

H. Aguilar^a, D. Conceição^a, A. Barros^a, V. Bouça^a, M. Ornelas^a,
R. Malgueiro^a, A. Carvalho^a, A. Portela^a, C. Silva^a, E. Döpelheuer^b,
S. Grishchuk^c, L. Gryshchuk^c, M. Gilberg^c, B. Wetzel^c

^a CeNTI, Centre for Nanotechnology and Smart Materials, V. N. Famalicão, Portugal

^b KORENA, Kroppenstedter Ölmühle Walter Döpelheuer GmbH, Kroppenstedt, Germany

^c IVW, Institut für Verbundwerkstoffe GmbH, Kaiserslautern, Germany

Uso de nanopartículas de sílica biogénica derivadas de la biomasa en las formulaciones poliméricas y sus aplicaciones

RESUMEN

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Avanzando hacia una sociedad post-petrolera, se hacen varios intentos para conciliar la escasez de recursos y objetivos ambientales con el uso de biomasa para aplicaciones industriales multisectoriales. El proyecto ReInvent objetiva entregar nuevos biomateriales como aditivos/bio-nanofillers para aislantes y estructurales para edificios y espumas suaves ligeras para interiores de vehículos. Los procesos de extracción/fraccionamiento de las biorrefinerías objetivan proporcionar materias-primas sostenibles para el desarrollo de bio-nanosilica funcionales para incorporar en matrices poliméricas, produciendo nuevos materiales celulares y compuestos avanzados. Este trabajo se basa en la extracción, purificación y caracterización de bio-nanosilica de residuos ricos en silicatos (cáscaras de arroz y cáñamo, fibras de cáñamo, residuos sólidos de prensado de aceite). Los extractos se examinaron mediante microscopía electrónica de barrido, mediciones de superficie y poros. Se estudió la influencia de la bio-nanosilice en los comportamientos reológicos de las bioresinas de furano y de poliurea indirecta para posible preimpregnado de ambas. La influencia de bio-nanosilica dispersada en componentes de isocianato y vidrio soluble (WG) sobre el comportamiento quimiorreológico de la resina, mostró un fuerte aumento de la viscosidad en condiciones ambientales, pero sin diferencias obvias a temperaturas de procesamiento entre 60-90 °C. Se garantizaron condiciones de procesamiento similares, mejor capacidad de manipulación y almacenamiento de preimpregnados relacionados. La reducción de la velocidad de reacción, confirmada por un aumento lento de la viscosidad, fue característica de la resina de IPU conteniendo bio-nanosilica, cuando se dispersó en WG, potenciando una vida útil más prolongada de estos preimpregnados altamente reactivos en condiciones de almacenamiento en frío.

Use of biogenic silica nanoparticles derived from biomass in polymeric formulations and their applications

ABSTRACT

Keywords:

Sustainable bio-(nano)fillers

Circular economy

Sustainability

Adhesives and composites

Construction & Automotive applications

In view of moving towards a post-petroleum society, several attempts are being made to reconcile resource scarcity and environmental objectives with the use of biomass for multisector industrial applications. ReInvent project aims to deliver novel bio-based materials as additives/bio-nanofillers for insulation and structural products used in buildings and lightweight soft foams for vehicle interior products. The extraction/fractionation processes from biorefineries aim to provide sustainable raw-materials for the development of functional bio-nanosilica particles to be incorporated in polymeric matrices, to produce new advanced cellular and composite materials. Particularly, this work lies on the extraction, purification and characterization of bio-nanosilica extracted from rich-silicate residues (e.g. rice husks, hempshells, hempfibres, oil pressing solid residues). The extracts were examined using scanning electron microscopy, and their textural properties were evaluated by surface area and pore measurements. Influence of bio-nanosilica on the rheological behaviours of biobased furan and greened indirect polyurea resins was studied in terms of possible prepregging of both resins. A comparison of influence of bio-nanosilica dispersed in isocyanate and waterglass (WG) components on the chemo-rheological behaviour of the resin was performed, showing a strong increase of viscosity at ambient conditions, but no obvious difference at typical processing temperatures between 60-90 °C. Thus, similar processing conditions, improved handling and storage ability of related prepregs were ensured. Obvious reduction of reaction speed, confirmed by slower increase of viscosity, was characteristic for IPU resin containing bio-nanosilica particles, especially when dispersed in WG, potentiating longer shelf-life of such highly reactive prepregs at cold storage conditions.

