detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

CITRUS WASTE FIBRES FOR NATURAL COSMETIC AND BIOPLASTIC PACKAGING

Vesna Žepič Bogataj [1,*], Peter Fajs [1], Carolina Peñalva [2] and Georgios Tsatsos [3]

[1] TECOS, Slovenian Tool and Die Development Centre, Kidričeva 25, 3000, Celje, Slovenia
[2] AITIIP Centro Tecnológico, Romero 12, 50720, Zaragoza, Spain
[3] COSMETIC, Ioannou Metaxa 56, 19400 Karellas, Koropi, Greece

Article Info:
Received:
11 September 2023
Revised:
18 December 2023
Accepted:
18 December 2023
Available online:
31 December 2023

Keywords:
Citrus peels
Waste fibres
Bioplastic
Cosmetic Packaging
Composites
Circular Economy

ABSTRACT

In this work new biocomposite materials from wasted citrus peels have been validated for value-added packaging and new cosmetic products. Extracted natural fibres and dehydrated pulp from citrus fruit were combined with polylactic acid and other additives as materials for the production of bio-based packaging jars and cosmetic products. Orange powder (dehydrated waste) was found to be the best performing for the composition of packaging, while orange comminute, which results from milling orange peel revealed to be the most suitable for the composition of cosmetic formulations. Polylactic acid was compounded with citrus fibres by up to 25 wt.% by using twin screw extrusion and processed via injection moulding, one of the most widespread processing technologies for the production of rigid packaging containers. Composites were characterized and their mechanical, morphological and thermal properties were defined. Validation of packaging thermostability performance was performed by heat deflection temperature in compliance with ISO-75 and VICAT softening temperature in accordance with ISO-306. Compatibility tests of packaging demonstrators with newly formulated cosmetic products were researched as well. An accelerated compatibility test of the cosmetic jars with water- and oil-based simulants was performed at the ambient temperature, -5°C and 45°C. The results have indicated that new cosmetic packaging is not consistent with water-based cosmetic formulations yet is compatible with products based on natural oils. While the price of these products is generally higher than those using conventional plastics, they are competitive for premium cosmetic brands.

1. INTRODUCTION

Citrus fruits are considered to be the most popular and abundant crops worldwide. However, their industrial process and consumption produce a large amount of waste, especially peels, seeds, and pomace. Citrus processing waste normally occupies up to 60% of the total fresh fruit mass (peels, membranes, pomace, seeds), wastewater and semi-solid residues, such as centrifugation pulp that results from the extraction of juice. Approximately 10 million tons of citrus waste is produced each year (Zema et al., 2018) and, due to its large quantity and perishable nature, citrus by-products are considered as problematic waste. Citrus peels rot quickly, which attracts microbes, flies, mould, and results in the production of mycotoxins. Proper management of these wastes or their conversion into further process streams is, therefore, a necessity and not just an attempt to increase income (Berk, 2016). Proper disposal of citrus waste requires significant investment as unauthorised disposal leads to soil and water pollution, and destruction of the aquatic ecosystem (Zema et al., 2018). However, this type of waste can be also viewed as a potential bio-resource material for several application purposes. Many studies have already demonstrated that citrus processing waste contains numerous phytochemicals and bioactive components, such as polyphenols, vitamins, pectin, essential oils, fibres, terpenoids, etc. (Yun and Liu, 2022). The use of citrus processing waste is, therefore, effective as it aids in recycling valuable compounds and reduces environmental pollution.

In the past few years, citrus processing waste has shown good application potential in the food sector (Kumar et al. 2022, Yun and Liu, 2022, Iqbal et al. 2022, Suri et al. 2022), especially for the preparation of superfoods and nutraceuticals (Zhu et al., 2020). These bioactive components not only serve as functional ingredients, but also prevent the invasion of microbes, allergies, and illnesses (Babbar et al. 2011). Citrus waste usually becomes livestock feed, but it can also be used as a substrate for mushroom

* Corresponding author:
Vesna Žepič Bogataj
email: vesna.zepic.bogataj@tecos.si

Detritus / Volume 25 - 2023 / pages 24-32
https://doi.org/10.31025/2611-4135/2023.18330

production, an accelerator for the preparation of compost, certain biofuels and bioethanol (Bernal-Vicente et al., 2008, Casquete et al., 2015). If combined with bioplastics, it can act as an ideal material for packaging applications (Yun and Liu, 2022; Peñalva et al., 2019; Žepič et al., 2016). The world of bioplastic packaging brings about a solution for ecological products by creating a more sustainable and greener world with a smaller environmental footprint. In combination with citrus peel powder, bioplastic materials can be shaped into jars, bottles, dispensing pumps, cosmetic packaging, and other innovative ideas that can be the next selling product on the market. Moreover, due to the presence of high-value compounds, such as essential oils and a unique fragrance, citrus processing waste proves its suitability for incorporation in cosmetic products (Pinto et al. 2021).

This paper investigates the use of citrus peel powder in novel biocomposite materials for value-added packaging and cosmetic products. Polylactic acid (PLA) was compounded with citrus powder in different ratios in order to valorise its application potential for cosmetic packaging. Composites were characterized for mechanical, morphological, and thermal properties, while the validation of packaging demonstrators was carried out via optical 3D scanning measurements, thermostability analyses and compatibility performance tests with cosmetic simulants and newly formulated cosmetic products.

The implementation of this study was possible with the cooperation of the industrial partner OLVETIA and the research institutions of TECOS and AITIIP, within the LIFE CITRUSPACK project (LIFE Citruspack, 2021), co-financed by the LIFE Programme, EU's funding instrument for the environment and climate action.

