Synthesis and Characterization of Maleic Anhydride-grafted Orange Waste for Potential Use in Biocomposites

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The purpose of the study was to develop a less hydrophilic, and therefore more useful, material from orange waste produced in large quantities by the food industry. A new derivative of industrial orange waste was synthesized *via* esterification with maleic anhydride. The reaction was confirmed *via* Fourier transform infrared spectroscopy (FTIR), and the degree of substitution of the hydroxyl groups was 0.39 ± 0.01, as determined by a back-titration method. A major change in physical structure was confirmed by scanning electron microscopy (SEM). The flake-like structure of orange waste changed to a sponge-like structure after the reaction, which involved an increased volume and a reduced density by approximately 40%. The sponge-like structure was represented as an agglomeration of particles with a low specific surface area of 2.18 m^2/g and a mean pore diameter of 10.7 nm. Interestingly, the grafted orange waste seemed to become more hydrophobic, which was confirmed by a contact angle test; however, the material absorbed more water vapor. Thermogravimetric analysis (TGA) confirmed a thermally more uniform, though, less heat-resistant material. This work suggests a possible way of utilizing orange waste *via* synthesizing a renewable material with possible applications as a filler in biocomposites.

Keywords: Biopolymers; Esterification; Grafting; Maleic anhydride; Orange waste; Pectin

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INTRODUCTION

In a zero-waste approach, the valorization of the abundantly available lignocellulosic materials has been gaining elevated attention for the production of a wide range of applications (Arevalo-Gallegos *et al.* 2017; Bilal *et al*. 2017; Iqbal *et al*. 2017). Such products include bio-chemicals, bio-fuels, animal feed, enzymes, and biocomposites (Asgher *et al*. 2017; Ahmad *et al.* 2017). The use of natural fibres and biopolymers has been of great research interest for the production of biocomposites and bioplastics. While commodity plastics are hydrophobic substances, most of the natural fibres bear hydrophilic properties. Biopolymers are also hygroscopic substances, and when used they result in thermoplastics sensitive to water (Zuo *et al.* 2013). In general, these hydrophilic plastics have low mechanical properties, and blending is necessary with water-resistant polymers to obtain good mechanical properties (Zuo *et al.* 2013). In polymeric blends and composites, interfacial adhesion between the components plays a crucial role in achieving adequate physico-mechanical features (Zhang and Sun 2004; Zuo *et al.* 2013; Yu *et al.* 2014). Establishing the necessary adhesion between the hydrophilic biopolymers or natural fibres and the hydrophobic commodity plastics is a major challenge. In such cases when interfacial tension is low, compatibilizers are often used to enhance the interfacial adhesion of the often immiscible substances to overcome the weaknesses (Khalid *et al.* 2008; Arias *et al.* 2013).

Maleic anhydride has been used as a compatibilizer to modify polysaccharides (Zhang and Sun 2004; Zuo *et al.* 2013; Yu *et al.* 2014). In one study, the less polar poly-lactic acid was grafted with maleic anhydride in order to make it compatible with the polar ramie fibres (Yu *et al.* 2014). In another study, corn starch was esterified with maleic anhydride to replace the hydrophilic hydroxyl groups with hydrophobic ester groups (Samain *et al.* 2011) for developing some hydrophobic characteristics in the starch (Zuo *et al.* 2013). The modification of biopolymers with maleic anhydride also enables chemical cross-linking between polymer chains through vinyl sites (Almeida *et al.* 2015). Maleic anhydride is an industrially available and bio-based material that is also used in the cosmetic and food industry (Fischer Scientific 2018; PubChem 2018). Therefore, it is a safe material for the fabrication of environmentally friendly biomaterials.

An example for a lignocellulosic raw material for the fabrication of biomaterials is orange waste. The global orange production in 2017/18 was forecast to tumble to 49.3 million tons from the previous year (USDA 2018) and *e.g.* juice production produces at least 50% waste of the initial mass. Orange waste is a by-product with low use; however, it contains interesting biopolymers, such as pectin, cellulose, and hemicellulose. Therefore it can potentially be used for producing bio-based materials in the bioplastic industry (Rezzadori *et al.* 2012; Lopez-Velazquez *et al.* 2013). A drawback of orange waste is the hygroscopic nature of pectin and cellulose, which makes it difficult to blend with any other hydrophobic polymer, whether natural or synthetic.

The goal of this study was to reduce the hydrophilicity of orange waste by grafting with maleic anhydride, thereby making it suitable for applications, *e.g.*, in biocomposites and polymer blends. By grafting of maleic anhydride into the orange waste structure, several major chemical and physical changes occurred. The results were analysed by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC), and tests were performed to examine the density, water affinity, specific surface area, degree of substitution, and contact angle.

