Journal of Physics:
Conference Series

PAPER • **OPEN ACCESS**

Eco-friendly composites with specific functional properties

To cite this article: J Passaro *et al* 2024 *J. Phys.: Conf. Ser.* **2716** 012042

Eco-friendly composites with specific functional properties

J Passaro[1], A Bifulco[2], L Guadagno[3], A Aronne[2], F Cimino[1] and P Russo[1]

[1]Institute for Polymers, Composites and Biomaterials, National Research Council, Pozzuoli (Naples), Italy
[2]Department of Chemical, Materials and Production Engineering (DICMaPI), University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy
[3]Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (Salerno), Italy

jessica.passaro@ipcb.cnr.it

Abstract. The development of sustainable hydrophobic composite coatings is of high interest for aircraft applications. Currently, the use of natural derived functionalized microparticles as filler to obtain hydrophobic epoxy-based coatings was not deeply investigated. In this scenario, a novel hydrophobic epoxy-based composite including waste hemp microparticles functionalized with silica layer, 3-aminopropyltriethoxysilane, polypropylene-graft-maleic anhydride and silanes (hexadecyltrimethoxysilane and 1H,1H,2H,2H-Perfluorocotyltriethoxysilane) is presented. The resulting coating was casted on typical aeronautical panel, based on carbon-fiber-reinforced polymers, to achieve an improved hydrophobicity and anti-icing property induced by functionalized hemp microparticles.
The wettability and anti-icing property were investigated. Compared to unfilled epoxy resin, the obtained composite coating achieved a greater water contact angle of 30° and doubled increase in icing time. Despite the low content (2 wt.%) of hemp particles, DSC analysis displayed a relevant increase in Tg value, confirming an efficient interaction between the epoxy matrix and the functionalized hemp filler. AFM analysis proved how the presence of hemp filler leads to an increase in roughness due to the hierarchical structure formed by the long chains of silane molecules. The combination of silane activity and rough morphology allows the development of hemp composite coatings with enhanced hydrophobicity, anti-icing behavior and thermal stability for aircraft applications.

1. Introduction

Polymer composites and nanocomposites play an important role for several manufacturing industry, such as automotive and aerospace [1-3]. Recently, much work has been focused on the development of polymer composite coatings due to their strong damping capacity, high specific modulus and strength, anti-icing and self-monitoring properties [4-6]. The physical and mechanical enhancements result from the interaction (e.g., hydrogen bonds) between filler (e.g., inorganic particles and fibers) and polymer matrix at the nanometre scale [7-8].
Nowadays, the increased awareness of the environmental impact of composite materials at the end of their life has directed both academic and industrial research towards alternative solutions with almost similar performance and functionality but, at least partially, derived from renewable resources or recyclable raw materials, even for advanced applications [9 -10].

In this scenario, natural fibers (e.g., hemp, flax) have been widely validated as a promising alternative to conventional ones as reinforcement of polymeric matrices because of their renewability, lightness, high specific mechanical properties, ease of surface modification, cost effectiveness, etc [9, 11-12].
However, the incompatibility between natural fiber and matrix, the fiber size variability, their flammability and difficult processability limit the use and development of natural fiber composites. [13] Such drawbacks need to be overcome by fostering further investigations. Additional research efforts for the development of eco-friendly materials are crucial to achieve a more sustainable future.
In the present study, thermosetting composite coatings with enhanced hydrophobicity were deposed by casting on carbon-fiber-reinforced (CFR) polymer panels typically employed for aircraft structures. The novelty of this work was to demonstrate the possibility of using waste hemp functionalized particles to obtain innovative hemp-epoxy coatings with improved hydrophobicity and anti-icing performances for aircraft applications [14]. Specifically, morphological, structural, thermal and hydrophobic/anti-icing properties of hemp composite coatings are discussed.