1 Introduction

On the verge of depletion of oil sources and of a more environmentally conscious society, several attempts are being made to create synergies between biomass production and processing sectors as means to solve natural resource scarcity and fulfil environmental objectives using biomass residues and by-products for multisector industrial applications. Within this scope, the ReInvent project intends to deliver novel bio-based materials and frameworks as additives/bio-nanofillers for insulation and structural products used in buildings and lightweight soft foams for vehicle interior products.

The agro-industry wastes are by-products resultant from the procedure of energetic crops (biomass). Their incineration provides a solid waste named ashes, which can be thrown away in disposals because of their low added value. An incorrect management of these wastes could raise serious questions about human health and environment issues. A possible solution for this problem is an encouragement to a sustainable and rational environment recovery of these wastes. In the present study, an alternative ending is proposed for the Si-enriched wastes, that can be used to provide a sustainable and rational environment source of silica. In the literature, there is work reporting the extraction, quantification and characterization of silica present in different vegetable residues, that could be used for several industrial applications. L. Jones and A. Milne studied the silica content in different parts of oat plant. From this study, they concluded that the most promising plant parts for the extraction of silica were the leaves and the stems, with silica content of 0.1% - 3.49% and 0.08% - 1.03%, respectively [1]. Elmoniem *et al.* studied the distribution of silica in cucumber leaves harvested with different maturation periods. In this study it was found that the silica content present in the soil directly influenced the maximum silica content bioaccumulated in the plant. Additionally, the authors also concluded that, the longer the maturation period, the higher was the silica content bioaccumulated, ranging from 13% to 43.9%. [2] F. Lanning determined the silica content of different rice plant parts, namely roots (5.82%), stems (5.10%), sheaths (13.13%) and leaves (10.13%). [3] J. Amick extracted and purified silica from rice husks to produce a solar grade silicon for solar cells, which had a silica content of 20% - 25%. [4] Sharma *et al.* have performed a mapping of the silica distribution in the husks by energy-dispersive X-ray analysis (EDAX), and they have shown that it is concentrated primarily within the outer epidermis, although a small amount of silica was found within the inner epidermis adjacent to the rice kernel. [5] In the investigations carried by Mishra *et al.* and Chakraverty *et al.*, the white ash obtained from the combustion of this raw material at moderate temperature, contains ~92% - 97% amorphous silica and some amount of metallic impurities that can be removed further by a simple acid-leaching treatment. [6, 7]

In the present work alternative agro-industry residues, such as hemp shells, hemp fibres, solid residues of oil pressing, with potential for biogenic silica nanoparticles extraction were studied. This work contemplates not only the extraction process, but also the quantification methodology and morphological characterization of the extracted materials. As it is intended that these nanomaterials are used as bio-nanofillers in insulation and structural products used in buildings and lightweight soft foams for vehicle interior products, their rheological behaviour

in polyfurfuryl alcohol (PFA) and greened indirect polyurea (IPU) bio-based resins, results of the ReInvent project, was also accessed.

Biomass derived furan resins, also called PFA resins are well known in the field of bio-composites due to their high potential for replacement of common phenolic resins and versatile properties such as nearly 100% renewable content, carbon footprint neutrality, no emission of formaldehyde, good mechanical and thermal properties, high fire resistance, etc. Usually, hemicellulose-rich biomass residues like corn cobs, natural fibre husks, sugarcane bagasse are used for its extraction and conversion in furfural, being sequentially converted via catalytic hydrogenation to furfuryl alcohol. Finally, oligomerisation of furfuryl alcohol in acidic conditions take place, resulting in variety of PFA resins of various molecular mass and functionality, depending on time and temperature of reaction. [8-11] Therefore, high-viscosity PFA prepreg resin was selected as the first candidate for the investigation of rheological behaviours of formulations containing novel biogenic silica nanoparticles.

