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Sustainable Utilization Strategy of Organic Waste via Fabrication of Bioelastomer with Antibacterial and Antioxidant Activities Using Mandarin Peel Extracts

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Abstract: Mandarin peels (MPs), a food-processing residue, have several restrictions on their disposal and can cause serious environmental pollution. In this study, MP was used to fabricate a functional bioelastomer with antioxidant and antibacterial activities. Bioactive compounds were recovered from MPs in liquid form and added to the bioelastomer during fabrication to maintain the mechanical strength of the bioelastomer. The radical scavenging activities of the fabricated bioelastomer (B–MPE 15%) were 3.3% for DPPH and 20.8% for ABTS, respectively. In addition, B–MPE 15% exhibited antibacterial activity against gram-positive (*Staphylococcus aureus*), gram-negative (*Escherichia coli*), and antibiotic-resistant bacteria (Methicillin-resistant *S. aureus* and Vancomycin resistant *Enterococcus*). The chemical properties of B–MPE 15% were not significantly different from those of the control group (bare PDMS). Tensile strength, elongation at break, and water vapor transmission rate of B–MPE 15% were found to be 5.1 N/mm^2, 649%, and 33.3 g/(m^2 day), respectively. Therefore, the addition of MP extracts did not significantly affect the physical properties. The fabricated bioelastomer with antibacterial and antioxidant activities is expected to be utilized in the food packaging, pharmaceutical, and medical industries. Our research is expected to represent a future-oriented strategy for realizing carbon neutrality by upcycling food waste.

Keywords: bioelastomer; mandarin peel; flavanone; antioxidant; antibacterial

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1. Introduction

Mandarin is one of the most popular fruits because of its sweet taste and ease of consumption, as well as its antioxidant, anticancer, antibacterial, and anti-adipogenic properties [1,2]. An estimated 630,000 tons of mandarins were produced in Korea [3], and it has been reported that approximately 50,000 tons of mandarin-processing residues are generated annually [4]. However, only 30% of the mandarin residues are used as medicinal herbs. While the remaining 70% used to be disposed of into the ocean [5], Korea has strictly forbidden this disposal method for food wastes since 2013 in accordance with the 1996 Protocol of the London Convention [6], as it leads to disruption of the marine food chain and loss of marine biodiversity [7]. Food waste is typically disposed of through landfilling, incineration, and composting [8]. However, in Korea, direct landfilling of food waste has

been prohibited, by law, since 2005 to alleviate the shortage of landfills, protect groundwater and soil, and promote the conversion of food waste into value-added materials [9]. Meanwhile, incineration of food waste with a high moisture content can generate dioxins during combustion with other low-humidity wastes [10]. During composting, nitrate- and phosphorus-contacting leachates and greenhouse gases (GHGs) get generated, causing eutrophication and global warming, respectively [11]. As a result, various developed countries other than Korea, including the USA, EU, Japan, and China, are also suffering from social and environmental issues related to the disposal of food waste [12,13]. Therefore, it is necessary to propose a sustainable food-waste management plan that not only prevents environmental pollution but also converts food waste into value-added materials.

Traditionally, value-added materials, such as fuels and chemicals, have been produced in petroleum refineries [14]. However, these refineries are considered the main contributors to GHG emissions because they release carbon that was buried in the ground into the atmosphere. The CO_2 emissions from this sector alone were estimated to be 1079 million tons in 2015 [15]. Many countries around the world are seriously concerned about environmental pollution caused by these GHG emissions, so they participated in the UN Framework Convention on Climate Change (UNFCCC) and adopted the Kyoto Protocol (1997), the Lima Call for Climate Action (2014), the Paris Agreement (2015), etc. [16]. Consequently, biorefineries, which utilize biomass as raw materials instead of petroleum-based materials, have been attracting attention as a strategy to achieve net-zero CO_2 emissions [17]. In biorefineries, food waste is considered an ideal feedstock because it satisfies economic feasibility, owing to its low transport and storage costs, year-round availability, and ease of handling [18]. Mandarin peels (MPs), which account for approximately 7–11% of mandarins generated during juice processing, are mostly discarded because they are considered to have no economic value [19,20]. However, these residues contain cellulose, hemicellulose, pectin, essential oil, and flavonoid, which have the potential to be converted into value-added materials [21]. Although various studies have been carried out regarding the production of biofuels, such as ethanol [22] and methane [23], energy-based products have limitations that currently prevent them from completely replacing low-cost fossil fuels [24]. Therefore, in consideration of economic feasibility, it is necessary to produce bio-based products with high market values [25], such as flavonoids [26] and essential oil [27].

