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# Ionic Liquid Surface Treatment of Calcite for Improved Compatibility with Polyolefin Matrix

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**Abstract.** Preliminary surface treatment of crystalline marble powder filler with a dominantly hydrophobic ionic liquid, namely triethylsulfonium-bis(trifluoromethylsulfonyl) imide has been employed to design a filler with improved compatibility towards non-polar polymer matrices, such as polyolefins. The maximum uptake of ionic liquid per 1g of marble powder was 132 mg. The surface coating of the crystalline phases has been proved by XRD and FTIR spectroscopy, making our method useful in designing fillers with improved dispersibility/ compatibility in/with polyolefins. The floating test method has proved the efficiency of the alkylsulfonium ionic liquid in hydrophobization of the crystalline calcite-rich phase, thus proving useful in obtaining composites with improved properties.

## 1. Introduction

Calcium carbonate is the most widely used filler for particulate-reinforced polyolefin composites. Its low price, coupled with good thermal stability, workability, and neutral color [1-3]. It has been reported to efficiently increase the impact resistance, fire-resistance and water stability in various combinations with high density polyethylene (HDPE) and polypropylene (PP) matrices [3].

However, due to its high surface polarity and hydrophilicity it is mainly incompatible with hydrophobic polymer matrices such as polyolefins [4].

To improve its dispersibility in polymer media, calcium carbonate is often surface treated with a variety of modifiers/dispersion agents such as silanes, phosphates, titanates, fatty acids (mainly stearic acid), etc [5,6]. Because of this treatment, a layer of hydrophobic organic molecules is attached to the mineral surface, via physical bonding. The structure and properties of such layers, being the interface between the inorganic filler and the polymer matrix bears a strong influence on the final properties of the composites [5].

Among the most frequently used calcite coating techniques at laboratory scale, include dry coating (through mixing with the additive at different temperatures, dependent on its nature) and the solution method. In the solution method, the calcite surface is usually treated with the solution of the acid in a nonpolar solvent (n-alkanes, toluene) [7].

Ionic liquids (ILs) have been scarcely used as dispersing agents for inorganic fillers so far. Their use as surface hydrophily-enhancing agents could impart also some useful properties to the composites, such as antimicrobial character, improved UV-resistance, fire retardancy and so forth [8,9].

In this study, crystalline marble powder has been surface treated with triethylsulfonium-bis(trifluoromethylsulfonyl) imide by treatment of the particles with different amounts of ionic liquid



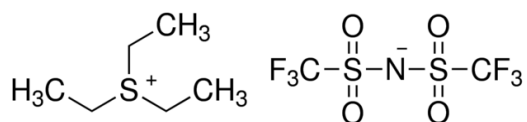
dissolved in ethanol. The structure and properties of the obtained products were determined by SEM microscopy, XRD and FTIR spectroscopy. The effect of surface modification has been evaluated by the floating test, confirming the efficiency of the studied ionic liquid use as surface functionalizing agent.

## 2. Materials and methods

### 2.1. Materials

Marble dust powder (sieved, average particle diameter < 0.01mm) has been provided by TITAN MAR Co., Chiajna, Romania.

The ionic liquid used in this study (figure 1), namely triethylsulfonium-bis(trifluoromethylsulfonyl) imide (TesIm) has been purchased from IoLiTec-Ionic Liquids Technologies GmbH, Germany (99.5% purity) and was used without further purification.



**Figure 1.** Chemical structure of used ionic liquid.

### 2.2. Methods

**2.2.1. Marble powder IL surface treatment.** Due to the high viscosity of the pure ionic liquid, to obtain a uniform coating of the marble powder with the ionic liquid, three solutions with concentrations of 30%, 50% and 50% vol. TesIm in 98% ethanol have been prepared. A determined amount of marble powder (10g) have been immersed in 50 mL of the TesIm ethanol solutions and magnetically stirred for determined time periods at 25°C. For the IL uptake kinetic determination, aliquots of the solutions have been extracted at specified time intervals and analysed by UV spectrophotometry at 235 nm, based on the absorption maximum of the IL in ethanol (determined previously).

