:

i) assess the effect of filler content on PLA storage modulus in 30-120°C range;

ii) assess the effect of filler content on PLA Young's modulus, elongation at break and maximum tensile strength.

As already described in our previous study [33], models of Voigt (**Equation (2)**) and Halpin-Tsai (**Equation (3)**) can be used to assess the filler modulus.

$$E_c = \phi_m E_m + \phi_f E_f$$

Equation (2)

$$\frac{E_c}{E_m} = \frac{1 + 2\eta\phi_f}{1 - \eta\phi_f}$$

$$\eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + 2}$$

Equation (3)

where E_c, E_m and E_f are composite, matrix and filler moduli, respectively, and ϕ_m and ϕ_f the corresponding volumetric fractions.

For the application of these micro-mechanical models, it is necessary to know the volumetric fractions, and thus the silica real content and density within PLA composites. In order to assess silica density, Archimede's law was exploited, performing weight measurements in air and water and estimating the silica real content by TGA final residues. Subsequently, the found density values were used for calculating the volumetric fractions (ϕ) required by micro-mechanical models, from the weight fractions, once again estimated as TGA final residues.

Finally, the best fitting line of the experimental modulus values of bio-composites was calculated using the two micro-mechanical models cited above; by this way, also the silica modulus was assessed.

2.6 Evaluation of filler-matrix interactions

The effect of polymer-filler interactions can be quantitatively described by using Pukanszky's model for particle-based composites, as described in **Equations (4)** and **(5)** [34]. More specifically, **Equation (5)** derived from **Equation (4)** and allows to investigate a linear relationship existing between the natural logarithm of reduced yield stress σ_{red} (defined as follows) and the filler content [35,36].

$$\sigma_c = \sigma_m \frac{1-\phi_f}{1+2.5\phi_f} \exp\left(B\phi_f\right)$$

Equation (4)

$$log(\sigma_{red}) = log\frac{\sigma_c\left(1+2.5\phi_f\right)}{\sigma_m\left(1-\phi_f\right)} = B\phi_f$$

Equation (5)

where σ_c and σ_m are the yield stresses of composite and matrix, respectively; B is a term corresponding to the load carrying capability of the filler and depends on filler-matrix interactions; ϕ_f is the filler volumetric fraction within polymer matrix (the same already adopted in Voigt and Halpin-Tsai models).

In our manuscript, such model was used for assessing PLA-silica interactions and for establishing if some differences occur in relation to the silica type (namely, extracted or commercial silica).

3. Results and Discussion

3.1 Silica characterization

Infrared spectroscopy provided suitable information on the chemical structure of the original RH and extracted silica: their ATR spectra are reported in **Figure 3**.

As far as RH is concerned, numerous peaks are evident: in particular, a broad band between 3750 and 2800 cm^{-1} (centered at 3374 cm^{-1}) and a peak at 1542 cm^{-1} can be assigned to the O-H stretching and bending vibrations of adsorbed water, respectively. The most intense adsorption peaks are located at 1047 and 800 cm^{-1} that can be ascribed to the presence of silica (Si-O-Si stretching and bending vibrations) [37]. The other peaks can be referred to cellulose, hemicellulose and lignin, the main components of RH, as already described in the Introduction [5]. Among these peaks, it is possible to discriminate the contribution of each component, even though, most of them are ascribed to cellulose and hemicellulose (namely, ν(OH) at 3374, ν(CH_2) at 2920, δ(OH) at 1637, δ(CH_2) at 1463, δ(CH), and δ(OH) at 961 cm^{-1}. In addition, for the hemicellulose a less intense peak at 1730 cm^{-1} can be attributed to the C=O stretching vibration of carboxyl groups). On the other hand, the presence of lignin is detectable only for the presence of methyl groups and aromatic skeletal vibrations (at 2851 and 1637 cm^{-1}, respectively).

After silica extraction, all the bands of cellulose, hemicellulose and lignin disappear and only the Si-O-Si stretching and bending vibrations are still detectable (i.e. 1047 and 800 cm^{-1}, **Figure 3**).

From the morphological point of view, RH is characterized by an ordinated structure in which regular and geometric elements are repeated in the space (**Figures 4A** and **4B**). In addition, some elongated structure like "whiskers" are well visible on the shield tips (**Figure 4A**). The elemental analysis reported in **Figure 4C** inlet and the corresponding map (**Figure 4D**) show a homogeneous distribution and fine dispersion of Si element in all the area take in consideration.

When silica is extracted from RH, its morphology is extremely inhomogeneous (**Figure 5A**); only after a milling treatment, a more homogeneous distribution of polyhedral "chips" can be achieved (**Figure 5B**). However, a broad distribution of silica particles has been observed (from 10-20μm to 0.5-2 μm). Further confirmation about the smallest particles came from light scattering analyses: once again, a broad distribution consisting of three peaks centered at 0.25, 1.15 and 5.50 μm with a proportion of 74, 25 and 1%, respectively, has been found.