The predominant flavonoids in MP are hesperidin and narirutin [28], which have antioxidant [29], antibacterial [30], antidiabetic [31], and anti-inflammatory properties [32]. In addition, bioactive compounds derived from natural sources are in increasing demand, as alternatives to synthetic compounds, because of their safety and non-toxic effect on the human body [33]. Extraction techniques, including maceration, Soxhlet, microwave-assisted, ultrasound-assisted, and enzyme-assisted extraction, have been used to extract bioactive compounds from MP [34]. Among the various extraction methods, microwave-assisted extraction (MAE) has the distinct advantages of short extraction times, high extraction yields, and low solvent usage [35]. In addition, this technique is suitable for industrial-scale application [36]. The recovered bioactive substances are mixed with various polymers to fabricate bioelastomers that are used as functional materials in the food, pharmaceutical, and medical industries [37]. Dordevic et al. [38] produced edible chitosan films for food packaging using extracts of blueberries, red grapes, and parsley. Meanwhile, non-biodegradable synthetic polymers, such as polyethylene glycol (PEG), polyvinyl alcohol (PVA), polypropylene (PP), polyethylene (PE), and polydimethylsiloxane (PDMS), are also widely used in bioelastomer fabrication because they have stronger physicochemical properties than natural polymers [39].

Following these research trends, we previously fabricated a bioelastomer with antioxidant and antibacterial activities [40]. In our previous study [40], PDMS, which has higher flexibility, thermal stability, and biocompatibility, as well as lower toxicity than other synthetic polymers [41], was used as the polymer. In addition, by-products of aronia juice processing were used as the raw materials for natural bioactive compounds. However, the direct use of by-products in powder form dramatically reduced the mechanical strength of

the fabricated bioelastomer. These barriers accentuate the disadvantage of PDMS, which is its relatively low mechanical strength due to its major structure composed of Si–O bonds, unlike the C–C bonds constituting PVA, PP, and PE [42]. Therefore, it is necessary to design a strategy for fabricating bioelastomers with antioxidant and antibacterial activities while maintaining their mechanical strength.

In this study, a strategy for the sustainable utilization of food processing residue was designed by fabricating a functional bioelastomer using bioactive compounds extracted from MPs. First, a mixing ratio of extraction solvents suitable for recovering the flavonoids, hesperidin and narirutin, from MP was selected. Microwave-assisted extraction was utilized to recover hesperidin and narirutin from MP with high efficiency in a short time. Furthermore, the effects of microwave power and irradiation time on flavonoid extraction were investigated. The recovered bioactive compounds were used to fabricate functional bioelastomers with antioxidant and antibacterial activities. Finally, the biological properties, chemical structure, and mechanical strength of the fabricated bioelastomer were compared with those of the control group. This study is the first attempt to produce a functional material by mixing flavonoid extracts obtained from MP, a waste resource, with PDMS to design a sustainable biorefinery.

2. Materials and Methods

2.1. Materials

Mandarin peels (MPs) were purchased from Cheongmyeongyagcho (Chungju-si, Chungcheongbuk-do, Korea). The MPs were ground with a blender and sieved to a size of 90 μm. Polydimethylsiloxane (PDMS; Elastosil E43) was obtained from Wacker (Munich, Germany). Hesperidin, narirutin, dimethyl sulfoxide (DMSO), 1,1-diphenyl-2-picrylhydrazyl (DPPH), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), and potassium persulfate were purchased from Sigma-Aldrich (St. Louis, MO, USA). Methanol (MeOH), phosphoric acid, acetonitrile, and heptane were purchased from Samchun Chemical (Seoul, Republic of Korea). All reagents used in this study were of analytical grades.

