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Electromagnetic transparency of composites of unsaturated polyester and nanolignin: Morphological and surface energy considerations

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Nanoparticles, LNPs, aerosol flow, dielectric property, gas inverse chromatography, surface energy, wave transparent

Abstract

We introduce a simple spray drying method for the scaleup production of spherical organic (lignin) microparticles with controlled size distribution (0.85 to 1.57 μm). We assess the surface energy of the lignin particles by inverse gas chromatography and determine its role in nanocomposites synthesized from unsaturated polyester. Such nanocomposites are shown to be irradiation transparent (millimeter frequency region). The permittivity and $\tan\delta$ of the composite material reached values between 0.01 and 3.1 (28 GHz) with 10 per hundred resin filler content. Vinyl groups were introduced on the surface of the particles to achieve enhanced interfacial adhesion, and resulted in a reduced relative permittivity (2.75). Together with wave

interactions, the mechanical and thermal properties of the composites are placed in perspective, opening new opportunities in next generation bio-based devices for 5G high-speed communication.

Introduction

Technical lignins are isolated from the wood biomass by using processes such as Kraft, soda, and sulfite pulping, which generate Kraft and alkali lignin as well as lignosulfonates, respectively.(Kai et al. 2016) During the efficient isolation protocol at pulping process, lignin molecules are altered by chemical reactions(Chakar and Ragauskas 2004) (Gierer 1980) *via* cleavage of inter-unit linkages in the native macromolecule, including β -O-4', α -O-4', β - β ', 5-5' bonds and associated formation of new covalent bonds. Such process leads to be distinctly diverse lignin profiles, for instance, as far as molecular structure, alkyl-aryl ether content, degrees of secondary condensation, and molecular weight.(Sjostrom 1993) Isolated lignin represents an important and abundant biopolymer resource the behavior of which is highly predictable and adaptable based on its functionality and modifiability.(Glasser 2019) Despite its attributes (i.e., low cost, abundance, biodegradability, non-toxicity), valorization of technical lignins may be challenged by their molecular structure and the isolation processes,(Berlin and Balakshin 2014) *e.g.*, given the changes in physico-chemical properties. To overcome the drawbacks associated with their diversity, developing spherical colloidal particles, herein called 'nanolignin', is an appealing option. Indeed, molecular assemblies into sizes ranging from the nano- to micron scales, can be employed as a new class of materials with interesting properties (microstructure and surface chemistry). Because of their large surface-to-volume ratio, nanolignin can have a great influence on the physicochemical properties of materials. In fact, the field of polymer nanoparticles is quickly expanding and

playing a pivotal role in a broad spectrum of areas;(Rao and Geckeler 2011)(Khan et al. 2019)
the same can be said for those derived from lignin.(Abbati de Assis et al. 2018)

Nanolignin has been previously synthesized by precipitation methods initiated with
electrolyte(Fritz et al. 2017), acids(Frangville et al. 2012), CO₂ saturation(Myint et al.
2016), continuous solvent exchange,(Qian et al. 2014) and dialysis(Lievonen et al. 2016),
as well as by sonication(Gilca et al. 2015) and emulsion templating methods(Nypelö et al.
2015). Studies related the synthesis protocols and their applications are referred to in available
review articles.(Österberg et al. 2020)(Ago et al. 2017) The physical properties of these
particles, such as hydrophobicity, surface charge, and stability, are dependent on the type
of lignin precursor and the synthesis procedure. The wide range of morphological
properties of nanolignin makes it suitable for controlled functionalization for
environmentally benign applications. Additionally, by varying the synthesis conditions
(solvent/anti-solvent, atmosphere, temperature, *etc.*) and sources (Kraft, sulfonate,
organosolv, milled wood), the surface chemistry of the lignin, and consequently surface
energy of the resultant particles, can be conveniently controlled. Therefore, understanding
surface energy of nanolignins is critical to develop sustainable nanomaterials as well as to tailor
their performance.