2. Materials and Methods

Waste hemp rugs supplied by by MAEKO S.r.l. (Italy) and, as shown in Figure 1, were functionalized in 3 steps procedure:

- Initially hemp rugs surfaces were modified by employing sodium metasilicate in a sol−gel procedure allowing the formation of a silica layer on the hemp surface, making them brittle and suitable for obtaining hemp-silica powder (HEMPSi).
- In the second step, a second functionalization with amino groups of HEMPSi (HEMPN) was carried out by using the coupling agent 3-aminopropyltrimethoxysilane (APTS).
- Finally, to confer hydrophobic character to hemp particles HEMPN, the amino groups were left to react with polypropylene-graft-maleic anhydride (PPgMA), leading to HEMPP microstructures.

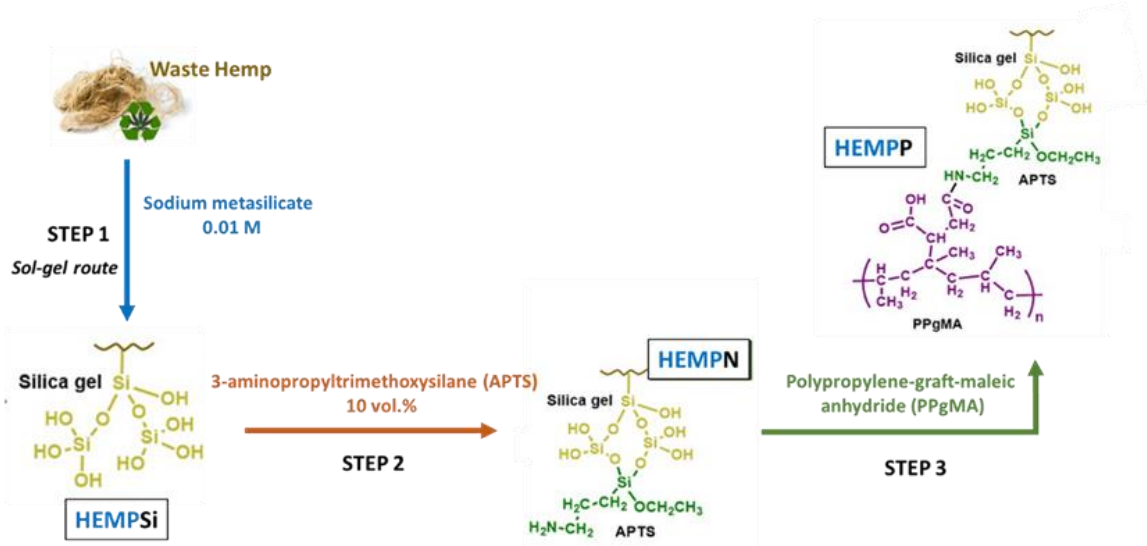

Figure 1. Procedure for the preparation of hydrophobic hemp particles (HEMPP) (reprinted with permission from [14]).

For the preparation of polymer-based coatings, as shown in Figure 2, the epoxy resin system bisphenol A diglycidyl ether (DGEBA) and modified cycloaliphatic polyamines hardener, purchased from MATES S.r.l. (Italy), were mixed with 2 wt% of functionalized hemp particles HEMPP and 1 wt% of silanes (hexadecyltrimethoxysilane (HDTMS) or 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES)). All the coatings were cured for 24 hours at 60 °C and post-cured for 4 hours at 80 °C. The functionalization and fabrication of hemp particles and the manufacturing of fiber-reinforced epoxy composite coatings are well described in [14]. All the investigated samples are listed in Table 1.

Table 1. Chemical composition of epoxy composite coatings.

