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Sol-gel Chemistry Approaches for the Manufacturing of Innovative Functional Composites for the Aerospace Sector

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Abstract. Sol-Gel is a "bottom-up" synthesis method that enables the production of films, nano/microparticles, fibers, gels, and bulk materials, both glassy and crystalline. Sol-Gel chemistry can be a vital tool for solving problems in several industrial applications where nanotechnology is necessary to overcome constraints. Here, various examples involving silicate-based materials are discussed. Silicatic materials with a variety of morphologies and applications, e.g., monodisperse SiO₂ particles ranging in size from a few nanometers to a micron, can be synthesized through hydrolysis and polycondensation reactions of silicon alkoxide precursors. Using an environmentally friendly electrospinning process, silica nanoparticles can be incorporated into polyvinylpyrrolidone (PVP) fibers to create novel, fire-resistant sound absorbers. Additionally, by employing hybrid techniques based on Sol-Gel, the flame retardance of nanocomposites made of silica and epoxy resin as well as epoxy-based composites including hemp, even cured with cycloaliphatic hardeners, can be enhanced. The development of novel materials beneficial for aviation applications, such as hydrophobic (potentially self-anti-icing) coatings, is a further proof of the effectiveness of Sol-Gel chemistry.

1. Introduction

Innovative materials with improved functionality, safety, and sustainability are increasingly in demand in industrial sectors based on quickly evolving technologies, such as the aircraft industry. The manufacturing of soundproofing polymeric materials, reducing the noise pollution, represents one famous example [1, 2]. Sound absorbing blankets composed by nanofibers can be easily synthesized by electrospinning [1]. The current soundproofing materials exhibit low performances in the medium and low medium frequency range [3]. In recent years, soundproofing materials based on electrospun polyvinylpyrrolidone (PVP) were obtained [3]. One drawback refers to the good solubility of PVP in water, which significantly restricts the use of the blankets. To prevent this, the electrospun mats are thermally treated, causing the polymer chains to crosslink [3]. However, the heat treatment often results in unwanted fiber shrinkage. A solution for this issue was found out by including silica nanoparticles



into the PVP matrix [3]. The thermally treated electrospun PVP-based materials including silica nanoparticles showed both sound absorption properties and improved fire retardance.

Epoxy resins have a combination of chemical resistance and thermal stability, making them appropriate for a wide range of industrial applications, particularly in the aerospace industry [4]. Cycloaliphatic amines are increasingly being used as greener hardeners because of the health hazards of aromatic amines [5]. Cycloaliphatic epoxy resins show high flammability and thus the addition of flame-retardant additives is required for most applications [6]. Though Halogen-containing flame-retardants have been frequently employed for improving the fire behavior of resins, many of these additives have been recently banned due to their potential toxicity [4-7]. A very intriguing method to improve the flame-retardant behavior of an epoxy matrix cured with cycloaliphatic amine, with a relatively low loading of phosphorus (i.e., 2 wt.%), involves the use of an in-situ sol-gel methodology for the preparation of silica-epoxy nanocomposites, combined with a strong phosphorous(P)-nitrogen (P-N) synergism [6-8] or the in situ generation of magnesium hydroxide nanocrystals [9, 10].

In the last ten years, fiber-reinforced polymer composites employing available natural fibers, such as hemp, are growing of interest in several aerospace applications, due to their low-cost and high sustainability [11]. However, hemp-containing composites are easily flammable [12]. This characteristic strongly limits the use of these materials, as often severe standards and fire tests must be passed. The authors manufactured hemp fabric/epoxy composites by vacuum bag molding, also tailoring the surface of hemp fabric fibers with silica through a simple and green process [13]. Besides, the effect on the mutual presence of treated hemp fibers and ammonium polyphosphate (APP) on the fire performances of the obtained composites was assessed.