2. MATERIALS AND METHODS

2.1 Materials

Citrus waste powder (CWP) was supplied by AMC Innova Natural Drinks (Murcia, Spain), a subsidiary of AMC Group, Spain's third-largest international exporter in the food and beverage sector. CWP was extracted from the orange juice production process, blended in a certain percentage (trade secret), milled, and finally dried for further processing into composite materials. CWP was added to biodegradable polylactic acid (PLA) with the trade name IngeoTM Biopolymer 3251D by NatureWorks® LLC in different weight ratios, namely 0, 15 and 25 wt.%. Acetyl tributyl citrate (ATBC), supplied by Traquisa S.L. (Barcelona, Spain), was added as a plasticizer to improve the final performance of materials in a conventional extrusion compounding process (Coperion ZSK26 co-rotating twin-screw extruder, semi-industrial) at AITIIP facilities (Zaragoza, Spain). The compounded materials were afterward dried (Mini dryers Moretto X DRY AIR T) to ensure a low water level content that could, otherwise, negatively affect the product properties. The blend composition and sample designations used in this study are presented in Table 1.

TABLE 1: Sample composition for cosmetic jars (CJ).

Composite Sample	PLA [wt. %]	CWP [wt. %]	ATBC [wt. %]
CJ10	100	0	--
CJ11	80	15	5
CJ12	70	25	5

2.2 Production of cosmetic packaging jars

Compounded materials were transformed into a three-part set of cosmetic packaging (Figure 1), assembled by an inner insert, an outer case, and a lid, with an injection moulding machine (KraussMaffei 80/380 CX) with newly designed and manufactured injection moulds. For compatibility tests with cosmetic simulants and final products, 50 prototype jars were injected, of which 25 inner inserts were made of pure PLA and 25 were made of CJ11 formulation. Specimens for mechanical testing were obtained by injection moulding with the Fanuc Roboshot ALPHA S50IA/330/IT electric injection machine (Tokyo, Japan) following the ISO 527 standard.

2.3 Characterization analyses

2.3.1 Tensile testing

Tensile tests using Zwick Roell Z 2.5 (Zwick GmbH & Co. KG, Ulm, Germany) were carried out in compliance with ISO 527-1-2 under ambient conditions. The distance be-

a)

b)

FIGURE 1: Cosmetic Jars with (a) plain PLA insert, and (b) CJ11 composite variation.

tween the grips was set to 60 mm. The presented values of elasticity modulus (E_t), tensile strength (σ_M), and elongation at break (ε_b) are an average from at least six replicates from each tested material.

2.3.2 Scanning electron microscopy

The morphology of the composite fractured surfaces was examined after a tensile test using the Hitachi S3400N (Tokyo, Japan) scanning electron microscope (SEM). An operating voltage of 10 kV and magnifications of 500x and 50x were used.

2.3.3 Thermogravimetric analysis

Thermal characterisation was carried out by using thermogravimetric analysis (Mettler-Toledo TGA/SDTA 851e, Greifensee, Switzerland). The samples were heated from 20 to 1000°C at 20°C/min under N_2 atmosphere (100 mL/min).

2.3.4 Optical 3D measurement

A high-resolution optical 3D scanner (ATOS CS 5M; GOM, Braunschweig, Germany) was used to explore the surface quality of cosmetic jars. The initial step in the optical 3D scanning process involved conducting a calibration procedure to ensure the dimensional consistency of the measuring volume. To minimize the scan noise and surface gloss, a 2 µm thick layer of an anti-reflective TiO_2 coating spray was manually applied on the jars' surface jointly with adhesive reference markers. Each jar was then mounted on the rotating table and scanned at a resolution of 5 megapixels (MP) in 20 positions through 360° with a working distance of 590 mm. A dedicated software (GOM Inspect Suite 2020; GOM, Braunschweig, Germany) was used to automatically obtain a triangulated mesh in STL format from the point cloud.

2.3.5 Heat deflection temperature

Heat deflection temperature (HDT) was determined according to ISO 75-2:2013 with the Zwick/Roell HDT/Vicat 4-300 (Zwick GmbH & Co. KG, Ulm, Germany), operating at a voltage of 0.45 MPa and a heating rate of 120°C h^{-1} (method B). The temperature was determined after the specimen deflecting 0.33 mm. Before testing, specimens were preconditioned for 88 hours at (23 ± 2)°C and (50 ± 10)% rh. The presented results are an average of three conducted experiments.

2.3.6 Vicat softening temperature

Vicat softening temperature (VST) experiment was performed according to ISO 306: 2013. The examination was accomplished according to the test method A50 (10 N; 50°C/h) in silicone oil. The samples were stored in standard climate 23/50-2 (DIN EN ISO 291: 2008-05) for a minimum of 24 hours before the examination.

2.3.7 Compatibility testing

Different cosmetic simulants were tested with cosmetic jars and stored for four months at three different temperature zones: -5°C, 25°C and 45°C. The compatibility tests were conducted with the inserts made of plain PLA and a newly developed composite (formulation CJ11) with five different simulants, namely paraffin oil, caprylic/capric triglyceride, and water samples with 4, 7 and 10 pH values. The water solutions were prepared by adding citric acid to water and adjusting pH by a solution of sodium hydroxide. All the solutions contained 1% phenoxyethanol as a preservative. pH values of the simulant samples were measured again after 14 days and compared to the initial conditions. Appearance, odour, and mass change of the simulated sample were evaluated after four months. Subsequently, compatibility tests of the cosmetic jars with three newly formulated cosmetic products based on citrus waste were carried out to validate their suitability for cosmetic packaging application.