Sample	Description
EPO	DGEBA resin cured with polyamines hardener (Epoxy System)
EH-HDTMS	Epoxy system with 2 wt% of HEMPP and 1 wt% of HDTMS
EH-PFOTES	Epoxy system with 2 wt% of HEMPP and 1 wt% of PFOTES

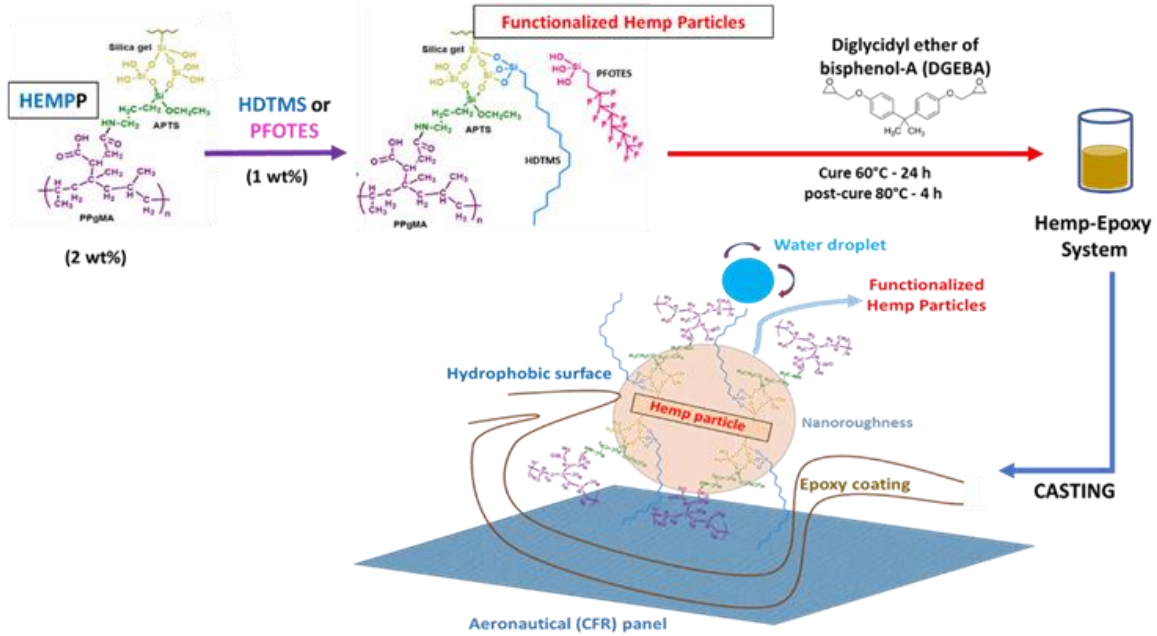

Figure 2. Overall procedure for obtaining the hemp-epoxy composite coatings (reprinted with permission from [14]).

2.1. Wettability and anti-icing tests

To evaluate the wettability of hemp-epoxy coatings, the contact angle (CA) and hysteresis contact angle (CAH) were measured by placing a water droplet on the coated surface of aeronautical panels. The anti-icing performances of hemp-epoxy coatings were evaluated by determining the freezing time of water droplet in a rigorous climate environment (-30°C for 10 minutes) and simulating the ice formation on aircraft structures during the winter season.

2.2. Structural, Morphological and Thermal Analysis

Structural analysis was performed on functionalized hemp particles and hemp-epoxy composites by using Attenuated Total Reflectance–Fourier Transform Infra-Red (ATR-FTIR) analysis and Scanning Electron Microscopy (SEM), coupled with an EDX system for a semi-quantitative elemental exploration. Atomic force microscopy (AFM) was used to evaluate the surface roughness of pristine epoxy and hemp-epoxy coatings. For all the specimens, the roughness average (Ra) and the root mean square roughness (Rq) parameters were evaluated according to equations shown in [14]. Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) were carried out to assess the thermal behavior of pristine epoxy and hemp-epoxy coatings.

3. Results

SEM-EDX analysis was conducted on the hemp particles after the three steps of functionalization procedure. Figure 3 shows the typical web-like structure and unregular morphology of the hemp microfibrils, with diameter from tens of nanometers to tens of microns.

Table 2. Elemental composition (wt.%) of functionalized hemp particles evaluated by EDX analysis.