On the other hand, authors are working intensively on the development of indirect polyurea resins, so called 3P resins (from polyisocyanate + phosphate + polysilicate) originally marketed by Polinvent Ltd (Budapest, Hungary) [12], their hybrids and phosphate-free alternatives (also called 2P resins). [13-17] Recently, an IPU resin was developed by total replacement of organic phosphate by relatively low amount of epoxidized linseed oil (ELO). [18-19] In contrary to organic phosphates in 3P resins being able to diffuse out, there are no concerns with change of material properties and pollution of environment due to migration and/or extraction of the plasticiser when ELO is used. Thanks to epoxy groups in its structure, this bio-based material remains chemically bounded to the matrix, e.g. via reactions with isocyanate groups and partially due to certain reaction with formed amines, despite low reactivity of epoxidized plant oils toward primary amines. Therefore, this type of resin was selected for investigation of the influence of new biogenic silica nanoparticles on its chemo-rheology at RT in order to be able to evaluate potential of such nano-reinforced IPU resins for the development of highly reactive prepreps.

2 Experimental

2.1 Materials

Several agro-residues were used in this work: rice husks, hemp shells, hemp fibres, wheat, and mustard seeds, as well as hemp press cake (by-product of the oil pressing process) were all supplied by Korena, DE. Non-catalysed prepreg furan resin (PFA) was supplied by Coventive Composites, UK and served for rheological studies (specific details not published for commercial reasons). Ammonium molybdate tetrahydrate was acquired from Alfa Aesar. Oxalic acid dehydrate, sodium metasilicate and metol (p-methylaminophenol sulfate) were purchased from Sigma-Aldrich. Sodium sulphite anhydrous was purchased from VWR. Polymeric diphenylmethan diisocyanate (PMDI) Lupranate® M20S was acquired from BASF, DE. Epoxidized linseed oil (ELO) Lankroflex™ L was acquired from Akcros Chemicals Ltd., UK. PI-Liner 3P Komp. A, a ~50 wt.% aqueous sodium silicate solution with a Na₂O/SiO₂ ratio of



1:1.6–2.6, viscosity 600 mPa·s and density 1.55 g/cm³, was purchased from Polinvent Ltd., HU. Unless otherwise stated, all solutions were prepared using Milli-Q ultra-pure deionized water.

2.2 Methods

2.2.1 Biogenic silica nanoparticles extraction

Initially, the residues were washed with deionized water, under stirring, at ~22 °C. Then, acidic extraction was performed by adding an acid and stirring the mixture at 60 °C for 2 hours. After this time, the residues were filtered and neutralized with deionized water, followed by drying at 110 °C for 12 h. The dried residues were then pyrolyzed in a muffle furnace, which was heated from 22 °C to 700 °C for 2h30 and maintained at 700 °C for 3h30, to obtain silica powder.

2.2.2 Quantification and characterization of the extracted biogenic silica nanoparticles

2.2.2.1 Quantification of silica in the extracted powder

The quantification of the silica content in the powder resulting from the extraction process was performed based on a colorimetric method described by Nelson and Arrington [20]. Briefly, an 8 g/L solution of acidified ammonium molybdate was prepared in 5% (v/v) HCl. A metol-sulfite solution (reduction reagent) was prepared by dissolving 0.3 g of anhydrous sodium sulfite in 15 mL and then adding 0.5 g of metol. Solutions of 50% (v/v) of sulfuric acid and 10% (w/v) oxalic acid were also prepared. Different working solutions with different concentrations (0 - 35 µM) of silicic acid were also prepared and quantified in order to draw a calibration curve.

For the quantification of silica, 2 mg of each extracted sample was solubilized in sodium hydroxide 1 M at 100 °C for 2 h, in an oil bath. After solubilization, the obtained silicate was dissolved in 1300 µL water.

To perform silicomolybdate assay, each tube was loaded with 1994 µL of the standard working solution or sample and 800 µL acidified ammonium molybdate solution. After 15 minutes, a freshly prepared mixture solution of metol-sulfite reagent, 10% oxalic acid, 50% acid sulfuric and water was prepared, and 1205 µL were added to each tube. The blue colour was left to develop over 2 h at room temperature, before measuring the absorbance at a wavelength of 810 nm in a spectrophotometer (Lambda35, Perkin Elmer).