3.2 PLA-silica bio-composite characterization

3.2.1 Morphological analysis

The morphology of the prepared bio-composites has been investigated by Scanning Electron Microscopy (SEM): **Figures 5C** and **5D** report two micrographs of PLA10S and PLA30S as examples. Extracted silica exhibits a homogeneous distribution and a quite fine dispersion within the polymer matrix, notwithstanding the presence of micrometric particles (30 - 0.5 μm distribution), as confirmed by elemental analysis (**Figures 5C** and **5D** inlets). Despite this, there is no segregation of the filler, rather a good adhesion between silica and PLA, as well.

When homologous samples containing 10 and 30 wt.-% of a commercial silica were observed by SEM (**Figures 5E** and **5F**), no significant differences in terms of aggregate sizes have been easily detected; only the shape of the aggregates formed by the two fillers can be considered slightly different: polyhedral-like for extracted silica and globular-like for commercial one.

However, in some areas, the aggregates are bigger than those observed with extracted silica (up to 100 μm of one size, **Figure 5F**).

3.2.2 Thermal properties

The thermal properties of the prepared bio-composites have been investigated by using thermogravimetry and compared with those of neat PLA.

Such technique has been primarily used to check the thermal stability of the bio-composites containing extracted silica in air in comparison with the behavior of PLA. **Figure 6** reports the weight loss as a function of temperature (TG curve) and **Table 1** summarizes the collected data.

As far as PLA is concerned, its thermal degradation occurs in air by a single step in which the maximum weight loss is registered (347°C). Taking in consideration the accuracy of the employed TG, hence an experimental error of 0.5 wt.-%, neat PLA leaves an almost negligible residue at the end of the test (residue at 800°C).

Referring to bio-composites, regardless of their silica content, T_{max} remains constant within the experimental error; on the other hand, the final residue at 800°C increases by increasing filler loading (**Figure 6** and **Table 1**). These findings were expected as silica is thermally stable up to 800°C, and therefore the prepared materials are stable at the PLA processing temperature (namely, 180°C).

Comparing the final residues with the theoretical contents of silica within bio-composites, the real content of filler inside was estimated: these data were reported in **Table 1** (last column). We concluded that PLA5S, PLA10S, PLA20S and PLA30S actually contain 5.0, 8.0, 16.5 and 26.5 % of silica, respectively. This suggests a not precise control of the gravimetric feeder during extrusion; this is probably due to silica particles that exhibited a high tendency to agglomerate and compact themselves. Such disadvantage was not spotted using the commercial silica under investigation: indeed, the real contents of filler for PLA10SIDI and PLA30SIDI were 10.0 and 29.0% (**Table 1**), respectively.

3.2.3 Mechanical properties

The mechanical properties of the prepared bio-composites have been thoroughly investigated; to this aim, two different techniques (namely, dynamic thermo-mechanical and stress-strain analyses) have been employed. In the packaging field, the mechanical properties play a key role to correctly choose the most suitable material/formulation (type and thickness) for obtaining the desired performances.

The dynamic thermo-mechanical analysis in strain controlled mode has been used in order to establish the effect of the temperature and filler content on the storage modulus of PLA: **Figure 7** reports the trend of the storage modulus (E') *vs*. temperature. This aspect is fundamental for those applications at different conditions from room temperature, in particular if some significant temperature leaps occur. From an overall consideration, a general increase of E' has been observed under glass transition temperature (T_g) for all the prepared bio-composites, revealing that the filler modulus could be higher than that of PLA, as expected (**Table 2**). In addition, E' turned out to be a function of the silica content: indeed, it increases, by increasing filler content. For all the formulations and neat PLA, the mechanical property collapse occurs at 65°C, estimated as maximum of tanδ. At high temperatures (>100°C), the bio-composites exhibited higher storage modulus than that of PLA, although very low.

DMTA data confirm that PLA and also the bio-composites, regardless of their filler content, may be used only under 60-65°C, where the mechanical properties fall down.

Pursuing our research, some stress/strain analyses at room temperature have been performed for assessing the toughness of composites. The collected data are listed in **Table 2**. As expected, a significant increase of the Young's modulus of PLA as a function of the filler content has been found (4.04, 4.32, 4.94, 5.62 vs. 3.72 GPa for PLA5S, PLA10S, PLA20S, PLA30S and PLA, respectively). Referring to the deformation at break, a significant decrease, depending on filler content, has been observed.

Surprisingly, the presence of extracted silica, regardless of its content, slightly reduces the maximum strain value of PLA (σ_{max}). Actually, such trend is an unusual behavior that could be ascribed to the broad distribution of silica, already discussed in heading *3.2.1 Morphological analysis*. These findings confirm the possibility to use such bio-composites for applications where the deformation or maximum loading required should be similar to that of PLA.