Composition (%)	C	O	N	Si
HEMPSi	39.5	57.3	-	3.2
HEMPN	37.9	53.2	6.7	2.2
HEMPP	46.5	45.6	-	7.9

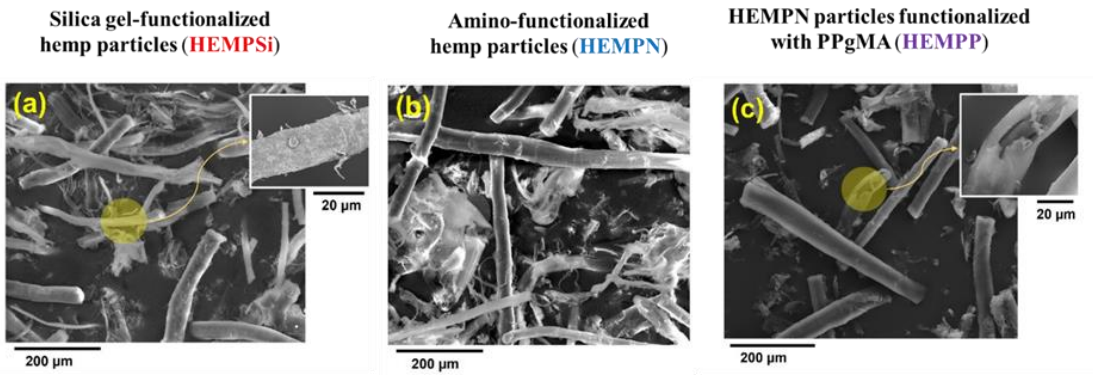

Figure 3. SEM micrograph of functionalized hemp particles with: (a) sodium metasilicate, (b) APTS and (c) PPgMA. (Reprinted with permission from [14]).

The presence of the silica layer on HEMPSi and amino groups on HEMPN surface was confirmed by EDX analysis (Table 2). Figure 3(c) reveals that the surface of HEMPP particles appears slightly waxy and different compared to the ones of HEMPSi and HEMPN microfibrils. This was ascribed to a thin layer of polypropylene covering the primary wall of hemp particles. Furthermore, the presence of PPgMA on HEMPP was confirmed by a higher amount of carbon (46.5%) recorded by EDX (Table 2), compared to the carbon amount found on HEMPSi particles. The successful functionalization of hemp microfibrils was also assessed by ATR-FTIR analysis, as shown in Figure 4.

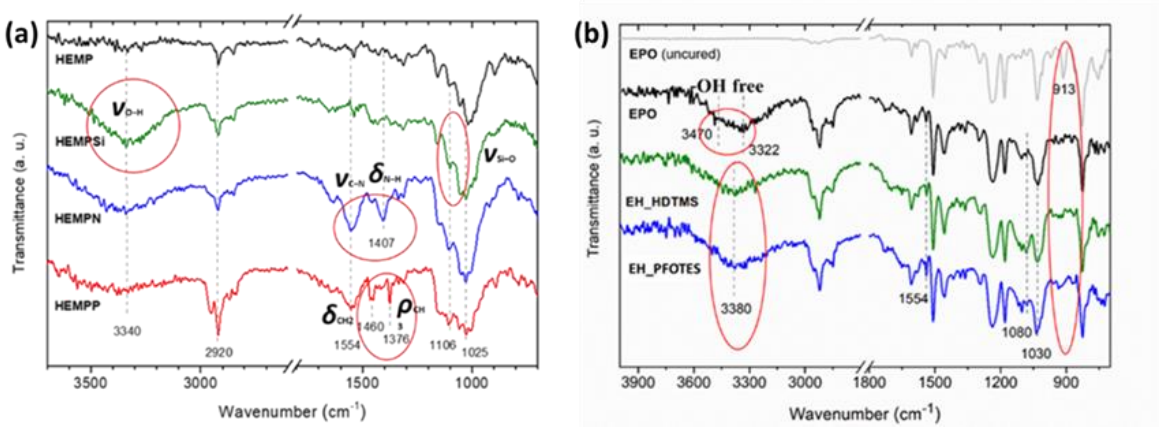

Figure 4. ATR-FTIR Spectra of (a) functionalized hemp particles, (b) uncured epoxy resin, resin cured with the amine hardener, composite coatings EH_HDTMS and EH_PFOTES. (Reprinted with permission from [14]).

