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Chapter

Lignin as Sustainable Antimicrobial Fillers to Develop PET Multifilaments by Melting Process

Juliette Minet, Aurélie Cayla and Christine Campagne

Abstract

Nowadays, textiles functionalization is developing increasingly, fabrics are not only defined by the intrinsic properties of the fiber but some properties are also brought to provide them added value. Among the desired properties, antibacterial activity is targeted to improve the comfort and durability of textiles but many commercial products use chemical substances which are harmful for the environment (regulation 528/2012). The goal of this study was to use bio-based biocide which can be incorporated in the polyethylene terephthalate (PET) by melt spinning for the development of functional PET. This biocide had to resist to the PET processing temperature up to 264°C which was the maximum temperature of implementation. Two kinds of Kraft lignin and titanium dioxide as reference were added by melting way. The antimicrobial activity was characterized at low concentration (1 and 2 wt.%), to avoid a significant decrease in mechanical strength for the multifilaments and to maintain optimal rheological properties of the polymer for the melt spinning process. Filled PET pellets were obtained by twin screw extrusion step and the multifilaments by melt spinning step. Finally, knitting structures were developed for the evaluation of the antibacterial activity. The mechanical (tensile test) and thermal (DSC and TGA) properties of the filaments were characterized.

Keywords: antibacterial activity, melt spinning process, lignin, sustainable, filaments

1. Introduction

The textile industry is constantly in movement to develop functional and sustainable materials. Additional properties can be added to the intrinsic properties of the textile through its functionalization. One of the targeted properties is antibacterial activity to develop more durable textile because microbes damage fabrics or can develop bad odor. Antimicrobial textile is used in different fields such as medical, clothing or building. On the market, different kinds of textile structures developed with antimicrobial activity are commercialized, as example the X-static® product which is made by permanently bonding metallic silver to the surface of the fiber to inhibit the growth of bacteria [1]. Polyrey Sanitized® uses [2] silver ions for

hospital bedding or Cupron® which develops fabrics of natural or synthetic fibers with pure copper incorporate inside [3]. Textile can be functionalized at all stages of its transformation, during the extrusion for the mass-functionalization, by diffusion for the small molecules or with various surface treatments. The diffusion technic is similar to dyeing process, the diffused agent is carried within the fiber whereas others treatments as surface-functionalization, the agent is placed on the surface by padding or coating. Many textiles and filaments are marketed with antimicrobial activity by mass incorporation of fillers produced by extrusion. The active products are either organic or mineral agents and have to present a good thermal stability during the extrusion step for the incorporation of antibacterial component in the polymer. Amicor's® acrylic fibre used organic agent as triclosan for bringing the antibacterial properties [4]. Mineral agents as silver can be also incorporated in synthetic monofilament, for example, Trévira Bioactive® [5] and Meryl® Skinlife [6], respectively polyester and polyamide which present permanent antimicrobial properties. Nowadays, more and more commercial products are produced by extrusion with the addition of fillers into the thermoplastic polymer and silver nanoparticles are often selected [7–9]. However, environmental concerns of these particles are pointing despite the effective antibacterial properties and good resistance to high temperature because they are very toxic to aquatic life with long lasting effects. Its environmental impact leads to a European regulation (regulation 528/2012) of its use [10]. One way to reduce environmental impact is to substitute silver particles by sustainable, ecofriendly and efficient agents. The challenge, to continue the development of synthetic fiber by melt spinning, is the thermal resistant of agents to processing temperatures of polymer. For reducing the diffusion of the antibacterial agent in the environment, the mass functionalization by extrusion and melt spinning process seems to be the best way to obtain durable textile. Some bio-based agents as chitosan [11] or eugenol [12], present interesting antibacterial activity. Chitosan, obtained after a deacetylation of chitin which is structural element in the crustaceans exoskeleton, may interact with the bacteria membrane and damage it. Indeed, chitosan can alter permeability of membrane cell leading to release of the protein material and other intracellular components and can be accompanied by some lysis of the cell [11]. Eugenol, major constituent of cloves, is effective against a wide range of bacteria, Gram-negative as *E. coli*, *P. vulgaris* or Gram-positive as *S. aureus* [12]. However, a lot of these agents cannot be used for extrusion because of their degradation temperature too low during this step. One other kind of sustainable product which can be incorporate in a polymer to give antibacterial properties is lignin [13–17]. Lignin is a complex and irregular biopolymer and the International lignin institute [18] describes it as an organic substance that binds the cells, fibres and vessels together. It composes wood and the lignified elements of plants and gives the rigidity to the cell wall of the vascular plants [15, 18, 19]. This is the second most abundant organic polymers after cellulose on earth [18] however, it is considered as waste material and low value by-product in the paper industry [19]. Lignin is derived from the polymerization of *p*-coumaryl, coniferyl and sinapyl alcohols, it is cross-linked phenolic polymers [19, 20] but chemical structure cannot be precisely defined because all lignins have some variations in their composition [18]. Indeed, lignin contains many different functional groups, like hydroxyl, methoxyl, carbonyl and carboxylic groups which can be found in different proportions in its structure according to its origin and extraction processes applied [20]. This functional groups lead to polymers several different properties such as specific antioxidant properties [14, 16, 21], UV stabilization effect [22, 23] or antibacterial activity [18, 19, 22–25]. Cazacu et al. define antibacterial activity of several lignin (Alcell® lignin, Kraft lignin and hydrolysis lignin) according to the nature bacteria, its origin, its chemical structure and also its