Bio-composites containing commercial silica have exhibited a different mechanical behavior if compared with those containing silica derived from RH. Indeed, apart from the increase of Young's modulus observed also in this case, and comparable with that of extracted silica (**Table 2**), the elongation at break and the maximum strain value of PLA have been strongly reduced by the presence of commercial silica. At the highest filler content (30 wt.-%), ε passed from 9.2 (PLA) to 2.46 or 0.69% as well as σ_{max} from 57.15 to 50.71 or 32.35 MPa for PLA30S and PLA30SIDI, respectively. This finding can be ascribed to a different interaction level between filler and matrix: for confirming our hypothesis Pukanszky's model was applied. **Figure 8** plots reduced stress at yield data (log σ_{red}) as a function of volumetric fractions. If such model works a straight line should be obtained, the slope of which represent B parameter of Equation 4 and 5. As already explained, B is a term corresponding to the load carrying capability of the filler and depends on filler-matrix interactions and is influenced by all factors affecting the load-bearing capacity of the filler, i.e. on the strength of interaction (which depends on surface energy/chemistry of the constituent) and on the size of the contact surface [35]. It means that higher B, higher are filler-matrix interactions.

Comparing the two silica, it is noteworthy that at 10 wt.-% loading, the trend and thus B value of the two silica are almost comparable; on the contrary, at 30wt.-%, silica derived from RH still exhibits a linear trend, the slope of which is significantly higher than that of composite containing commercial silica (2.575 vs. 1.930, **Figure 8**). By this way, we can conclude that a higher filler-matrix interaction level was verified when silica from RH is used. This can explain the mechanical properties discussed above.

The mechanical analysis has been completed by fitting the experimental E data by micro-mechanical models. As already mentioned, this study could be useful for correctly choosing of the composite formulation when a specific E is required. To this aim, an estimation of the silica density with Archimede's law and silica modulus were carried out. A density value of 1.82, 1.88 and 1.25 g/cm^3 for the extracted silica, commercial silica and PLA has been found, respectively. Subsequently, these values have been used for calculating the volumetric fractions (ϕ) required by micro-mechanical models (0.035, 0.056, 0.119 and 0.207 for PLA5S, PLA10S, PLA20S and PLA30S, respectively) determined from the weight fractions estimated from TGA residues (**Table 1**, column of the estimate filler content).

As already described in a previous study [33], models of Voigt (**Equation (2)**) and Halpin-Tsai (**Equation (3)**) can be used to assess the modulus of a filler in a polymer matrix. Referring to pure polymer, the E_m value adopted was 3.72 GPa, obtained from the stress-strain tests on PLA (**Table 2**). At the same time, the evaluation of E_f has been proven to be enough difficult. Thus, Voigt and Halpin-Tsai models have been used to valuate E_f from E_c values measured by stress-strain tests (**Table 2**). As results, E_f values calculated using Voigt and Halpin-Tsai models are 13.8 and 65 GPa with a maximum punctual error of 0.8 and 1% (up to 20 wt.-% loading), respectively. Subsequently, (E_c - E_{PLA})/E_{PLA} values as a function of the volumetric fraction obtained from both models have been plotted (**Figure 9)** and the experimental results with corresponding error have been included, as well. It is noteworthy that Halpin-Tsai model gave a theoretical value of silica modulus that is very close to that of a glass.

Referring to the volume fraction calculation, the bio-composites have showed a density higher than unloaded PLA, due to the presence of silica; this aspect can be considered relevant for the packaging transport cost. In this optics, for evaluating if the weight increase is higher than the modulus one, the specific modulus was calculated as E/density: these data (**Table 2**) showed that the presence of silica favors an increase of E, even though the values were normalized on density.

3.2.4 Oxygen barrier properties

Another important aspect for the materials suitable to the packaging industry is the possibility to protect or limit the contact between foods and oxygen, gases, water, or to prevent the aroma dispersion. To this aim the barrier properties of a film are important and must be evaluated.

The oxygen barrier properties of the prepared bio-composites have been tested and the collected data are summarized in **Table 3**, where the permeability was calculated following the **Equation (1)**. These data showed that the oxygen permeability of PLA is significantly affected by the presence of both silica, but the trend is completely opposite. Indeed, with extracted silica OP decreases, while with commercial one increases. In both cases, the reduction or improvement is significant and almost linearly depending on silica content (**Table 3**). The reduction may be in part due to the silica particle which turns out to be less permeable to the oxygen diffusion than matrix. In addition, the presence of silica particles within PLA may create a more tortuous pathway in the matrix through which oxygen diffuses more difficultly. The last aspect can be ascribed to the good adhesion and filler-matrix interaction level (demonstrated with Pukanszky's model) as well as the homogeneous distribution of the filler within the polymer matrix (observed by SEM).

Conversely, with commercial silica, the aggregates are bigger than those observed with extracted silica (as already discussed in heading *3.2.1 Morphological analysis*) and the filler-matrix interaction level is lower. Probably, some aggregates may also have sizes comparable with film thickness, causing some defects able to increase the oxygen permeability.

In addition, the aggregates seems to be formed by a large number of nanometric particles not completely adherent among them. All these aspects result in the formation of a film that is more permeable to the oxygen diffusion with respect to that containing extracted silica.

