

Reinforcement of Thermoplastic Starch Films with Cellulose Fibres Obtained from Rice and Coffee Husks

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ABSTRACT: Cellulosic fibres from coffee (CF) and rice (RF) husks have been obtained applying chemical treatments and characterized as to their microstructure and thermal behaviour. These materials have been incorporated into glycerol plasticised thermoplastic starch (TPS) films obtained by melt blending and compression moulding at 1 wt%, 5 wt% and 10 wt%. Microstructure, thermal behaviour and optical, tensile and barrier properties of the composites were analysed. Both kinds of micro-fibres improve the film stiffness while reduced the film stretchability. However, CF better maintained the film ductility at 1 and 5 wt%. A network of fine oriented fibres was observed on the surface of the films, while internal fibres exhibited a good adherence to the polymer network. The water vapour permeability of TPS films was not reduced in composites, although oxygen permeability was lowered by about 17%. Film transparency decreased by fibre addition in the UV-VIS range. Thermal stability of composites was slightly higher than net TPS films.

KEYWORDS: Cellulose fibres, coffee husk, reinforcing properties, rice husk, starch composites.

1 INTRODUCTION

The increasing concern about the environmental preservation points to the replacement of most common non-biodegradable petroleum-derived plastics, causing high environmental problems, by more environmental-friendly materials which are biodegradable materials and, boarding a more sustainable approach, which are bio-based [1]. Food packaging involves a high consumption of plastics, which in many cases are non-recyclable due to the load of organic compounds. One of the most important groups of biodegradable and bio-based plastic materials is polysaccharides obtained from renewable resources. These biopolymers are directly extracted from biomass and, depending on their origin, different types of starch, cellulose, chitosan, gums or alginates can be found [2, 3].

Starch is the most widely studied thermoplastic sustainable biopolymer for food packaging applications because it is abundant, low cost and able for food contact purposes. It is composed of different ratios of amylose and amylopectin, depending on the plant source (cassava, corn, potato, rice, etc.). Native starch can be transformed in thermoplastic starch through the gelatinization process induced by temperature and plasticisers (mainly water or glycerol).

Thermoplastic starch exhibit very good filmogenic capacity, forming homogenous and transparent polymeric matrices with barrier properties to high oxygen, carbon dioxide or lipids [4] although they are water sensitive, present low barrier properties to water vapour and exhibits relatively poor and unstable mechanical resistance and extensibility; all of this due to its hydrophilic nature and to its natural tendency to retrogradation [5]. In order to enhance their limited properties as packaging materials, different strategies has been developed, such as the addition of plasticisers which reduce the intermolecular forces in the native starch increasing the flexibility or stretchability [6, 7], incorporation of cross-linking agents, such as citric acid [8], blending with other polymers [9], or incorporation of inorganic [10-12] and organic fillers [13-16]. Many studies analysed the behaviour of different organics fillers as reinforcing agents of TPS matrices. Micro- and nano-fillers derived from lignocellulosic wastes have been used in different studies to develop enhanced starch biocomposites, including eucalyptus wood pulp [17], sugarcane bagasse [18], wood [19], cotton, hemp or kenaf fibres [20]. In this sense, the use of agro-waste to obtain micro or nano-fillers able to reinforce packaging films represents a good alternative to, additionally, valorise the waste product.

Lignocellulosic residues are attractive materials because of their biodegradability, excellent mechanical properties, such as great stiffness and strength, and low density [21]. The manufacture of soluble coffee is the

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main industry of different countries like Brazil, Vietnam, Indonesia, Colombia, Ethiopia, India or Mexico [22] which generates a significant amount of waste that is usually burned causing great environmental contamination. Coffee husk (endocarp of coffee beans) is the residue obtained after de-hulling operation in coffee dry processing, being rich in cellulosic (~57%) and lignin (~22%) components [23]. Studies of the extraction and characterization of cellulosic materials from coffee husk have not been previously reported at the best of our knowledge. Sung et al. [24] studied the incorporation of other similar coffee agro-waste such as cellulose nanocrystals from coffee silverskin (tegument of green coffee beans liberated as the primary by-product during the coffee roasting process) into polyester matrix. On the other hand, rice husk is one of the main renewable by-products of rice milling operations with similar composition in lignocellulose content of coffee husk (~55% cellulose and ~35% lignin; [25]). The high cellulose content makes these residues interesting materials to obtain cellulosic materials for different uses. Johar et al. [26] applied the traditional alkali and bleaching treatments to obtain and characterise cellulose fibres from rice husk. But no previous studies were carried out for coffee husk. Cellulose fractions obtained from these kinds of biomasses can be transformed into micro-scale materials to be incorporated into starch matrices in order to improve their functional properties as packaging materials.

In this study, cellulose fibres from coffee and rice husks have been obtained by alkali and bleaching treatment and analysed as to their reinforcement properties into starch matrices. The changes induced in the film microstructure and tensile, barrier and optical properties of the films containing different ratios of microfibrils have been analysed, as well as their effect in the thermal stability of the composites.

2 MATERIALS AND METHODS

2.1 Materials

Rice husk was provided from Dacsa (Almàssera, Valencia, Spain) and coffee husk was obtained by Centro Surcolombiano de Investigaciones en Café de la Universidad Surcolombiana (Neiva, Colombia). Corn starch was purchased from Roquette (Roquette Laisa, Benifaió, Spain). Glycerol and sodium hydroxide, for alkali treatment, were obtained from Panreac Química, S.A. (Castellar del Vallès, Barcelona, Spain). Sodium chlorite and acetate buffer for bleaching treatment were provided by Sigma Aldrich Química S.L (Madrid, Spain). For conditioning samples, Phosphorus pentoxide (P_2O_5) and magnesium nitrate-6-hydrate ($Mg(NO_3)_2$) were obtained from Panreac Química, S.A. (Castellar del Vallès, Barcelona, Spain).