3. RESULTS AND DISCUSSION

3.1 Mechanical properties

The effect of citrus waste powder on the tensile modulus (E_t), tensile strength (σ_M) and elongation at break (ε_b) is shown in Table 2. The results indicate that the addition of a CWP filler has a positive effect on Young's modulus, which is a vital factor for illustrating the stiffness of the materials under tensile loading. The elevated values for Young's modulus of composite formulations C11 and C12 were 3599 MPa and 3819 MPa respectively, which means a 4% and 9% improvement of the E_t value when compared with plain PLA. Nevertheless, these are only marginal enhancements that indicate a good filler distribution across the polymer matrix, but not the desired reinforcement potential.

The last statement coincides with the tensile strength results, showing that CWP addition has a negative effect on this property. The σ_M value falls to 46,15 MPa from 58.13 MPa when the percentage of a filler is 15% and the drop is further pronounced when the percentage of CWP is increased to 25%. It is well stated in the literature that the tensile strength of polymer composites depends on interfacial adhesion (Li et al. 2007). The cause for poor adhesion can also be found in the non-modified surface of CWP, as the surface charge treatment of fillers usually results in improving the final material properties (Fu et al. 2008). On the other hand, CWP particles in the PLA matrix may act as sites for stress concentration, thereby leading to the failure of the biocomposites. Elongation at break was also lower for composite samples compared to plain PLA, indicating extremely brittle materials.

Overall, the mechanical characterisation demonstrated that the filler-matrix interaction in composites produced in the present study followed general trends universally observed for particulate fillers, rather than fibrous elements (Fu et al. 2008). Due to the tendency of citrus residues in water blends to collapse during spray drying protocols,

TABLE 2: Tensile results.

Sample	E_t (MPa)	σ_M (MPa)	ε_b (%)
CJ10	3456,10 ± 145,95	58,13 ± 1,63	2,72 ± 0,12
CJ11	3599,20 ± 209,58	46,15 ± 1,01	1,78 ± 0,06
CJ12	3819,84 ± 172,10	42,81 ± 0,23	1,45 ± 0,03

their geometry is particulate, rather than fibrous (Fig. 2c). As elucidated by Fu et al. (2008), this particulate geometry entails an increase in stiffness, a decrease in strength, and an improvement in toughness.

3.2 Morphology analysis

The fractured surfaces of samples tested under tensile load were observed under SEM. It was found that the voids due to air entrapment are minimum in PLA matrix (Figure 2a), whereas the number of voids kept on increasing with the addition of CWP. Pure PLA sample exhibited large smooth surfaces without any irregularities (Fig. 2a), indicating a brittle fracture behaviour (Todo and Takayama, 2011). The addition of CWP filler dramatically changed the appearance of the fracture surface, which became rougher (Figs. 2b, c and d). Furthermore, the morphological structure of CWP is clearly visible in Figure 2c and can be clearly correleated to the spherical particulates. Higher magnifications also provide an evidence of a weak filler matrix adhesion (Fig. 2c and d) that leads to poor mechanical properties as discussed in the previous section. This lower affinity between the hydrophobic matrix and the hydrophilic filler leads to a decrease in the strength properties of the resulting composites. The agglomeration of CWP particles can also be a reason for poor mechanical properties. Frequently, fibre pull-out and cavities created by debonding of CWP from the surrounding PLA matrix were observed (Fig. 2c). This fracture mechanism is common for fibre reinforced composites under tensile load (Faludi et al. 2014). It is an indication of relatively poor surface adhesion between the CWP and the PLA matrix. As local stress concentration is occurring at these defects, this explains the reduced strength of the PLA/CWP composites.

TABLE 3: Thermogravimetric analysis results.

Sample	T_{onset} [°C]	$T_{50\%}$ [°C]	T_{max} [°C]	FR [%wt]
CJ10	379	433	466	1,26
CJ11	257	402	661	4,23
CJ12	198	391	749	6,47

3.3 Thermogravimetric analysis

The TGA results can be analysed in different phases to recognize the degradation behaviour of the composite materials. The results of the thermogravimetric analysis are presented in Table 3. Initially, the weight loss observed below 285°C corresponds to the thermal decomposition of the polymer chains in plain PLA, where a random scission of ester bonds occurs, resulting in the release of low molecular weight fragments. At approximately 350°C, a significant weight loss indicates a secondary degradation stage, involving further breakdown of residual fragments and the elimination of volatile species, like carbon dioxide, water, and small organic molecules (Peñalva et al. 2019). The presence of CWP particles influences the thermal behaviour of PLA (Table 3). The addition of citrus waste powder led to a lower onset of decomposition temperature (T_{onset}),