3.2.5 Economic analysis

In the present work, we have proposed a simple extraction of silica derived from an industrial waste (rice husk) for using it as filler for conferring new performances to PLA. This process should be economically sustainable if an industrial exploitation is foreseen. To this aim, an economic analysis was carried out, firstly considering the extraction process of silica, and after the preparation of PLA-based composites. For a complete economic analysis, the cost of an industrial plant should be considered, but this aspect is very complex and, for this reason, not taken in consideration at the moment.

Referring to silica extraction, our attention was focused on material and energetic costs. First of all, we have calculated the total cost of 1 kg silica production, on the basis of the unit costs of each material used during extraction (namely, rice husk, sulfuric acid and water), following the recipe previously described in heading *2 Materials and methods*; these data are summarized in **Table 4**. It is important to highlight that costs taken in consideration in our calculations refer to industrial (and not laboratory) quantities. The total cost for silica production was estimated 0.92 €/kg. In addition, costs due to water heating and rice husk burning were considered (**Table 5**). As far as water heating is concerned, a consumption of 5.88 kWh has been assessed, taking into account that the efficiency of a common electrical heater is approximately 0.9. Otherwise, the RH burning occurs with a heat release, and thus an energetic gain may be obtained (namely, 9.34 kWh with an efficiency of 0.3). In conclusion, the total energetic balance of such process is positive with a production of 3.46 kWh, corresponding to a gain of 0.69 € (considering the 2012 Italy energy cost).

Pursuing our economical assessment, the cost of PLA-silica-based bio-composites has been compared with that of pure polymer. To this aim, the concept of Break-Even Point (BEP) has been considered: on the basis of its value, it is possible to establish if the investigated formulations are economically sustainable. More specifically, BEP represents the percentage of silica that should be added to PLA in order to have the cost of the bio-composite equal to that of pure polymer. Thus, the process turns out to be economically advantageous only when the employed silica amount exceeds the BEP. On the basis of the costs reported in **Table 6** for PLA, silica and extrusion process, it was calculated that approximately 25 wt.-% filler is needed to exceed the BEP value, and thus this amount guarantees economical outcomes, notwithstanding the environmental aspect. In addition, such material exhibited higher mechanical and barrier properties with respect to neat PLA.

BEP value is strongly reduced from 25 down to 18 wt.-% filler, when the energetic gain of 0.69 € for 1 kg of silica is included in its calculation.

It is noteworthy that the cost used for extrusion (0.4 €/kg) is a typical industrial cost for 10 tons of materials in 2012; obviously, this cost can be further reduced by increasing the produced quantity. Furthermore, the cost of polymer was quoted 2.5 €/kg, although such value strongly depends on market requests. Finally, the improved mechanical and barrier properties of composites may allow a reduction of package thickness with respect to the use of unloaded polymer, making even more economic our approach.

4. Conclusions

In the present study, bio-composites consisting of poly(lactic acid) and silica derived from rice husk have been prepared by melt compounding. The possibility to obtain injection molded objects or films was verified obtaining samples for the characterization analysis. The collected data by thermogravimetry and mechanical analyses have shown that all the formulations under investigation can be taken into account as materials for several applications in the packaging field like boxes, containers, crates, other objects and thick films. Indeed, the presence of extracted silica has induced significant improvements of the Young's modulus as well as a slight reduction of the oxygen permeability of PLA. The achieved mechanical properties turned out to be higher than those exhibited by the homologous samples prepared by using a commercial silica.

The economic analysis of the materials and whole process (namely, silica extraction and bio-composite preparation) has highlighted that the production of a formulation containing 20 wt.-% silica can be considered economically sustainable, when the energy recovered from the rice husk burning is reused.

Acknowledgements

The Authors would like to thank the ECOFOOD project within "Ricerca & Innovazione per il Miglioramento della Sostenibilità della Filiera Agro-alimentare" program, economically supported by the POR-FESR resources of the Economy and Finance Ministry, the European Union and the Piedmont Region. - Publication n. 13.

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Figure captions

Figure 1. Pictures of rice husk (a), rice husk ash (b) and extracted silica (c).

Figure 2. Twin screw and temperature profiles.

Figure 3. ATR-FTIR spectra of rice husk and silica.

Figure 4. SEM magnifications of rice husk (A and B) and corresponding elemental analysis (C).

Figure 5. SEM magnifications of silica powder (A and B) and bio-composites containing 10 and 20wt.-% silica (C and D).

Figure 6. TG curves of PLA and bio-composites in air.

Figure 7. Storage modulus E' and tan δ of PLA and bio-composites as a function of temperature.

Figure 8. Reduced stress data of PLA and bio-composites with extracted and commercial silica with the fitting lines according to Pukanszky's model.

Figure 9. Experimental modulus (E) increase, oxygen permeability (OP) decrease and modulus fitting curves with Voigt and Halpin-Tsai models.

Table list

Table 1. TGA data of PLA and bio-composites in air.

Sample	T_{max} [°C]	Residue at 800°C [%]	Estimate filler content [%]
PLA	347	1.0	0.0
PLA5S	346	6.0	5.0
PLA10S	345	9.0	8.0
PLA20S	347	17.5	16.5
PLA30S	346	27.5	26.5
PLA10SIDI	348	11.0	10.0
PLA30SIDI	348	30.0	29.0

Table 2. Stress-strain and DMTA data of PLA and bio-composites.