2.2 Extraction of Cellulose Fibres from Coffee and Rice Husks

The extraction process of cellulose fibres (CeF) from coffee and rice husk was carried out according to the method reported by Johar et al. [26] with some modifications. Rice or coffee husk, previously ground (mean particle size about 2-3 mm), were alkali treated to purify the fibres by removing hemicelluloses, pectin, waxes, part of lignin and other impurities. For this purpose, the samples were treated with 4 wt% of NaOH at 80°C for 3 h, at a 1:15 solid-liquid ratio, with mechanical stirring. Then, the solid was filtered and washed with distilled water several times, with the subsequent filtration, until the alkali solution (brown) was removed (colourless filtrate).

Bleaching process was performed to remove the lignin content. Equal parts of acetate buffer solution, sodium chlorite (1.7 wt%) and distilled water were mixed with the alkali treated solid (at 1:15 solid: Liquid ratio) and submitted to reflux temperature (about 100°C) for 4 h. This process was repeated as many times as necessary until the samples were completely white, as an indicator of the lignin removing. Then, the samples were filtered and washed with distilled water several times, with the subsequent filtration, until the solution was removed and dried in a desiccator containing P_2O_5 and grounded in a Moulinex grinder DJ200031 350W. The fibres were characterised as to their thermal properties (Thermogravimetric Analyzer TGA 1 Star^e System analyser, Mettler-Toledo, Inc., Switzerland) and microstructure (Scanning Electron Microscope, JEOL JSM-5410, Japan).

2.3 Preparation of TPS Composite Films

Cellulose fibres from coffee or rice husk, glycerol (as plasticiser) and native corn starch were dispersed in water and hand-blended till a homogenous blend was obtained. Starch:glycerol:water ratio (w/w) was 1:0.3:0.5, according to previous studies [6, 8] and fibres were incorporated at 1 wt%, 5 wt%, and 10 wt% respect the starch. Seven formulations were prepared identified as S (starch-glycerol), S-CF or S-RF (starch with fibres from coffee or rice husk) and 1, 5 or 10, referred to percentage of fibre contents. In Table 1 the mass fraction of each component in the dry blends and their identification codes are reported.

Each formulation was melt blended in a two-roll mill (Model LRM-M-100, Labtech Engineering, Thailand) at 160°C and 8 rpm for 30 min until a homogeneous paste sheet of TPS was obtained. The TPS sheets were cut as pellets and conditioned at 25°C and 53% relative humidity (RH) for one week before the film performance. The films were obtained by compression

moulding using a hot plate press (Model LP20, Labtech Engineering, Thailand). Four grams of the conditioned pellets were put onto Teflon sheets and preheated on the heating unit for 5 min. Films were obtained by compressing at 160°C for 2 min at 30 bars, followed by 6 min at 130 bars; thereafter a cooling cycle was applied for 3 min [6]. The obtained films were conditioned at 25°C and 53% RH for 1 week before their characterization.

Table 1 Mass fraction of the different components (Starch: S, Glycerol: Gly and Cellulose: C) in the TPS film (S) and composites with 1%, 5% or 10% of coffee fibres (CF) or rice fibres (RF).

Formulations	X _S	X _{Gly}	X _C
S	0.77	0.23	---
S-CF1	0.76	0.23	0.01
S-CF5	0.73	0.22	0.05
S-CF10	0.69	0.21	0.10
S-RF1	0.76	0.23	0.01
S-RF5	0.73	0.22	0.05
S-RF10	0.69	0.21	0.10

2.4 Characterization of Fibres and Composites

2.4.1 Optical Properties

The internal transmittance of the films was determined through their transmittance in the UV-VIS range using a UV-VIS spectrophotometer (Perkin Elmer Instruments, Lambda 35, Waltham, USA), within 300-950 nm wavelength range. The film gloss was determined at an incidence angle of 60°, according to the ASTM standard D523 method [27] using a flat surface gloss meter (Multi.Gloss 268, Minolta, Germany). All results are expressed as gloss units (GU), relative to a highly polished surface of black glass standard with a value near to 100 GU.

2.4.2 Microstructure Analysis

Light microscopy (Optika Microscopes B-350 connected to an Optikam B2 camera, Italy) was used to measure the length range of the cellulose fibres. A drop (20 microliter) of the 1.5% solid dispersions was spread over the slide and observed at 10X magnification level. Fibre length range was estimated by measuring more than 100 fibres elements in at least 10 different microscopic observations for each sample (Optika Vison Lite 2.1). A Scanning Electron Microscope (JEOL JSM-5410, Japan) was used to analyse the microstructure of cellulose fibres, previously conditioned in P₂O₅ for 2 weeks at 25°C. Samples were gold coated and

observed, using an accelerating voltage of 15 kV. Field Emission Scanning Electron Microscopy (FESEM Ultra 55, Zeiss, Oxford Instruments, UK) was used to analyse the surface and cross-sections microstructure of the films, previously conditioned at the same condition as fibres. Film samples were adequately mounted on support stubs and platinum coated. Observations were carried out at 1.5 kV.

2.4.3 Film Thickness and Equilibrium Moisture Content

The film thickness of conditioned films was measured using a Palmer digital micrometer at six random positions around the film. The water content of conditioned film at 53% RH and 25°C was determined, in triplicate, gravimetrically, by drying for 24 h at 60°C using a convection oven (J.P. Selecta, S.A. Barcelona, Spain) and subsequent conditioning in a desiccator at 25°C with P₂O₅ (a_w=0) for 2 weeks.