The prepared maleic anhydride-grafted orange (OW-MA) could potentially be used as a filler for a biopolymer such as polylactic acid (PLA). PLA is still an expensive polymer and, since orange waste is cheap, renewable and available in huge quantities, adding it to a biopolymer would reduce the cost. Furthermore, for many biopolymers, there is still a need to improve the technical properties. The addition of a filler could modify some of the technical properties. As an example, PLA has been reinforced with various renewable materials such as wood flour (Zhang *et al.* 2018). The feasibility of OW-MA as a filler merits future study.

EXPERIMENTAL

Materials

Orange waste (OW), consisting of peels, pulp, and seeds was obtained from Brämhults Juice AB (Borås, Sweden). According to a previous analysis (Bátori *et al.* 2017), OW contained 29.84 ± 0.29% pectin, 18.66 ± 0.48 cellulose, and 20.89 ± 0.89% hemicelluloses. Until further use, the OW was stored at -20 °C. Maleic anhydride (MA) (≥ 99%, Sigma-Aldrich, St. Louis, USA), dimethyl sulfoxide (DMSO) (≥ 99.5%, Sigma-Aldrich, St. Louis, USA), pectin (from citrus peel – galacturonic acid content ≥ 74.0% (dried basis), and methoxyl groups ≥ 6.7% (dried basis), Sigma Aldrich, St. Louis, USA) used in the experimental process were all of analytical grade.

Pretreatment of Orange Waste for Esterification

Soluble sugars in the OW were removed prior to use by dissolution in water, where the ratio of OW to water was 1:1.5 (kg/L) in all washing steps. First, the OW was soaked in tap water overnight at room temperature. Two further washing steps were conducted at 35 ° C for

20 min. The OW was collected using a metal sieve and rinsed under tap water after each washing step. The OW was cut to small pieces with a knife and further dried at 40 °C for 16 h according to a previous study (Bátori *et al.* 2017). The dried OW was milled to a fine powder using a variable speed rotor mill (Pulverisette 14, Fritsch, Idar-Oberstein, Germany) with a sequence of sieve sizes of 1 and 0.2 at 10,000 rpm, for a maximum of 1 min each.

Synthesis of Maleic Anhydride-grafted Orange Waste

Orange waste and maleic anhydride were pre-dried in a vacuum oven (Vacucell, Buch & Holm, Herlev, Denmark) (at less than 0.05 bars) at 40 °C for 12 h prior to use. The synthesis was performed as described by Almeida *et al*. (2015), with two major differences. N,N-dimethylformamide (DMF) was replaced with dimethyl sulfoxide (DMSO), a safer and less toxic solvent, and the dialysis step was not performed. Briefly, the dried OW (1 g) and MA (3 g) were dissolved in 10 mL and 15 mL of DMSO solvent, respectively, and continuously stirred at room temperature for 12 h. The MA-solution was added to the OW-solution dropwise under continuous stirring at room temperature. The mixture was maintained for 24 h at 70 °C. The grafted OW was then precipitated in acetone (200 mL) under continuous stirring and separated by vacuum filtration. Instead of the dialysis step, the filtered maleic anhydride-grafted orange waste (OW-MA) was washed with acetone three times, after filtration. The material was vacuum-dried at 20 °C under 0.5 bars pressure for 12 h. The pressure was then reduced to less than 0.05 bars and drying was continued for 24 h. The same reaction was also performed on pure pectin (PEC), as a reference material, and some comparative analyses were carried out on maleic anhydride-grafted pectin (PEC-MA).

Characterization of Maleic Anhydride-grafted Orange Waste

Determination of degree of substitution of hydroxyl groups

The degree of substitution (DS) was determined by titration according to Zou *et al.* (2013), with slight modifications. 0.5 g of dried OW-MA was weighed accurately and placed in a 100-mL bottle. Then, 10 mL of 75% ethanol solution and 10 mL of 0.5 M $NaOH_{(aq)}$ solution were added. The closed bottle then was stirred and kept at 30 °C for 30 min. The excess alkali was then back-titrated with 0.5 M standard solution of $HCl_{(aq)}$, and a blank titration was carried out using unmodified OW. The DS was calculated according to the following equations,

$$W_{MA} = \frac{M_{MA} * C * (V_0 - V_{sample})}{1000 * 2W_{sample}} * 100\% \qquad (1)$$

$$DS = \frac{M_{OW} * W_{MA}}{M_{MA} * (100 - W_{MA})} \qquad (2)$$

where W_{MA} is the content of MA substituted (%), M_{MA} is the molecular weight of MA (98 g/mol), C is the concentration of $HCl_{(aq)}$ solution, V_0 is the volume of $HCl_{(aq)}$ consumed by the blank sample (mL), V_{sample} is the volume of $HCl_{(aq)}$ consumed by the esterified sample (mL), and M_{OW} is the theoretical molecular weight of OW (166 g/mol) based on a previous component analysis (Bátori *et al.* 2017).