			Filler content			
		PLA	5 wt.-%	10 wt.-%	20 wt.-%	30 wt.-%
DMTA of silica from RH at 30°C	E' [GPa]	3.34±0.07	3.62±0.07	3.86±0.08	4.40±0.09	5.14±0.1
	ΔE’ [%]*	-	+8	+16	+32	+54
DMTA of commercial silica at 30°C	E' [GPa]	3.34±0.07	-		-	
	ΔE’ [%]*	-	-		-	
Stress-strain analysis of silica from RH at 23°C	E [GPa]	3.72±0.07	4.04±0.07	4.32±0.02	4.94±0.05	5.62±0.47
	ΔE [%]*	-	+9	+16	+33	+51
	ε [%]	9.21±1.72	5.42±1.29	5.48±1.12	2.75±0.94	2.46±0.43
	σ_{max} [MPa]	57.15±1.56	47±2.52	52.65±1.66	54.43±2.55	50.71±1.32
	E/density [MPa · m^3/Kg]	2.98±0.05	3.16±0.05	3.33±0.02	3.68±0.05	3.93±0.1
	ΔE/density [%]*	-	+6	+12	+24	+32
Stress-strain analysis of commercial silica at 23°C	E [GPa]	3.72±0.07	-	4.27±0.13	-	5.51±0.17
	ΔE [%]*	-	-	+15	-	+48
	ε [%]	9.21±1.72	-	2.68±0.62	-	0.69±0.04
	σ_{max} [MPa]	57.15±1.56	-	51.39±1.55	-	32.35±1.59

* Δ = x PLA-x biocomposite/ x PLA, x can be E, E’ or E/density

Table 3. Oxygen permeability data of PLA and bio-composites (23°C, 65% R.H.).

Sample	Thickness [mm]	OTR [cc/(m² bar 24h)]	OP [cc mm/(m² bar 24h)]	δ* [%]
PLA	0.32	47.5	15.2	-
PLA5S	0.24	58.6	14.1	-7
PLA10S	0.30	41.2	12.4	-19
PLA20S	0.29	37.1	10.8	-29
PLA30S	0.35	15.6	5.4	-64
PLA10SIDI	0.29	195.5	55.7	+267
PLA30SIDI	0.31	817.2	253.3	+1567

* δ = (OP bio-composite - OP PLA)/OP PLA.

Table 4. Economic analysis of 1 kg silica extraction.

Material	RH	H_2SO_4	Water
Cost [€/kg]	0.07*	0.14**	0.002***
Material amount for 1kg silica [kg]	6.67	2.33	65.33
Cost of material for 1kg silica [€]	0.47	0.33	0.13
Total cost for 1kg silica [€]		0.92	

*Associazione Granaria di Milano - Borsa dei Cereali (http://borsa.granariamilano.org/visualizza_listino.php3)

** Italian leader for sulfuric acid production (http://www.marchi-industriale.it/web/index.php/It/home/)

*** Italian quotation for 2012 (http://www.ilsole24ore.com/art/impresa-e-territori/2013-05-10/litalia-acqua-prezzi-geografia-201003.shtml?uuid=AbSBMtuH)

Table 5. Energetic balance for 1 kg silica extraction.

Process step	Water boiling	RH burning
Material amount for 1kg silica [kg]	65.33	6.67
Energy [kWh/kg]	-0.10*	+4.67**
Efficiency	0.9	0.3
Total energy [kWh]	-5.88	+9.34
Total energetic balance [kWh]	+3.46	
Energetic gain [€]	0.69***	

* Evaluation carried out in our laboratory

** Tsai et al. 2007 [3]

*** in order to evaluate the energetic gain, 0.2 €/kWh was used following the Italian National table of electric energy provided by "Autorità per l'energia elettrica e il gas" 2012, independent organism of Italian Government (http://www.autorita.energia.it/it/che_cosa/presentazione.htm).

Table 6. Analysis of Break-Even Point (BEP).

	Cost [€/kg]	BEP on material costs [wt.-% silica]	BEP on materials and energy costs [wt.-% silica]
PLA	2.50	25	18
Silica	0.92		
Extrusion	0.40		
Energetic gain	-0.69		

Figure 1.