2.4.4 Water Vapour Permeability and Oxygen Permeability

The ASTM E96-9532 [28] gravimetric method was used to determine the Water Vapour Permeability (WVP) of the films, considering the modification proposed by McHugh et al. [29]. Distilled water was placed in Payne permeability cups (3.5 cm diameter, Elcometer SPRL, Hermelle/s Argenteau, Belgium) to expose the film to 100% RH on one side. Each cup was placed in a cabinet equilibrated at 25°C and 53% RH, with a fan placed on the top of the cup in order to reduce the resistance to water vapour transport, thus avoiding the stagnant layer effect in this exposed side of the film. The relative humidity of the cabinet (53%) was held constant using Mg(NO₃)₂ oversaturated solutions. The cups were weighed periodically (0.0001 g) and the water vapour transmission rate (WVTR) was determined from the slope obtained from the regression analysis of weight loss data versus time. From this data, WVP was obtained according to Ortega-Toro et al. [6,8].

The oxygen permeability (OP) was determined using an OX-TRAN Model 2/21 ML (Mocon Lippke, Neuwied, Germany), in samples conditioned at 53% RH and 25°C. The oxygen transmission values were determined every 20 min until equilibrium was reached. The film area used in the tests was 50 cm². From these values OP was obtained, considering the measured film thickness. All barrier properties were determined in triplicate for each film sample.

2.4.5 Tensile Properties

A universal test machine (TA.XTplus model, Stable Micro Systems, Haslemere, England) was used to determine the tensile properties of films. The tensile strength (TS), the elastic modulus (EM), and the

elongation at break (E) of the films were determined from the stress-strain curves, estimated from force-distance data obtained for different films (2.5 cm width; 10 cm length), according to the ASTM standard method D882 [30]. Equilibrated samples were mounted in the film-extension grips (with 5 cm of separation) of the testing machine and stretched at 50 mm/min until breaking. Tests were carried out at 25°C and 53% RH. Ten replicates were performed for each film formulation. The measures were carried out at initial time (1 week conditioned films) and final time (28 weeks conditioned films).

2.4.6 Thermal Analysis

The thermal stability of the different samples (fibres and films) was analysed using a Thermogravimetric Analyzer TGA 1 Star^e System analyser (Mettler-Toledo, Inc., Switzerland) under nitrogen atmosphere (gas flow: 10 mL min⁻¹). Samples (about 4-5 mg) were heated from 25°C to 600°C at 20°C/min. At least two replicates for each sample were obtained. Initial degradation temperature (T_{Onset}) and peak temperature (T_{Peak}) corresponding to the maximum degradation rate, were obtained from the first derivative of the resulting weight loss curves using the STAR^e Evaluation Software (Mettler-Toledo, Inc., Switzerland).

2.4.7 Statistical Analysis

Statgraphics Plus for Windows 5.1 (Manugistics Corp., Rockville, MD) was used for carrying out statistical analyses of data through analysis of variance (ANOVA). Fisher's least significant difference (LSD) was used at the 95% confidence level.

3 RESULTS

3.1 Microstructure and Thermal Behaviour of Cellulose Fibres

Figure 1 shows the appearance of both cellulose fibres after the chemical treatments. The sample colour drastically changed from brownish in raw material to the characteristic whiteness of cellulose (Figure 1a) thus indicating the high removing degree of lignin compounds [26]. The particle size of the ground raw materials (2-3 mm) was highly reduced, as observed in the light microscopy images Figure 1b. The estimated fibre length from the image analyses ranged between 70-570 μm for coffee husk and 60-490 μm for rice husk. Particle size reduction provoked by bleaching treatment was similar for both samples where the effective attacks of the chemical agents disrupted the internal structure of the material, removing the non-cellulosic components. Bleaching treatment with the sodium chlorite solution, which becomes chlorine dioxide in acetate buffer solution,

provokes the oxidation of the lignin aromatic ring [31, 1], releasing purified cellulose materials. SEM images (Figure 1c) revealed the different shape of both fibres; coffee fibres were flatter and helically folded, whereas rice fibres were more cylindrical with less than 10 μm in diameter as previously reported by Johar et al. [26]. The obtained cellulose fibres showed a good aspect ratio (relationship between the length and the diameter). The length range was 60-570 μm with very small diameters, as can be observed in Figures 1a and 1b. This provides adequate properties as reinforcing materials for composite applications [1].

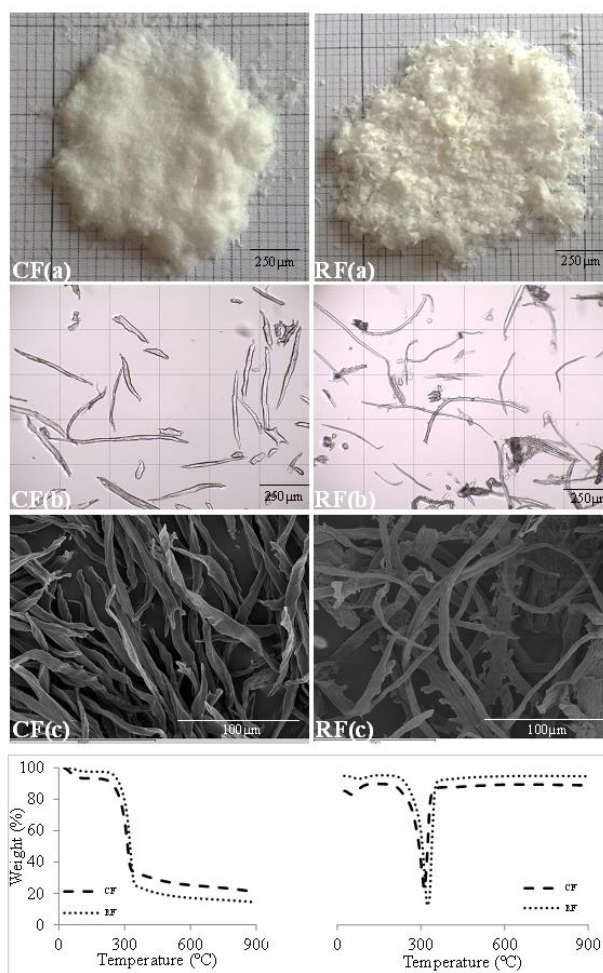


Figure 1 (a) Appearance of coffee (CF) and rice (RF) fibres after bleaching treatment, (b) light micrographs of fibre water dispersions (grid: 250 μm) (c). SEM micrographs of isolated fibres and (d) TGA and DTGA curves of the fibres.