**2.2.2. Coated marble powder characterization.** For structural characterization, the marble powder has been removed from the ethanol ionic liquid solution and dried in vacuum (300 mbar, 50°C). To determine the modification in crystalline phases that occur in marble after ionic liquid treatment, XRD spectra have been obtained, with a Bruker Discover diffractometer ( $K_{\alpha 1} = 0.154$  nm, scan speed 5 degrees/min). To characterize the surface of the calcite particles, FTIR spectra have been acquired in the 4000-600  $\text{cm}^{-1}$  interval (Bruker VERTEX 70 spectrophotometer working in reflectance mode). A QUANTA 200 scanning electron microscope was used to study the morphological appearance of the IL-treated marble powder and reference.

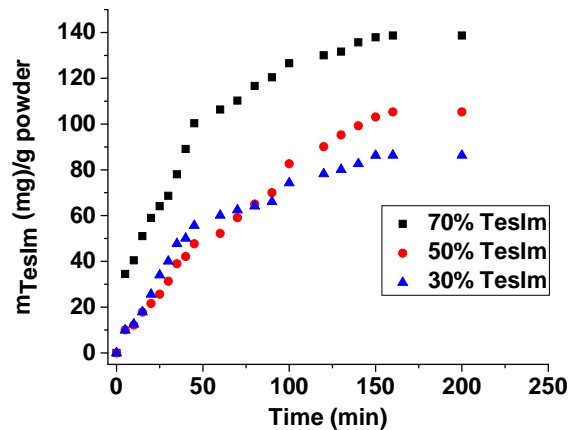
The effect of surface modification has been evaluated by the floating test, initially reported by Sheng et al. [10], which represents the ratio of the free-floating functionalized powder to the overall weight of the powder after being magnetically stirred in water at 1000 rpm and room temperature (the active ratio). To assess the modification in surface energy of the coated marble powder, surface energy measurements have been performed. The powder has been dried at 105°C for 5 hours then it was pelleted by means of a hydraulic press at 100 atm for 10 s. The surface energy of the pellet (related to the sample polarity) has been determined through contact angle measurements. As a general methodology, three drops (5  $\mu\text{L}$  each) of distilled water, respectively octanol, with different surface tensions have been placed on the sample's surface, and the contact angles have been assessed by ImageJ software (contact angle plugin). With the help of SCA software (DataPhysics GmbH), the surface energy has been assessed, based on the Owens, Wendt, Rabel and Kaelble (OWRK) method.

Untreated marble powder and neat PP and HDPE powders have been pelleted and analysed in a similar manner.

### 3. Results and discussion

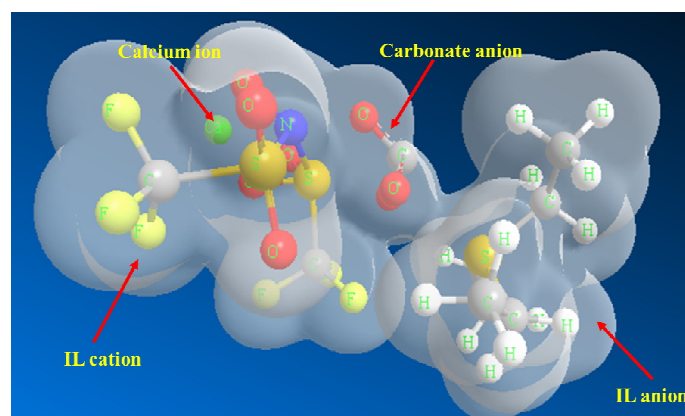
The ionic liquid uptake kinetic of the calcite powder is presented in figure 2. It can be observed that equilibrium uptake of IL is reached in approx. 150 min of contact with the IL ethanol solution.

A pseudo-equilibrium zone could be registered at the 40-80 min interval, which could be due to the concurrent elimination of several crystalline phases from the inorganic material because of the magnetic stirring process, as well as of different hydrophobic IL monolayers stacking. The active ratio of the functionalized powder is 32.45% for the marble immersed in the 30% vol. TesIm ethanol solution; 57.23% for the marble immersed in the 50% vol. TesIm ethanol solution and 65.23% for the 70% vol. solution, respectively.