concentration in cultivation medium and the type of microorganisms [19]. Therefore, lignin has shown antibacterial properties, and also in polyvinyl alcohol (PVA), in polyethylene (PE) and in poly(lactic acid) (PLA) [18, 19, 22–25]. Indeed, the activity of the PVA with lignin nanoparticles (LNP) for active packaging was demonstrated for two kinds of bacteria (*Xanthomonas arboricola* pv. pruni and *Pectobacterium carotovorum* subsp. Odoriferum) by Yang et al. [24]. They have demonstrated a well dispersion of the LNP could generate a nucleation effect in PVA and they have validated the synergetic antioxidation effect of LNP with the chitosan [24]. LNP and cellulose nanocrystals (CNC) at 1 and 3 wt.% in PLA present also a synergetic effect but in terms of transparency and UV light blocking aptitude not for antibacterial effect, LNP had better result without the addition of CNC as showed Yang et al. [22]. The antibacterial efficiency of 2 wt.% Björkman lignin was also described in PE film by Gregorova et al., against *E. coli* and *S. aureus* and its activity was compared with common used synthetic antibacterial effective additives [25]. Lignin showed good antibacterial activity compare to known biocides which is harmful for the environment [25]. Without mention antibacterial activity of lignin, Faruk et al. [35] showed the influence of lignin incorporation (Kraft lignin, organosolv lignin and soda lignin) in thermoplastics mostly in polypropylene and polyethylene but also in polyamide, polystyrene, polyvinyl chloride and even more at 0–80 wt.% of lignin were tested. They concluded that the addition of lignin can improved greatly the thermal stability but it depends on the miscibility between lignin and thermoplastics and the types of lignin had an influence on the blending [24]. Unfortunately, in most cases the mechanical strength decreased because of their low compatibility but can be improved with the change of lignin and new blending methods [24]. Furthermore, lignin enhanced the flame retardancy and allows to use it as a carbon source in intumescent systems [13, 24]. This review mentioned the study of Canetti and Bertini which dealt with thermal properties of the composites (PET + lignin) [26]. The analysis showed the degradation temperature and thermal stability in nitrogen decreased with the addition of filler, therefore the lignin content had not to be too high [26].

In this study, polyethylene terephthalate (PET) which is the synthetic polymer the most common in textile [27], was chosen for its high mechanical strength, toughness and fatigue resistance [27, 28]. Different antimicrobial products were incorporated in PET and the purpose was to identify agent with optimal antibacterial properties and with sufficient thermal stability for resisting to the extrusion and spinning process. Rheological property of the polymer had to be adapted to present fluidity compatible with the melt spinning process. The antimicrobial activity had to be observed with small concentration of product, without causing a considerable decrease in the textile's mechanical strength, antimicrobial product selected as a reference was titanium dioxide (TiO_2) because of its high photoactivity, it had been the subject of many studies as antibacterial, self-cleaning or antifogging surfaces [17, 29] and for the bio-based compounds were two kinds of Kraft lignins: Domtar lignin (DL) and Kraft lignin (KL).

2. Materials and methods

2.1 Materials

PET RT 5120 used in this study was supplied by INVISTA Resins & Fibers GmbH. The glass transition temperature of pellets is 82°C and its crystallization temperature 174°C with crystallinity content around 34%. Two kinds of Kraft lignins were incorporated in PET: Kraft lignin (KL) and Domtar lignin (DL).

KL was purchased from Sigma Aldrich and DL from UPM Biochemicals, Finland (European distributer of Domtar BioChoice™ lignin). KL was a pure grade lignin with purity level >98%, with a pH between 5.5 and 7.5 and DL represented industrial grade lignin with a lower purity level (~95%). Titanium dioxide (TiO_2), known for his antibacterial property [17, 29], had been used as a reference. Aeroxide® TiO_2P_{25} was purchased from EVONIK Industries.

2.2 Textile structures development

Production of antibacterial textile structures requires firstly functional pellets (PET + lignin or TiO_2) produced by extrusion. Then PET nanocomposites were used in melt spin equipment for the development of multifilaments. Finally, a textile structure was obtained by knitting for the characterization of antibacterial activity.

2.2.1 Extrusion

The preparation of PET/fillers compounds by extrusion, requires a drying stage in a vacuum oven at 80°C during 12 h for removing any absorbed water and for avoiding the hydrolyze phenomena of PET. Lignins or TiO_2 incorporation into the PET, with different weight percentages (1 and 2 wt.%), was realized thanks to a co-rotating intermeshing twin-screw extruder from Thermo Haake (L/D = 25). For each blend, the rotational speed was 100 rpm and the five heating zones temperatures of the extruder were fixed ranging from 252 to 260°C. A granulator cut the extruded rod into cylindrical pellets which were dried again for the spinning step.

2.2.2 Melt spinning

Multifilament yarns were obtained by a melt spinning process using the Spinboy I manufactured by Busschaert Engineering spinning device. The extruded blend (PET + fillers) pellets passed through a single-screw extruder heated from 255 to 265°C which brought them in molten state. The spinning temperatures of extruder zones were defined in **Table 1**. They were injected through two dies, containing each 40 holes with a diameter of 1.2 mm, thanks to a volumetric pump. Two bundles of monofilaments were obtained, cooled down by air and then covered with a spin finish oil to ensure multifilament cohesion along the process. The multifilament continuous yarn was hot drawn between two rolls with varying speeds (S1 and S2 defined in **Table 1**) before winding. The theoretical drawing of multifilament was given by the draw ratio (DR), Eq. (1):

$$DR = \frac{S_2}{S_1} \quad (1)$$

Two draw ratios were applied, 2 and 4 by keeping the first roll at the same speed (200 m/min). DR = 4 was obtained when rollers reach the maximum speed at which the multifilaments were spinnable, for optimal drawing. The blend PET/KL

	Extruder zones					Dies	S1 (m/min)	S2 (m/min)	DR
T°C	257	255	264	264	260	262	200	200	2
							400	800	4

Table 1.
Spinning temperatures and roller speeds according to draw ratio (DR).

was not spinnable with DR = 4 because the heap of LK powder blocks the dies which prevents the formation of filaments.