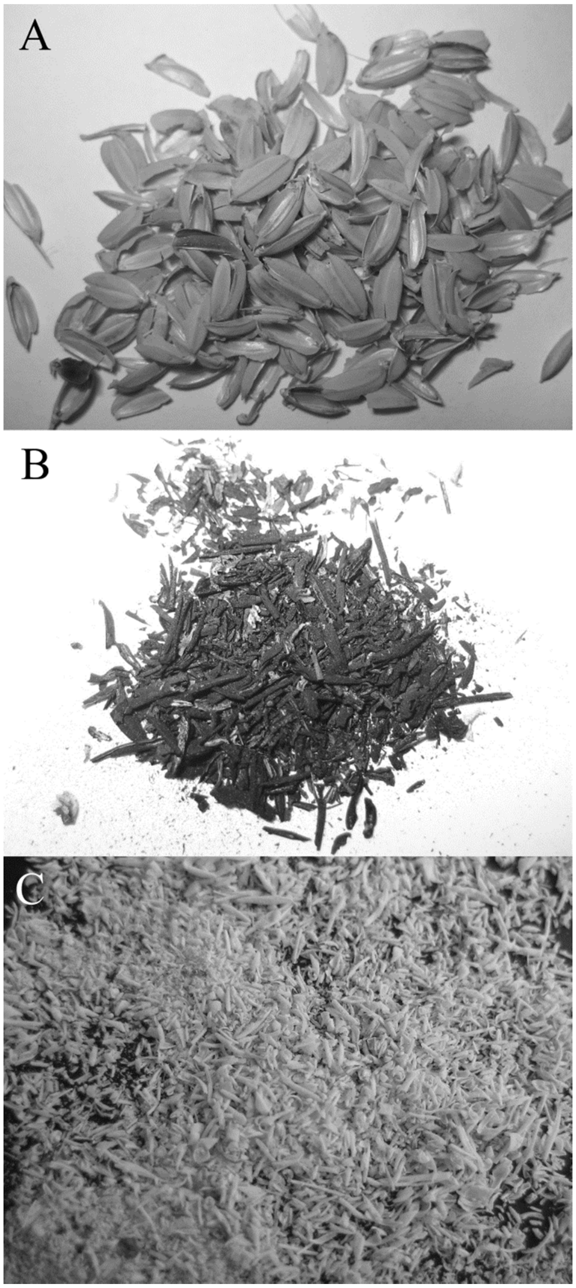


Figure 2.

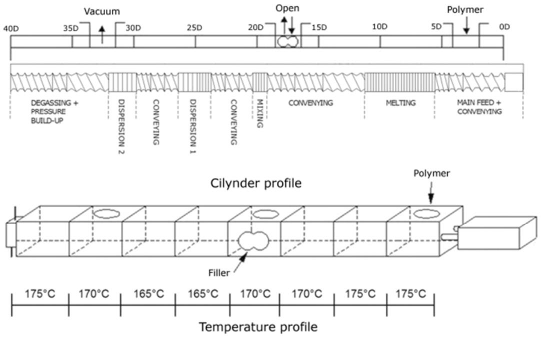

Vacuum
Open
Polymer
40D
35D
30D
25D
20D
15D
10D
5D
0D
DEGASSING + PRESSURE BUILD-UP
DISPERSION 2
CONVEYING
DISPERSION 1
CONVEYING
MIXING
CONVENYING
MELTING
MAIN FEED + CONVENYING
Cilynder profile
Polymer
Filler
175°C
170°C
165°C
165°C
170°C
170°C
175°C
175°C
Temperature profile

Figure 3.

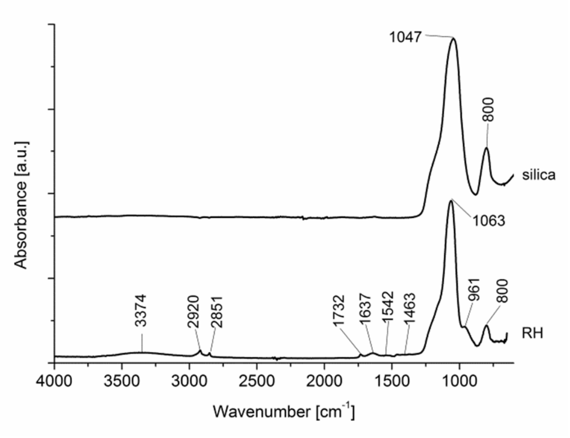

1047
800
silica
1063
3374
2920
2851
1732
1637
1542
1463
961
800
RH
Absorbance [a.u.]
4000
3500
3000
2500
2000
1500
1000
Wavenumber [cm^{-1}]

Figure 4.