2.2.2.2 Particle characterization

The extracted powders were observed by a Field Emission Gun/Scanning Electron Microscopy (FEG/SEM) - Nova NanoSEM 200 (FEI Company) with an integrated system EDS/EBDS - EDAX - Pegasus X4M (EDS - energy dispersive spectrometer/EBSD - Electron Backscatter Diffraction) to obtain EDS (chemistry) data. The samples were fixed by mutual conductive adhesive tape on aluminium stubs and covered with carbon palladium using a sputter coater.

The superficial area of the extracted silica powders was determined by the N₂ desorption isothermals at -196 °C,

recurring to a multipoint analysis performed at a Quantachrome NOVA 4200e (Quantachrome Instruments) equipment. The BET specific surface area (S_{BET}) was obtained according to the Brunauer-Emmett-Teller (BET) method. For the analysis, 150 mg of each sample was previously degassed for 5 h at 120 °C. The mesopore surface area (S_{meso}) and the micropore volume (V_{micro}) were determined by the t method. The total pore volume (V_p) was determined for $P/P_0 = 0.95$ (in which P is the pressure and P_0 is the saturation pressure). The average pore diameter (d_p) were calculated using the BJH method applied to the desorption branch of the isotherm.

2.2.3 Incorporation of bio-silica on polymeric matrices

Lab scale ultrasonic bath was used for dispersion of new biogenic silica nanoparticles. Three concentrations of bio-nanosilica, i.e. 0.25 (PFA-0.25 phr SiO_{2_US}), 0.5 (PFA-0.5 phr SiO_{2_US}), and 1.0 phr (PFA-1.0 phr SiO_{2_US}) have been selected for investigation of its dispersibility. Non-filled PFA resin was used as the reference (PFA-Ref). For this purpose, silica was firstly mixed into the resin at 60 °C for 30 min at 300 rpm and then subjected twice to ultrasonication for 15 min at 60 °C and finally vacuum-degassed. Obtained dispersions were cooled down to the room temperature (RT, i.e. 25 °C) prior to rheological measurements.

For further dispersion method comparison, mechanical dispersion of the bio-nanofiller in the PFA resin at 60 °C for 10 min at 200 rpm using a tooth stirrer was also studied. After removal of entrapped air bubbles under vacuum the samples were cooled down to RT prior to the rheological measurements. PMDI with average functionality of 2.7, 31.5% NCO-content, viscosity at 25 °C of ~210 mPa·s, and density at 25 °C of 1.24 g/cm³ was mixed at RT for 1 min at 500 rpm with ELO with ~100% renewable content, epoxy equivalent weight 182 g/eq., viscosity 1300 mPa·s and density 1.034 g/cm³. Obtained mixture was served as “greened” isocyanate component of IPU resin. PI-Liner 3P Komp. A, served as water glass (WG) component of IPU resin.

Based on rheological results for PFA resin, concentration of 0.5 phr of biogenic silica nanoparticles and mechanical dispersion with tooth stirrer at RT for 10 min at 2000 rpm were selected for processing of filled IPU-resin mixtures. For comparison purposes, biogenic silica nanoparticles have been dispersed in PMDI (IPU-0.5 phr SiO₂ in PMDI) and WG (IPU-0.5 phr SiO₂ in WG) components. Non-filled IPU resin was served as reference (IPU-Ref). Volumetric ratio of PMDI to WG of 2:1 was used in all final mixtures being mixed at RT for 1 min at 500 rpm directly prior to chemorheological experiments.

2.2.4 Rheological characterization of the polymeric matrices

Temperature sweeps in the range of 25-90 °C in oscillation mode with frequency of 62.8 rad/s, ~100% strain were collected for PFA based systems using plate-plate rheometer ARES from Rheometric Scientific with parallel plates of 45 mm in diameter and gap in-between of ~0.5-1 mm. Similar parameters were also set for IPU resins, i.e. oscillation mod with frequency 62.8 rad/s, 45 mm parallel plates with a gap of 0.5-1 mm. However, time



sweeps for 60 min reaction time at 25 °C using ~18% strain were collected in this case.

