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SURFACE ENERGY DETERMINATION OF PARTICLES USED AS FILLERS IN POLYMERS: APPLICATION TO LIGNIN/PLA COMPOSITES

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Abstract: *This study has the aim to propose a new simple method to determine the surface energy components of particles used as fillers in polymers. An experimental protocol coupled to a modified Jurin law is proposed. This protocol was applied to lignin particles used as reinforcement in polylactic acid (PLA). Some treatments were performed on lignin to improve the adhesion with PLA and the modifications due to the treatments were characterized. The originality of this method was to extend the theory of Jurin to porous media and compare it to the well-known theory of Washburn. Results showed that the Washburn theory had some limits for the application to these materials, since some hypotheses were not respected or no longer valid. Reliable surface energy and components of untreated and treated lignin were obtained revealing the efficiency of the proposed method.*

Keywords: *Capillary wicking; interface; surface energy; lignin; biocomposite.*

1. Introduction

The addition of some biofillers like lignocellulosic biomass is an effective way to improve polylactic acid (PLA) properties and to extend its range of applications. Lignin, in powder form, has a wide set of applications as filler in composites, such as UV blocker, antioxydant, charring agent in flame retardancy, mechanical reinforcement or surfactant [1]. However, the strong polar nature of lignin, due to the presence of hydroxyl groups, makes it incompatible with the non-polar PLA matrix, resulting in a poor interfacial filler-matrix adhesion. Acetylation and phosphorylation are two lignin chemical modifications used to enhance the mechanical and thermal properties of lignin/PLA composites respectively. These properties are strongly related with the interfacial adhesion between fillers and PLA [2].

To characterize the interfacial adhesion, the determination of lignin and PLA surface energy components is required. Surface energy is an intrinsic property of each liquid and solid material and, for a solid, it is obtained by means of equilibrium contact angle measurements. However, for powders assumed as porous media more issues arise, notably due to the imbibition of the liquid into the medium. An apparent contact angle can be obtained using wicking tests and the well-known modified Washburn equation for porous materials. However this method, that theoretically allows the determination of apparent advancing contact angles, does not always give reliable results due to the Washburn hypotheses that are not respected or no longer valid (typically the non-linearity of wicking curves for which apparent advancing contact angles could not be obtained).

A new simple method using a modified Jurin law for porous media is proposed here in order to determine reliable apparent equilibrium contact angles and obtain surface energy of fillers [3].

An experimental protocol based on capillary wicking and coupled to the modified Jurin law was set and applied to lignin particles used as reinforcement in PLA. Some treatments were performed on lignin to improve the adhesion with PLA and the modifications due to the treatments were characterized. Reliable surface energy and dispersive and polar components of untreated and treated lignin were obtained revealing the efficiency of the proposed method. Lignins were then used as reinforcements for PLA. The microstructure of the biocomposites was characterized to highlight the modification of adhesion at the filler/matrix interface due to the modification of fillers surface properties [3]. This characterization will be discussed during the oral presentation.

2. Materials and Methods

2.1 Materials

The lignin used in this study is an alkali lignin supplied by TCI (Tokyo, Japan). This was named untreated or reference lignin (Ref-Lig). The content of methoxyl group is between 10 and 12 % and the median particle diameter is around 50 μm . For the surface energy determination, four liquids were tested with lignin. Table 1 shows density ρ , dynamic viscosity η , surface tension γ_L and dispersive γ_L^D and polar γ_L^P components for each liquid at standard conditions [4]. The n-Hexane (99 % pure and supplied by Chem-Lab) was used as totally wetting liquid. The water and the ethylene glycol (99.5 % pure and supplied by Chem-Lab) were used because of their polarity. The lactic acid (90 % pure, supplied by Sigma-Aldrich), was used expecting to have similar wetting properties of PLA. Dynamic viscosity of lactic acid was measured using a AR2000ex rheometer (TA Instrument) with a coaxial cylinder system. Surface tension and dispersive and polar components were determined using a K100SF tensiometer (Krüss) and performing a three-step procedure detailed in a previous work [5]. As expected, lactic acid was found to have a quasi-totally dispersive nature, with dispersive and polar components very close to ones of PLA [6].