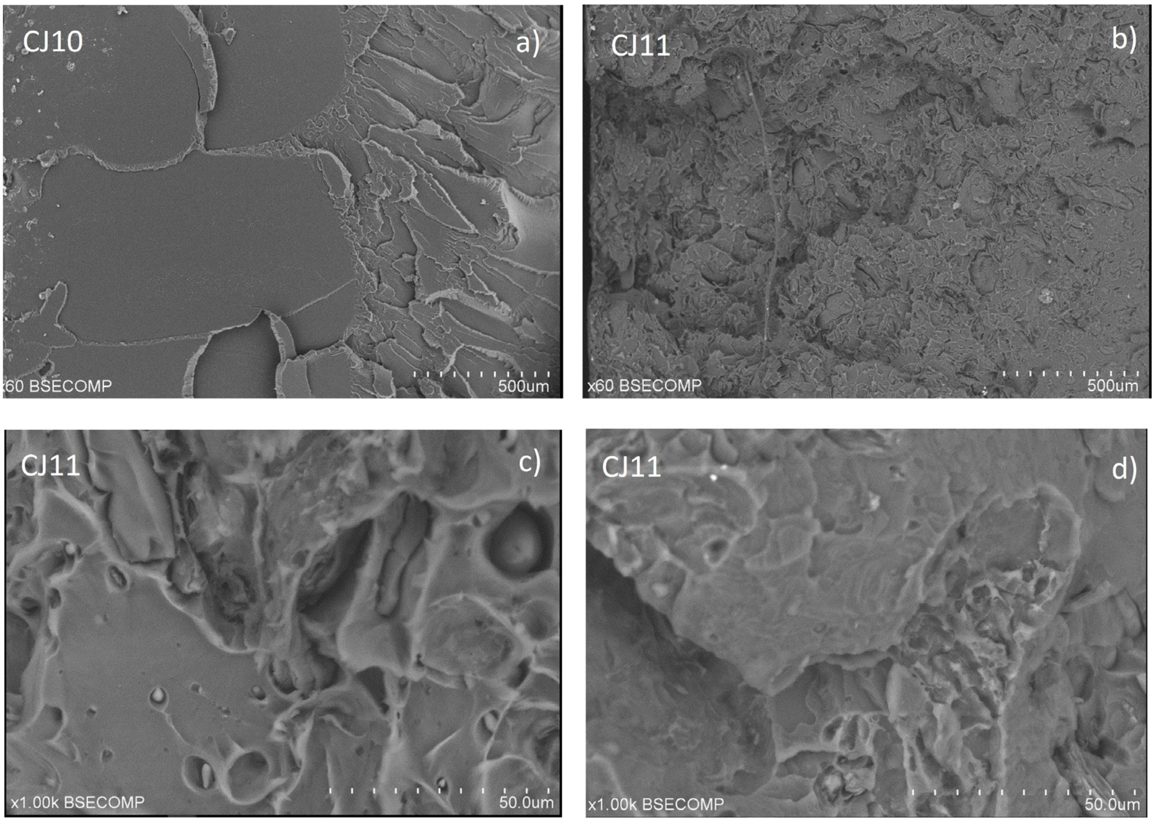

FIGURE 2: SEM images of (a) PLA sample (CJ10) (500 µm), (b) composite sample with 15% CWP (CJ11) at 500 µm magnification, (c) and (d) composite sample with 15% CWP (CJ11) at 50 µm magnification.

which was pronounced with raised CWP contents. This indicates that samples with 25 wt.% CWP show the lowest thermal stability. On the contrary, T_{max}, which is a temperature where the maximum mass loss rate occurs, was found to be increased with elevated CWP contents. The same observation was made for the mineral content and non-volatile fraction of the samples. In addition, the results of the final residue (FR) were consistent with the amount of CWP added to the samples; the higher the amount of CWP, the higher the percentage of FR.

3.4 Optical 3D-scanning and geometrical analysis

3D scanning is one of the important technologies used for designing, inspection, and quality control and it is becoming an essential tool for producers who need an accurate dimensional inspection of their final products (Javaid et al., 2021). This non-contact measuring technology converts a physical model into a digital 3D Computer-Aided Design (CAD) with the help of paired scanning software. To confirm the dimensional compliance, 3D scanning measurements were performed, involving 20 scans (14 on the upper and 6 on the bottom side) captured from various angles (Figure 3a). These scans were aligned using the reference markers and the resulting point cloud was polygonised to create a hole-free mesh in the .stl format for further inspection (Figure 3b). Subsequently, the mesh was refined, including smoothing and thinning, to improve its quality and precision. In the last step, best-fit alignment was used to align the mesh (actual data) to the nominal CAD data (Figure 3c). With the ATOS inspection module, a "surface comparison on actual" analysis was performed, involving the quantifying of positional deviations between the nominal and actual surfaces. By employing the deviation labels (points), multiple positions were validated. The results indicated that the dimensional aspects in all spatial directions (x, y, z) fall within a 0.1 mm tolerance on the labelled surface and a 0.3 mm tolerance on the helix surface (Figure 4). This outcome signifies that the injection mould

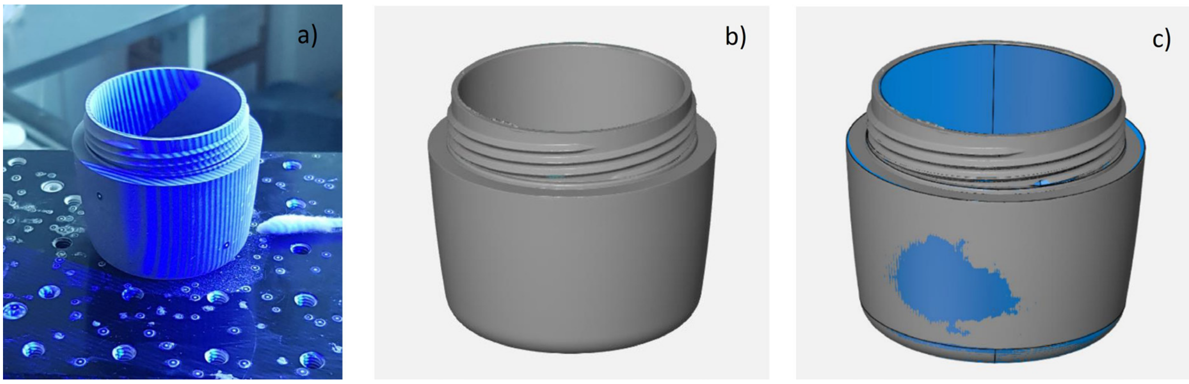

FIGURE 3: Cosmetic jars demonstrators (a) during the 3D scanning procedure; (b) polygonised mesh prepared for measurements (.stl file); and (c) local best-fit alignment between the nominal (blue) and actual (grey) data (c).