3 Results and Discussion

3.1 Biogenic silica nanoparticles

The extraction of biogenic silica from agro-residues begins with a washing step (first with water and then the extraction in acidic medium) to assure the removal of impurities and to avoid the contamination of the extracted powder. The washed material is then calcinated to allow the removal of the organic matter from the residue and a white powder rich in silica is produced. In this work, several agro-residues were used as a source of bio-silica and the yield of the process was, in average, 1.3%, except for the rice husk extract, that yielded 9% of ash. After the process of extraction, each bio-nanofiller was structurally and morphologically characterized by different techniques. The analysis by SEM revealed a powder that comprises large aggregates of spherical silica particles with diameter in the range of 52 nm to 76 nm (Figure 1 shows the images obtained for rice husk ash, as an example). The chemical characterization of the samples by EDS confirmed the presence of silicon in all the extracted powders.

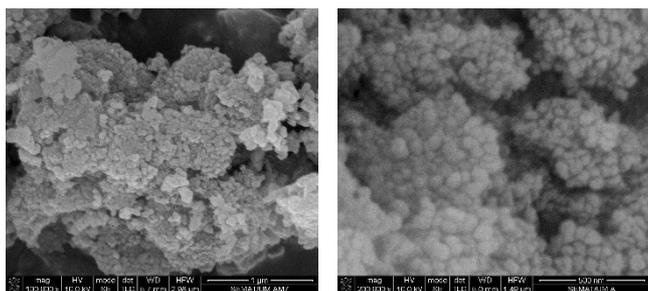


Figure 1. Micrographs obtained by SEM for the silica nanoparticles extracted from rice husks (scale bar: 1 µm on the left image and 500 nm on the right image).

The surface area, as well as the pore parameters of some samples are critical parameters for future functionalizations of the biogenic silica nanoparticles, as well as for their behaviour when added to polymeric formulations. The BET results obtained for the different silica rich extracted powders, presented in Table 1 show the results obtained for the textural characterization of the samples. All the samples showed low surface areas (less than 5 m²/g) except the particles extracted from rice husk and from wheat, that presented a surface area of 120 m²/g and 50 m²/g, respectively. The total pore volume was in the range of 0.01 cm³/g to 0.04 cm³/g for the hemp and the mustard derived silica particles and was around 0.18 cm³/g for the particles obtained from rice husks and wheat. All the samples presented a pore diameter of approximately 1.8 nm.

Table 1. Textural characterization of the extracted particles.

	S_{BET} (m ² /g)	S_{meso} (m ² /g)	V_{micro} (cm ³ /g)	$V_{p/Po=0.95}$ (cm ³ /g)	dp_{BJH} (nm)
Rice husk	120	0	0	0.186	1.82
Hemp fibre	<5	0	0	0.022	1.78

Hemp press cake	<5	0	0	0.035	1.80
Hemp shells	<5	0	0	0.036	1.78
Mustard seeds	<5	0	0	0.022	1.78
Wheat	50	0	0	0.177	1.80

3.1.1 Quantification of silica in the extracted powder

Although the EDS analyses indicated that all the extracted samples had silicon, it was necessary to determine the purity of the extracted bio-Si-nanoparticles, thus the quantification of the extraction bio-Si powder was performed. Initially, different standard working solutions were analysed in order to plot a calibration curve that correlates the amount of silicon in a sample and the absorbance of the sample at 810 nm. The data was adequately described by the regression equation $A=0.0207C_{Si} + 0.0035$ ($R^2 = 0.9988$). The quantification was only performed for the samples extracted from rice husk, hemp shells and wheat, which were the agro-residues with a higher yield after the extraction process. The quantification by the silicomolybdate test revealed 93 %, 79 % and 82 % of pure silica on the ash from rice husk, hemp shells and wheat, respectively.

3.1.2 Incorporation of bio-silica on polymeric matrices and their rheological properties

With a higher yield during the extraction process and a higher content of silica in the extracted powder, the nanoparticles obtained from rice husks were selected for further studies as nanofillers for PFA and IPU resins.