Fourier transform infrared measurements

An FTIR spectrometer (Nicolet iS10, Thermo Fisher Scientific, Waltham, USA) was used to collect spectra of the modified OW. Spectra were recorded by Nicolet OMNIC 4.1 software from 500 to 4,000 cm^{-1}, and 64 scans were averaged. Essential FTIR® (eFTIR, Madison, WI, USA) software was then used to analyse the data.

Specific surface area by Brunauer-Emmett-Teller analysis

Gas sorption measurements were carried out using a Belsorp (Bel Japan, Inc., Osaka, Japan) apparatus with N_2 gas at 77 K. The Brunauer-Emmett-Teller (BET) equation was used for calculating the specific surface area with WIBU-KEY software (Wibu Systems, Karlsruhe, Germany).

Scanning electron microscopy

Scanning electron microscopy of the samples was performed with an FEI Quanta 200F with Oxford-EDS system IE 250 X Max 80 equipped with a field emission gun (FEG) electron source (Thermo Fisher Scientific, Waltham, MA, USA). The samples were pre-coated with gold before SEM imaging.

Thermogravimetric analysis

Thermogravimetric analysis (Q500 TA instruments, Waters LLC, New Castle, DE, USA) was performed to determine the thermal properties of the substances. Approximately 5 mg of each sample was heated from room temperature up to 700 °C at a rate of 20 °C/min. The analysis was performed under nitrogen atmosphere and in triplicates.

Differential scanning calorimetry

Differential scanning calorimetry analysis was performed on a TA Instruments Q2000 apparatus (Waters LLC, New Castle, DE, USA). Approximately 6 mg of the modified OW sample was heated in an enclosed aluminium pan from -20 °C to 200 °C at a rate of 20 °C/min in the first scan and in the re-scanning under nitrogen atmosphere.

Measuring water uptake capacity

The water uptake of the samples was measured at 20 °C and at 30 °C by keeping 1 g of each sample in a climate chamber (TK 120 Test Cabinet, Nüve, Ankara, Turkey) with 85% humidity for 24 h. The water content of the samples was determined with a gravimetric method after 2, 4, 6, 8, 12, and 24 h.

Contact angle

Contact angle measurements were performed using an Attension Theta optical tensiometer (Biolin Scientific, Espoo, Finland). OneAttension software (Biolin Scientific, Espoo, Finland) was used for data collection and analysis. The sessile drop method was used to apply the droplet on the substrate surface. A 4 µL drop was dispensed on the surface, and the images were captured. Approximately 0.35 g of orange waste or grafted orange waste powder was weighed and then placed between two insulating polyester sheets. The sandwich was then pressed (78 MPa) for approximately 5 min to make a compressed film. The thickness of the obtained samples became less than 1 mm. The samples then were placed in the equipment for contact angle measurement.

RESULTS AND DISCUSSION

Industrial orange waste (OW), which is difficult to handle, was used in this study to develop a useful and renewable material that can potentially be used for the fabrication of biocomposites and biopolymer blends. For this matter, orange waste was modified with maleic anhydride. By grafting of maleic anhydride into the OW structure, several major chemical and physical changes occurred. First, a number of the hydrophilic hydroxyl groups attached to the OW were converted to the less polar ester groups, which are represented in the maleic anhydride side groups. Maleic anhydride is a bifunctional molecule in the structure, with one side connected to OW and the other side available to connect with another polymer chain, enabling it to crosslink polymer chains and to increase the dimensional stability. The less polar nature of the modified polysaccharide could trigger enhanced adhesion with a less polar or more hydrophobic natural or synthetic resin. The results of the modification are interesting and, in certain cases, contradictory due to the complexity of the starting material.

Chemical Reaction of Maleic Anhydride with Orange Waste

The reaction of OW was performed with a degree of substitution of 0.39 ± 0.01, meaning that almost 40% of all possible hydroxyl groups in the substance had reacted with maleic anhydride. For the pectin, the degree of substitution was similar at 0.38 ± 0.03. In a study by Almeida *et al*. (2015), a similar method was used, except that the solvent was dimethylformamide, and a degree of substitution of 0.24 was obtained. The differences between the results might be because of the choice of solvent, which warrants further investigation. The reaction is demonstrated in Fig. 1.