Many plant leaves exhibit extremely hydrophobic surfaces, which makes them capable of self-cleaning [14]. Because of this high water repellency, which may be advantageous in aerospace applications, the scientific community is interested in mimicking such function on the surface of high-performing materials [14]. The authors prepared wrinkled silica nanoparticles, using the Sol-Gel process, because they have a nanoscale wrinkled structure able to provide a hierarchically structured morphology on the surface where these nanostructures are laid [15]. These mesoporous wrinkled silica nanoparticles can be changed to a Janus type, where each half of the surface is distinguished by a different kind of chemical moieties and functionalities. A Cassie-Baxter surface and consequently superhydrophobic capabilities were demonstrated by the deposition of Janus nano-structured wrinkled colloidal particles on a microscope glass after they had been fractionalized with a hydrophobic silane compound [16]. The Janus nano-structured wrinkled colloidal particles can also be utilized as functional supports for polymers, such as polypropylene grafted maleic anhydride (PPgMA), opening new industrial applications for these particles. Alternatively, a similar strategy based on well-controlled surface functionalization was applied to hemp microparticles, turning them into a hydrophobic filler providing epoxy coatings with anti-icing properties [17].

2. Experimental

2.1. Manufacturing of Electrospun Polyvinylpyrrolidone-Based Materials

The Stöber Sol-Gel method, which produces monodisperse particles through hydrolysis and polycondensation of low molecular weight alkoxides (i.e., tetraethyl orthosilicate) in alkaline solution at room temperature, was used to generate the silica nanoparticles (SiO_2Np), with an average diameter of 250 nm. To achieve a final concentration of polymer and silica of 10 and 20 wt.%, respectively, the SiO_2Np were dispersed in an ethanol solution of PVP (MW: 1,300,000 g mol⁻¹). The suspension in ethanol was electrospun at room temperature with a controlled humidity of 45±10% [13], obtaining thin mats of PVP/silica composite (PVP_ SiO_2NT). To enable successful PVP crosslinking, a second series of mats were thermally treated up to 200 °C (PVP_ SiO_2HT) [6]. Figure 1 shows scanning electron microscopy (SEM), FESEM - Zeiss SIGMA, images of electrospun fibers in the thermally treated sample, with in section some visible silica nanoparticles emerging from the polymer matrix [13]. The thermal

treatment enables the electrospun mat to maintain its integrity and original properties while submerged in water.

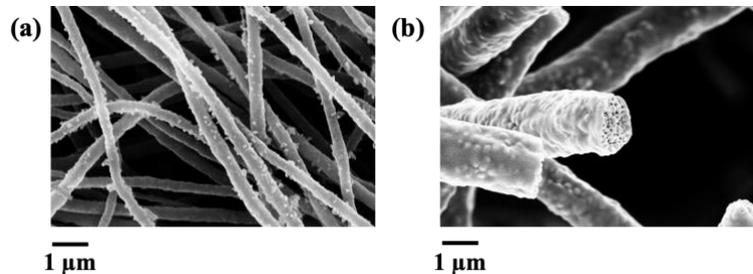


Figure 1. (a, b) SEM images of thermally treated mat (PVP_SiO₂HT) [6].

2.2. Manufacturing of Hemp Fabric/Epoxy Composites

Hand lay-up was the methodology used to prepare composite laminates. These latter were made of a certain number of hemp fabric layers (supplied by MAEKO S.r.l. (Milan, Italy)) impregnated by epoxy resin and cured with cycloaliphatic amine. The curing was performed in a vacuum bag through a curing cycle of 48 h at room temperature. Finally, the fabrication process led to four composites made of resin infiltrated with unmodified hemp sheets (H) or treated hemp sheets (HT), also incorporating 15 wt.% APP. Treated hemp fabric samples were obtained by repeatedly soaking the sheets into a waterglass (Na₂SiO₃, waterglass) solution 0.1 M acidified to pH = 2.5 [13].

2.3. Preparation of in-situ silica-epoxy composites

Silica precursors, i.e. 3-aminopropyltriethoxysilane (APTS) and tetraethyl orthosilicate (TEOS), were used to form, by in-situ sol-gel methodology, 2.0 wt.% of silica nanoparticles into a bisphenol A diglycidyl ether (DGEBA) epoxy matrix. Also, 3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)propanamide (DA) or 6H-dibenz[c,e][1,2]oxaphosphorin,6-[(1-oxido-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-yl)methoxy]-, 6-oxide (DP), melamine (M) and a cycloaliphatic amino hardener (i.e., isophorone diamine) were incorporated into DGEBA to obtain the final epoxy composites [6, 7]. The employed amounts of DA and DP were calculated to produce final composites with 2.0 wt.% of phosphorus (P). The P content was empirically determined by inductively coupled plasma optical emission spectrometry (Optima 3000 instrument, PerkinElmer AG, Rotkreuz, Switzerland). The resulting mixtures were taken for curing and post-curing, after being degassed and placed into a steel mould.