Viscosity dependences of PFA resins containing different amount of biogenic silica nanoparticles dispersed using ultrasound bath are presented in Figure 2. For better observation of related differences at lower and higher temperatures, the results are presented using linear and logarithmic y-axis, respectively. Obvious increase of viscosity at ambient temperature is characteristic for filled systems (cf. Figure 2a). Interestingly, the lower the concentration of biogenic nanosilica used, the higher were the viscosities achieved. This indicates that lower content of bio-nanofiller resulted in better dispersion quality of the related resin. However, this effect was continuously diminished upon heating, i.e. viscosities of the resins containing biogenic silica nanoparticles became more and more similar to that of reference resin. Starting from ~60-70 °C, viscosities of both reference and filled systems are in the range of below 1 Pa·s (cf. Figure 3b). This means that, despite the quite low viscosity, but still higher compared to PFA-Ref system (differences up to ~400 mPa·s at ~70 °C and up to ~50 mPa·s at 90°C), nanoreinforced PFA resins can be properly processed to prepregs at temperatures in the range of 60-90 °C similarly to the reference non-filled resin, resulting in quite similar impregnation quality. Furthermore, higher viscosity of filled systems at lower temperatures provide potential for improvement of resin drop-off effect upon cooling stage due to strong reduction of the flowability, their storage ability at ambient conditions and sterical and diffusion limitations. Finally, an



optimised tackiness at room temperature is expected. This has potential for more convenient handling with related prepreps.

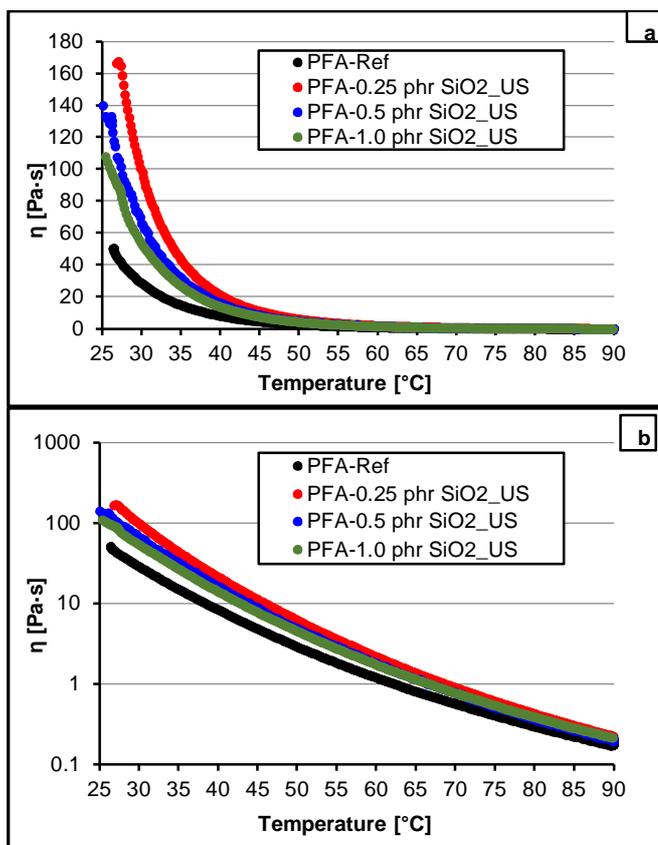


Figure 2. Influence of biogenic silica nanoparticles on the temperature dependencies of viscosity of PFA resin in the temperature range related to prepreg processing and storage represented using linear (a) and logarithmic (b) y-axis.

Figure 3 provides comparison of the viscosity profiles achieved using tooth stirrer vs. ultrasound bath as alternative dispersion technique based on two selected concentrations of silica nanoparticles, i.e. 0.25 and 0.5 phr. It is worthy to note that similar dispersion qualities were obtained in both cases, especially when higher concentrations of novel nanofiller were used. Only small differences could be seen in the plots with both linear (Figure 3a) and logarithmic (Figure 3b) y-axis. This allows conclusion that even simple dispersion methods like dissolving techniques, broadly available at many industrial companies, provide economic benefits compared to ultrasound assisted methods, that can be applied for proper dispersion of new biogenic silica nanoparticles.