Thermal analysis of cellulose fibres (Figure 1d) shows the characteristic peaks for these materials. A small weight loss was observed in all cases in the range of 100°C, attributable to the evaporation of bonded water in the films. The temperatures of the

onset and main peak, around 270°C and 300°C, respectively, are typical of cellulose decomposition, as reported by several authors for cellulosic materials such as cotton ($T_{\text{peak}} 349^\circ\text{C}$ [32]), bleached garlic straw ($T_{\text{peak}} \sim 290^\circ\text{C}$ [33]), cellulose recycled office paper ($T_{\text{peak}} 361^\circ\text{C}$ [34]) or bleached rice husk ($T_{\text{peak}} \sim 305^\circ\text{C}$ [26]). Mensaray and Ghaly [35] reported that lignocellulosic materials decompose in the temperature range of 150-500°C; depending on the initial raw material. Very similar behaviour was observed for both kinds of fibres, although a higher residual mass was noted for the coffee material, thus indicating a greater content of ashes or thermostable degradation products. Nevertheless, the observed thermal stability of these materials allows for their effective use for obtaining composite polymer films applying the usual thermoprocessing (extrusion, melt blending and injection moulding) of the plastics industries.

3.2 Properties of Composite Films

3.2.1 Optical Properties

Figure 2 shows the internal transmittance (T_i) of the films in the wavelength range of 300-950 nm as an indicator of the film transparency to both near UV and VIS radiation. Gloss values are also indicated in Figure 2 for each film sample. The low transparency of the starch and composite films in the low wavelength range is remarkable, as observed by other authors [7, 36]. This aspect can be considered positive since this implies potential protection ability in food applications, to reduce UV-induced oxidation reactions [13]. Incorporation of fibres reduced the films transparency in the whole wavelength range, according to the introduction of a dispersed phase in the polymer matrix with the subsequent anisotropy in the refractive index and light dispersion effects. The higher fibre ratio, the greater the film opacity. This effect was also remarkable in the UV region, reinforcing for the mentioned protective function. At low fibre ratio (1 wt%) the transparency reduction of coffee fibres was significantly lower than that promoted by rice fibres, which could be related with the different particle size or aggregation or orientation in the films. At higher ratios, the differences were mitigated probably due to the fact that from a determined concentration of dispersed phase, the high light interferences masked the possible structural differences between the composites with the different fibres, which would affect the light dispersion behaviour.

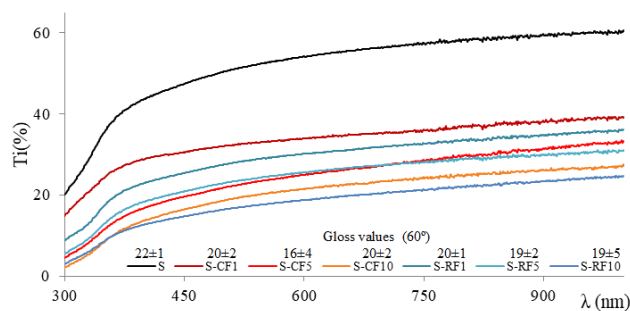


Figure 2 UV-VIS Transmittance spectra of the corn starch films containing different ratios of cellulose fibres from coffee (CF) or rice (RF) husks. Gloss values are also indicated for each sample.

The gloss of the films is mainly associated to their surface roughness, which can be also affected by the film processing method [8]. Figure 2 shows the obtained values for the different films. In general, the composite films exhibited low gloss compared with neat starch films. Their values ranged between 16-20 GU for coffee fibres and 19-20 GU for rice fibres, with high variability, and without clear tendencies as a function of filler content. The addition of fillers induced irregularities at the films surface where fibre fragments will be present, which contributes to light dispersion, giving a matt appearance to the composites, as previously observed by other authors when micro- and nano-fillers were incorporated into the polymer matrices [15, 37, 20, 38].

3.2.2 Tensile Properties

Reinforcing materials, such as cellulosic fibres can contribute to improve mechanical properties of starch films which possess poor mechanical properties not enough adequate for food handling [39]. Figure 3 shows the typical tensile curves of corn starch films containing different ratios of the isolated cellulosic fillers from coffee or rice husks, in comparison to the film control sample (S), every one conditioned at 53% RH and 25°C for 1 week. A clear tendency of increasing stiffness of the samples was observed for all of the composites with increasing the fibre content, such as also observed Kargarzadeh et al. [40]. On the other hand, fibre inclusion provoked a marked decrease in the film extensibility, except in composites with 1 wt% of coffee fibres, which did not significantly affect the stretching capacity and resistance to break of the TPS films. Composites with 10 wt% of both fillers and 5 wt% of rice fibres were considerably less extensible than TPS films. Table 2 shows the tensile parameters (Elastic modulus: EM, tensile strength: TS and percentage deformation $E\%$ at break), for both 1week conditioned films and 28 weeks stored films under the same ambient conditions,

to also observe the effect of fillers on the starch ageing in the films. The obtained EM values reflect the above commented reinforcing effect of both cellulosic fillers, since a considerable increase in EM was observed when the filler content rose. Composites with only 1 wt% of filler improved the elastic modulus of films in about 60% regardless of the fibre source, whereas more than 100% and 200% increase was observed for 5 wt% and 10 wt% of fibre content, respectively. The increase in the film stiffness was higher than that observed by Kargarzadeh et al. [40], for cassava starch matrix incorporated with 10 wt% of rice husk cellulose (only 55%). Taking into account the variability in the values, no significant differences in the EM enhancement were detected for both kinds of fibres. This high improvement in EM could be due to the purity degree of cellulose in the obtained fibres (62% and 74% respectively for coffee and rice fibres, quantified in a previous study), also implying a higher crystallinity degree of the material, which enhanced interaction between the fibres and starch, in line with the chemical affinity between cellulose and starch domains in the film structure [31], avoiding the weakening effect of other components of the lignocellulosic fraction in the starch matrix.