Table 1: Test liquids properties at 20°C.

Liquid	ρ (g/cm ³)	η (mPa.s)	γ_L (mN/m)	γ_L^P (mN/m)	γ_L^D (mN/m)
n-Hexane	0.659	0.32	18.4	0.0	18.4
Water	0.998	1.00	72.8	51.0	21.8
Ethylene gl.	1.113	21.81	48.0	19.0	29.0
Lactic acid	1.248	69.01 \pm 1.01	42.2 \pm 0.1	4.5 \pm 0.4	37.7 \pm 0.3

2.2 Lignin treatments

The chemical treatment of acetylation was performed on lignin using an adapted protocol from the literature [7]. A volume of 250 mL of acetic anhydride was introduced in a 500 mL round-bottomed flask and equilibrated at 65°C with reflux. After that, 1 mL of 1-methylimidazole working as catalyst was added. A mass of 40 g of alkali lignin was added slowly in the flask. The mixture was equilibrated at 65°C for 24 h. The reaction was stopped by introducing the mixture in 1.5 L of cold deionized water. Then the treated lignin was separated from the reaction mixture

by centrifugation (Hettich, Rotina 380). The lignin was washed from 3 to 5 times with deionized water in order to obtain a neutral pH (to remove acid residues). Then the lignin was dried in an oven at 80°C for 24 h. The treated lignin was named acetylated lignin (or Ac-Lig).

The phosphorylation treatment was also adapted from the literature [8]. A 60 % phosphoric acid was prepared using 85 % phosphoric acid and deionized water. The phosphoric acid was poured in a round-bottomed flask and stabilized at 80°C with reflux. Then 12.5 g of urea were slowly added to the acid. The mixture was put under agitation. When the urea was fully dissolved, 25 g of alkali lignin were slowly added to the mixture under vigorous agitation. After 1 h of reaction the mixture was dried in an oven at 70°C overnight, then it was heated at 150°C during 2 h for the thermal curing. After that, the lignin was cooled at room temperature and washed with ethanol using centrifugation. Finally, the treated lignin was dried at 80°C overnight. This lignin was named phosphorylated lignin (or P-Lig).

After both treatments, treated lignins were manually ground using an agate pestle and mortar set due to the agglomerates created during the chemical modifications. Thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) characterizations and scanning electron microscopy (SEM) observations showed the effectiveness of both treatments on lignin.

2.3 Lignin surface energy characterization

Using more than two liquids with known surface tensions (γ_L) and components (γ_L^D , γ_L^P) for contact angle measurements, the dispersive and polar components (γ_s^D , γ_s^P) of solid surface energy (γ_s) can be determined via a linear form of the Owens-Wendt equation [5]:

$$\frac{\gamma_L(1+\cos\theta_e)}{2(\gamma_L^D)^{0.5}} = (\gamma_s^P)^{0.5} \frac{(\gamma_L^P)^{0.5}}{(\gamma_L^D)^{0.5}} + (\gamma_s^D)^{0.5} \quad (1)$$

It is important to point out that for surface energy determination, equilibrium contact angles (θ_e) are defined in Eq. 1, which might be significantly different from the advancing contact angles.

Advancing contact angles are defined in the well-known Washburn equation. This equation, originally describing the capillary rise in a tube, has been extended to describe the capillary wicking into porous media packed in a cylindrical column and assumed as capillary tube arrangements:

$$m(t)^2 = \left[\frac{(c\bar{r}) \cdot \varepsilon \cdot (\pi R^2)^2}{2} \right] \frac{\rho^2 \cdot \gamma_L \cdot \cos\theta_a}{\eta} t \quad (2)$$

where $m(t)^2$ is the squared mass gained during the liquid rise, c is a parameter inversely proportional to the tortuosity and \bar{r} is the mean capillary radius. The $c\bar{r}$ is defined as a geometric factor. R is the inner radius of the column (or the cylindrical sample holder), ε is the porosity of the medium and θ_a is the apparent advancing contact angle, representative of the interaction between the liquid and the porous medium during the capillary rise.