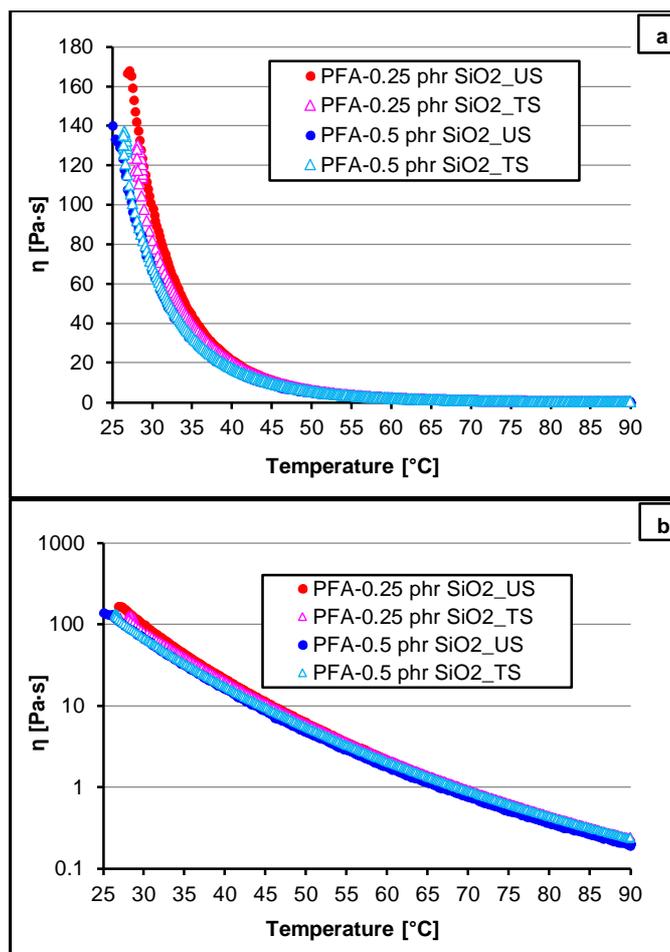


Figure 3. Comparison of mechanical and ultrasound assisted dispersion techniques regarding influence of biogenic silica nanoparticles on the temperature dependencies of viscosity of PFA resin represented using linear (a) and logarithmic (b) y-axis.

Incorporation of 0.5 phr biogenic silica nanoparticles in both PMDI and WG components of IPU resin using tooth stirrer resulted in similar initial mix viscosity in the range of 1.4-1.6 Pa·s. However, obvious depression of its increase over reaction time was observed. This was especially prominent, when WG was used as dispersion medium. Interesting is the fact that several different slopes are characteristic for the viscosity curves of IPU resins. Particularly, a slower viscosity increase is observed during the first ~12 min of reaction time in the case of IPU-Ref resin. Then, some acceleration of the process is observed (cf. Figure 4a). However, as it can be seen in Figure 4b, acceleration stage is slowing down with the reaction time, i.e. after ~20 min. Similar behaviour was also detected for nanoreinforced IPU system, when PMDI was used as dispersion medium for biogenic silica nanoparticles. However, the initial slope of viscosity curve was slightly lower, whereas an acceleration process started earlier (after ~6 min of reaction) in this case (cf. Figure 4a). In addition, slow-down of the acceleration effect characteristic for this system (cf. Figure 4b) occurred at earlier stages of reaction (i.e. at ~12 min) compared to that of IPU-Ref. Nevertheless, this behaviour changes, when biogenic silica nanoparticles were dispersed in WG. In fact the slope of respective viscosity curve during the first ~12 min of reaction time is similar to that for IPU-Ref resin (Figure 4a). Then, even some slight slowdown of the process is



observed. According to Figure 4b, almost no acceleration stage was observed in case of this system. Based on these observations it could be assumed that initial allocation of biogenic silica nanoparticles in PMDI or WG component influences differently the diffusion of reacting components through the in situ formed IPU membrane. Based on these observations, slower reaction speed is expected for IPU resin containing novel biogenic silica nanoparticles. This allows assumption that prolonged shelf life and storage ability of such highly-reactive prepregs can be expected upon their storage at low temperatures. It is worthy to note that similar mechanical properties of natural fibre reinforced composites produced of fresh prepared non-filled IPU resin and of that stored for 1 week at $-20\text{ }^{\circ}\text{C}$ (not presented here) were realised. Therefore, similar effect is expected for prepregs based on biosilica filled IPU even after longer storage time. This provides potential, not only a more convenient process window for preprepping, but also for more flexible logistic and on-side processing of new IPU based prepregs.