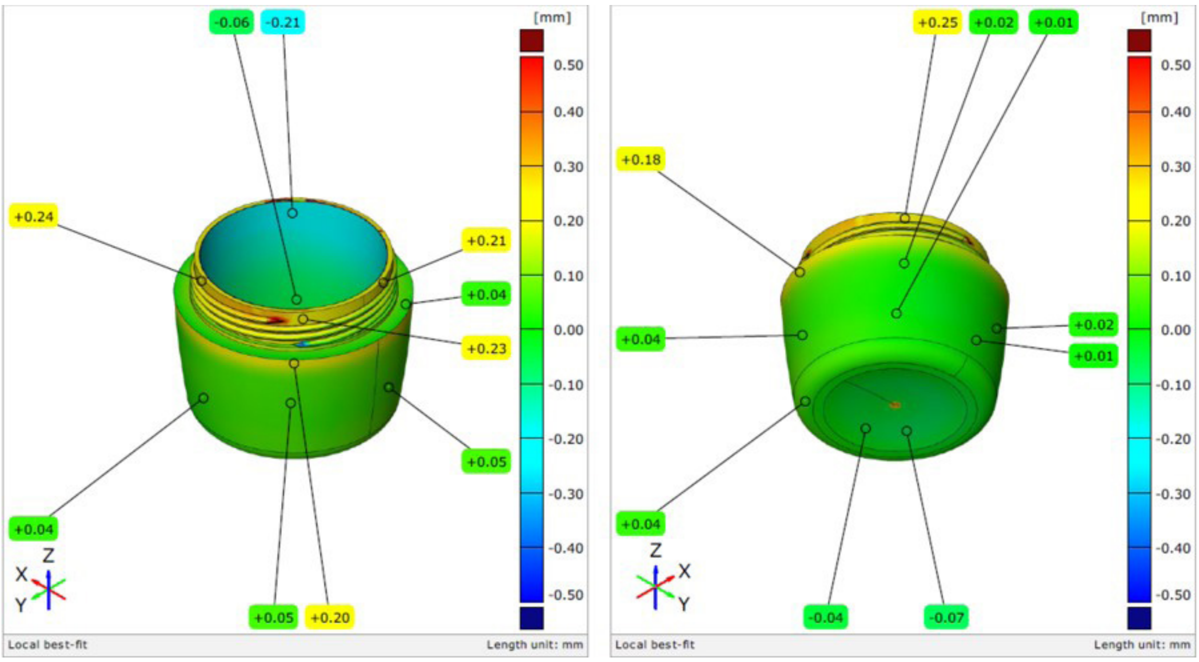

FIGURE 4: Surface comparison on actual CJ specimens with deviation labels.

was manufactured and installed with precision well within the specified tolerances and that the specimens' injection was moulded with appropriate processing parameters, thereby ensuring its operational functionality.

3.5 Thermostability analysis of cosmetic packaging jars

The dimensional stability of PLA is a big concern for its application under high-temperature conditions. Thus, heat deflection temperature (HDT) was employed as a technical requirement by packaging product designers (Narendar et. al., 2018). The HDT measurements of CWP composites are shown in Figure 5. The HDT value of plain PLA is around 55°C. After incorporating the CWP filler, the heat deflection temperature gradually decreased to 45.1°C and 44.8°C for the CJ11 and CJ12 samples respectively.

Vicat softening temperature (VST) is the temperature at which a sample is penetrated to a depth of 1 mm by a tip flat needle with a square or circular cross-section of 1 mm^2. This is an important measure used to characterize a material's thermomechanical strength (He et al. 2015). It can be a useful property for quantifying the filler effects in polymers. Similarly, to HDT, it is important in technical terms during the shaping and projection of industrial applications. The VST of the CWP composites are shown in Figure 6. The VST of plain PLA is around 56.2°C according to the manufacturer data provided (Natureworks LCC). With the CWP addition, the VST of the composites decreased to 51.8°C and 50.9°C for CJ11 and CJ12 respectively. These results are consistent with the TGA results, which also implies the degraded thermal stability of the composites with citrus waste powder. Safe application for the resulting

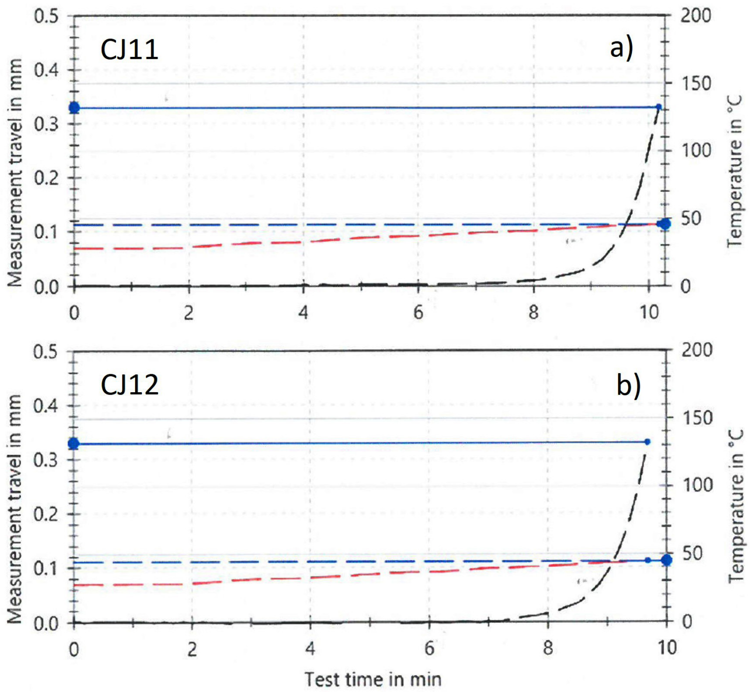

FIGURE 5: HDT diagram as a function of deflection/temperature vs. testing time for (a) composite sample with 15% CWP (CJ11), and (b) composite sample with 25% CWP (CJ12).