Generally, the capillary rise in a tube is stopped when the capillary force is balanced by the liquid weight in the tube. From this equilibrium, the well-known Jurin law defines the equilibrium height achieved by the liquid. An extension of the Jurin law for porous media packed in a column is proposed here. The Jurin law has been expressed as a function of the liquid mass at the

equilibrium (m_{eq}) and modified for powders or porous media packed in a cylindrical sample holder [3] as follows:

$$m_{eq} = \frac{2 \cdot \gamma_L \cdot \cos(\theta_e)}{(c\bar{r}) \cdot g} \varepsilon \cdot (\pi R^2) \quad (3)$$

where g is the gravitational acceleration and θ_e is here an apparent equilibrium contact angle, representative of the liquid/porous medium interaction at equilibrium. The benefit and the originality of using this approach consist in taking advantage of the recorded equilibrium mass achieved after capillary wicking to obtain an apparent equilibrium contact angle.

The dynamic test of capillary wicking was carried out using a K100SF tensiometer (Krüss, Germany). The K100SF is provided with an electronic microbalance (resolution of 10^{-7} g) where the sample holder containing the porous medium is clamped (Figure 1A). The sample holder consists of a hollow cylinder with an inner radius of 4.6 mm and a graduated height of 20 mm (Figure 2B). The lignin was inserted in the sample holder in order to achieve a filled height of 10 mm. Knowing the density of each type of lignin (measured by the pycnometer) and the sample-holder volume that had to be filled, the lignin mass was determined in order to set the same powder volume fraction V_p for each test and lignin. A V_p of 45% (resulting in a porosity of 55%) was then chosen for all wicking tests.

Wicking tests were carried out with reference, acetylated and phosphorylated lignins using n-Hexane, water, ethylene glycol and lactic acid. All tests were performed in standard conditions. Both modified Washburn equation (Eq. 2) and Jurin law (Eq. 3) were applied for these experiments in order to characterize the $c\bar{r}$ and the contact angles corresponding to each theory.

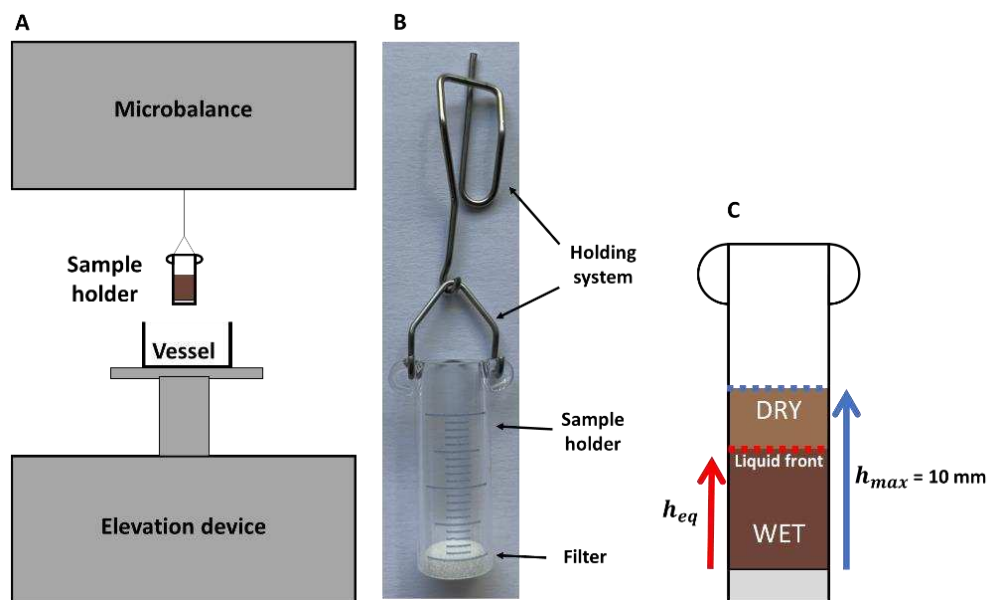


Figure 1. Capillary wicking: A) experimental set-up B) sample holder C) wicking representation.