2.2.3 Knit fabric

Developed multifilaments (PET + lignin; PET + TiO_2) were used for the development of A4 format textile structures by manual knitting machine. The knit fabric had to have a large pore structure for the antibacterial test (agar), so that bacteria can breathe underneath the knit. Indeed, bacteria used in this study, multiply in the presence of oxygen, they are called aerobic. All samples were knitted in rib 1 × 1 with 69 needles and E8 gauge. For antibacterial test, the knitting structures were desired for removing the presence of oil and surfactant at the yarns surface. Three steps were required for the desizing; the first one is several cycles in a soxhlet containing petroleum ether during 4 h. Fabrics were dried during at last 12 h, and then underwent a second soxhlet in ethanol during the same time as before. Three cleanings in distilled water under ultrasound (37 Hz) for 20 min released residual products from the sizing. After drying the knits during 12 h, they could be characterized.

2.3 Characterizations methods

2.3.1 Thermal properties

Thermogravimetric analyses (TGA) under air were performed using a TA 2050 Instruments. A sample of 10 ± 0.5 mg of filler or pellet was placed in an open platinum pan. Loss weight measurements were carried out from 20 to 700°C at a heating rate of 10°C/min in a 50 ml/min flow of nitrogen. Degradation temperature was studied after 5 wt.% loss weight. Differential scanning calorimetry (DSC) characterizations of multifilaments were performed on a 2920 Modulated DSC (TA Instruments) with typically 10 ± 0.2 mg of dry material. The manipulation carried out under nitrogen atmosphere (with a flow of 50 ml/min) consisted in two identical cycles, the first one being devoted to the elimination of the thermal history of the nanocomposite previously extruded. The first and the second cycle had the same temperature variation: from −20 to 200°C at 10°C/min, an isotherm at 200°C during 3 min and a cooling stage at 10°C/min to return to −20°C. Analyses were made on the second cycle. The crystallinity degree (χ) of PET in blend was calculated according to Eq. (2):

$$\chi(\%) = \frac{\Delta Hm}{(1 - m_{filler}) * \Delta Hm^0} \quad (2)$$

where m_{filler} is the theoretical content (wt.%) of fillers introduced in PET; ΔHm^0 is the reference enthalpy defined as heat of a 100% crystalline sample (117.6 J/g); ΔHm is the melting enthalpy.

2.3.2 Mechanical properties

Mechanical properties were tested to control that the multifilaments with fillers keep sufficient mechanical properties for undergoing to a textile transformation. The mechanical tests were realized on monofilaments extracted from the multifilament yarn. The count of 10 samples was measured in decitex (dTex) by Vibroskop LENZING INSTRUMENTS and each monofilament was tested to define

its tensile strength. These tests were carried out following the standard NF EN ISO 5079 on a tensile testing machine from Zwick (1456). The force sensor used was 10 N. All the tests were made at standard atmosphere (20 ± 2°C; 65 ± 5%). The length of the sample was 20 mm and the deformation rate 20 mm/min. All the results represented an average value of 10 tests.

2.3.3 Morphology

The longitudinal view of multifilaments was observed with an optical microscope. The Nikon eclipse LV100POL with advanced research image analysis was used to analyze the dispersion of the fillers into PET. The morphology of PET with 1 and 2 wt.% KL and DL blends was studied using a Field Emission Gun-Scanning Electron Microscope (FEG-SEM) to analyze the distribution of lignin in the polymer. The technology used was Jeol JSM7600F with Oxford EDX (energy dispersive X-ray spectrometry) analysis.

2.3.4 Interfacial energy

The interfacial energy between the PET and the fillers were determined from the surface energy of each components by the sessile drop technique. Lignins films were created and were tested with a drop of water and diiodomethane which were polar and apolar liquid with a known surface tension (**Table 2**). Surface energy could be expressed as a sum of several components as in Eq. (3): polar (p), dispersive (d), ionic (i), covalent (c), metallic (m), etc. [30].

$$\gamma_S = \gamma_S{}^p + \gamma_S{}^d + \gamma_S{}^i + \gamma_S{}^c + \gamma_S{}^m + \ldots \quad (3)$$

Only two components, polar and dispersive, are taken into account; the other terms are defined as negligible.

γ_L^d is the dispersive component and γ_L^p is the polar component of liquids.

θ was considered as the angle of the liquid on the solid. The Fowkes method allows to determinate the polar and dispersive components of the surface energy from the contact angles obtained on this solid with various liquids [31, 32].

The equation of Owen and Wendt [33] (4) with two unknowns allows to define the surface energy of the solid:

$$\gamma_L(1 + cos\theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p} \quad (4)$$

γ_S is the surface tension of lignins (mN/m); γ_L is the surface tension of the liquid (mN/m); γ^p is the polar component (mN/m); γ^d is the dispersive component (mN/m).

Surface energy of lignins and PET allow to measure interfacial energy with Eq. (5) between x/PET and x is the lignin KL or DL [34]:

(mN/m)	γ_L	γ_L^d	γ_L^p
Water	72.6	21.6	51.0
Diiodomethane	50.8	48.5	2.3

Table 2.
Water and diiodomethane components of the surface tension (γ_L).

$$\gamma_{x/PET} = \gamma_x + \gamma_{PET} - \frac{4\,\gamma_x^d\,\gamma_{PET}^d}{\gamma_x^d + \gamma_{PET}^d} - \frac{4\,\gamma_x^p\,\gamma_{PET}^p}{\gamma_x^p + \gamma_{PET}^p} \quad (5)$$

x is the lignin KL or DL.