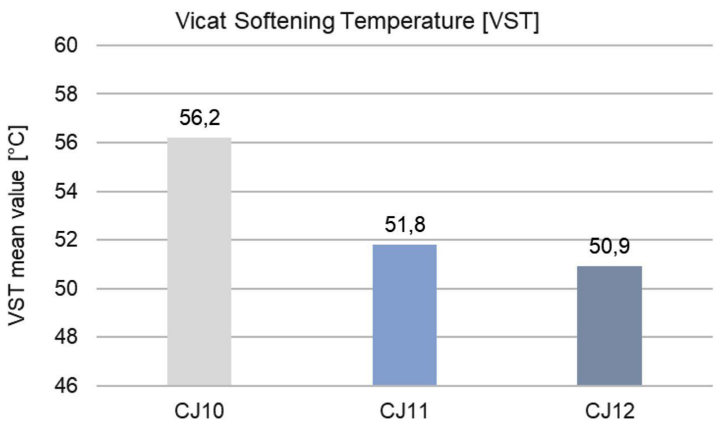

FIGURE 6: Vicat softening temperature for plain PLA and composite samples.

composites without a deformable phenomenon is, therefore, feasible at temperatures below 45°C.

3.6 Compatibility testing of cosmetic packaging

An accelerated (room temperature, freezer, and oven at 45°C) compatibility test of cosmetic jars with different simulants (aqueous solutions of different pH values and oils of different polarity) was performed to evaluate the materials' suitability for cosmetic packaging applications. The performance results of cosmetic jars are shown in Table 4. Compatibility tests were validated with inserts made of plain PLA and the composite sample CJ11.

After monitoring various parameters (pH, weight change, appearance, swelling, odour, colour), compatibility results of cosmetic jars and cosmetic products revealed that newly formulated composites are not compatible with water-based cosmetic simulants, as the brown colour migrates into the cosmetic product, which can be attributed to the hydrolytic effect of the PLA matrix (Dreier et al. 2021). Moreover, composite jars are not resistant to chemical ingredients in cosmetic formulations based on aqueous solutions since the inserts started to show cracks and fractures at low pH values (pH = 4) and elevated temperatures (T = 45°C), The maximum change in mass loss was observed in the composite samples with water-based solutions of pH 7 for all three tested temperature zones (Table 4). On the contrary, the jars made of CWP composites are validated as appropriate for oil-based cosmetic products, which was also indicated by the results of accelerated tests with oil-based media simulants (paraffin oil or caprylic/capric triglyceride) where no or minor changes were noted in terms of appearance, odour, or mass change, even under the most stringent conditions.

Simultaneously, compatibility tests of the cosmetic jars with three newly developed cosmetic formulations based on the citrus waste streams from the AMC's juice production plant were tested. The first product developed was a facial scrub (O/W scrub) presented in Figure 7a, containing 4% pomegranate peel, 0.05% orange essential oil as a perfume, and 1% orange fruit powder for improving the antioxidant and hydrating properties. The second product developed was an eye serum (water-based gel) with 0.5% orange fruit powder and 0.05% mandarin essential oil (Figure 7b). the third cosmetic product developed was a facial mask with kaolin clay for a smooth and clean skin sensation with 0.3% orange essential oil as a perfume and 0.5% orange fruit powder (Figure 7c).

Essential oils of orange, lemon and mandarin citrus waste constituents were found to be suitable for the use of aromatic ingredients in cosmetic products, as they provide a very pleasant citrus fragrance. Orange fruit powder and orange water peel extract were validated as compatible and may be used in various cosmetic formulations. At a high percentage (~ 10 wt.%), they may cause skin irritation depending on the product composition; a measure of caution is, therefore, necessary when using these extracts. Pomegranate seed powder, which was also validated as a potential scrub filler, was found to have the right granulometry for a face scrub, however, due to its strong and unpleasant smell, the use in cosmetic formulations for face masks is not recommended. On the other hand, pomegranate fruit cuts have a pleasant smell and are appropriate for use in body scrubs, which was also exploited in the formulation of the first cosmetic product based on CWP. All products were developed to comply with the COSMOS natural cosmetics standard.

TABLE 4: Compatibility test of cosmetic jars with simulants from water to oily mediums performed at -5°C, ambient temperature, and 45°C. Odour, appearance and mass change evaluated after four months.