The highlighted signals on ATR–FTIR spectrum (Figure 4(a)) confirm the effective functionalization of the hemp fiber particles:

- the bands at 3340 cm^{-1} ($\nu_{O–H}$) and 1100 cm^{-1} ($\nu_{Si–O}$) confirm the presence of silanol groups on HEMPSi particles;
- the bands at 1554 cm^{-1} ($\delta_{N–H}$) and 1407 cm^{-1} ($\nu_{C–N}$) support the presence of primary amino groups on HEMPN particles;
- the typical bands assigned to C–H bending (1376 cm^{-1} and 1460 cm^{-1}) and the increase of the C–H stretching bands at 2900–3000 cm^{-1} prove the t grafting of PPgMA on the primary wall of the HEMPP particles.

The chemical structure of the composites was also investigated by ATR-FTIR (see Figure 4(b)). The disappearance of the vibration band at 913 cm^{-1} indicates the complete cure of all the samples. For the epoxy composites EH_HDTM and EH_PFOTES, the presence of a single signal (3380 cm^{-1}) of O–H stretching band indicate the establishment of H-bonding interactions between the cured oxirane rings of resin and the functional groups on hemp particle surfaces.

The wettability of the composite samples was investigated by measuring the water contact angles (CA) and contact angle hysteresis (CAH). The CAH is a dynamic parameter provides information on the droplet mobility on the surface.

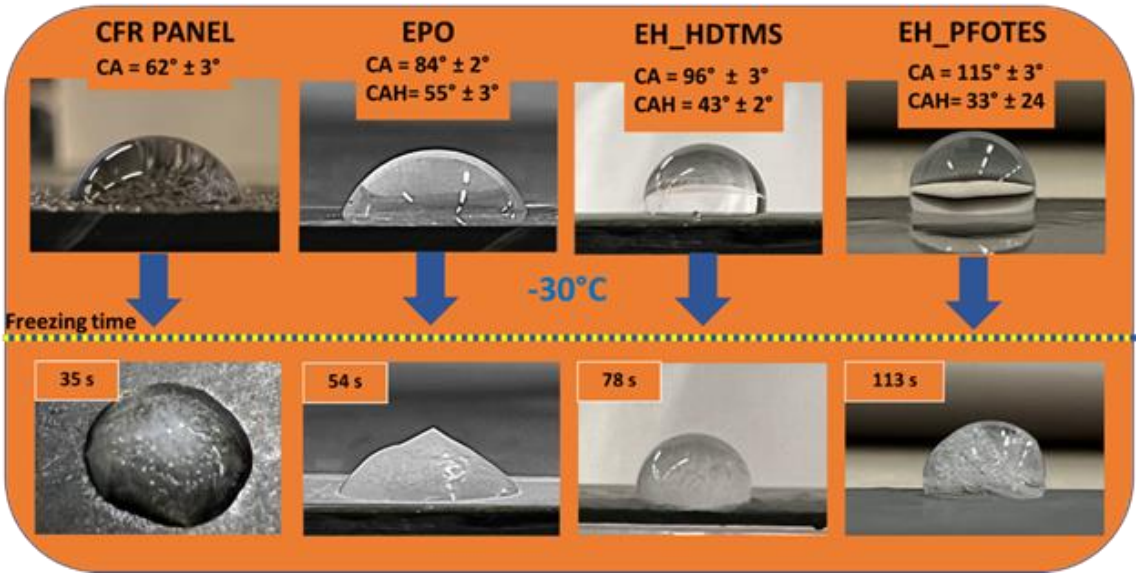

Figure 5. Pictures of water droplets at room temperature (above) with relative CA and CAH values, and after freezing process at −30 °C (below the dot line). The freezing time of water droplets on CFR panels and substrates coated with pristine resin (EPO), EH_HDTMS, and EH_PFOTES samples are shown. (Reprinted with permission from [14]).