In recent years, dynamic sorption methods have become increasingly important, including
dynamic sorption techniques such as inverse gas chromatography (IGC).(Lloyd et al. 1989)
Therein, a solid adsorbent of unknown surface energy is placed in a column, in contact with a
selected gas-phase, used as adsorbate. As in analytical gas chromatography, the retention time
is measured and converted into a retention volume, which is directly related to several physico-
chemical properties of the adsorbent). Key thermodynamic parameters, such as surface energy,
heat sorption and kinetic parameters (diffusion constant and the activation energy) can be
determined following the uptake *via* physisorption on the surface area and considering the

heterogeneity profiles of the biomaterial.(Belgacem et al. 1995) (Beaumont et al. 2017) The lignin spherical particles, firstly synthesized by an aerosol flow method, exhibited very interesting characteristics(Ago et al. 2016a) and were found to be effective in the stabilization of oil-in-water (O/W) Pickering emulsions. The results were related to the surface hydrophilicity of the solid emulsifier (Kraft lignin nanoparticles, KLNP). Overall, understanding of the surface energy of the lignin particles is essential in considering their applications. Hence, here we assess the surface energy of lignin spherical particles obtained though aerosol flow method by inverse gas chromatography.

The discussed KLNP and their surface energy are factored in applications related to millimeter waves, relevant to high-speed, large-capacity communication, a field of recent rapid growth. Wave-transparent polymer composites that can transmit electromagnetic waves at a certain frequency have been widely used, for example, in antenna windows, microwave relay stations, radomes, among others. In this sense, polymeric materials commonly possess low dielectric constant and good mechanical properties and are favored for their processability compared to inorganic materials.(Blattmann and Pratsinis 2019)(Wang et al. 2020) Electromagnetic losses are mainly due to the polarization phenomenon of the medium in the external electric field, *i.e.*, electric, atomic, ionic, orientation, and interfacial polarization.(Wang et al. 2020) In composite materials, the interface between filler and matrix is prone to interfacial polarization. A poor interfacial adhesion would cause multiple reflections and losses of electromagnetic waves at the interface.(Tang et al. 2021) (Hu and Ishikawa 2020) Thus, in order to achieve nanocomposites with low dielectric constant (ϵ) and dielectric loss tangent ($\tan\delta$), it is crucial to reduce interfacial polarization by reducing the polarization molecular density or by improving the interfacial adhesion between the filler and the matrix.

We propose a method that departs from efforts reported so far by the fact that dry, perfectly spherical, non-fused lignin particles are used for their high structural integrity. Considering

these characteristics, we apply KLNP as reinforcing filler in nanocomposites with or without surface modification and using a low-polarity functional group containing silane nanofillers in an unsaturated polyester matrix. The dielectric and mechanical properties, as well as thermal stability are evaluated aiming to provide a rationale for a new class of nanocomposites for uses in (5G) communication network.

In this study, firstly of its kind, we unveil the influence of precursor concentration on surface tension, particle formation and yield. The surface energy of the lignin particles is assessed *via* gas inverse chromatography and applied as a reinforcing filler for nanocomposites to demonstrated a wave transparent material in the millimeter frequency region, relevant to 5G high-speed communication.

Experimental

Materials. Kraft lignin (Indulin AT, Ingevity, USA) was used as received. Polyester resin (FLH-350R, U-pica, Co., Ltd. Japan), a curing agent (Parmek N, NOF corporation, Japan), Trichlorovinylsilane (TVCS) (Sigma-Aldrich, St. Louis, MO, USA), dimethyl formamide (DMF), and toluene (Wako Fujifilm, Osaka, Japan) were used as supplied.

Synthesis of KLNP and surface modification. The synthesis of spherical particle of lignin has been discussed in our previous reports.(Ago et al. 2016b)·(Kämäräinen et al. 2019)·(Abbati de Assis et al. 2018) Briefly, Kraft lignin was dissolved in DMF at a concentration of 5 % and above. The experimental set up used to synthesize the particles included a nebulizer, a heated reactor, and a cyclone collector. The generated lignin droplets at the nebulizer were suspended on nitrogen or air flow (3 l/min) and carried to a heated laminar flow system that was kept at 153 °C; finally, dried lignin particles were collected with a cyclone. In this work, another set up for synthesis spherical particles from lignin/DMF solution was applied, e.g., to increase the yield capacity, using a spray dryer (ADL311S-A, Yamato Co., Ltd. Japan), consisting of two

fluid nozzle atomization, a heated reactor, and a cyclone collector. In this method, the concentration of lignin solution ranged from 1 to 10 % and the processing condition included 160 °C, atomizing pressure of 0.16 MPa and flow rate of 0.27 l/min. The original Kraft lignin powder and the synthesized spherical lignin particles thereafter denote as KL and KLNP, respectively.