**Figure 2.** TesIm IL sorption kinetic onto the marble powder.

The maximum loading amount of ionic liquid is 132 mg/g of marble powder, registered for the solution with the highest IL content (70% vol.).

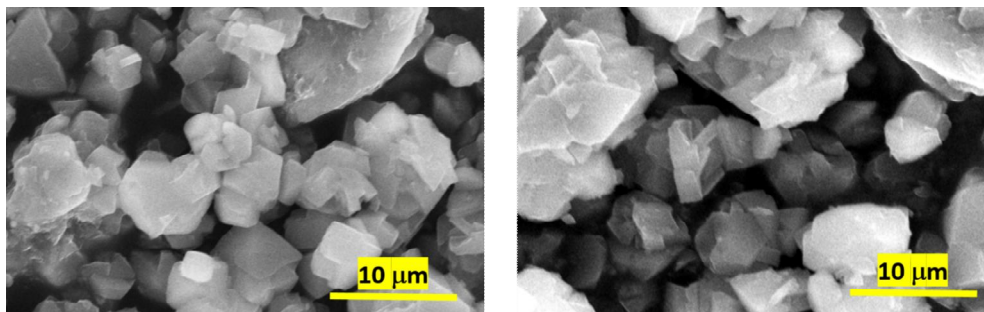


**Figure 3.** Calcium carbonate interactions with the TesIm IL.

It is expected that the calcium and carbonate ions in the marble filler interact with the anion/cation of the ionic liquid. Molecular dynamics simulations (MMF94 interface, 5000 iterations, minimum

RMS gradient of 0.1) have indicated that calcium carbonate molecule is placed within the “solvation surface” of the ionic liquid. The  $\text{Ca}^{2+}$  anion surface charge is efficiently “masked” by the  $-\text{CF}_3$  groups of the bis(trifluoromethylsulfonyl) imide anion (effective charge of +0.041) while  $\text{CO}_3^{2-}$  anion is attracted by charge-dipole interactions by the  $\text{S}^+$  atom in the ionic liquid cation (effective charge of the two  $\text{O}^-$  ions being -0.64 and -0.71).

The highest IL uptake speed has been registered for the solution with the highest concentration gradient. The irregularities present on the powder surface (figure 4) favour the sorption of the IL, which probably is oriented with the polar end towards the calcite phase and with the hydrophobic alkyl chains towards the exterior, possibly favouring the interaction with dominantly hydrophobic polymer matrices, such as polyolefins.

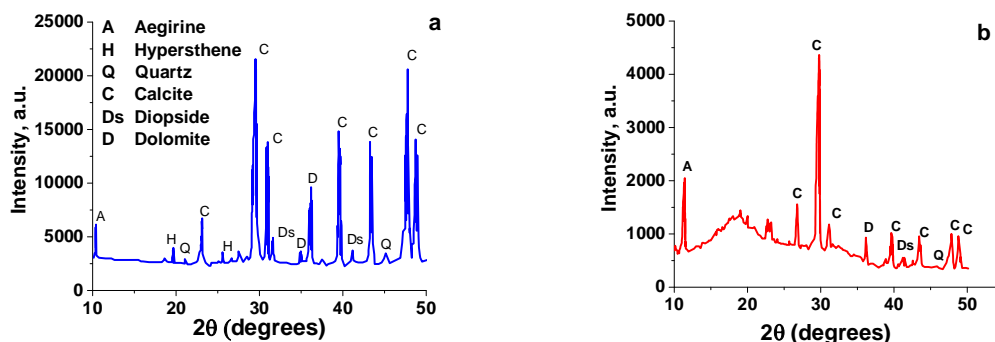


**Figure 4.** Initial marble powder (left) and TesIm-treated marble powder (right).

Ionic liquid treatment of the marble powder seems to increase the surface roughness of the particles, probably due to the leaching of several weakly bonded crystalline phases, aided by the magnetic stirring process.

The marble dust powder presents a dominantly crystalline structure, as determined from the XRD diffractogram (figure 5a). The as-received marble powder comprises mainly of trigonal calcite, rhombohedral dolomite, and several aluminosilicate minerals, such as aegirine, hypersthene, diopside, alongside quartz.