Temp. Condition	Simulant	pH value				Appearance		Odour Change		Mass Change	
		C10		CJ11		CJ10	CJ11	CJ10	CJ11	CJ10	CJ11
		0 day	14 days	0 day	14 days						
T= -5°C	Paraffin oil					N	C	N	N	+1.2%	+1.0%
	Caprylic/capric triglyceride					N	C	N	N	+1.2%	+ 0.9%
	Water (pH=4)	4.05	4.36	4.05	4.05	N	S, C	N	S	+1.3%	+1.3%
	Water (pH=7)	6.94	7.02	6.94	4.94	N	S, C	N	S	+1.3%	+ 2.2%
	Water (pH=10)	10.01	10.00	10.01	7.48	N	S, C	N	S	+1.3%	+1.3%
T= 25°C	Paraffin oil					N	N	N	N	+ 0.7%	+ 1.3%
	Caprylic/capric triglyceride					N	N	N	N	+ 1.4%	+ 0.9%
	Water (pH=4)	4.05	3.99	4.05	8.67	M	S, C	N	S	+ 2.6%	+ 4.6%
	Water (pH=7)	6.94	6.33	6.94	7.10	M	S, C	N	S	+ 2.7%	+ 4.9%
	Water (pH=10)	10.01	6.79	10.01	9.10	M	S, C	N	S	+ 3.3%	+ 4.7%
T= 45°C	Paraffin oil					N	N	N	M	+ 1.3%	+ 0.1%
	Caprylic/capric triglyceride					N	N	N	M	+ 1.0%	+ 0.7%
	Water (pH=4)	4.05	3.66	4.05	3.35	S, C	S, C	N	S	+ 5.0%	+ 3.6%
	Water (pH=7)	6.94	6.30	6.94	3.16	S, C	S, C	N	S	+ 2.9%	+ 7.6%
	Water (pH=10)	10.01	4.16	10.01	3.44	S, C	S, C	N	S	+ 3.9%	+ 1.6%

N – no changes; M – minor change; S – substantial change; C – colour change

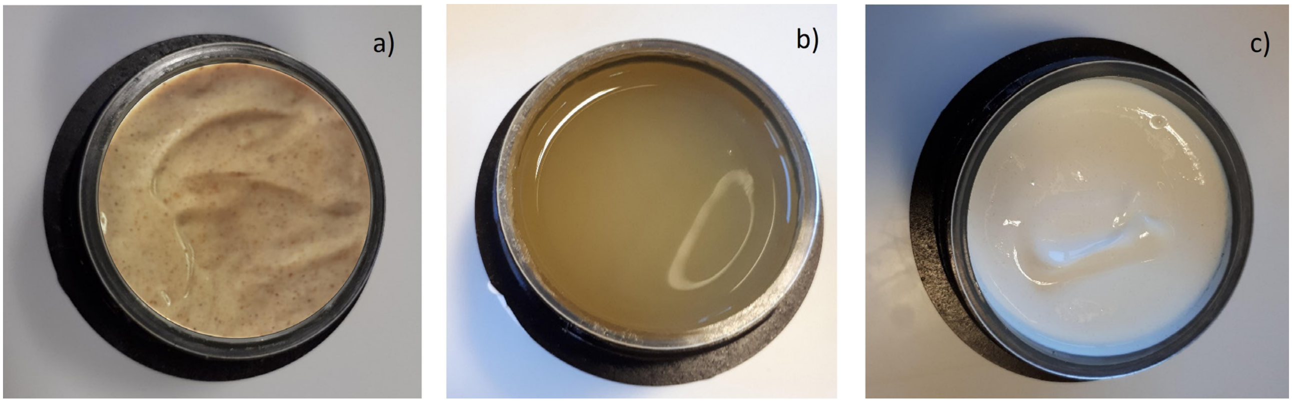

FIGURE 7: Photomacrographs of newly developed cosmetic products based on CWP: a) facial scrub, b) eye serum, and c) facial mask with kaolin clay.

4. CONCLUSIONS

This study has validated the utilization of citrus fruit waste in PLA composites for packaging and cosmetic applications. It has shown that such a secondary resource can be an interesting substitute for a certain plastic percentage in biobased sustainable packaging. Moreover, it can serve as a valuable ingredient in novel cosmetic formulations for antioxidant and hydrating properties. The results presented in this work show a good filler distribution across the biopolymer matrix, but not the desired reinforcement potential. The reinforcing potential is mainly attributed to two effects: (i) the formation of a physically bonded flexible filler network and (ii) strong polymer–filler couplings. Both of these effects arise from a high surface activity and the specific surface of the filler particles. Considering the aggregate morphology and surface structure of CWP fillers after drying the strengthening potential is drastically reduced and such additives serves only as fillers for the natural aesthetics of the final products, or a cheaper phase in the final composite materials. The negative impact on the mechanical properties of the resulting composites could be due to the fact that citrus waste filler was not given any kind of treatment, as a surface modification usually results in improving the final material properties. Poor interfacial adhesion was further proved with morphology results, indicating a weak affinity between the hydrophobic matrix and the hydrophilic filler that leads to decreased strength properties of the resulting composites. The addition of citrus waste powder led to a lower onset of decomposition temperature which was pronounced with increased filler contents. The results of the cosmetic jars' heat deflection and Vicat softening temperature were consistent with the TGA results, which also implies the degraded thermal stability of the composites with citrus waste powder. Safe application of the cosmetic packaging jars made of new composite materials without a deformable phenomenon was, therefore, feasible at temperatures below 45°C. Although newly formulated composites have been found to be incompatible with water-based cosmetic ingredients, they are appropriate for oil-based cosmetic formulations. Overall, the results indicate that the incorporation of citrus waste powder as a filler in PLA composite cosmetic packaging can be a market-appealing advantage. However, in order to meet safety conditions when in contact with cosmetic products, the use of inserts made of pure PLA in operating conditions between -5 and 45°C is strongly advised.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European LIFE Programme under the sub-program for environment and resource efficiency with a grant agreement n° LIFE16 ENV/ES/000171. Special acknowledgement to all project partners: AMC INNOVA NATURAL DRINKS, EROSKI, OWS, PLASTIPOLIS, TECOS, and project coordinator AITIIP.

REFERENCES

Babbar, N., Oberoi, H.S., Uppal, D.S., Patil, R.T. 2011. Total phenolic content and antioxidant capacity of extracts obtained from six important fruit residues. Food Research. International, 44 (1), 391-396, https://doi.org/10.1016/j.foodres.2010.10.001.

Berk Z. 2016. By-products of the citrus processing industry. Berk Z. (Ed.) In Citrus fruit processing, Academic press, San Diego (2016), 219-233.