In contrast, notable differences were observed in the film extensibility reduction for both fibres. At 1 wt%, coffee fibres did not significantly reduce the stretching capacity of TPS film, whereas rice fibres provoked a 40% reduction. At 5 wt%, about 40 and 75% extensibility reduction were respectively produced by coffee and rice fibres, while 75% was observed with 10 wt% of both fillers. These results suggest a better performance of coffee fibres in the corn TPS films in terms of reinforcement effect, since films become harder with lower increase in brittleness.

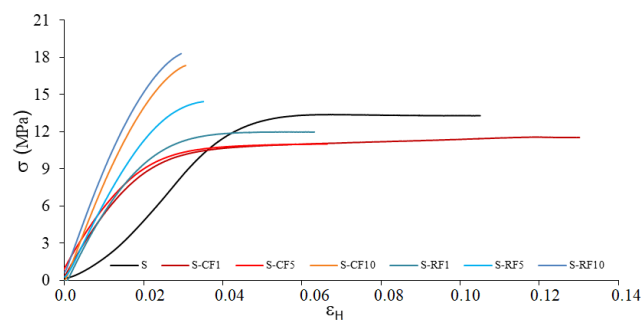


Figure 3 Typical stress-Hencky strain curves for starch films with 1 wt%, 5 wt% and 10 wt% of cellulose fibres from coffee (CF) and rice (RF) husk.

As concerns the development of the mechanical behaviour of the films after 28 weeks storage time, a

sharp decrease in the elastic modulus was observed for all formulations (40-55% depending on the film sample), but in composites with 5 wt% and 10 wt% of filler, still remained higher than in TPS films conditioned for 1 week. Comparison of EM values of composites with that of TPS films in stored samples revealed similar improvement percentages to those non stored films. As concerns elongation at break all films became much more extensible after storage, this effect being more marked when the fibre content increase. As compared with the stored TPS films, the brittleness effect induced by fibres, observed in one week conditioned samples, especially at higher fibre concentration, was notably mitigated and, even in for composites with 1 and 5 wt% coffee fibres and 1 wt% of rice fibres there were not significant differences in the film elongation at break respect TPS film. These changes in tensile behaviour of the films during the relatively long storage time could be attributed to a progressive water sorption in the films in the relatively wet storage ambient (53% RH), which could cause the polymer-glycerol-fibres rearrangement in the matrix, leading to a higher ductility, or even to a partial degradation of the starch matrix under these conditions. Nevertheless, even taking these changes into account, reinforcing materials exerted beneficial effects at maintaining mechanical resistance of the films.

3.2.3 Barrier Properties

Table 3 shows the moisture content and barrier properties of the conditioned films. The moisture content did not show significant differences among film formulations with different content or type of fillers. This agrees with the similar hygroscopic nature of starch and cellulose, which led to similar water sorption capacity in the composites, as compared with TPS films. Likewise, WVP of the TPS films was not affected by the fibre incorporation (different type or content) (Table 3). Although an increase in the tortuosity factor in the matrix could be expected by fibre dispersion, the high water affinity of cellulose did not imply a limitation for the transport of water molecules in composites. However, Wattanakornsiri et al. [34] found a 63% reduction in WVP of cassava starch films incorporating 8 wt% of cellulose fibres from recycled paper. Differences in the amylose: Amylopectin ratio (which is higher in corn starch) could play a key role in the composite nanostructure, provoking a different effect of fillers on the WVP of the films.

Table 2: Mean values and standard deviation of tensile properties of TPS and composite films conditioned (1 week) and stored (28 weeks), at 53% RH and 25°C. (Elastic modulus: EM; Tensile strength: TS; Percentage deformation E% at break).

Formulation	EM (MPa)	TS (MPa)	E (%)	EM (MPa)	TS (MPa)	E (%)	Thickness (mm)
	Initial time (1week)			Final time (28 weeks)			
S	260±80 ^a	13.0±1.5 ^b	12±7 ^b	126±4 ^a	7.0±2.0 ^a	22± 12 ^b	0.22±0.02 ^{ab}
S-CF1	399±106 ^b	9.0±2.0 ^a	13±4 ^b	181±74 ^a	8.3±2.1 ^{ab}	18 ± 4 ^b	0.21±0.01 ^a
S-CF5	563±75 ^c	12.2±1.4 ^{ab}	7±3 ^a	330±20 ^{bc}	9.8±1.0 ^b	23 ± 1 ^b	0.26±0.01 ^c
S-CF10	822±38 ^d	19.0±1.0 ^c	3±1 ^a	401±35 ^c	8.7±0.7 ^{ab}	14 ± 1 ^a	0.22±0.01 ^{ab}
S-RF1	430±70 ^b	11.3±1.8 ^{ab}	7±1 ^a	268±34 ^b	7.4±0.9 ^a	33 ± 3 ^b	0.23±0.01 ^b
S-RF5	671±105 ^c	16.5±2.7 ^c	4±1 ^a	339±31 ^{bc}	7.9±2.7 ^{ab}	14 ± 2 ^a	0.21±0.01 ^a
S-RF10	863±2 ^d	17.0±3.0 ^c	3±1 ^a	387±60 ^c	8.1±0.6 ^{ab}	16 ± 5 ^a	0.24±0.02 ^b

Different superscript letters within the same column indicate significant differences among formulations ($p < 0.05$).