2.4. Synthesis of wrinkled silica-gel particles and Janus nano-structured wrinkled colloidal particles

A modified Sol-Gel procedure was used to produce wrinkled silica nanoparticles. The operational parameters of this methodology allow for a wide range of surface roughness adjustment. Cetylpyridinium bromide (CPB) surfactant and solutions of TEOS, water, and cyclohexane were employed for the synthesis. Throughout the whole procedure, the temperature was maintained at 100 °C, and the generation of a stable emulsion was observed. A TEM (FEI TECNAI G12 Spirit-Twin [16]) image of the synthesized wrinkled silica nanoparticles, which show a highly roughened nano-structured mesoporous surface, is presented in Figure 2a [16].

Since suitable roughness and low surface energy are required for superhydrophobicity, a protocol based on the formation of colloidosomes was used to hydrophobize half of the surface of silica wrinkled particles (i.e., Janus particles) through silanization with dichlorodimethylsilane [16]. These Janus nano-structured wrinkled colloidal particles (JWSNs) have a high propensity to self-assemble, making rougher the surface of a microscope glass on which they are deposited.

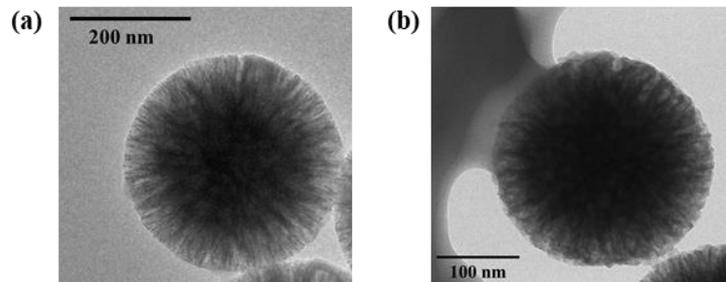


Figure 2. (a) TEM micrograph of the rinsed wrinkled silica-gel particles. (b) TEM micrographs of Janus wrinkled silica particles after functionalization through APTS and PPgMA [16].

3. Results and Discussion

3.1. Innovative Electrospun Polyvinylpyrrolidone-Based Materials for Soundproofing

The electrospun PVP_SiO₂HT mats exhibit the typical characteristics of non-woven fabrics, including a bimodal distribution of fiber diameters, according to SEM analysis [2]. It was shown that the silica particles are embedded inside the PVP fibers and finely separated by thin polymer layers, likely because of the occurrence of physical interactions between the polar groups of PVP and the silanols (Si-OH) on the particle surface [2]. The heat-treated samples exhibited water resistance without experiencing shrinkage. The structure and morphology of these composites are responsible for their specific functional properties.

3.1.1. Thermal and fire behavior of Electrospun Polyvinylpyrrolidone-Based Materials

Polymeric materials are required to fulfill several regulations to be considered in the fabrication of secondary aircraft structures. PVP_SiO₂HT sample passed the smoke density tests outlined in the Aircraft Materials Fire Test Handbook, as well as the 12-s vertical Bunsen burner tests required by Federal Aviation Regulations FAR 25.853 and FAR 25.855. The vertical Bunsen burner test evaluates the flammability of the materials; specifically, the extinguishing time must be shorter than 15 seconds. The self-extinguishing capability of the mats is probably due to their structure, made up of closely packed silica particles forming a ceramic backbone, as well as to the partial thermal degradation that happened during heating up to 200 °C [2].

3.1.2. Acoustic Properties of Electrospun Polyvinylpyrrolidone-Based Materials

The soundproofing capability of electrospun disks was assessed according to ASTM E 1050-12 and ISO 10534-2: the acoustical data were gathered using an impedance tube and reported as frequency vs. sound absorption coefficient [2, 3]. It was discovered that the bell-shaped curves with a sound absorption coefficient higher than 0.9 best describe the acoustical response of the PVP_SiO₂HT mats. By increasing the number and thus the total mass of the disks, the curves move toward a lower frequency and become sharper. For some curves, a second relative maximum can be observed, whose frequency was around three times that of the first maximum. Finally, the impedance tube tests reveal that PVP-based samples may have better sound absorption properties in the lower frequency range than materials of the same thickness that are typically used in the civil and aerospace engineering fields. This is demonstrated by comparing PVP_SiO₂NT and PVP_SiO₂HT electrospun mats with commercial products [2].