An example of experimental curve is given in Figure 2 for the reference lignin with n-Hexane. The Washburn equation is verified if the curves recorded by the tensiometer during capillary wicking (m^2 vs t) have a linear trend. Firstly, n-Hexane is used as totally wetting test liquid ($\cos \theta$ is approximated to 1) which allows the determination of $c\bar{r}$ from fit of the experimental

wicking curve with Eq. 2, as shown in Figure 2. In the same way, once $c\bar{r}$ is known, the linear fit of wicking curve with other liquids can be used to determine the apparent advancing contact angles (θ_a).

It is now interesting to observe that the curve in Figure 2 reaches an equilibrium weight (m_{eq}) due to the saturation of the porous medium by the test liquid. As for the Washburn approach, also for the Jurin law application, the squared equilibrium mass (m_{eq}^2) obtained with n-Hexane was used for the calculation of the $c\bar{r}$. Afterwards, the m_{eq}^2 obtained with the other test liquids were used to determine the apparent equilibrium contact angles (θ_e).

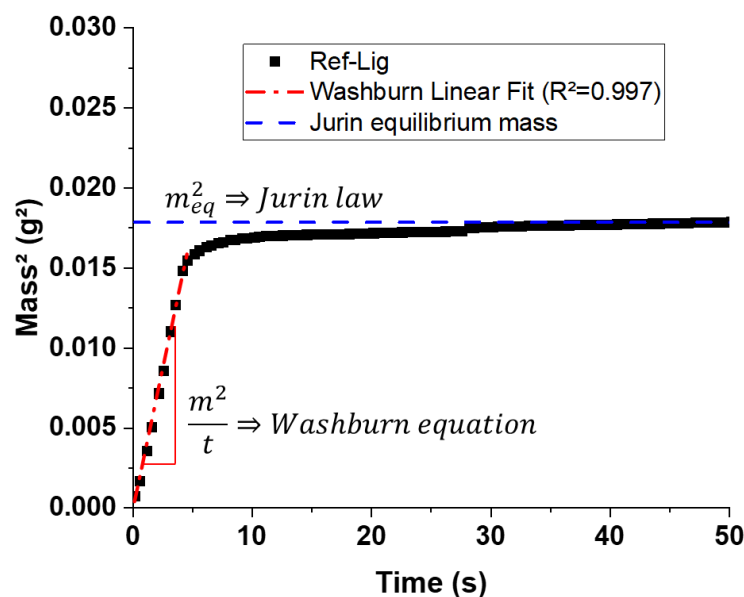


Figure 2. Washburn linear fit of experimental test of reference lignin with n-Hexane and Jurin squared equilibrium mass.

3. Results and discussion

3.1 Characterization of morphological and wetting parameters

Five tests were firstly performed with n-Hexane (Figure 3) in order to determine the $c\bar{r}$ for each lignin. It is possible to observe that the curves show a rapid wicking (less than 10 s) for untreated and treated lignins. All the samples were fully wetted showing a linear trend of wicking and the squared equilibrium mass was in a range between 0.0125 and 0.030 g² for all lignins. The slope of the curve (m^2/t) and the equilibrium mass (m_{eq}) were then used for the respective calculation of $c\bar{r}$ based on Washburn and Jurin equations.

Using the respective $c\bar{r}$, the determination of the contact angles was made applying both Washburn and Jurin approaches with the other test liquids, according to the experimental procedure.