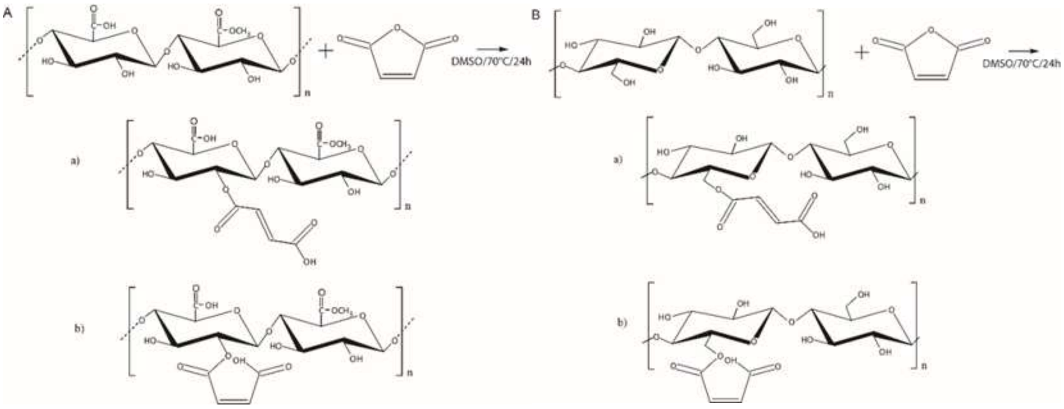

Fig. 1. (A) Schematic representation of chemical reaction between pectin and maleic anhydride (image based on information in Almeida *et al.* 2015), (B) Schematic representation of chemical reaction between cellulose and maleic anhydride. a) and b) represent the trans fumarate and cis maleate isomers of the polysaccharides (Almeida *et al.* 2015). Hemicelluloses have been neglected due to the complexity of their chemical structure.

Characterization of the Maleic Anhydride-grafted Orange Waste

Chemical structure

Maleic anhydride is prone to nucleophilic attack by nucleophiles, such as hydroxyl or amino groups, whereas hydroxyl groups that are commonly present in polysaccharides are prone to esterification reaction (Almeida *et al.* 2015). Esterification of OW was confirmed by FTIR spectroscopy (Fig. 2). As the largest fraction of OW is pectin (approximately 30%), the peaks describing the degree of esterification of pectin were also analysed. Changes of the broadband from 1750 cm^{-1} to 1700 cm^{-1} and from 1630 cm^{-1} to 1600 cm^{-1} were observed for esterified and free carboxyl groups, respectively (Putiev *et al.* 1964; Tsaryuk and Frantsesson 1991). The incorporation of maleic anhydride into OW and pectin increased the intensity of the ester carbonyl (C=O) stretching peak. Consequently, the increase of the area related to the peak at 1737 cm^{-1} and 1734 cm^{-1}, respectively, was noticeable. Both peaks shifted slightly to the right and resulted in a higher peak at 1723 cm^{-1} in both maleic anhydride-grafted pectin (PEC-MA) and maleic anhydride-grafted orange waste (OW-MA), thus representing the ester linkages between maleic anhydride and the polysaccharides. A study claimed that the peak at 1632 cm^{-1} was related to the vibration of vinyl groups (C=C) in the modified substance (Li *et al.* 2014). It is clearly visible in the spectra of OW-MA and PEC-MA that there is a peak at 1638 cm^{-1}, very possibly representing the vinyl groups; however, the peak could also be a modified version of the peaks referring to the free carboxyl groups at 1630 cm^{-1} to 1600 cm^{-1}. The first case is the more probable one, as the peak shifted to the left (1638 cm^{-1}), and the carboxyl peak is exactly the same for PEC-MA and OW-MA, regardless of the initial composition of the carbohydrates. The potential masking effect caused by water absorption at 1631 cm^{-1} has been neglected in this analysis as only dry powders were subjected to FTIR testing. The broadband ranging from 3550 cm^{-1} to 3200 cm^{-1} corresponds to the hydroxyl groups (O-H) and for OW-MA and PEC-MA, a reduction of the peaks can be seen, providing further demonstration of esterification. The hydroxyl groups in the polysaccharides can form hydrogen bonds with the carboxyl groups arising from the hydrolysed anhydride (Zhang and Sun 2004), and could result in the shift of the carbonyl (C=O) peak. A double band (one stronger than the other) also appears at 1300 cm^{-1} to 1000 cm^{-1} in the modified spectra, representing C-O in the esters (Putiev *et al.* 1964). Two other smaller peaks show up at 3008 cm^{-1} and 3063 cm^{-1}, referring to the C-H stretch of *sp*^{2}-hybridized carbons in maleic anhydride, which usually occurs at 3000 cm^{-1} to 3100 cm^{-1} (Wade 2014). The increased bands at 821 cm^{-1} are related to the out of plane deformation of carboxyl (-COOH) groups (Almeida *et al.* 2015), which arises in the maleic anhydride side groups. Changes in the FTIR spectra were remarkable, confirming the replacement of O-H groups with the maleic anhydride groups via ester linkages, which could demonstrate the reaction between maleic anhydride and the carbohydrates, as described.