2.3.5 Antibacterial activity

Antimicrobial tests have been run on each lignin powder and desizing knitted structures. First of all, knits were cut and autoclave steam sterilization was carried out at 120°C during 20 min to ensure other bacteria were not going to grow during the test. In test tubes, nutrient broth and bacteria were mixed and then cultured for 24 h at 37°C, which was the optimal temperature for bacteria growth. The culture solution was diluted and 250 μL of this solution with a concentration of ~105 CFU/ml was poured onto sterilized petri dishes with the solid culture medium (agar) that was adapted to the bacteria. Then 50 mg of each lignin powder was spread or knit fabrics (4 × 3 cm) were positioned in different petri dishes. Qualitative test was made with the Agar diffusion test. During this test, two different types of bacteria, described lower, were studied. This difference could be detected by staining technique: Gram-negative has an outer membrane. Indeed, antibacterial effect depends on the gram and the genus of the bacteria. The first was a Gram-positive bacterium, genus *Staphylococcus epidermidis* ATCC® 12228™, it is a bacterium that is found on the skin and is therefore constantly in contact with clothing textiles. The second bacterium tested was Gram-negative, genus *Escherichia coli* ATCC® 25922™. It is found mainly in the intestines of mammals and will serve as a reference for all Gram-negative bacteria.

Once the knits or the powders were positioned in contact with bacteria in petri dishes, they were placed in an oven for 24 h at 37°C for incubation. The antibacterial halo around the powder could be defined but for the textile, there is no diffusion of agent out of the fiber. Therefore, knits have been removed for defining antibacterial activity by contact underneath the knit.

3. Results and discussion

The comparison of the two lignins properties was realized with several tests out of characterization. First, fillers were tested to evaluate their antibacterial efficiency and their thermal resistance to high temperatures. Secondly, dispersion variations between fillers in PET were analyzed thanks to the mechanical properties of monofilament and finally the thermal and antibacterial properties of the textile material were characterized. Mechanical tests were also used to check if the yarn could be used and be enough resistant for an outdoor textile application.

3.1 Fillers properties

TGA tests on fillers were performed to define each degradation temperatures of lignins and the antibacterial test characterized their activities against two bacteria.

3.1.1 Thermal stability properties

The results in **Table 3** showed that the fillers presented thermal stability with the processing temperature of the PET (264°C) during melt spinning. In **Table 3**, degradation temperature (Td) of KL and DL were close to the PET processing

Fillers	KL	DL	TiO_2
Td (°C)	253	232	>700
Loss weight at 264°C (wt.%)	6.1	7.6	1.6

Table 3.
Degradation temperature of KL, DL and TiO_2.

temperature at 264°C whereas TiO_2 was very resistant up to over 700°C. The degradation at 264°C for both lignins was <8 wt.%. Therefore, KL and DL could be used by melt spinning as filler in the PET.

3.1.2 Antibacterial properties

Lignins powder were first tested with the agar diffusion test and qualitative test as explained in Section 2.3, antibacterial activity to confirm the antibacterial properties of lignins and the results are shown in **Figure 1**.

The black line delimits the halo which means that no bacteria are present around the lignin thanks to its antibacterial activity. Two kinds of bacteria were tested: *S. epidermidis* and *E. coli*, as explained. Against Gram-positive bacteria, halos were created around powders, so KL and DL were efficient. However, there was less diffusion of lignins with Gram-negative bacteria but a small halo could be noticed. Their effectiveness after an exposition at high temperature during 5 min were verified. The powders still demonstrated antibacterial activity with the same inhibition zone against bacteria after this thermal treatment.

3.2 Influence of dispersion on mechanical properties

The influence of fillers dispersion was characterized by the mechanical properties of the monofilaments. Optical microscope and SEM observations have completed the characterization of the dispersion. The interfacial energy of polymer and fillers gave information concerning the affinity of fillers and explained this dispersion.

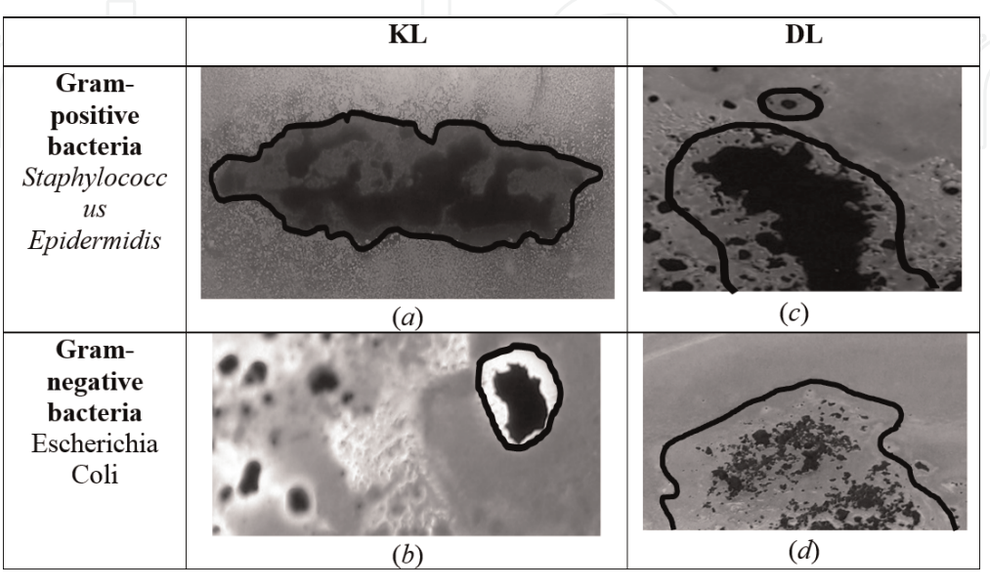

Figure 1.
Anti-bacterial results on (a) KL against S. epidermidis, (b) KL against E. coli, (c) DL against S. epidermidis, and (d) DL against E. coli.