Figure 4 shows wicking curves obtained for all lignins with ethylene glycol and photos of one sample per lignin after the test. One can observe that wicking kinetics were very different as a function of lignin. However, no curves showed a linear trend and then the Washburn equation could not be applied to determine the advancing contact angles. This was probably due to a

change in morphology occurring when the liquid is in contact with the lignin and then Washburn hypotheses (with a constant $c\bar{r}$) are not valid [9]. This interaction between lignin and ethylene glycol was observed in the literature and here, it causes a slight decrease of mass before achieving the equilibrium. Moreover, it is important to observe that the liquid reached different equilibrium heights depending on the lignin type. Using the Jurin approach, different apparent equilibrium contact angles were then found.

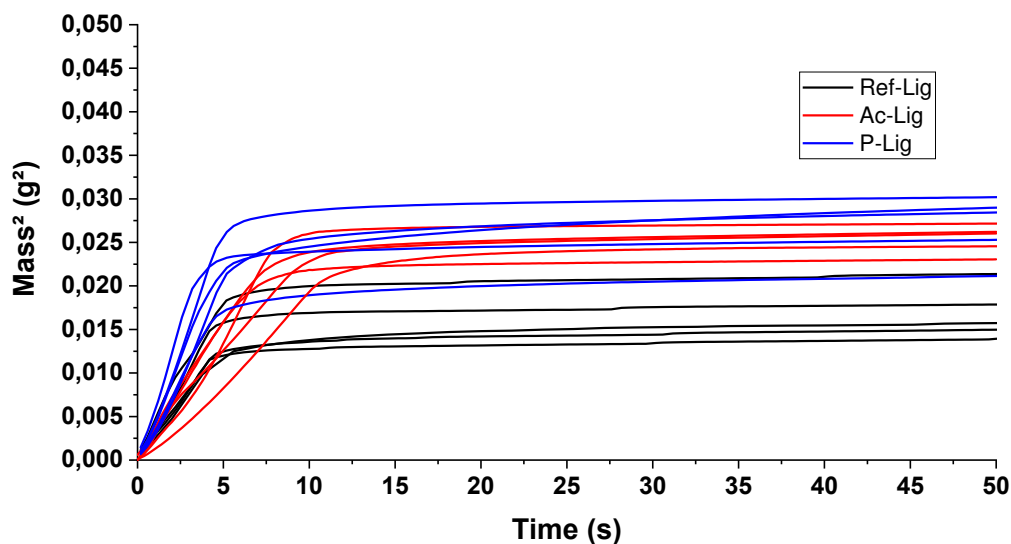


Figure 3. Wicking curves with *n*-Hexane for Ref-Lig, Ac-Lig, P-Lig.