In Figure 5 it is possible to observe that in the absence of functionalized hemp filler, the pristine EPO shows a hydrophilic character, due to the presence of hydroxyl groups which can form H-bonds with water molecules. By contrast, a hydrophobic behavior is observed for the two composite samples EH_HDTM and EH_PFOTES, due to the presence of silanes alkyl chains at the surface, which provides higher CA and lower CAH compared to pristine EPO sample. This result highlights the effects of structural and chemical contributions of HEMPP particles on the surface wettability. Besides, Figure 5 displays the change of water droplet shapes on samples after the freezing tests. The semicircular shape droplets were observed for the CFR panel and pristine EPO. By contrast, on the composite coatings, the water droplets remained more spherical with a delaying of the freezing time. These results can be justified by the reduction of the contact area between the hydrophobic coating surface and the water droplet, leading to a lower heat transfer rate.

The calorimetric analysis (DSC) shows the increase of T_g values (up to ~26%) of hemp-epoxy composites compared to the pristine EPO sample. This effect is ascribed to the chemical functionalization of hemp particles, which promotes the formation of many secondary interactions (i.e. H-bond) between the polymer matrix and the functional groups on HEMPP particles.

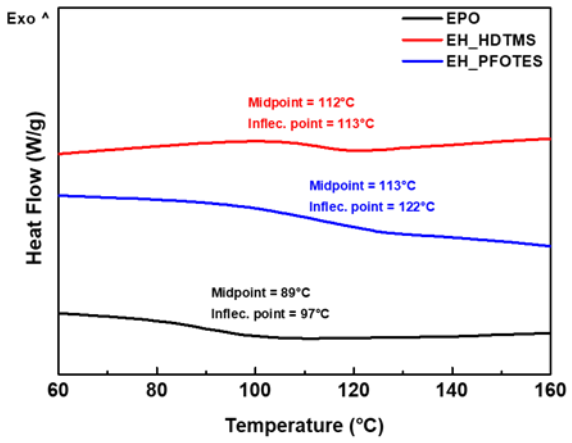

Figure 6. DSC curves (2nd heating) for the samples EPO, EH_HDTMS and EH_PFOTES.

The presence of these secondary interactions is also confirmed by TGA analysis carried out in air, showing an increase of the initial degradation temperature of the hemp-epoxy composites by ~20 °C compared to pristine EPO, as shown in Figure 6. Furthermore, in Table 3, the temperatures of second degradation step (T_{max2}) of composite coatings were up to 30 °C higher than pristine EPO. These values, together with the higher residual masses, prove that the addition of functionalized hemp particles lead to an enhanced thermal stability of the hemp-epoxy composites.

Table 3. Results of TGA in air atmosphere for pristine resin and epoxy composites: temperatures at which 5% weight loss is recorded ($T_{5\%}$), temperatures at which the weight loss rate reached maximum values (T_{max1} and T_{max2}), residue masses at the final temperature of 800°C.

Sample	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Residue (%) at 800°C
EPO	204	366	541	1.5
EH-HDTMS	222	372	563	3.2
EH-PFOTES	221	368	571	2.8

Table 4. Roughness parameters evaluated by AFM analysis.

Sample	Ra (nm)[a]	Rq (nm)[b]
EPO	16.0	19.9
EH-HDTMS	31.4	36.1
EH-PFOTES	55.9	76.1

[a] Average Roughness.
[b] Mean Square Roughness.