3.2. Hybrid Strategies for the Improvement of the Flame Retardancy of Epoxy Composites Cured with Aliphatic Hardener

3.2.1. Thermal and fire behavior of in-situ silica-epoxy composites

Silica-epoxy hybrid nanocomposites (NCs) were produced by modifying the resin with silane precursors and incorporating different flame retardants in the matrix, as described in the Experimental (Section 2.3). Unfilled epoxy resin and silica-epoxy NCs without any flame-retardant could not be classified in the UL 94 tests [6, 7]; however, the presence of silica ensures the formation of a continuous and stable char during the burning of the composites [6]. Although silica nanoparticles were necessary to get a V0 non-dripping rating in the UL 94 vertical burning test (IEC 60695-11-10, sample of $13 \times 125 \times 3 \text{ mm}^3$), epoxy resin having DA alone and 2 wt.% P was still able to achieve the V0 rating (self-extinguishing). On the other hand, epoxy samples containing DP (2 wt.% P) alone burned without any dripping phenomenon. However, to attain a V0 rating when DP was used as a flame retardant, the combined effects of melamine and silica nanoparticles were required. When DA and DP were utilized as flame-retardants in the NCs, cone calorimetry tests (Fire Testing Technology, East Grinstead, London, UK, irradiative heat flux of 35 kW/m^2 (ISO 5660 standard) on specimens ($100 \times 100 \times 3 \text{ mm}^3$)) revealed a striking reduction (up to 75%) in the heat release rate (HRR) (Figure 3). When both additives were used in the production of epoxy NCs, the CO/CO₂ ratio increased, demonstrating their gas phase flame inhibition activity [6, 7]. Additionally, due to a main flame retardant action in the condensed phase, samples containing DA and DP with melamine showed a greater rate of char formation and intumescence, particularly in the case of DP.

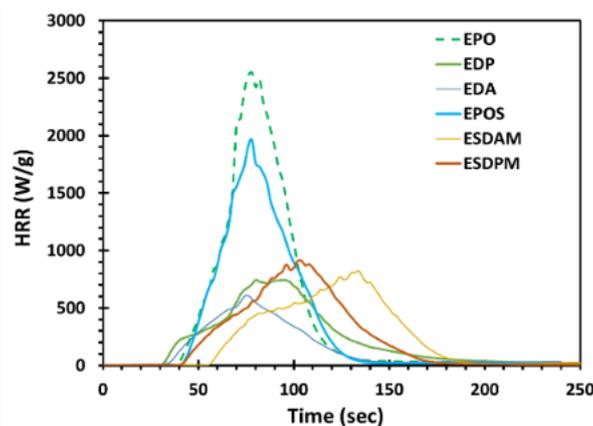


Figure 3. Heat release rate (HRR) curves measured by cone calorimetry for EPO, EDP, EDA, EPOS, ESDAM, ESDPM [6, 7].

3.2.2. Analysis of the residual char and evolved gas and flame-retardant mechanism

After the flammability test, it was shown that residual char of DP-containing samples retained a considerably larger percentage of phosphorus. This high P content in the char residue, obtained from UL 94 vertical spread tests, confirms the predominant condensed phase action of DP. Additionally, the presence of melamine encourages a greater P retention in the residue of ESDPM (8.9%) compared to EDP (4.5%) and ESDP (2.9%), which further supports their activity in the condensed phase [6, 7]. Evolved gas study of epoxy samples performed by direct inlet probe mass spectroscopy (DIP-MS, Finnigan/Thermoquest GCQ ion trap mass spectrometer (Austin, TX, USA)) and pyrolysis-gas chromatography mass spectrometry (PY-GC-MS, Type 5200, CDS Analytical, Inc., Oxford, PA, USA) revealed the release of a notable amount of flame inhibitors (i.e., active phosphorus species), responsible for a gas flame inhibition mechanism, particularly in the case of DA, for which a predominant gas phase activity was demonstrated. Based on the results of the fire studies and residue analysis, it was discovered that DP was mainly active in the condensed phase, where its decomposition products reacted with the

ammonia released by the decomposition of melamine to form P-N-O polymeric substructures and polyphosphoric acids in the char [6, 7] Such char had a greater P retention and, particularly when silica was present, served as a heat shield and oxygen barrier during combustion [7]. Considering the pivotal role of P in flame retardance mechanisms, an innovative sol-gel procedure was recently proposed to incorporate P in silica-based nanostructures by in situ modification of the epoxy resin [8].