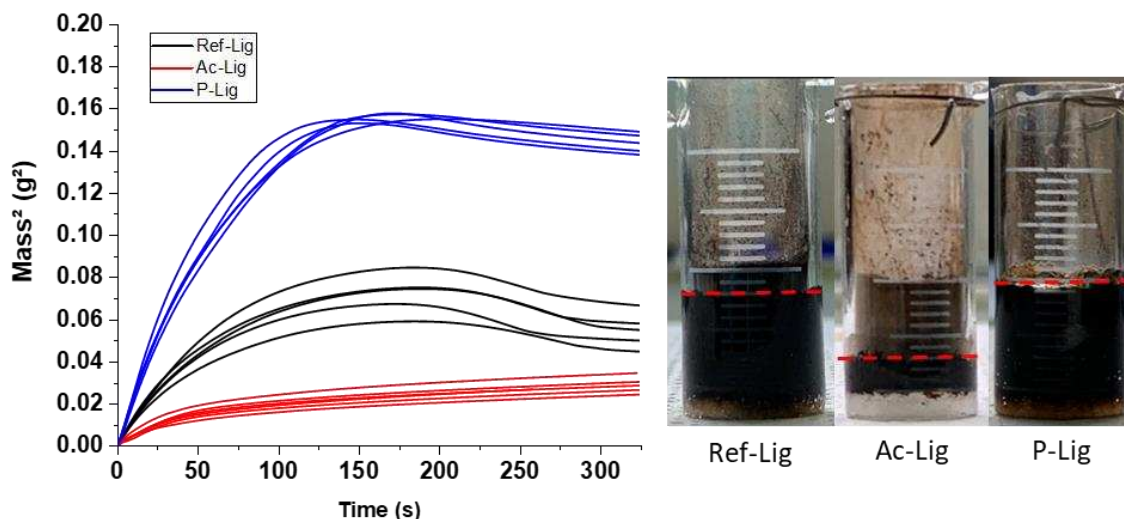


Figure 4. Wicking curves with ethylene glycol for Ref-Lig, Ac-Lig, P-Lig and respective liquid equilibrium heights (dash lines in red).

All equilibrium contact angles obtained applying the Jurin approach were then used to determine the surface energy and the dispersive and polar components of lignins.

3.2 Determination of lignin surface energy

The determination of lignin surface energy and their dispersive and polar components was possible using the Eq.1 and the apparent equilibrium contact angles obtained via the modified Jurin approach for porous media. Results are shown in Table 2.

Table 2: Surface energy and components of the different lignins.

	Ref-Lig	Ac-Lig	P-Lig
γ_s^D (mN/m)	13.60 ± 0.18	11.64 ± 0.14	23.31 ± 0.34
γ_s^P (mN/m)	39.25 ± 2.85	29.17 ± 1.36	17.88 ± 1.42
γ_s (mN/m)	52.85 ± 3.03	40.81 ± 1.50	41.19 ± 1.76

Ref-Lig was found to have the highest surface energy ($\gamma_s = 52.85 \pm 3.03$ mN/m) with a very high polar component (39.25 ± 2.85 mN/m). In the literature, Notley et al. [10] found a quite similar surface energy (57.1 mN/m) for a kraft lignin film using contact angles determined with a goniometer. Even if the two methods and the material form are different, the surface energies were close. However, the dispersive and polar components were not similar. The Ref-Lig is more polar than the Ac-Lig and the P-Lig, probably due to the OH and the Na⁺ content. The Ac-Lig ($\gamma_s = 40.81 \pm 1.50$ mN/m) and the P-Lig ($\gamma_s = 41.19 \pm 1.76$ mN/m) have a lower surface energy with a widely reduced polar component. This is consistent with the fact that the chemical treatments removed a part of Na and grafting new functional groups on hydroxyl sites. Due to the effectiveness of treatments, the lignin clearly lost a large part of polar components. Reducing the polarity of lignin should have a beneficial effect on the adhesion with PLA that is known as a hydrophobic matrix [6]. P-Lig showed the lowest polar component (17.88 ± 1.42 mN/m) and, in addition, an increase of the dispersive component compared to Ref-Lig and Ac-Lig. This is due to the addition of phosphorus, which has a heavier electron cloud and facilitates instantaneous dipolar moments formation [11].

4. Conclusion

Surface energy results were found to be consistent with the literature and with lignins characterizations. This proves that the modified Jurin approach coupled to an adapted experimental procedure for powders and porous media can be an effective and simple solution to determine suitable surface energy of these materials. Another interesting result is that the phosphorylation, known to be efficient for improving thermal stability of composites, could be also promising to improve the adhesion at the lignin/PLA interface compared to the acetylation, which is already known as an efficient treatment for this aim. Knowing filler surface energy components is also relevant to determine the work of adhesion between the filler and the matrix. For PLA matrix, surface tension components should be determined at the molten state [12, 13]. However, as a first approximation, lactic acid dispersive and polar components could be used to calculate the work of adhesion. All these aspects will be discussed during the oral session. Further studies about the enhancement of interface adhesion and the mechanical behavior of this interface represent the perspectives of this work.

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