Table 3: Mean values and standard deviation of moisture content, water vapor permeability (WVP) and oxygen permeability (OP) of TPS and composite films conditioned at 53% RH and 25°C.

Formulation	Moisture content (g water/g dried film)	WVP (g·mm·kPa ⁻¹ ·h ⁻¹ ·m ⁻²)	OP x10 ¹⁴ (cm ³ ·m ⁻¹ ·s ⁻¹ ·Pa ⁻¹)
S	0.093±0.002 ^a	11.1±0.4 ^{ab}	4.8±0.7 ^b
S-CF1	0.086±0.004 ^a	12.5±1.7 ^b	4.9±0.1 ^b
S-CF5	0.094±0.016 ^a	12.7±1.3 ^b	4.8±0.2 ^b
S-CF10	0.082±0.003 ^a	10.7±1.0 ^a	3.9±0.2 ^a
S-RF1	0.087±0.003 ^a	10.4±0.5 ^a	4.0±0.2 ^a
S-RF5	0.093±0.020 ^a	11.5±1.1 ^{ab}	4.3±0.4 ^{ab}
S-RF10	0.086±0.004 ^a	10.6±0.2 ^a	4.3±0.5 ^{ab}

Different superscript letters within the same column indicate significant differences among formulations ($p < 0.05$).

Table 3 also shows the values of oxygen permeability of the different composites and TPS film. The presence of cellulose fibres in starch matrices slightly improved the oxygen barrier (about 17% reduction in OP) especially for rice fibres at any ratio and coffee fibres at the highest ratio. The formation of a more tortuous pathway for transport of the oxygen molecules explains the OP reduction in the starch matrix already in itself with great resistance to oxygen transport [39]. Similar results were obtained by López et al. [41] in starch films containing inorganic filler (talc). The improvement of barrier properties by fillers depends on many factors such as the structure of the matrix, crystallinity, polarity and type of reinforcement agent [39].

3.3 Microstructure of the Composites

The interaction and dispersion degree of the fibres into starch matrix was studied by FESEM analysis. Figures 4 and 5 show the surface and cross-section of TPS films and composites. In contrast with the smooth surface of TPS film a rougher surface can be appreciated in composites, evidencing the fibre presence at surface level. Individualised fibres uncoated or infiltrated in the starch matrix can be observed in all composites, resulting in surface irregularities, which explain the lower observed gloss of composites, compared to TPS films. Kargarzadeh et al. [40] also studied the incorporation of multiscale rice husk into cassava starch and observed that the reduction in particle size of the fibres after alkali and bleaching treatments allowed starchy materials to infiltrate inside the fibre bundles.

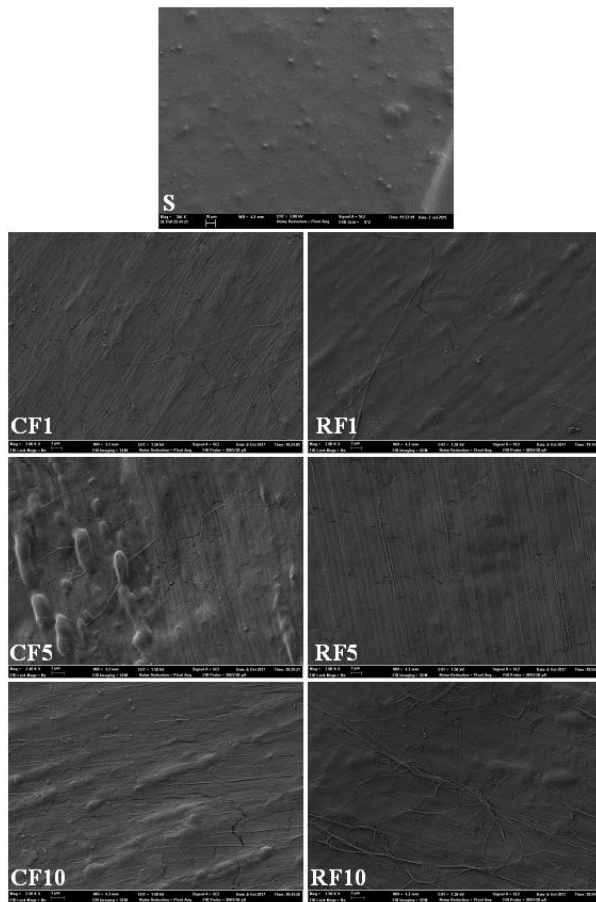


Figure 4 FESEM micrographs of the surface of TPS and composite films with different ratios of cellulose fibres.

A similar fibre distribution at surface level was observed for all composites, regardless the fibre ratio, whereas the internal fibre dispersion clearly reflected the different amount incorporated in the films, which exhibited a different fibre density as a function of total concentration (Figure 5).

This fact indicates the particular tendency of fibres to adsorb at the film surface, especially the finest ones, reaching an oriented distribution (quasi-parallel) on the film surface. This fibre arrangement explains the increase in the film stiffness, in line with the formation of an oriented fibrous tissue with offers greater resistance to deformation, even at low fibre ratio. The addition of higher amount of fibres will also lead to a weakening effect in the starch matrix due to the interruption of the polymer network. Figure 6 shows the FESEM images at higher magnification, where the above commented arrangement are more clearly observed. It is remarkable that in the fractured cross-section of the films the fibre bundles break practically

at the same level than then the polymer matrix, which suggests high interaction forces between fibres and polymeric matrix. The elimination of more hydrophobic compounds (hemicelluloses and lignin) provided a notable adhesion capacity to the fibre with starch chains, as be observed in the micrographs. Similar results were obtained by Zainudin et al. [31] using of multiscale kenaf fibres as reinforcing filler in cassava starch matrices. Likewise, the fibre di-stribution observed in the film cross-section is quite homogeneous, mainly exhibiting the bundle arrangement, in contrast with the more individualized form present at the film surface. A similar behaviour was observed by Chen et al. [36] with the incorporation of pea hull micro-fibres into pea starch; some cracks, holes and fibres aggregates appeared in the cross-sections of films.