Surface tension, surface energy and acid-base chemistry. The surface tension of all the solutions of lignin in DMF was measured with a du Nouy ring tensiometer (Surface tension metre, Ito Seisakusyo, Co. Ltd., Japan) operated at room temperature. The analyses for the surface energy of KL and KLNP were carried out using inverse gas chromatography (iGC Surface Energy Analyser). The data were analysed using both standard and advanced SEA Analysis Software. About 100 mg of the samples were packed into individual iGC silanised glass column, and were run at a series of surface coverages with alkanes and polar probe molecules to determine the dispersive surface energy (γ_s^D) as well as the acid-base free energy of adsorption (ΔG_{SP}). The sample column was pre-conditioned for 2 h at 30 °C and 0 % RH with 10 ml/min helium carrier gas. The experiment was conducted at 30 °C with 10 ml/min total helium flow rate, and using methane for dead volume corrections. BET specific surface area of the samples was determined *via* physical adsorption of octane molecules using the IGC-SEA unit.

KLNP treatment. 5% KLNP suspension in toluene containing 125 ppm water was prepared. Then 625 ppm trichlorovinylsilane were added and agitated for 18 h at 40 °C. The treated KLNP were filtered and rinsed with toluene several times followed by distilled water. The treated particles were dried at room temperature and then *in vacuo* at 100 °C. The treated KLNP is herein denote as V_KLNP.

Preparation of KL or KLNP/unsaturated polyester composites. Given amounts of KL or KLNP, 0, 5, 10, 20, 30 per hundred resin (phr), were dispersed in the precursor solution of

polyester resin, containing unsaturated polyester, styrene, methyl methacrylate, and maleic anhydride and sonicated (sonication bath) for 3-5 min and then further mixed with a planetary mixer with the combination of planetary mixing and defoaming modes (ARE-310, Thinky Co., Ltd. Japan) to obtain homogeneous suspensions without agglomeration of lignin and free of air bubbles. Then, 1 wt% curing agent was added, and the suspension was mixed again with a planetary mixer for 3 min. The suspension was poured on Teflon sheet and allowed to cure at room temperature for 20 h followed by a post-curing process at 40 °C for 2h.

Characterization of unsaturated polyester composites with KL or KLNP.

Scanning Electron Microscopy (SEM): KLNP and the fracture surface of the KLNP/Polyester composites were observed using a FE-SEM (S-4700, Hitachi, Co. Ltd., Japan). The samples were placed on a carbon tape followed by a metal coating with Pt/Pd to guarantee the secondary electrons on the samples during the observation. The images were obtained at 1.6 kV. The particle size and the distribution were estimated from SEM micrographs by using Fiji Image J.

Bending Tests: The mechanical properties of the composites containing KL or KLNP compositions, were performed by three-point bending tests (STB-1225L (A&D Co., Ltd. Tokyo, Japan)). The dimensions of the specimens were 30 mm in length, 14 mm in wide, and 2 mm in height. The crosshead speed was set to 1 mm/min for all the test and the applied force and the strain were monitored until the specimen break. The modulus was calculated from each S-S curve. The values for all the samples were averaged over three to five specimens. All the specimens were preconditioned at 20 °C and 65 % RH before the measurement.

Thermal analysis: The thermal properties for all the composites were examined by thermogravimetry (Themo plus, TG8120, Rigaku Co., Ltd., Japan) (TG-DTA) from r.t to 800 °C under air flow, 0.4 l/min with heating rate, 10 °C/min.

Dielectric measurement: The dielectric constant (ϵ) and dielectric loss tangent ($\tan\delta$) values of the samples were measured using a dielectric analyzer (Anritsu MS46122A Vector Network Analyzers) at 24 °C, relative humidity 49 %. The corresponding specimen dimension was 30 mm $\times$ 30 mm $\times$ 0.8 mm. Three points in each sample were randomly selected for measurement.