3.2.1 Mechanical properties

Count (dTex) was measured on monofilament extracted from multifilament yarns and the same monofilament was used for tensile test.

Figure 2 represents counts of multifilaments realized, for 1 and 2 wt.% of TiO_2, KL and DL and for virgin PET. The monofilament with KL was less regular and the standard deviation of monofilament count with KL was higher than others. The count with DR = 4 was always slightly smaller than DR = 2, indeed multifilaments at DR = 4 were more stretched. Virgin PET was used as reference, and the introduction of TiO_2 or DL did not significantly modify the average count of the monofilaments extracted from the multifilament. On the other hand the incorporation of KL increased the count which could be explained by the agglomeration of fillers in PET.

Figure 3(a) represents the tenacity and **(b)** the elongation at break according to the fillers content. The dotted line is for DR = 4 and the continuous line for DR = 2. In **Figure 3(a)**, the incorporation of KL and DL fillers decreased the tenacity of the PET by almost 40% no matter the type of lignin. Both lignins weakened the monofilament but thanks to the good mechanical properties of PET, the multifilament could be still transformed into textile structure. The fillers content had low effect on the elongation at break except for KL, the tenacity continue to reduce with 2 wt.%. Moreover, when DR = 4 the material was more resistant than at DR = 2, because the macromolecules had been more oriented in the direction of the stress during drawing in the glassy state. In **Figure 3(b)**, all values of elongation

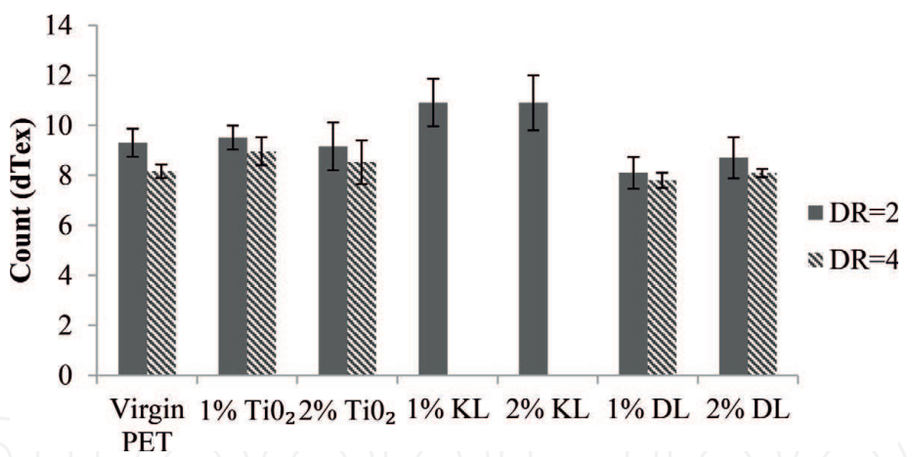

Figure 2.
Counts of monofilaments: virgin PET, 1 and 2 wt.% of TiO_2, KL and DL according the draw ratio (DR).

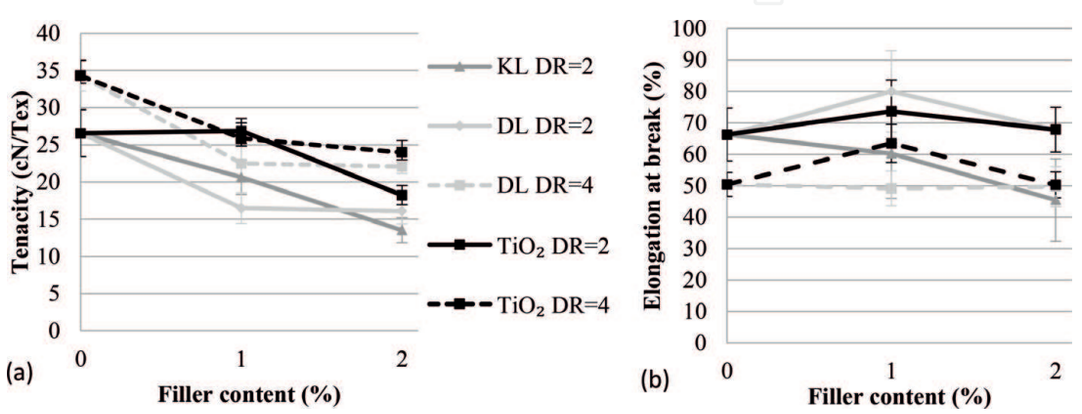

Figure 3.
(a) Tenacity at break and (b) elongation at break according to fillers content.

at break were between 50 and 80%, the latter being weakly impacted by the adding of fillers. Elongation at break increased slightly with 1 wt.% TiO_2 and DL (DR = 2) but not significantly according to standard deviation. Indeed, the standard deviation is higher for 1 wt.% DL in comparison with the other measures. The incorporation of 1 and 2 wt.% KL decreased the elongation at break and this value decreased with the draw ration leading to the orientation of the macromolecules. The more content of KL was, the weaker and less elastic the filament was. For DL there was no general trend, there was a decrease in mechanical properties with 1 wt. % and the properties were stable at 2 wt.%.