2.2. Preparation of Mandarin Peel Extracts

To select the most efficient extraction solvent, 1 g of MP was immersed in 10 mL of a MeOH:DMSO solution mixed in different proportions (1:9, 3:7, 5:5, 7:3, and 9:1, *v/v*). MP, then, was extracted in an incubator at 40 °C, with a shaking speed of 150 rpm, for 24 h. To design the MAE process for maximum flavanone recovery from MP, MP was immersed in the selected extraction solvent (1:10, *w/w*) and extracted at various microwave powers (70, 210, 350, 490, and 630 W) and irradiation times (5, 10, 15, 20, and 30 s). Each extract was centrifuged at 13,000 rpm for 10 min to separate the supernatant and, then, analyzed and used for bioelastomer fabrication.

2.3. Fabrication of Bioelastomer

PDMS was poured into a square Petri dish (24.5 × 24.5 cm), and 20 mL of heptane and mandarin peel extracts (MPEs) were recovered under the determined MAE conditions were added and mixed uniformly. The bioelastomer manufacturing conditions are listed in Table 1. The Petri dish was transferred to a vacuum oven and dried at 40 °C until the moisture was completely removed.

Table 1. Detailed manufacturing conditions of bioelastomers.

Sample	PDMS (g)	MPE (g)
B–MPE 0% (control, PDMS)	50	0
B–MPE 1% (*w/w*)	49.5	0.5
B–MPE 3%	48.5	1.5
B–MPE 5%	47.5	2.5
B–MPE 7%	46.5	3.5
B–MPE 10%	45	5
B–MPE 15%	42.5	7.5
B–MPE 20%	40	10

2.4. Antioxidant Activity of Bioelastomer

2.4.1. DPPH Radical Scavenging Activity

DPPH radical scavenging activity was determined using the DPPH assay with a slight modification [43]. The DPPH stock solution was prepared by dissolving the DPPH reagent in MeOH to a concentration of 0.5 mM. The DPPH working solution was prepared by diluting the prepared DPPH stock solution with methanol until the absorbance at 517 nm reached 1.2. Each bioelastomer (size: 1 × 1 cm) was immersed in 1 mL of the DPPH working solution and reacted at 25 °C for 30 min. The bioelastomer was then removed, and the absorbance of the supernatant was measured at 517 nm using a spectrophotometer (DU 730, Beckman Coulter, Brea, CA, USA). The blank was 1 mL of methanol, and the control was 1 mL of DPPH working solution without bioelastomer added. All experiments were performed in triplicate to obtain the standard deviations. Radical scavenging activity was calculated using the following Equation (1):

$$\text{Radical scavenging activity (\%)} = (1 - (OD_{sample}/OD_{control})) \times 100 \quad (1)$$

2.4.2. ABTS Radical Scavenging Activity

ABTS radical scavenging activity was measured using the ABTS assay with a slight modification [44]. An ABTS stock solution was prepared by reacting 7 mM ABTS solution and 2.45 mM potassium persulfate in a 1:1 ratio (*v/v*). ABTS working solution was prepared by diluting the prepared ABTS stock solution with methanol until the absorbance at 734 nm reached 1.0. Each bioelastomer (size: 1 × 1 cm) was immersed in 1 mL of the ABTS working solution and reacted at 25 °C for 30 min. The bioelastomer was then removed, and the absorbance of the supernatant was measured at 734 nm using a spectrophotometer; the blank was 1 mL of methanol, and the control was 1 mL of ABTS working solution without bioelastomer added. All experiments were performed in triplicate to obtain the standard deviations. The radical scavenging activity was calculated using Equation (1) above.