Table 1 Concentration of lignin in the precursor solution and diameter and yield of the resultant particles

Entry	Concentration, wt%	Particle size, μm	Yield, g/100ml
1	1	0.85 $\pm$ 0.04	0.15
2	3	1.00 $\pm$ 0.06	0.15
3	5	1.26 $\pm$ 0.05	0.34
4	7.5	1.57 $\pm$ 0.04	1.94
5	10	1.13 $\pm$ 0.07	3.11

Results and Discussion

KLNP was synthesized with a spray dryer using the respective precursor solution at 1, 3, 5, 7.5, and 10 % concentration. Table 1 shows the yield of KLNP, which was in the range 15-30 % based on consumed precursor solution and after running the instrument for the given time. The yield increased with increasing the concentration of the lignin solution. Note that the KLNPs yield was underestimated due to the large sample loss during the synthesis and collection, within a short period of running time. For the tested concentration range, the mean particle diameter ranged from 0.85 to 1.57 μm and it increased with the concentration. This can be explained by the increased viscosity of the precursor solutions, which produced larger

droplets from the nozzle, under the given pressure. However, when a 10 % precursor solution was used, the particle size was decreased to 1.13 μm . No significant change in surface tension was observed over the range of concentration tested; hence, no major effect on the particle size and distribution was expected (Figure 1S). The particle size distributions and the corresponding SEM images obtained from the various precursor concentration are compared in Figure 1. The particle size and the particle size distribution of KLNP obtained from the precursor solutions, from the given concentrations, was analyzed by measuring approximately 200 particles over several SEM images (Image J software).

Figure 1. Particle size distribution and SEM micrographs for KLNP obtained from KL precursor solutions at initial concentrations of (a) 1, (b) 3, (c) 5, (d) 7.5, and (e) 10 %. Scale bar in SEM images, 10 μm .

The particles were smooth and spherical. As the solution concentration of the precursor was increased, the most frequent particle size shifted toward larger diameters, namely, from ~ 0.5

216 μm for 1 and 3 % solutions to 1.5~2 μm for 5 and 7.5 % solutions. Using a 10 % solution, the
217 number density (frequency) of the smaller particles of <1.5 μm increased, which contributed
218 to a reduction in the average particle size. Overall, the most uniform particles were obtained
219 from the 5 % precursor solution. Although monodisperse size particles may be difficult to
220 obtain *via* an aerosol flow process, where the precursor solution is atomized into small droplets
221 followed by evaporation through a heating process into molecular assembled, the average
222 particle size and distribution was controlled by varying the concentration of the precursor
223 solution.(Ago et al. 2016b) (Ago et al. 2017) In order to investigate the surface energy for
224 KLNP, the particles obtained from the precursor solution with 5 % concentration were used.

225 The surface energies of KL and KLNP were evaluated by gas inverse chromatography. This
226 technique allows to assess differences in surface energy and surface chemistry of samples that
227 are known to affect processes involving interfacial interactions, such as nanocomposites,
228 coatings, and adhesions. (Klapiszewski et al. 2017), (Strzemieska and Voelkel 2012), (van
229 Asten et al. 2000) Dispersive (γ_s^D), acid-base (γ_s^{AB}) and total surface energy (γ_s^T) profiles
230 obtained directly from the IGC, for both samples, are shown in Figure 2.

Figure 2. Comparative plots of the surface properties of KL and KLNP for their surface energies versus percentage of surface area (a) Dispersive surface energy, (b) Specific surface energy, and (c) Total surface energy and the plots of surface energy versus percentage of surface (area increment) (d) Dispersive surface energy, (e) Specific surface energy, and (f) Total surface energy.