3.2.2 SEM and optical microscope

Figures 4 and **5** are respectively the SEM pictures and images from optical microscope. In the SEM pictures KL caused asperities on the surface of filaments and showed that it is not regular, unlike the wire with DL which is longitudinally regular. Microscopy analyzes show that KL forms agglomeration while DL is homogeneously dispersed. In **Figure 5(a)** and **(b)**, the optical microscope showed many agglomerates of KL in PET, especially with 2 wt.%. The higher the filler content, the more defects there were. Most of agglomerates were larger than 100 μm and some of them appeared to the naked eye as in **Figure 6**. DL presented a better dispersion in PET as seen in **Figure 5(c)** and **(d)**. The count of the yarn with KL was higher because of the poor dispersion and the heap of powder that increased the thickness. Agglomerates were arranged randomly along the filament which was explained the big standard deviation of the count in Section 3.2.1.

3.2.3 Interfacial energy

Interfacial energy was calculated with formulas in Section 2.3.3, Interfacial energy for explaining the difference of homogeneity between lignins in the PET. **Tables 4** and **5** show respectively the surface energy of DL, KL and PET and the interfacial energy between KL/PET and DL/PET.

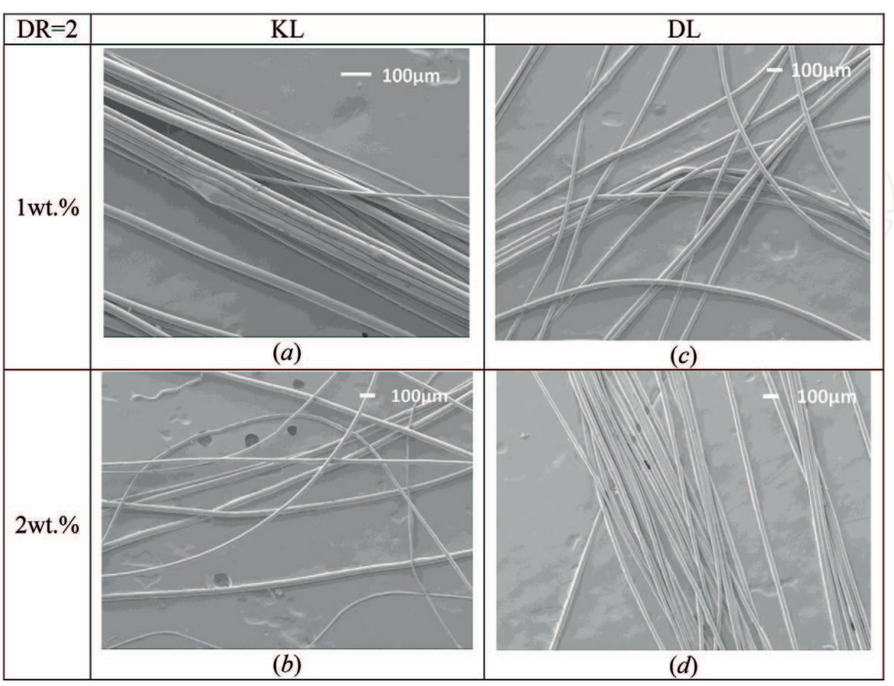

Figure 4.
SEM of multifilaments (a) PET + 1 wt.% KL, (b) PET + 2 wt.% KL, (c) PET + 1 wt.% DL, and (d) PET + 2 wt.% DL.

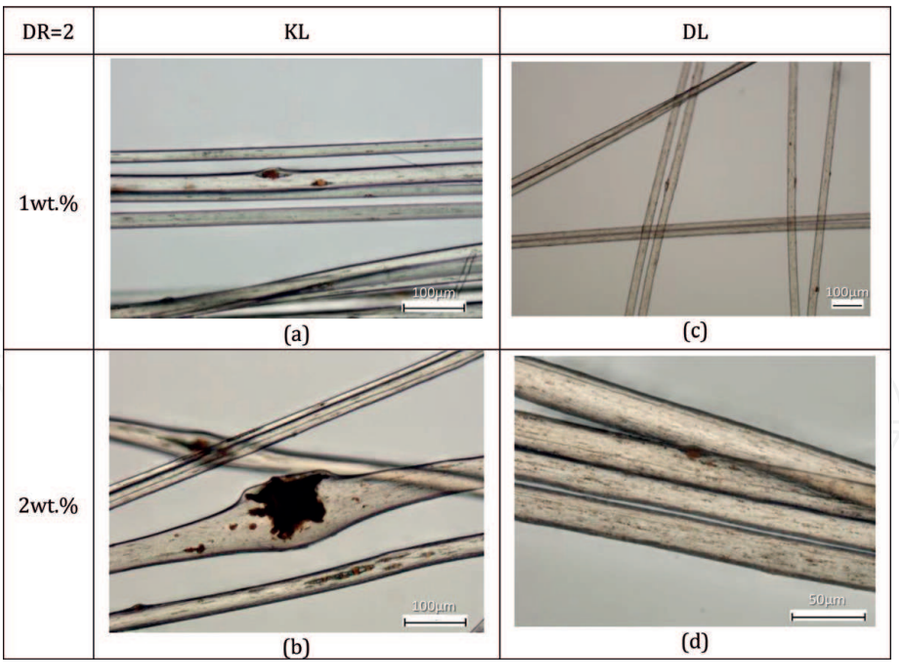

Figure 5.
Optical images of multifilaments (a) PET + 1 wt.% KL, (b) PET + 2 wt.% KL, (c) PET + 1 wt.% DL, and (d) PET + 2 wt.% DL.