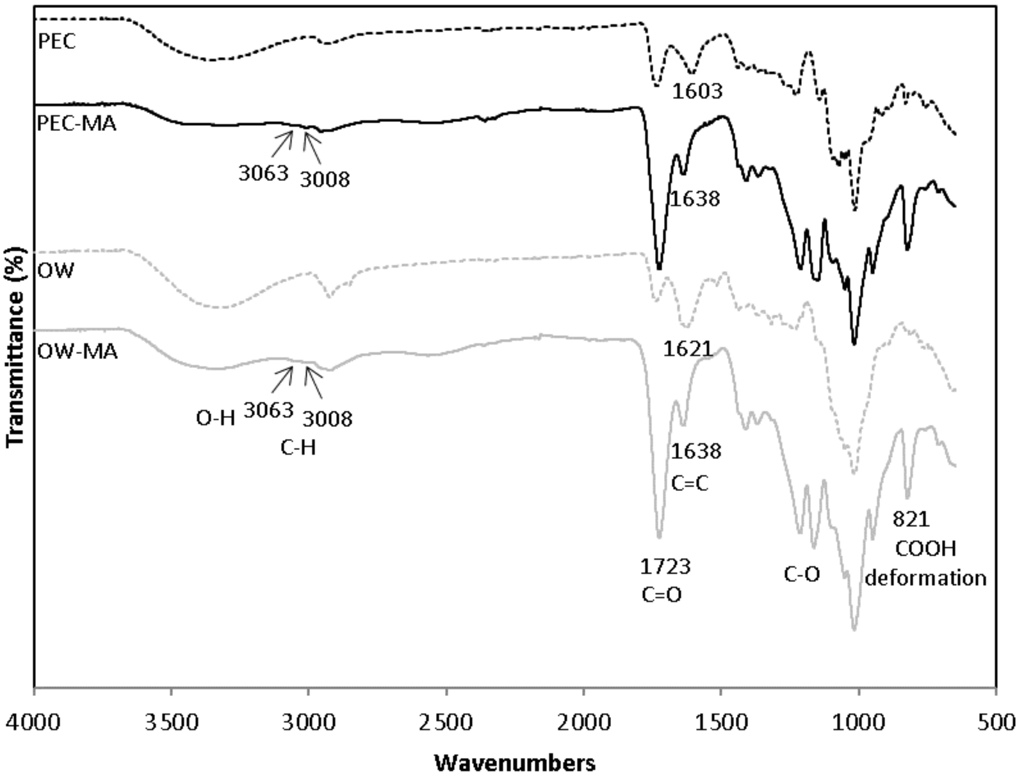

Fig. 2. Changes in FTIR spectra of orange waste (OW), OW-MA, pectin (PEC), and PEC-MA

Density and microstructure

When determining filling material for composites, density must be considered. It is important to make the lightest possible material. During milling and weighing processes, the density of OW-MA was less than that of unmodified OW; therefore, its density was measured. The same mass (2.5004 g) of samples was placed in a measuring cylinder, and the filling volume was read at ~5.6 mL and at ~9.5 mL for orange waste powder and OW-MA, respectively. Therefore, the density of the sample was decreased by approximately 40% after the reaction with maleic anhydride.

The lower density could suggest an increased specific surface area. Compared with superabsorbent materials, the specific surface area of modified OW was rather low at 2.18 m^2/g. The mean pore diameter of OW-MA was 10.7 nm. According to Li *et al.* (2008), dried orange peel powder (with a particle size between 0.1 mm and 0.2 mm) has a specific surface area of 128.7 m^2/g and an average pore diameter of 3.05 nm. The explanation for the decrease in specific surface area might be that the particles agglomerated during the reaction, which resulted in the increase of pore sizes, as well as the decrease of accessible surface area.

The proposal of the agglomeration of the particles is supported by SEM images, which was used to study the morphology of the grafted OW. The sizes of the OW-MA particles were generally greater than those of the OW particles, which can clearly be seen under the same magnification in Fig. 3 (A, B, C, and D). The structural change of OW-MA is also confirmed by Fig 3. During the esterification reaction, the structure of OW was changed from flake-like to a hollow and porous, sponge-like structure. The possible explanation for this change might be that at the molecular level, the previously packed polymer chains are no longer sitting close to each other because the incorporated maleic anhydride side chains are longer than the OH side groups. These peripheral chains provide a distance between the polymer chains and are responsible for opening up the structure. The same change in the structure can be seen in Fig. 3 E and F images taken on pure and modified pectin. The changes in the surface due to grafting of maleic anhydride are also reflected in a decreased specific surface area for the sample.