All the profiles show that both KL and KLNP are energetically heterogeneous, which means that surface energy changes as a function of surface coverage. In addition, it can be clearly observed that the dispersive component contributes to a major part of the surface energy. The combined plot of dispersive, specific (acid-base) and the total surface energy of the samples are presented in Figure 2a-2c. The narrower profile of the total surface energy of KLNP, ranging from 50 to 69 mJ / mm², indicates that such sample is more energetically homogeneous than KL. This highlights that the surface structure caused by isotropic shrinking during regeneration (drying) from the precursor solution resulted in a solidified and perfectly spherical shapes with atomic/molecular reconstruction on the surface. This energy homogeneity may provide more stable flow behavior of KLNP. KL is relatively more heterogeneous, possessing surface sites with different energy levels; hence, KL is more active, having higher dispersive and total surface energy. In order to represent the heterogeneity of these samples,

the surface energy distributions are obtained by a point - by - point integration of the surface energy profiles, resulting in plots of γ_s^D , γ_s^{AB} , and γ_s^T , surface energy versus percentage of surface (area increment), as shown in Figure 2d-2e. The y_{50} , the median, has been defined as the surface energy where half of the population lies below this value. Similarly, 90 percent of the distribution lies below the y_{90} , and 10 percent of the population lies below the y_{10} (Table S2). The specific (acid–base) Gibbs free energy of desorption, ΔG_{SP} , of polar solvents on both samples was also measured at different surface coverage (Figure 3a, 3b). The ΔG_{SP} profiles as a result of the interaction with all five or six polar probe molecules are displayed. Higher ΔG_{SP} values can be attributed to a higher concentration of polar surface groups or different surface groups with higher specific surface energy. Both KL and KLNP showed strong degree of interactions with all the polar probes and the rank of order of KL for decreasing ΔG_{SP} interactions goes in the order acetonitrile, ethanol, dichloromethane, chloroform, and toluene and for KLNP, as ethanol, dichloromethane, chloroform and toluene. The surface chemistry of the samples was assessed using the Gutmann acid (K_a) and base (K_b) numbers, determined with polar probes (dichloromethane, toluene, chloroform, ethanol, and chloroform). K_a and K_b values of the samples were calculated using the ΔG_{SP} values of polar probes at that particular surface coverage.

Figure 3. Specific free surface energy against area increment for (a)KL and (b) KLNP showing strongest interactions with the polar probes. (c) The Gutmann acid (K_a) and base constants (K_b) at a surface coverage of 0.005 n/n_m , (d) Thermodynamic work adhesion, and (e) Surface polarity/Wettability for KL and KLNP.

Figure 3d shows the K_b for both samples was consistently higher than K_a , indicating that the samples possess higher concentrations of electron-donating (basic) surface functional groups than electron-withdrawing (acidic) ones. Surface energy is directly related to the thermodynamic work of adhesion between two materials, which corresponds to the work required to reversibly separate an interface between two bulk phases. The total work of cohesion was determined according to geometric mean methods, as shown in Figure 3d. KL showed higher work of cohesion, which also indicated high tendency of aggregation in the samples compared to KLNP. The polarity of both samples, KL and KLNP was calculated from the specific and total surface energies, shown in Figure 3f. The results suggest that KLNP is relatively more polar and hydrophilic compared to KL. This result indicates that many critical functional groups in the lignin molecule, such as phenolic/aliphatic hydroxyl groups, alkyl-aryl

ether group, etc., can be exposed on the particle surface, thus allowing further chemical modifications effectively. More detailed surface composition analysis may be performed by ¹HNMR measurements (Pylypchuk et al. 2020) in combination with IGC. The surface properties of KLNP, with its energetical homogeneity and hydrophilicity, should play an important role in enhancing interfacial interactions, such as good dispersibility the particles and interfacial adhesion between KLNP and polymer matrices in composites.

KL and KLNP were applied as reinforcing fillers in unsaturated polyester resin to identify the impact of the size, the morphology, and the surface properties of KLNP on the mechanical and the electrical properties of the UPE-based composites. Figure 5 shows the results from the bending tests for KL or KLNP/UPE composites with different KL and KLNP loadings.

Figure 4. The mechanical properties of the KL or KLNP/UPE composites with different lignin addition (a) Flexural stress, (b) Strain, and (c) Flexural modulus.

The flexural strength for the KL/UPE composites dropped to nearly half of the reference polyester sample, from 68 to 35 MPa with the addition of KL with 5 phr of the matrix polymer. The values hardly changed when KL was increased up to 30 phr. When KLNP was incorporated in the polymer matrix, the decrease in flexural strength was suppressed; it even slightly increased to up to 59 MPa at 30 phr KLNP, Figure 4a.