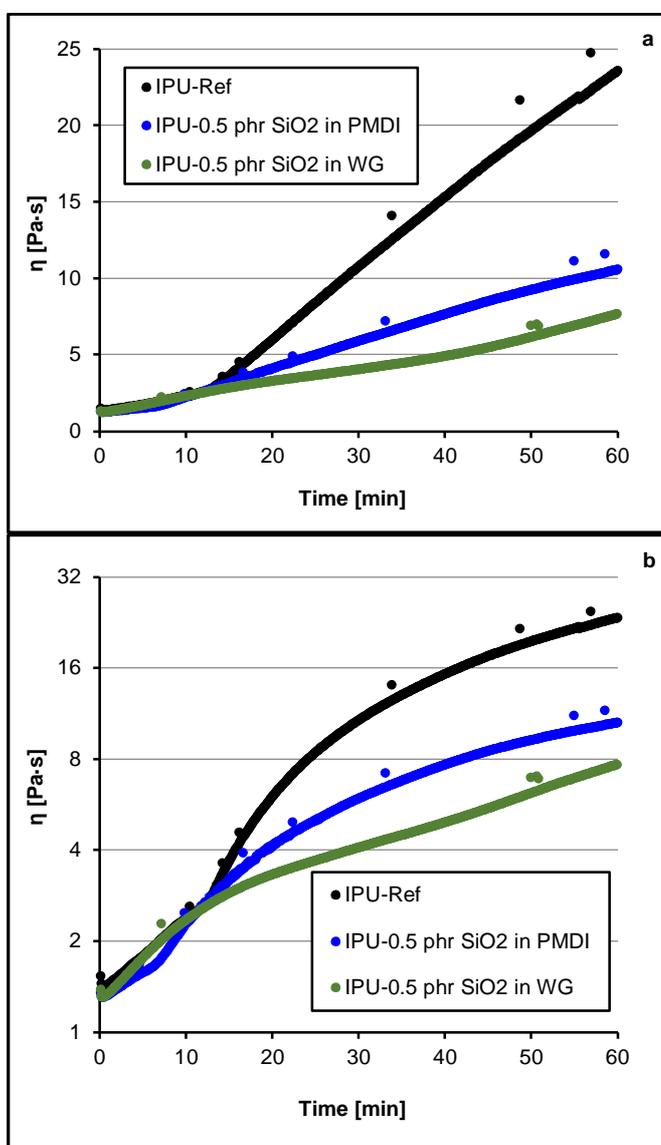


Figure 5. Influence of 0.5 phr biogenic silica nanoparticles dispersed mechanically in PMDI and WG components of IPU resin on its reactive viscosity profile during 60 min of reaction time at $25\text{ }^{\circ}\text{C}$ represented using linear (a) and logarithmic (b) y-axis.

4 Conclusions

The present work covered the extraction process of biogenic silica nanoparticles from different agro-industry residues, its characterization and influence in the rheological properties of bio-based polymeric matrices. For the agro-residues used as a source of bio-silica, the yield of the process was, in average, 1.3 %, except for the rice husk extract, that yielded 9% of ash. The characterization of silica rich extracted powders revealed the presence of large aggregates of porous nanoparticles with large surface area for the rice husk ash.

Proper dispersibility of new bio-silica nanoparticles using both tooth stirrer and ultrasound assisted techniques was confirmed by rheological experiments on filled PFA resin. Novel biogenic silica nanoparticles showed positive influence on rheological behaviour of PFA prepreg resin. This provides potential for improved handling and storage ability of PFA prepregs without negative impact on their manufacturing process.

Incorporation of new biogenic silica nanoparticles in PMDI and especially WG components of “greened” IPU resins resulted in obvious reduction of the reaction speed. This opens new possibilities for development of highly reactive prepregs with prolonged shelf-life upon storage at low temperatures.

This article shows that it is possible to extract bio-silica from agro-residues using a process that is suitable for industrialization. The extracted components have shown to be promising to be used as nanofillers on polymeric formulations.

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