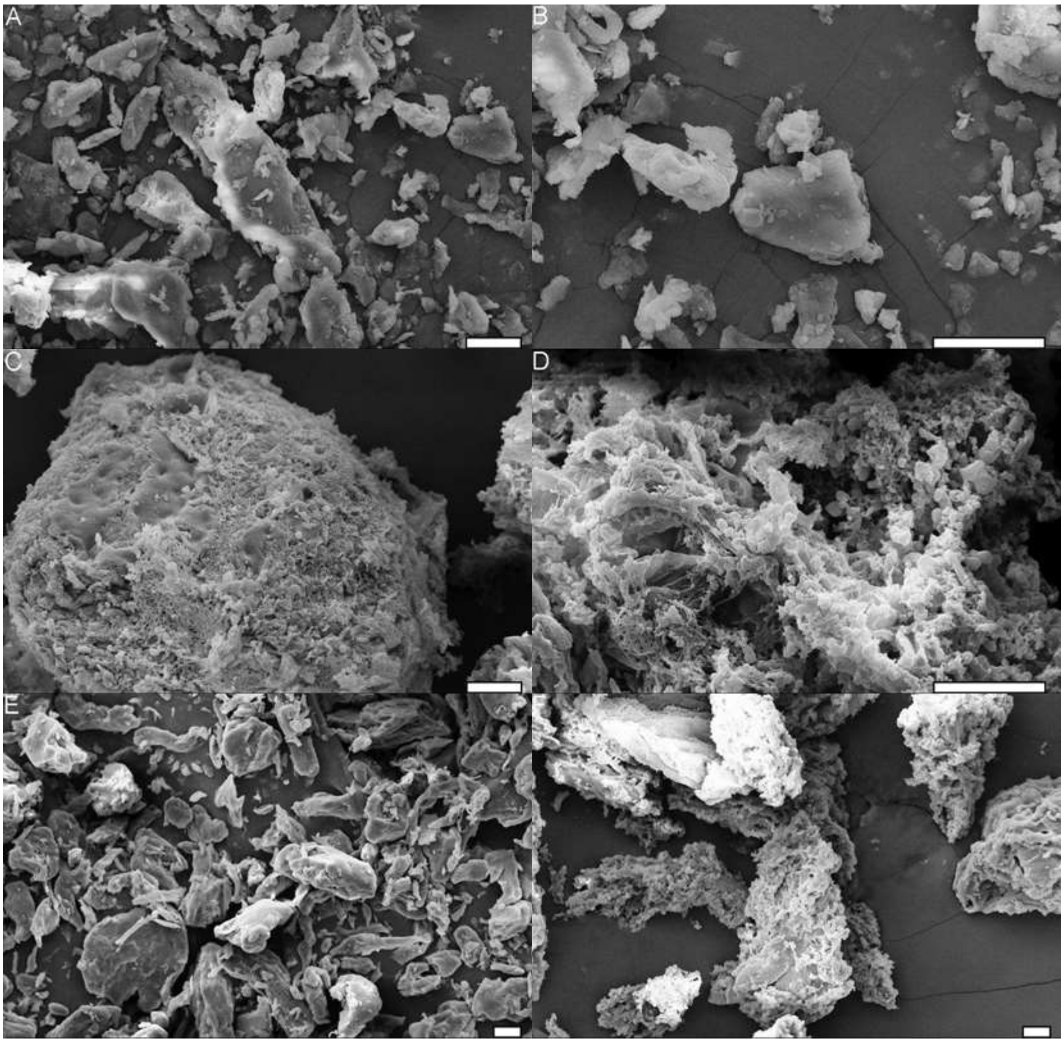

Fig. 3. (A and B) SEM (scanning electron microscopy) images of unmodified orange waste, (C and D) OW-MA (maleic anhydride-grafted orange waste) sample, (E) unmodified pectin, and (F) PEC-MA (maleic anhydride-grafted pectin) sample. By grafting orange waste with maleic anhydride, the chance of particle agglomeration increases. Scale bar values represent 25 µm. A: Mag=1.00 KX WD=6.5 mm EHT=20.00 kV; B: Mag=2.00 KX WD=6.5 mm EHT=20.00 kV; C: Mag=1.00 KX WD=6.5 mm EHT=20.00 kV; D: Mag=2.00 KX WD=6.5 mm EHT=20.00 kV; E: Mag=500 KX WD=7.5 mm EHT=20.00 kV; F: Mag=500 KX WD=11 mm EHT=20.00 kV.

Thermal properties

Because there was no major difference observed in the thermogram of grafted pectin and grafted OW, only one curve is shown. The degradation of the modified polysaccharides starts at a lower temperature than of the unmodified polysaccharides (Fig. 4). Degradation for both OW-MA and PEC-MA started with an onset decomposition temperature just above 100 °C; otherwise, it was above 200 °C for the unmodified samples. The possible explanation for this could be the same reason as discussed above: the introduction of peripheral chains broke the packed polymer structure and reduced the crystallinity of the material. Heat transfers easier in the modified structure, because there is more space between the chains due to the newly incorporated maleic anhydride side groups, which are longer in length than the short hydroxyl groups, and thus less energy is needed to decompose the polymers. Additionally, the oxygen present in maleic anhydride might catalyse the decomposition reaction (Jabbari *et al.* 2015).

A new thermal event is visible in both modified samples at approximately 150 °C. This first thermal event is attributed to the decomposition of the new, maleic anhydride side chains (decomposition pioneers), which counts for only approximately 30% of the decomposition in the first step.