The flexural strength, e.g., the capacity of a material to resist the bending force applied perpendicular to its longitudinal axis, indicated a good dispersity of KLNP, with no significant aggregation in the matrix. This is examined by the energetical homogeneity of the surfaces (see Figure 2 and 3). Another reason for the improvement of the flexural strength might be ascribed to the good mechanical strength of KLNP particles, due to the formation of extended networks intra- or inter molecular interactions, compared to KL powder, which consisted of undefined shapes with secondary particle agglomeration.

The flexural strain was considerably decreased with increasing of KL or KLNP loading shown in Figure 4b. As the strain is reciprocal to the stiffness of a material, the results show that the filler imparts a greater stiffening effect. It can be seen that by addition of 5 phr KL or KLNP, the strain dropped to approximately 65 % and 70 %, respectively. The reduction in strain at break implies that the ductility of the matrix was suppressed by the presence of the filler. The composites with KLNP showed a slightly higher ductility than the one with KL. The flexural modulus of the KL and KLNP/UPE composites are shown in Figure 4c. For KLNP /UPE composites, the elastic moduli were also increased with KLNP content and the highest value, 4.6 GPa, was achieved at 30 phr KLNP. However, when KL were incorporated, it decreased to 2.6 GPa at the same concentration.

Morphological analysis of the KL and KLNP/UPE composites. SEM was used to study the morphology and microstructure of the KL and KLNP/UPE composites. Figure 5 shows the SEM micrographs of the fractured surface of composites with different amounts of KL and KLNP. The fracture surface of the KL composites was observed to be very rough in the lignin filler domains and with many voids. By contrast, KLNP composites showed relatively smooth fractures and well defined spherical KLNP domains. It can be seen that KL and KLNP particles were under the stress concentration against force loading.(Ngo et al. 2019) It is noticeable that

KLNP was well dispersed, with no significant aggregates in the matrix and regardless of loading.

Figure 5. Scanning electron micrographs of the fractural surface for (a)-(d) KL/UP and (e)-(h) KLNs/UP composites with different the filler contents (a, e) 5 %, (b, f) 10 %, (c, g) 20 %, and (d, h) 30 %. Scale bar for (a) - (d), 100 μm , for (e) – (h), 50 μm .

The homogeneous morphology observed in KLNP/UPE composites should be reflected in the improvement in flexural strength and modulus, as mentioned above. In the higher magnification of the fractural surface of KLNP/UPE composites, gaps at the interface between KLNP and the matrix polymer were clearly observed, which indicates poor interfacial adhesion (Figure 5, insert). This interfacial phenomenon is consistent with the surface energy of KLNP, which was shown to be hydrophilic compared to KL (gas inverse chromatography, Figures 2 and 3). In order to improve the adhesion at the interface between KLNP and the matrix polymer, trichlorovinylsilane was used as a coupling agent. FT-IR studies for the particles after the silane treatment confirmed the occurrence of new bands around 2950, 2897 cm^{-1} for CH_2 stretching 1720 cm^{-1} for vinyl groups, at 770, 1152 cm^{-1} for Si-O-Si from the hydrolysis condensation reaction, that confirmed successfully introduction of the siloxane with vinyl group on the surface of the particles, V_KLNPS (Figure S2). (Kanimozhi et al. 2014) Further investigation was conducted by SEM and EDX measurements. SEM micrographs of the

particles after the silane treatment showed well-defined polysiloxane nanofilaments grown on the surface.(Artus et al. 2006) (Rollings et al. 2007) The typical length and diameter of the nanofilaments were 500 nm and 30 nm, respectively. Such nanostructure on the surface was responsible for the superhydrophobicity, as expected (Figure S2). EDX confirmed the presence of silicon on the surface (Figure 6). In addition, we confirmed a polysiloxane thin layer across the surface of the particles (see SEM image of the resulting the thin films collapsing onto the substrate after the removal of lignin dissolution). The thin film of polysiloxane with a size corresponding to the original particle size remained intact, which resulted from the formation of a polysiloxane thin layer, uniformly deposited over the surface of every particle, regardless its size (Figure 6c). Similar nano-structured material, with a hollow thin film induced by KLNP has been reported by using a Fe(III)-tannic acid chelation capsule(Tardy et al. 2018).