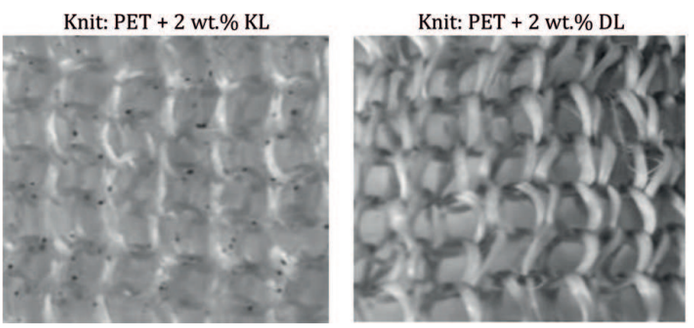

Figure 6.
View of knit fabrics PET + 2 wt.% KL and PET + 2 wt.%.

(mN/m)	γ_S	γ_S^p	γ_S^d
KL	55.4	25.3	30.1
DL	53.8	15.9	37.9
PET	44.6	4.9	39.7

Table 4.
Surface tension polar and dispersive of KL, DL and PET.

$\gamma_{KL/PET}$ (mN/m)	$\gamma_{DL/PET}$ (mN/m)
15.1	5.9

Table 5.
Interfacial energy of KL and PET ($\gamma_{KL/PET}$) and DL and PET ($\gamma_{DL/PET}$).

Table 5 had showed that the interfacial energy for Dl in PET was smaller than for KL, which means that the affinity between DL and PET is better than KL. A higher interfacial energy ($\gamma_{KL/PET}$) shows a low affinity which caused

agglomerates as seen in the optical microscope images. Omar Faruk et al. [24] have explained that when lignin was pure the blending was better, but in this case, it was the opposite because as seen in Section 2.1, KL has slightly higher purity than DL. The difference could be explained by the side-chain of each lignin, which account for the difference of the interfacial energy with PET.

3.2.4 Thermal properties

Knowing the thermal properties of the filament allowed to determine the crystallinity content of the polymer, to understand its behavior at different temperatures. DSC measured the crystallinity content, melting and glass temperature. The crystallinity content has been calculated as explain in Section 2.3, differential scanning calorimetry and are presented in **Figure 7**.

Figures 7 and **8** introduce the results obtained for the filaments with DR = 2 because results were similar for both DR. Tc is the crystallinity temperature measured on the second cycle of curves obtained by DSC analysis. **Figures 7** and **8** show the values according to the percentage of fillers in the PET. For all fillers, the incorporation enhanced the crystallinity content but for KL and TiO_2, the percentage of filler had no impact. For both lignins, crystallinity temperature increase and the crystallization start beforehand. The crystallinity content and temperature of DL increased with the percentage; therefore, DL can be defined as nucleating agent and its effect increase slightly with the fillers content.

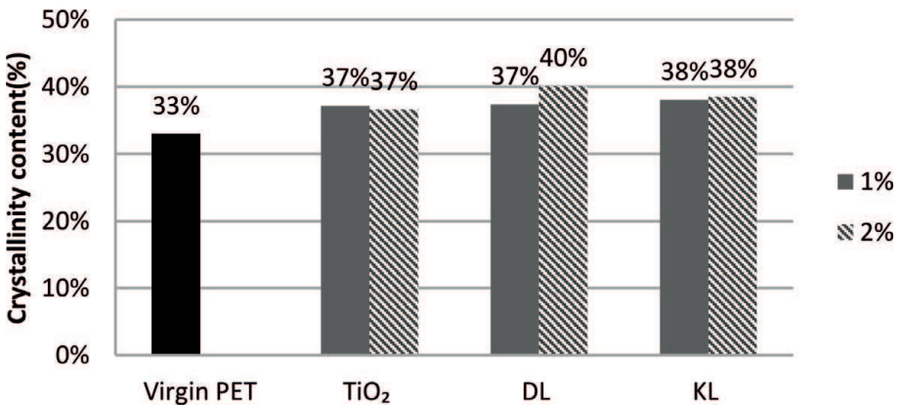

Figure 7.
Crystallinity content of multifilaments DR = 2 virgin PET, and filled PET with TiO_2, LD or LK at 1 or 2 wt.%.

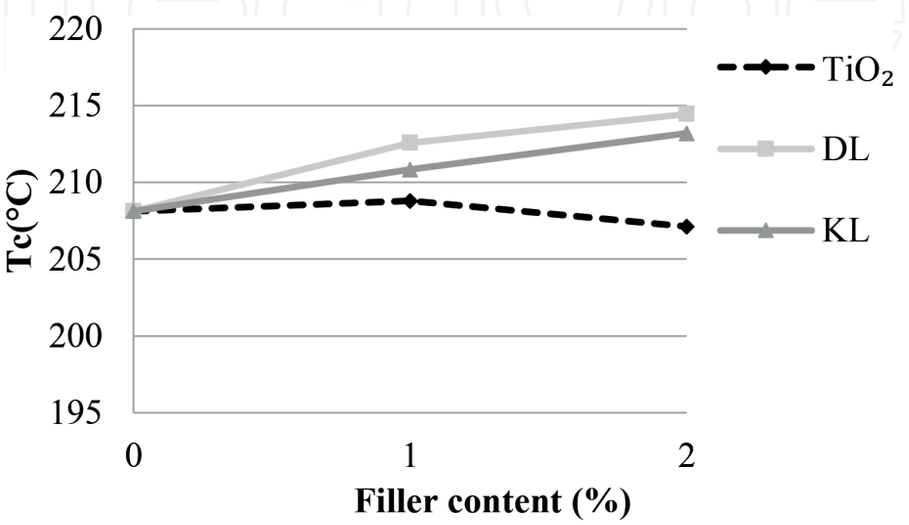

Figure 8.
Crystallinity temperatures according to filler content for TiO_2, LD and LK, DR = 2.