3.2.3. Characterization of the Silica Coating on hemp fabrics

The establishment of a silica-based coating can be seen in the Fourier transform infrared (FTIR, Nicolet 5700 FTIR spectrometer, Thermo Fisher, Waltham, MA, USA) spectra of hemp fabrics before and after treatment with the acidic waterglass solution. The bands between 1200 and 1135 cm^{-1} were attributed to the stretching vibrations of the -Si-O-cellulose and -Si-O-Si-bonds, respectively [13]. Washing fastness tests were carried out to confirm the water resistance of the silica-based coating [13]. It was found that the coating was resistant to washing and insoluble in the washing medium. SEM microscopy images related to hemp fabrics before and after acidic waterglass treatment (see Figure 4) reveal that the deposition of the waterglass coating smoothed the surface of the fibers [13]. The formation of -C-O-Si- moieties, ascribed to the reaction between Si-OH and cellulosic C-O-H groups, was proved by NMR (Bruker Bio Spin GmbH, Rheinstetten, Germany) analysis [13].

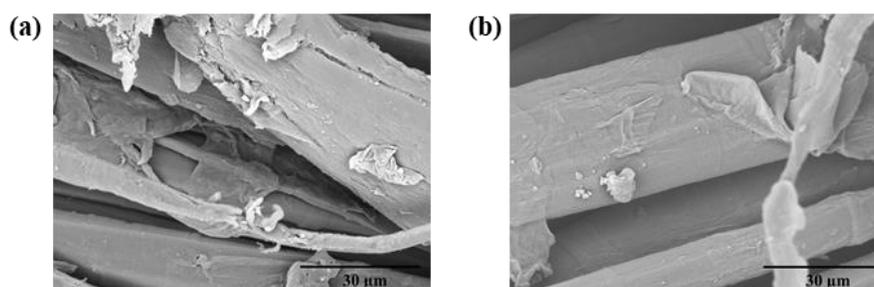


Figure 4. SEM images of: (a) untreated hemp fabric (scale bar: 30 μm); (b) hemp fabric after the waterglass treatment (scale bar: 30 μm).

3.2.4. Thermal, Mechanical and fire behavior of Hemp Fabric/Epoxy Composites

When combined with ammonium polyphosphate, the waterglass treatment appears to be quite successful in enhancing the fire behavior of hemp fabric/epoxy composites. In particular, the combined use of hemp surface treatment and 15 wt.% APP (sample HT/E-15APP) significantly improves such cone parameters as HRR, TSR (total smoke release), THR (total heat release), and SEA (smoke extension area), which show reductions of 83, 35, 45, and 44%, respectively, compared to untreated hemp/epoxy composites [13]. In an inert atmosphere, the generation of an extremely stable char is also encouraged. The low interfacial adhesion between the epoxy matrix and the fibers embrittles the composites, which also exhibit a quite lower stiffness compared to virgin resin. The fabric material reinforced by the waterglass-treated silica layer, on the other hand, is able to absorb more fracture energy, allowing the preservation of the mechanical behavior of the epoxy resin in the presence of both treated fibers and flame retardant additive.

3.3. Manufacturing of hierarchically structured hydrophobic and superhydrophobic coatings

3.3.1. Superhydrophobic coating through the deposition of Janus nano-structured wrinkled colloidal particles

Drop casting was used to deposit wrinkled colloidal silica particles showing a Janus nanostructure on glass substrates, which enabled Cassie-Baxter state to be reached with water contact angle hysteresis as

low as 2° . Atomic force microscope (AFM, Witec Alpha 300 RAS [16]) demonstrated that the JWSNs produced a hierarchical morphology on the glass surface that was controlled at several scales, including the wrinkle size (a few tens of nanometers), particle radius (a few hundreds of nanometers), and interparticle distance. Energy-filtered TEM was employed to study the surface the functionalization of Janus nanoparticles by PPgMA (Figure 2b) [16]. Water contact angle, contact angle hysteresis (CAH), and roll-off angle (ROA) measurements were carried out to deeply study the wettability of microscope glass slides covered by JWSNs. These experiments demonstrated that the surfaces exhibit superhydrophobic properties due to their high water contact angle (149°), and very low water CAH (2°) as well as low ROA (1.8°) [16]. These findings indicate that this sol-gel methodology has a huge potential for use in surface engineering and coating science applications in the aerospace industry.