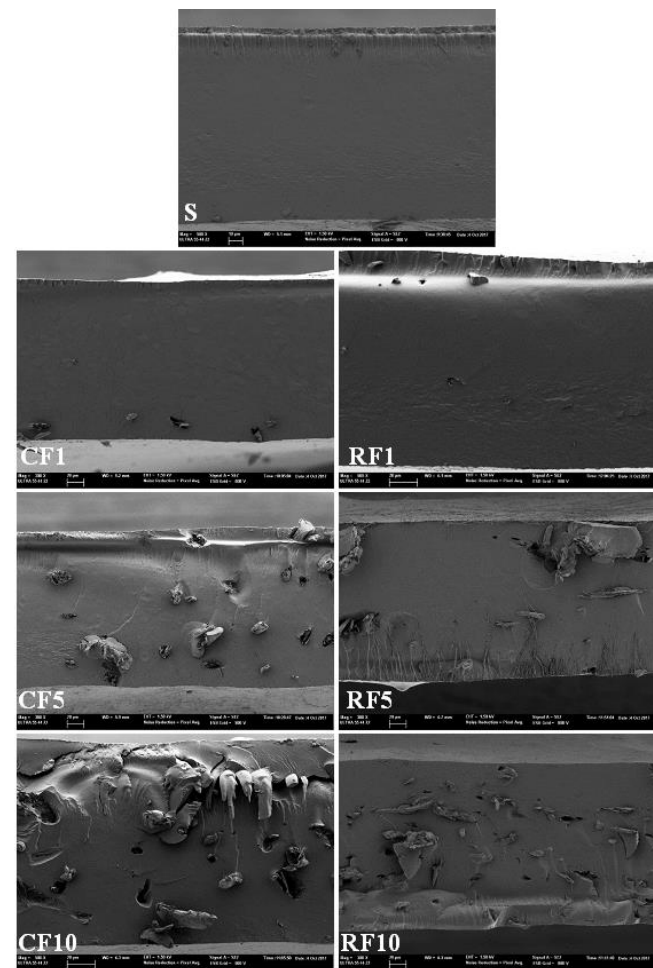


Figure 5 FESEM micrographs of the cross-section of TPS and composite films with different ratios of cellulose fibres.

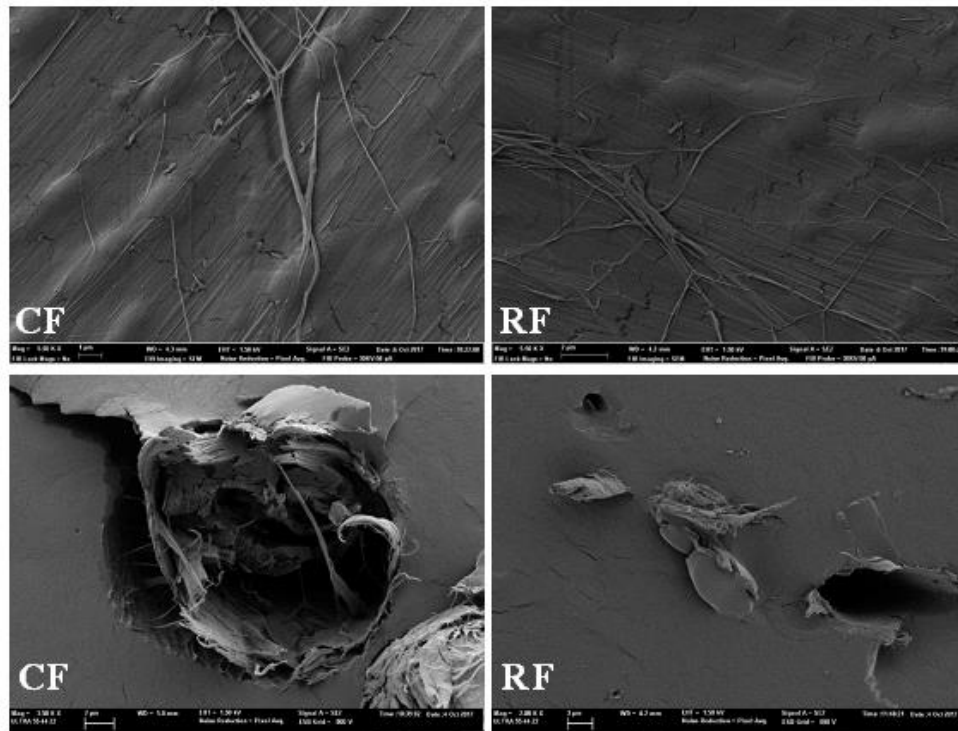


Figure 6 FESEM micrographs at higher magnification of fibres into the starch matrices, on the surface (top) and inside the film (bottom).