In the thermal degradation curve of pure pectin, two major decomposition stages are observed that are not related to the release of water molecules (Aburto *et al*. 2015). However, the temperature ranges related to these two stages are slightly higher than what is discussed in the literature (Aburto *et al*. 2015). A possible explanation could be differences in the degree of polymerization of the samples. The second major thermal event occurred at approximately 240 °C and 260 °C for pectin and PEC-MA sample. Thus, the modified pectin required a slightly higher temperature to decompose than the unmodified pectin, but decomposition occurred at a lower rate (Fig. 5A). The higher thermal stability for PEC-MA than for pectin could be attributed to the modification, which was also concluded by Almeida *et al*. (2015).

In the unmodified OW sample, the first thermal event is related to the decomposition of pectin in orange waste at approximately 250 °C, counting for a slightly higher decomposition rate. The second event is attributed to the decomposition of cellulose in OW at approximately 355 °C with a residue approximately 30% of the sample. In the OW-MA sample, decomposition of pectin occurred as the second thermal event at approximately 280 °C, and in the third thermal event, the decomposition of cellulose occurred at approximately 304 °C. These events were shifted compared with the unmodified sample. The decomposition of pectin in OW-MA occurred at a higher temperature (shifted to the right, same as for pectin and PEC-MA), while cellulose decomposed at a lower temperature (shifted to the left), compared with the unmodified samples, but at a lower rate (Fig. 4B). A similar tendency of maleic anhydride treated cellulose can also be seen in the study performed by Li *et al*. (2014). One possible explanation for the behaviour of cellulose and hemicelluloses in OW-MA could be the reduced crystallinity in the modified structure that allows a better heat transfer. The complexity of orange waste compared with pure pectin would require further investigations in order to better understand the processes.

The low thermal stability of OW-MA would not be suitable for applications where withstanding high temperatures is a requirement. In contrast, OW-MA could be suitable for applications that require degradation in a certain time interval, *i.e*., a biodegradable material.

DSC analysis indicated endothermic transitions during the first scan of the OW-MA sample. As it was also reported for orange waste films (Bátori *et al.* 2017), the endothermic transition disappeared during the re-scanning (data not shown). Similar to the OW films (Bátori *et al.* 2017), it was concluded that OW-MA does not bear a glass transition temperature or a melting point under the observed conditions, and it is more likely to be amorphous than crystalline. The DSC diagram has been left out for the sake of brevity.