AFM analysis was used to estimate the nanoscale roughness of the samples. The evaluated parameters (Ra and Rq) in Table 4 show a relatively low roughness values of pristine EPO. By contrast, both composite samples exhibit a much higher roughness value. This effect can be attributed to the high ability of silane chains (HDTMS or PFOTES) to migrate toward the solid-air interface, leading to an effective surface hierarchical structure in terms of hydrophobicity and anti-icing capability.

4. Conclusion

This research activity focused on the use of waste hemp as functional filler to produce innovative hydrophobic coatings for aircraft structures. The chemical modification procedure allows to convert the natural hemp hydrophilicity into hydrophobic behavior, making it a suitable filler for non-polar epoxy matrix. The rough morphology and non-polar character of the functionalized hemp particles exhibit a synergistic action with epoxy matrix, leading to an enhancement in terms of thermal behavior, hydrophobicity and anti-icing performances. In addition, the boosted hydrophobicity and roughness are due to the anchored fluorinated silane (PFOTES) or the greener and cheaper alkyl silane (HDTMS). It is important to underline that all the results have been achieved by using only 2 wt% of HEMPP through an easy one-pot procedure with mild operating conditions. In conclusion, the use of cellulose and its derivatives in non-wettable coatings have many potentials and would reduce both material and coating fabrication costs. In a context of circular economy, it is important to underline the novelty of this research aimed at developing new sustainable coatings starting from cellulose, alternatives to

conventional solutions based on fluorinated agents which are effective but nowadays rejected due to their environmental impact.

Acknowledgments
This research is funded by the University of Salerno, project code: 300395CIC22RAIMONDO.

References

[1] Passaro J, Russo P, Bifulco A, De Martino M T, Granata V, Vitolo B, Iannace G, Vecchione A, Marulo F and Branda F. 2019 *Polymers* **11(7)** 1205
[2] Das S, Kumar S, Samal S K, Mohanty S and Nayak S K 2018 *Ind. Eng. Chem. Res.* **57** 2727–2745
[3] Parveez B, Kittur M I, Badruddin I A, Kamangar S, Hussien M and Umarfarooq M A 2022 *Polymers* **14(22)** 5007
[4] Kopparthy S D S and Netravali A N 2021 *Compos. C: Open Access* **6** 100169
[5] Sanchez C, Belleville P, Popall M and Nicole L 2011 *Chem Soc Rev* **40(2)** 696-753
[6] Bragaglia M, Paleari L, Passaro J, Russo P, Fabbrocino F, Luciano R and Nanni F 2023 *Compos. Sci. Technol.* 110253
[7] Branda F, Passaro J, Pauer R, Gaan S and Bifulco A 2022 *Langmuir* **38(18)** 5795–5802
[8] Passaro J, Imparato C, Parida D, Bifulco A, Branda F and Aronne A 2022 *Compos. B. Eng.* **238** 109874
[9] Papa I, Formisano A, Lopresto V, Cimino F, Vitiello L and Russo P 2020 *J. Compos. Mater.* **54(24)** 3481-3489
[10] Sanjay M R, Madhu P, Jawaid M, Senthamaraikannan P, Senthi, S and Pradeep S 2018 *J. Clean. Prod.* **172** 566–581
[11] D'Angelo G A, Leone G, Pagliarulo V, Ferraro P, Vitiello L and Russo P 2022 Non-destructive evaluation of damage detection in hybrid basalt/flax fibres-polypropylene composites. *In Nondestructive Characterization and Monitoring of Advanced Materials, Aerospace, Civil Infrastructure, and Transportation XVI SPIE* Vol. 12047 pp. 12-17
[12] Bifulco A, Silvestri B, Passaro J, Boccarusso L, Roviello V, Branda F and Durante M 2020 *Materials* **13(8)** 1844
[13] Jawaid M and Khali H P S A 2011 *Carbohydr. Polym.* **86** 1–18
[14] Passaro J, Bifulco A, Calabrese E, Imparato C, Raimondo M, Pantani R, Aronne A and Guadagno L 2023 ACS Omega **8 (26)** 23596-23606