3.3.2. Hydrophobic and anti-icing coating through the functionalization of hemp microparticles

The hydrophobicity of epoxy resin was also enhanced through the addition of modified hemp microparticles (HMPs), obtained starting from hemp fabrics. The functionalization included waterglass and APTS, giving a reactive silica layer, PPgMA, and either hexadecyltrimethoxysilane (HDTMS) or perfluorooctyltriethoxysilane (PFOTES) [17]. The epoxy coatings cast on aeronautical carbon fiber reinforced panels were evaluated in terms of thermal behavior and wettability. The filler had improved compatibility with the epoxy matrix and tended to migrate toward the surface of the coating. The incorporation of only 2 wt.% of modified hemp particles resulted in an increased T_g and enhanced thermo-oxidative stability. In the case of coatings containing PFOTES, the water contact angle (CA) and contact angle hysteresis (CAH) reached 115° and 33° , respectively, and the freezing time of water droplets at -30°C was extended up to 1.8 min, whereas samples cast with pristine resin showed $\sim 84^\circ$ and 0.9 min, respectively (Figure 5).

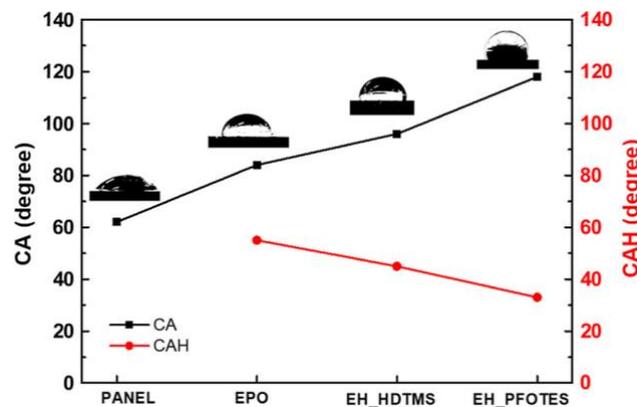


Figure 5. CA, CAH, and water droplet representations of untreated aeronautical panel (PANEL) and of the ones coated by pristine resin (EPO), epoxy formulation containing HDTMS (EH_HDTMS), and epoxy formulation based on PFOTES (EH_PFOTES) (reprinted with permission from [17]).

The improvement of hydrophobicity and anti-icing behavior was ascribed to the synergy of the hierarchical rough surface morphology and the non-polar nature of the modified HMPs [17]. The study presents an original approach to transform waste fabrics into functional fillers for composite coatings.

4. Conclusions

The purpose of this work is to demonstrate how Sol-Gel chemistry can effectively be used to create a variety of cutting-edge materials for specific aerospace applications. Hemp fibers coated with silica or in-situ silica-modified epoxy resins enable the manufacturing of polymer-based composites showing very good fire retardance without dripping phenomena. Silica-epoxy nanocomposites may also achieve

self-extinction by employing the flame retardant properties of DOPO derivatives. As regards thermoplastic polymers, electrospun polyvinylpyrrolidone mats can be fabricated in an environmentally friendly manner. When Stöber silica nanoparticles are added to the polyvinylpyrrolidone mats and a specific thermal treatment is applied, the result is a material that exhibits unheard-of sound absorption coefficients at very low frequencies and self-extinguishing behavior. Janus nano-structured wrinkled colloidal particles with an intrinsic hierarchical architecture can be obtained using sol-gel chemistry for the fabrication of superhydrophobic surfaces. A sustainable alternative toward coatings with increased hydrophobicity and anti-icing capability is offered by the suitable functionalization of hemp microparticles with silica, a thin polypropylene layer, and an alkyl silane. These results highlight the versatility of the Sol-Gel methodology in both the synthesis and modification of nanostructured materials to produce multifunctional composites.

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