Bernal-Vicente, A., Ros, M., Tittarelli, F., Intrigliolo, F., Pascual, J.A. 2008. Citrus compost and its water extract for cultivation of melon plants in greenhouse nurseries. Evaluation of nutriactive and biocontrol effects. Bioresource Technology, 99 (18), 8722-8728.

Casquete, R., Castro, S.M., Martin, A., Ruiz-Moyano, S., Saraiva, J.A., Cordoba, M.G. et al. 2015. Evaluation of the effect of high pressure on total phenolic content, antioxidant and antimicrobial activity of citrus peels. Innovative Food Science & Emerging Technologies, Vol. 31, 37-44.

Citruspack LIFE, Layman Report. 2021. Project Consortium under grant agreement n° LIFE16 ENV/ES/000171. Accessible at: https://citruspack.eu/wp-content/uploads/2021/02/laymans_report_en.pdf (09/09/2023)

Dreier, J., Brütting, C., Ruckdäschel, H., Altstädt, V., Bonten, C. 2021. Investigation of the Thermal and Hydrolytic Degradation of Polylactide during Autoclave Foaming. Polymers (Basel). 13(16):2624. doi: 10.3390/polym13162624.

Faludi, G., Dora, G., Imre, B., Renner, K., Mőcző, J., and Pukánszky, B. (2014). "PLA/lignocellulosic fibre composites: Particle characteristics, interfacial adhesion, and failure mechanism," Journal of Applied Polymer Science 131(4), 1–10. DOI: 10.1002/app.39902.

Fu, S., Feng, X., Lauke, B., et al. 2008. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate. Polym Compos, 39: 933–961.

He, S., Zhou, L., He, H. 2015. Preparation and properties of wood plastic composites based on tea residue. Polym Compos; 36: 2265–2274.

Iqbal, A., Schulz, P., Rizvi S.S. 2022. Valorization of bioactive compounds in fruit pomace from agro-fruit industries: present Insights and future challenges. Food Biosci., 44, p. 101384

Javaid, M., Haleem, A., Singh, R.P., Suman, R. 2021. Industrial perspectives of 3D scanning: Features, roles and it's analytical applications, Sensors International, Vol 2, 2666-3511.

Kumar, V., Kaur, R., Aggarwal, P., Singh G. 2022. Underutilized citrus species: an insight of their nutraceutical potential and importance for the development of functional food. Sci. Hortic., 296, 110909

Li, X., Tabil, L.G., Panigrahi, S. 2007. Chemical treatments of natural fiber for use in natural fiber-reinforced composites: a review. J Polym Environ.; 15: 25–33.

LIFE Citrsupack - Revalorization strategies within the circular economy for the use of citrus waste in green packaging and cosmetics. LIFE16 ENV/ES/000171. Available at: https://citruspack.eu/ (11/09/2023)

Narendar, R., Priya Dasan, K., Rajendran, K. 2018. Coir pith/nylon/epoxy hybrid composites and their thermal properties: thermogravimetric analysis, thermal ageing, and heat deflection temperature. J Vinyl Addit Techn; 24: 297–303.

Peñalva, C., Vidal, J., Verstichel, S., Fajs, P., Žepič Bogataj, V., Cruz Arcas, M. 2019 Revalorization strategies for the use of citrus waste in green packaging and cosmetics. In: Conference Proceedings Sardinia_2019 [Padova: Eurowaste SRL]. International waste management and landfill symposium (2019; Santa Margherita di Pula, Sardinia, Italy), p.11

Pinto, D., Cadiz-Gurrea, M.L., Silva, A.M., Delerue-Matos, C., Rodrigues F. 2021. Cosmetics - Food Waste Recovery. Galanakis C.M. (Ed.), Food waste recovery (2nd Ed.), Academic Press, San Diego, CA, 503-528.

Suri, S., Singh, A., Nema P.K. 2022. Current applications of citrus fruit processing waste: a scientific outlook. Appl. Food Res., 2, p. 100050. https://doi.org/10.1016/j.afres.2022.100050.

Todo, M., and Takayama, T. (2011). "Fracture mechanisms of biodegradable PLA and PLA/PCL blends," in: Biomaterials – Physics and Chemistry, R. Pignaletto (ed.), InTech, Rijeka, Croatia.

Vivek, S., Kanthavel, K. 2019. Effect of bagasse ash filled epoxy composites reinforced with hybrid plant fibres for mechanical and thermal properties. Compos B; 160: 170–176.

Yun, D., Liu, J. 2022. Recent advances on the development of food packaging films based on citrus processing wastes: A review. Journal of Agriculture and Food Research, Vol 9. https://doi.org/10.1016/j.jafr.2022.100316.

Zema, D.A., Calabro, P.S., Folino, A., Tamburino, V., Zappia, G., Zimbone, S.M. 2018. Valorisation of citrus processing waste: A review. Waste Management, 80, 252-273. https://doi.org/10.1016/j.wasman.2018.09.024.

Zhu, Z., Gavahian, M., Barba, F.J., Rosello-Soto, E., Kovacevic, D.B., Putnik, P., et al. 2020. Valorization of waste and by-products from food industries through the use of innovative technologies. Agri-Food industry strategies for healthy diets and sustainability, Academic Press, Cambridge, MA, USA, 249-266

Žepič Bogataj, V., Poljanšek, I., Oven, P. and Čop, M.. 2016. Properties of PLA films reinforced with unmodified and acetylated freeze dried nanofibrillated cellulose. Holzforschung, vol. 70, no. 12, 2016, 1125-1134. https://doi.org/10.1515/hf-2016-0096