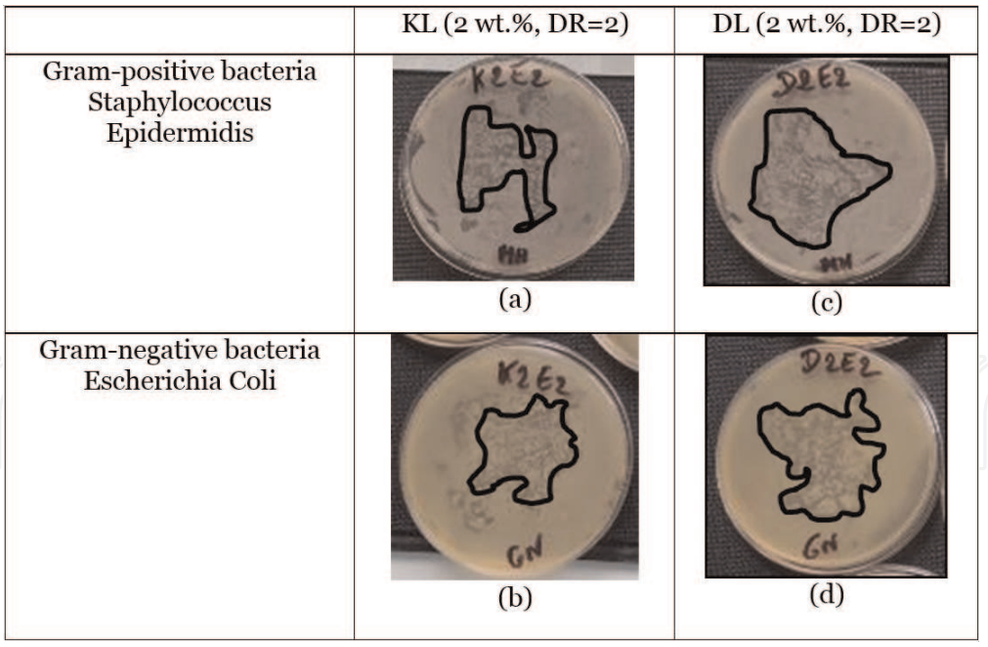

Figure 9.
Anti-bacterial results on desizing knitted fabric based on PET filled with (a) KL against S. epidermidis, (b) KL against E. coli, (c) DL against S. epidermidis, and (d) DL against E. coli.

Integration of lignin at 1, 2 wt.% or TiO_2 did not modify the thermal stability of the PET and the degradation temperatures were always around 400 ± 2°C (which was the accuracy of TGA device). These fillers did not have any influence on thermal transition, nor on the glass transition and melting temperature. Whatever the draw ratio, fillers and their content, the glass temperature was always the same, close to 78 ± 2°C and the melting temperature is 256 ± 2°C. The fillers did not impact the thermal properties except DL which behaves as a nucleating agent.

3.3 Antibacterial properties

Antibacterial tests were run on knit fabrics with 2 wt.% of lignins, results were shown in **Figure 9**. Black lines show the antibacterial halos after removing textile. Bacterial growth was analyzed below the desizing knit fabric for avoiding the presence of impurities.

For PET knitting structures, the results were good, in contact with *E. coli* bacteria. DL appeared to have slightly better efficiency. Nevertheless, the results with *S. epidermidis* bacteria were quite similar. Both of them were efficient against Gram-positive bacteria. As seen in SEM and optical microscope images, the poor dispersion of KL causes agglomerates which are randomly along the filament. The contact between KL and the bacteria is different according to the area of the yarn in contact during the test, the antibacterial effect will be better where agglomerates are present and ineffectual when no KL. Whereas, the homogeneous dispersion of the DL with PET allow to guarantee an uniform antibacterial effect everywhere in the textile.

4. Conclusion

Antibacterial properties create added value for textiles to be durable and prevent bad odors. However, many antibacterial products are noxious for the environment. The aim of the study was to replace harmful biocide by eco-friendly and durable

agent. Melt spinning process was chosen because it restrict the diffusion of the antibacterial product in the environment. The filler selected was lignin, a biopolymer and two kinds of Kraft lignins were compared. The dispersion of fillers in the PET, the thermal and the mechanical properties and antibacterial activity were taken into account. First of all, the incorporation of both lignins in PET was a success for the development of multifilaments by melt spinning. As seen before, they have a significant impact on mechanical properties of the monofilaments with the incorporation of lignin into PET and we have observed a decrease of the tenacity. But these new mechanical properties do not have effect on the use of yarns in textile process. The poor dispersion of KL does not have a significant influence on the tenacity of the monofilament in comparison with DL. KL presents a low affinity with PET, remains on the surface and creates thickness defects. The dispersion of KL is not homogeneous within the filament and does not guarantee an antibacterial activity along the multifilament. However, DL has low interfacial energy with PET, which allows intimate mixing with the polymer. The thermal properties demonstrate DL as a nucleating agent because its crystallinity content and temperature increase, so DL intensifies the crystallinity of the PET. Finally, KL and DL have a positive activity against Gram-positive bacteria. Nevertheless, DL appears to have slightly better efficiency against Gram-negative bacteria despite its smaller specific surface area. Consequently, Domtar lignin seems to be a good candidate to replace silver nanoparticles. From this point on, testing the durability of anti-bacterial properties will be interesting to see the behavior of DL at weather conditions (temperature, humidity, UV) and by washing to equate to rain.

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