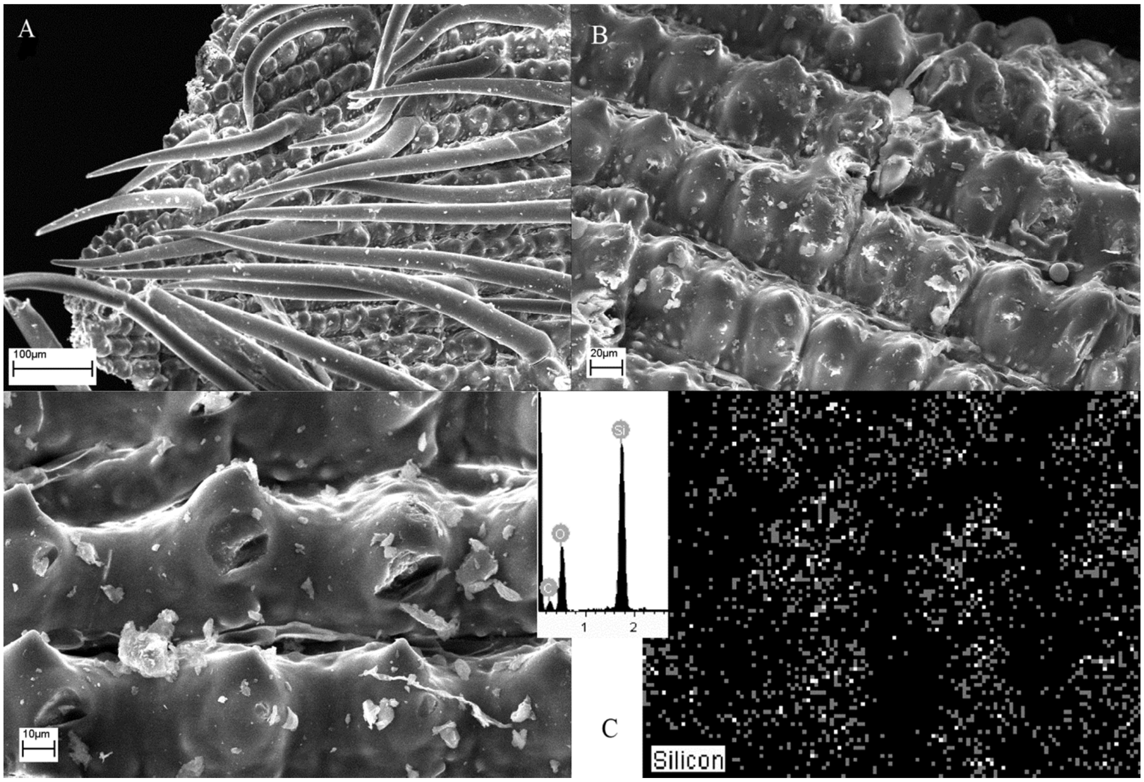


Figure 5.

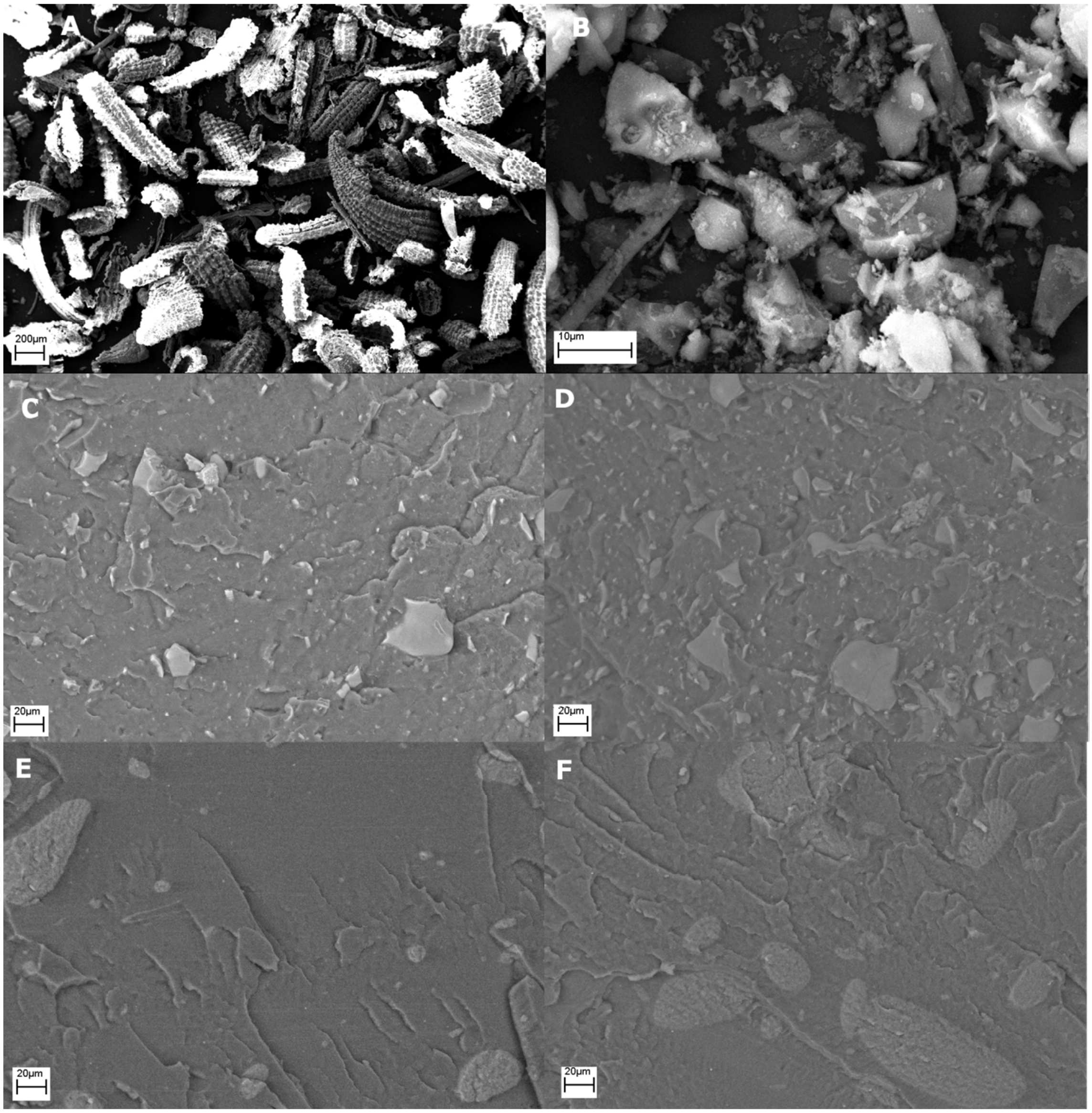


Figure 6.