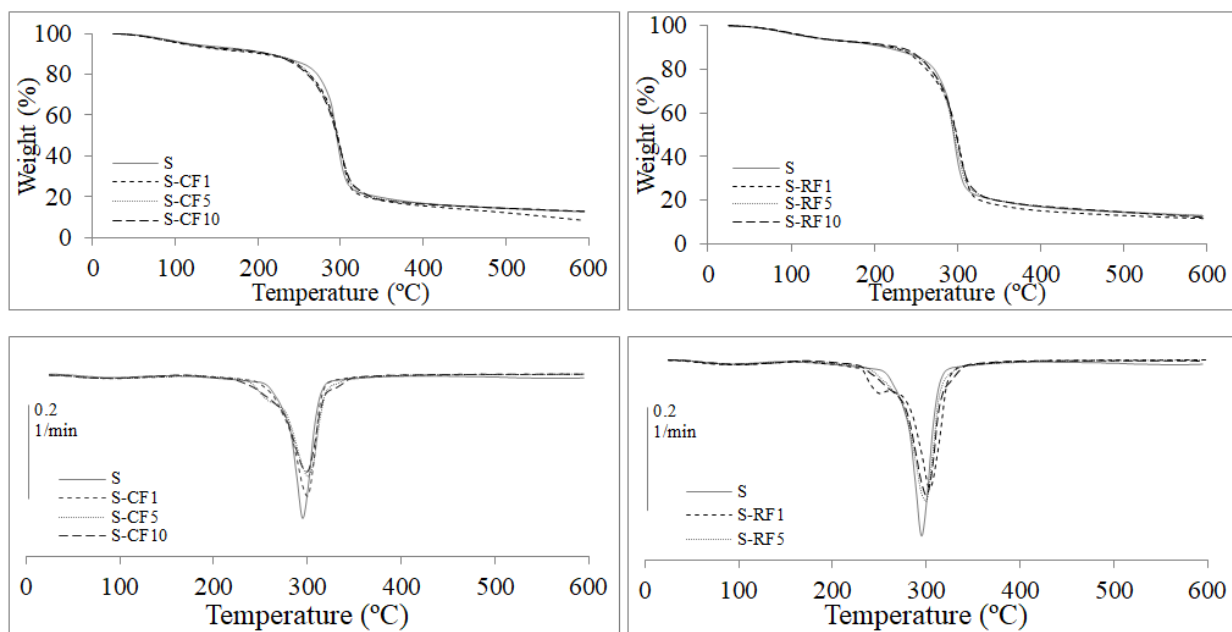


Figure 7 TGA and DTG curves of TPS films with different contents of coffee (CF) and rice (RF) fibres.

Table 4 Mean values and standard deviation of onset and peak temperatures for thermal degradation of TPS and composite films conditioned at 53% RH and 25°C.

Samples	[41-104]°C		[265-305]°C	
	Onset (°C)	Peak (°C)	Onset (°C)	Peak (°C)
S	46.3±2.1 ^{cd}	94.8±0.2 ^a	280±1 ^d	295.0±0.5 ^a
S-CF1	45.6±1.8 ^{cd}	94.8±0.2 ^a	271.5±0.2 ^b	300.3±0.5 ^b
S-CF5	41.8±0.7 ^a	95.0±0.1 ^a	270±3 ^{ab}	300±2 ^b
S-CF10	48.7±1.4 ^d	95.0±0.2 ^a	265.5±0.2 ^a	299±2 ^b
S-RF1	45.9±0.3 ^{cd}	96.8±0.2 ^a	276.5±1.4 ^{cd}	305±1 ^c
S-RF5	45.1±0.7 ^b	95.0±0.1 ^a	274±4 ^{bc}	299±0.4 ^b
S-RF10	48.0±1.4 ^{cd}	104.8±0.2 ^b	272±1 ^b	300±1 ^b

Different superscript letters within the same column indicate significant differences among formulations ($p < 0.05$).

3.4 Thermal Behaviour

The thermogravimetric analysis (TGA) was carried out to investigate the influence of fibres on thermal stability of the starch matrix. Figure 7 shows the TGA and DTG curves of starch films with 0 wt%, 1, 5 wt% and 10 wt% of cellulose fibres from coffee or rice husk. DTG curves shows the different peaks related to weight losses caused by thermal degradation. All samples exhibit a weight loss between 95-104°C, which corresponds to the loss of bonded water in the materials. The main peak is associated with the thermal degradation of the cellulosic compounds and starch matrix. Table 4 summarises thermal degradation temperatures, T_{onset} and T_{peak} , for TPS and composite films. Corn starch film exhibited the peak degradation around 295°C, in the range reported by Zainudin et al. [31] for degradation of cassava starch (275°C), associated with the scission of the main chains (1,4- β -D-glucopyranose). The thermal stability of starch matrices increased between 1% and 3% with the incorporation of the cellulosic fillers, especially with 1 wt% of rice husk cellulose fibres. Composites showed a degradation temperature range between 299-304°C without notable differences among them, in contrast with the lower interval (280-295°C) of TPS. Similar observations were described by Kargarzadeh et al. [40] when 6% of bleached rice husk fibres were incorporated into cassava starch. Niranjana Prabhu and Prashantha [39] reviewed the properties of TPS composites for food packaging applications, and also reported a greater thermal resistance of composites containing different lignocellulose fibres.

4 CONCLUSIONS

Coffee and rice husk cellulosic fibres provoked a relevant reinforcing effect on glycerol plasticised TPS

films, this being higher (more than 200%) when the fibre content increased till 10 wt%, while reduced the film stretchability. However, CF better maintained the film ductility than RF at 1 wt% and 5 wt%. This reinforcing effect was maintained during film storage (28 weeks). A network of fine oriented fibres was observed in the surface of the films, which could contribute greatly to the increase in the resistance to deformation of the films. The fibres distributed in the internal part of the matrix exhibited a good adherence to the polymer network as revealed by the FESEM analysis of the film cross-section. WVP of TPS films was not reduced in composites, although oxygen permeability was lowered by about 17%. Film transparency decreased by fibre addition in the UV-VIS range, which could be interesting to preserve foods from light-induced oxidation reactions. Thermal stability of composites was slightly higher than net TPS films. These results indicate the excellent capacity of fibres from coffee and rice husks to improve functional properties of TPS films while representing a good alternative to give added value to these agricultural wastes.

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