Figure 6. Scanning electron micrographs of (a) V_KLNP modified with silane, (b) V_KLNP/UPE composites with 10 phr of the filler, (c) The polysiloxane thin layers collapsing onto the substrate after the removal of lignin dissolution. EDX spectra detected Si for (d) the mapping image and (e) the spectrum.

V_KLNP/UPE composite at 10 phr filler content was prepared by the same procedure as explained for KLNP. As can be seen in Figure S2, some V_KLNP aggregated in the matrix, which may result from the drying process of the particles, from water/toluene suspension, followed by rinsing after silane treatment. This highlights that the redispersion of V_KLNP from the dry state into a polymer resin, with less aggregation, may require severe redispersion steps such as high shearing. In the high magnification image of Figure 6, the interaction between the fillers and the matrix polymer was significantly improved. No air gaps were observed at the interface. This result suggests that V_KLNP fillers efficiently formed covalent bonds, via vinyl groups, with the matrix polymer and during the curing process. Additionally, since the surface of V_KLNP became superhydrophobic, as already discussed, they had the tendency to interact with the hydrophobic polymer matrix. The enhancement of the interfacial adhesion may lead to improvements in the thermomechanical and dielectric properties of the composites, as will be discussed later. The improvement of interfacial adhesion has been reported for Kraft lignin and UPE and the effect of lignin on volume shrinkage and mechanical properties has been investigated.(Yeo et al. 2017)

TGA-DTA measurements were carried out to determine the thermal stability of the composites, at different loading and surface properties of the fillers. The temperatures at 5 % weight loss, $T_{5\%}$ and at the maximum rate of weight loss, T_d of the composites were determined from the TG thermographs and summarized in Figure 7. Compared to neat UPE, $T_{5\%}$ were found to be gradually decreased as the filler content increased (both for KL or KLNP). However, the $T_{5\%}$ of the KL/UPE composites decreased as the filler content increased, while the decrease of the $T_{5\%}$ of the KLNP/UPE composite was suppressed. This can explain the high thermal stability of KLNP, with excellent mechanical integrity resulting from intra- and intermolecular interaction formed during the aerosol regeneration (drying) process.(Ago et al. 2016a)

V_KLNP/UPE (10 phr filler content) improved the thermal stability at $T_{5\%}$ and T_d , 310 and

377 °C, respectively in comparison to KL, or KLNP/UPE composites. Th results can be explained from the strong interaction between V_KLNP and the matrix as well as the higher bond energy of Si-O bonds, consisting of a polysiloxane layer, as opposed to that of C-C or C-O bonds.(Kumar and Narayanan 2002) In addition, no air gaps were observed at the interface between KL or KLNP and UPE in the composites, given the better interfacial adhesion, which resulted in a restricted enhancement of thermal conductivity of the composites.

Figure 7. TG thermographs for KL or KLNP/UPE composites with different loading of the filler content from 0 to 30 phr and the star indicates $T_{5\%}$ or T_d from V_KLNP/UPE composites with 10 phr of the filler content.

The composites filled with the lignin spherical particles, KLNP and V_KLNP, were tested next as wave-transparent materials, towards 5G high-speed communication devices, which can transmit electromagnetic waves at a certain frequency. Therefore, the dielectric properties in the millimeter frequency region of the composites were examined. Wave-transparent

materials require a low permittivity, ϵ_s and dielectric loss tangent, $\tan\delta$ (ϵ_s and $\tan\delta$ decreases the electromagnetic wave loss also reduced during transmission).(Wang et al. 2020) The electromagnetic loss is mainly due to the polarization phenomenon of the medium in the external electric field, i.e. electric polarization, atomic polarization, ionic polarization, orientation polarization, and interfacial polarization.(Wang et al. 2020) In order to achieve low ϵ_s and $\tan\delta$ in the nanocomposites, it is important to reduce interfacial polarization by improving the interfacial adhesion between the filler and the matrix. The permittivity of V_KLNP/UPE composite (10 phr V_KLNP content) improved the permittivity, ϵ_s 2.75 (at 28 GHz) compared to the KLNP/UPE composite, ϵ_s , 3.01, which can result from better interaction between V_KLNP and the matrix. We note that the low polarity of Si-O bonds in the polysiloxane structure also contribute to a reduction in permittivity. A dielectric loss, $\tan\delta$ of 0.01 was measured for both samples, which can fit the demands of the intended application. The results of the dielectric properties of KLNP and V_KLNP composites are in the range of commonly used polymers and fillers (Table S3 (Ávila et al. 2013) (Krishnadevi et al. 2013)).