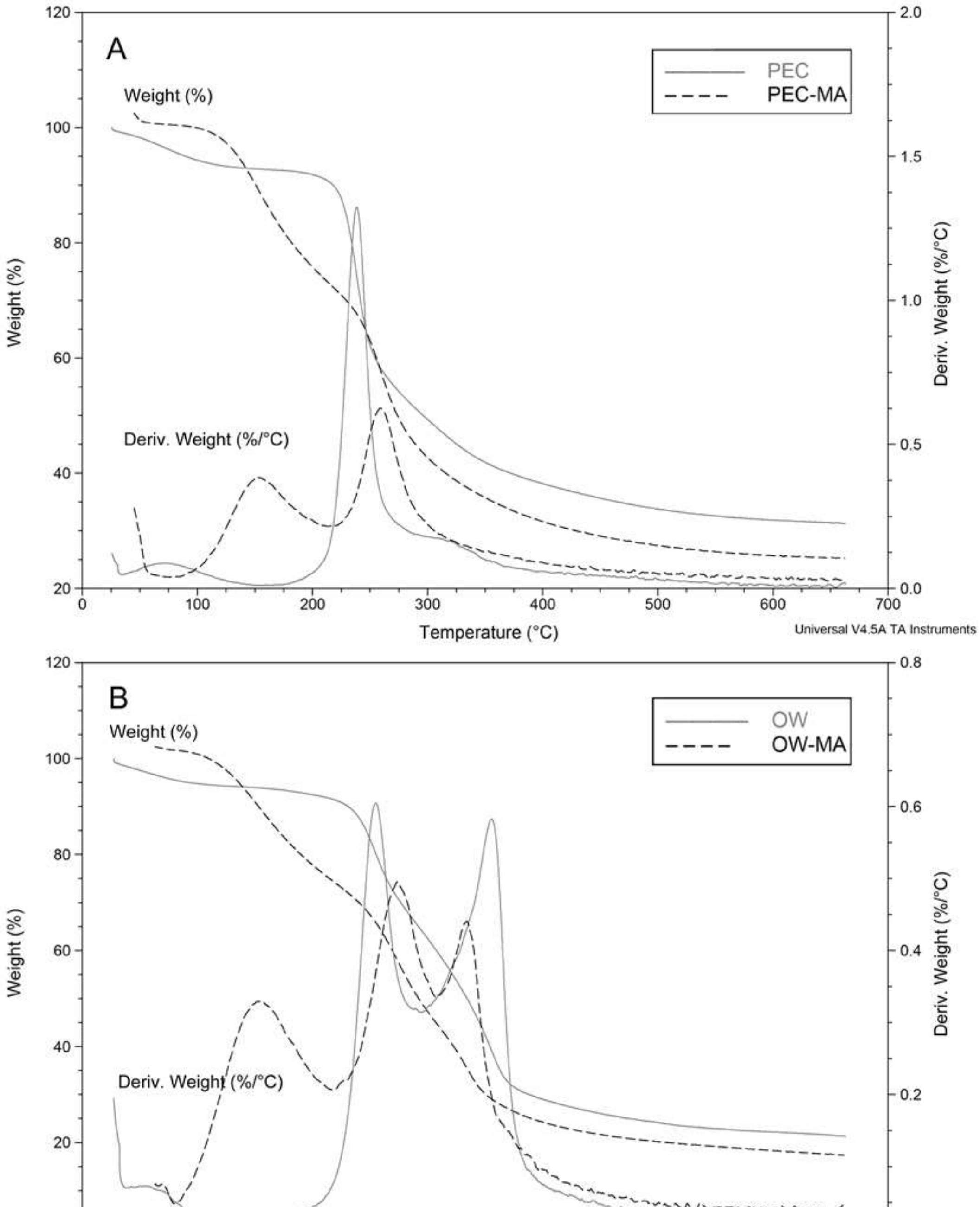

Fig. 4. (A) TGA thermogram of pectin (PEC) and PEC-MA, (B) and of orange waste (OW) and OW-MA. Diagrams are showing the weight % (left axis) and the derivatives of the weight % with respect to the temperature (right axis).

Affinity for water vapor and wettability

At relative humidity of 85%, the modified OW samples absorbed a higher amount of water vapour than the unmodified orange waste samples (Fig. 5). The higher water affinity could possibly be explained either by the changed structure or by the increased volume of the modified OW, facilitating the absorption of water vapour. Thus, in the modified OW, the water vapour molecules have a better access to interact with the carboxyl groups on the maleic anhydride and the remaining OH groups on the polymers, even though their number has been decreased. Contrary to these results, the contact angle test (Fig. 6) showed that the modified OW behaved more as a hydrophobic substance than the unmodified OW. The results of the contact angle test, which is performed in a short time (a maximum of 10s), was significantly dependent on the surface properties of the materials. Replacement of the OH groups with maleic anhydride groups, in the modified orange waste, resulted in a more hydrophobic surface. However, during the long-time exposure (in the affinity test), the water vapor molecule can more easily penetrate through the more porous structure of the modified material and therefore, this material exhibited a higher water affinity compared to the original orange waste.

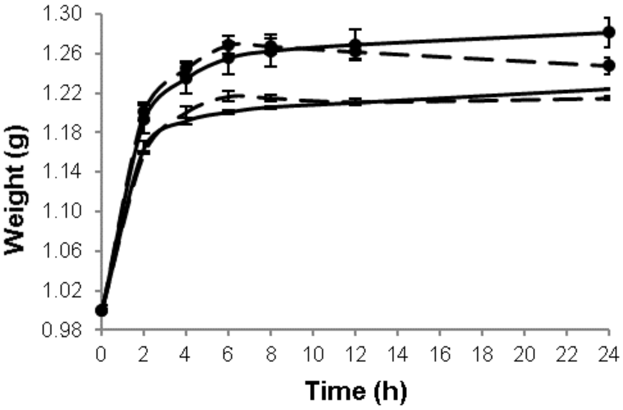

Fig. 5. Water uptake test was performed at 85 % relative humidity at 20 °C and 30 °C. The results are based on the average of triplicate samples of orange waste (OW) at 20 °C (solid line), maleic anhydride-grafted orange (OW-MA) at 20 °C (solid line with circles), orange waste (OW) at 30 °C (dashed line) and maleic anhydride-grafted orange (OW-MA) at 30 °C (dashed line with circles).

Fig. 6. (A) Water contact angle measurement of orange waste (OW) powder, and (B) maleic anhydride-grafted orange (OW-MA) powder

CONCLUSIONS

1. This study presents a new approach towards the valorisation of the lignocellulosic orange waste, which is produced abundantly during orange juice production. Therefore, grafting of orange waste was performed by replacing approximately 40% of the hydroxyl groups with maleic anhydride side groups via ester bonding.
2. The grafted orange waste behaved in a contradictory manner when interacted with water/water vapour: it had a higher affinity for water vapour (as a result of its high porosity),

but at the same time it showed more hydrophobic behaviour when the surface was directly exposed to water, compared to unmodified orange waste.

3. Esterification reaction made maleic anhydride-grafted orange waste to become lighter than orange waste. The change in density could be favorable for, *e.g*., composite fabrication.
4. The porous structure allowed a better heat transfer and created a thermally more uniform material. However, the maleic anhydride-grafted orange waste degraded at a lower temperature than orange waste; it could be more suitable for composites that are meant to biodegrade within a certain time interval.

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