Ionic liquid adsorption on the surface of the marble particles determines a decrease in the overall intensity of the spectrum, probably due to the coating of the crystalline phases with the dominantly amorphous ionic liquid.

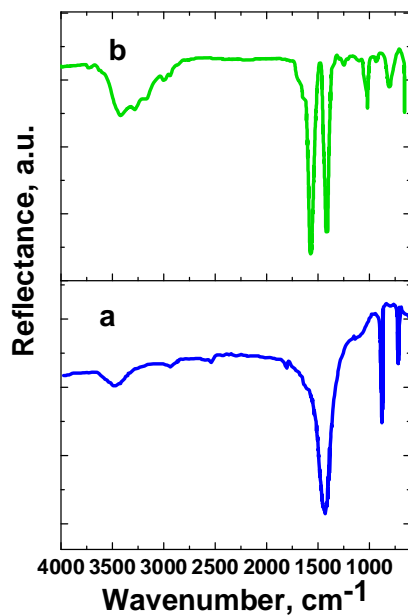


**Figure 5.** XRD diffractograms of: (a): neat marble powder; (b): TesIm-treated marble powder (70% vol. IL solution).

This hypothesis could be confirmed by the presence of the amorphous peak, centered at  $\sim 19.7^\circ$  (figure 5b). Also, several peaks, ascribed to hypersthene, diopside and dolomite disappear from the

diffractogram, being leached into the IL solution. As the calcite phase has the higher hardness among the minerals present in marble, leaching of compounds with lower mechanical resistance could prove useful for the hardness and impact resistance of particulate-reinforced polyolefin composites.

The surface sorption of ionic liquid is also confirmed by the FTIR spectra presented in figure 6.



**Figure 6.** FTIR spectra of (a): reference marble powder and (b): IL-treated marble powder.

The FTIR spectra of neat marble powder from Fig. 5a shows the presence of weakly bonded water (-OH group, band centered at  $\sim 3520\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$ ). Several intense bands are present, belonging to C-O bending vibration ( $\sim 1470\text{ cm}^{-1}$ ) and C-O rotation ( $\sim 870\text{ cm}^{-1}$ ) in the carbonate anion [11].

Ionic liquid-treated marble powder presents the spectral features of neat IL, namely, the presence of S-O and C-F vibrations ( $3000\text{--}4000\text{ cm}^{-1}$  domain), as well as of alkyl stretching vibration band ( $\sim 2920\text{ cm}^{-1}$ ) and the band associated with the C-F vibration in the trifluoromethanesulfonate anion ( $\sim 1230\text{ cm}^{-1}$ ) [12].

The values presented in table 1 for the IL-treated marble pellet indicate a decrease with up to 54% in the values of the surface energy comparing with the untreated marble powder indicating an optimum functionalization.

**Table 1.** Surface energy values of the analysed samples.

Sample	$\gamma$ (mN/mm)	Contact angle ( $^{\circ}$ )
Marble	75.4	23.5
Functionalised marble	34.1	68.7
PP	30.4	56.1
HDPE	29.9	50.9

Through functionalization it could be seen that the values for the surface energy of the functionalized marble resemble those of PP and HDPE, indicating a good potential compatibilization between the two phases, beneficial to the obtaining of composites, either through injection or thermoforming. Even if the surface energy is also affected by roughness and porosity (HDPE, PP and marble powder having rather different compressibility and particle dimensions), the determinations have clearly indicated a hydrophobization of the highly polar marble powder.

#### 4. Conclusion

Crystalline calcite-rich marble powder has been surface treated with ethanol solutions of different concentrations comprising the triethylsulfonium-bis(trifluoromethylsulfonyl) imide ionic liquid. An efficient hydrophobization of the marble powder has been achieved, determined by an active ratio of over 60%, for the most concentrated ionic liquid solution.

The XRD and the FTIR spectra confirm the presence of the ionic liquid on the surface of the inorganic phase, proving the potential usefulness of our method in designing particle-reinforced composites with polyolefin matrices.

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