Conclusion

We demonstrate the synthesis the spherical lignin nano-, micro- particles with a continuous aerosol process for pursuing mass-production of lignin nano- and microparticles using Kraft lignin/DMF solution. We investigated the effective yield for various particle sizes and distributions as a function of concentration of the precursor solution. It was found that 5 % lignin content in the precursor solution provided good yield, with narrower particle distribution. The lignin particles were perfectly spherical and smooth, in the range size from 0.85 to 1.57 μm . Inverse gas chromatography determined the surface energy of the spherical lignin nano-, micro-particles. KLNP showed a relatively high polarity and a higher hydrophilicity compared to KL. This result suggests that many critical functional groups, such as phenolic/aliphatic hydroxyl

groups, alkyl-aryl ether group, among others, are exposed on the particle surface. Importantly, total surface energy of KLNP indicated that it is more energetically homogeneous than KL. Therefore, spherical lignin particle formation may be adopted as a new class of lignin materials to overcome diversity at the molecular level. We applied lignin nano- micro-particles as fillers in unsaturated polyester composites, which were tested for their dielectric properties in the millimeter frequency, valuable in the design of next-generation 5G high-speed materials. The obtained KLNP composites exhibited ϵ and $\tan \delta$ values of 3.01 and 0.01 at 28 GHz. Further, ϵ , 2.75 was improved by improving interfacial interaction via silane treatment of KLNP. Overall, the results highlight that KLNP/UPE and V_KLNP/UPE composites display performance benefits for wave-transparent materials at extremely high frequency. We believe that the results of this study will help increase the value of lignin. Although lignin is a natural, biodegradable polymer, a systematic evaluation of size-dependent toxicity should be conducted.

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Declarations

The authors have no conflicts of interest to declare that are relevant to the content of this article.

This article does not contain any studies involving either animals or human participants performed by any of the authors.

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Figures

Figure 1

Particle size distribution and SEM micrographs for KLNP obtained from KL precursor solutions at initial concentrations of (a) 1, (b) 3, (c) 5, (d) 7.5, and (e) 10 %. Scale bar in SEM images, 10 μm.

Figure 2

Comparative plots of the surface properties of KL and KLNP for their surface energies versus percentage of surface area (a) Dispersive surface energy, (b) Specific surface energy, and (c) Total surface energy and the plots of surface energy versus percentage of surface (area increment) (d) Dispersive surface energy, (e) Specific surface energy, and (f) Total surface energy.

Figure 3

Specific free surface energy against area increment for (a)KL and (b) KLNP showing strongest interactions with the polar probes. (c) The Gutmann acid (K_a) and base constants (K_b) at a surface coverage of 0.005 n/n_m, (d) Thermodynamic work adhesion, and (e) Surface polarity/Wettability for KL and KLNP.

Figure 4

The mechanical properties of the KL or KLNP/UPE composites with different lignin addition (a) Flexural stress, (b) Strain, and (c) Flexural modulus.

Figure 5

Scanning electron micrographs of the fractural surface for (a)-(d) KL/UP and (e)-(h) KLNs/UP composites with different the filler contents (a, e) 5 %, (b, f) 10 %, (c, g) 20 %, and (d, h) 30 %. Scale bar for (a) - (d), 100 μm, for (e) - (h), 50 μm.

Figure 6

Scanning electron micrographs of (a) V_KLNP modified with silane, (b) V_KLNP/UPE composites with 10 phr of the filler, (c) The polysiloxane thin layers collapsing onto the substrate after the removal of lignin dissolution. EDX spectra detected Si for (d) the mapping image and (e) the spectrum.

Figure 7

TG thermographs for KL or KLNP/UPE composites with different loading of the filler content from 0 to 30 phr and the star indicates T5% or Td from V_KLNP/UPE composites with 10 phr of the filler content.

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