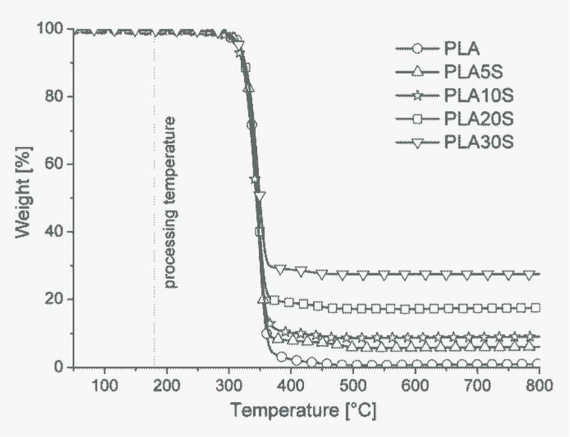

100
80
60
40
20
0
Weight [%]
processing temperature
100
200
300
400
500
600
700
800
Temperature [°C]
PLA
PLA5S
PLA10S
PLA20S
PLA30S

Figure 7.

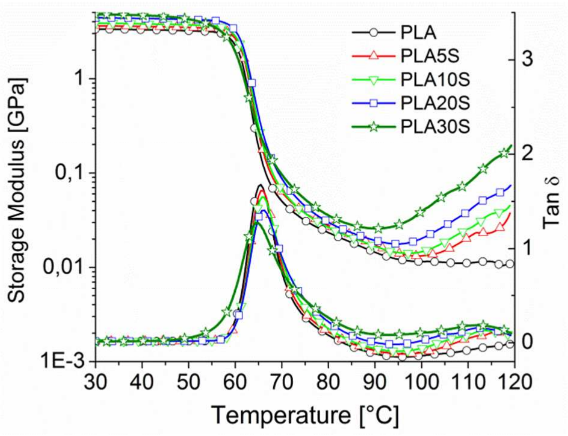

PLA
PLA5S
PLA10S
PLA20S
PLA30S
Storage Modulus [GPa]
1
0,1
0,01
1E-3
Tan δ
3
2
1
0
30
40
50
60
70
80
90
100
110
120
Temperature [°C]

Figure 8.

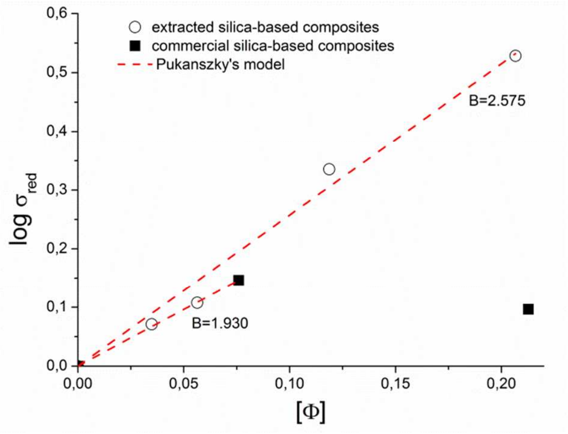
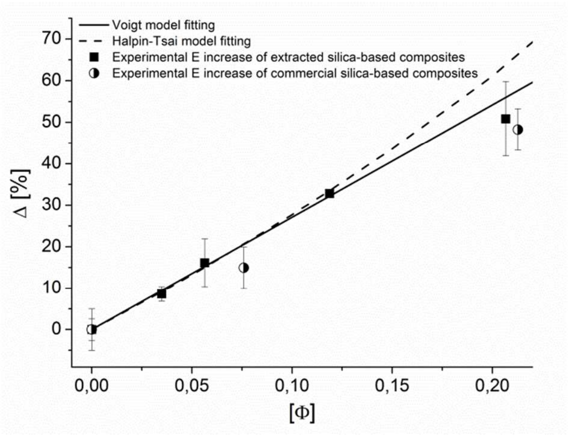

○ extracted silica-based composites
■ commercial silica-based composites
- - - Pukanszky's model
B=2.575
B=1.930
0,6
0,5
0,4
0,3
0,2
0,1
0,0
log σ red
0,00
0,05
0,10
0,15
0,20
[Φ]

Figure 9.


Voigt model fitting
Halpin-Tsai model fitting
Experimental E increase of extracted silica-based composites
Experimental E increase of commercial silica-based composites
Δ [%]
70
60
50
40
30
20
10
0
0,00
0,05
0,10
0,15
0,20
[Φ]