2.5. Antibacterial Activity of Bioelastomer

The antibacterial activity of the bioelastomer was determined following the method in our previous study [41]. *Staphylococcus aureus* was used as the gram-positive bacteria, *Escherichia coli* as the gram-negative bacteria, and methicillin-resistant *Staphylococcus aureus* (MRSA) and vancomycin-resistant *Enterococcus* (VRE) as the antibiotic-resistant bacteria. All the bacteria were cultured in a shaking incubator at 150 rpm, for 24 h, at 37 °C in 50 mL of nutrient broth. The bacteria were diluted to 10^6 CFU/mL and inoculated on nutrient agar plates. Bioelastomers (size: 1 × 1 cm) were placed in the center of the nutrient agar medium, inoculated with each bacterium, and then, incubated at 37 °C for 24 h. The antibacterial zone was determined using the Image J software (v1.52i, National Institutes of Health, Bethesda, MN, USA). All experiments were performed in triplicate to obtain the standard deviations.

2.6. Characterization of Bioelastomer

The chemical structures of the bioelastomers were investigated using Fourier-transform infrared spectroscopy (FT-IR; JASCO FTIR-4600, Jasco, Japan). Tensile strength and elongation at break were determined, according to ASTM D412, using a universal testing machine (Instron 3367; Norwood, MA, USA). Water vapor transmission rate (WVTR) was determined, according to ASTM F1249, using a Permatran-W 3/33 MA (Mocon, Minneapolis, MN, USA). The morphology of both bioelastomers was characterized using scanning electron microscopy (SEM, SNE-3000M, SEC Inc., Suwon, Republic of Korea) at a scanning voltage of 5 kV.

2.7. Analytical Methods

The hesperidin and narirutin contents in MPE were determined using high-performance liquid chromatography (HPLC). The analytical conditions were as follows: INNO column

C18 (5 μm, 4.6 mm × 250 mm, Young Jin Biochrom, Seongnam-si, Republic of Korea); diode array detector (DAD); wavelength, 250 nm; temperature, 25 °C; injection volume, 5 μL; flow rate, 0.8 mL/min. The gradient elution conditions were as follows: acetonitrile for solvent A and 0.03% (*v/v*) phosphoric acid in DW for solvent B; 0 min, 10% A; 0–15 min, 20% A; 15–28 min, 40% A; 28–36 min, 75% A; 36–38 min, 10% A; 38–50 min, 10% A. Standard curves for quantification were prepared using hesperidin and narirutin as the standard reagents.

3. Results and Discussion

3.1. Selection of Extraction Solvent for Flavanone Recovery from Mandarin Peels

To maximize flavanone recovery from MPs, appropriate mixing ratios of the extraction solvents were investigated. A MeOH:DMSO mixture was used to extract total flavonoids from MP [45]. Similarly, Magwaza et al. [46] demonstrated that a mixed MeOH:DMSO solution (1:1, *v/v*) effectively and rapidly extracts phenolic compounds, such as flavanone glycosides and phenolic acid, from mandarin rinds. Figure 1 shows the effects of the mixing ratio of MeOH:DMSO on the flavanone (hesperidin and narirutin) recovery from MPs. The extraction solvent was mixed with solutions of MeOH and DMSO that had MeOH:DMSO ratios of 1:9, 3:7, 5:5, 7:3, and 9:1 (*v/v*). The resulting flavanone recovery with each solution was 26.6, 31.9, 43.7, 28.0, and 18.4 mg/g-biomass for hesperidin and 5.2, 6.3, 8.7, 6.1, and 5.3 mg/g-biomass for narirutin, respectively. These results agree with those of a previous study [46], which showed that the MeOH:DMSO solution mixed in the same ratio is the most effective extraction solvent for recovering flavanone from MPs. Therefore, a 5:5 ratio (*v/v*) of the MeOH:DMSO mixture was selected as the extraction solvent for recovering flavanone from MPs (Figure A1).

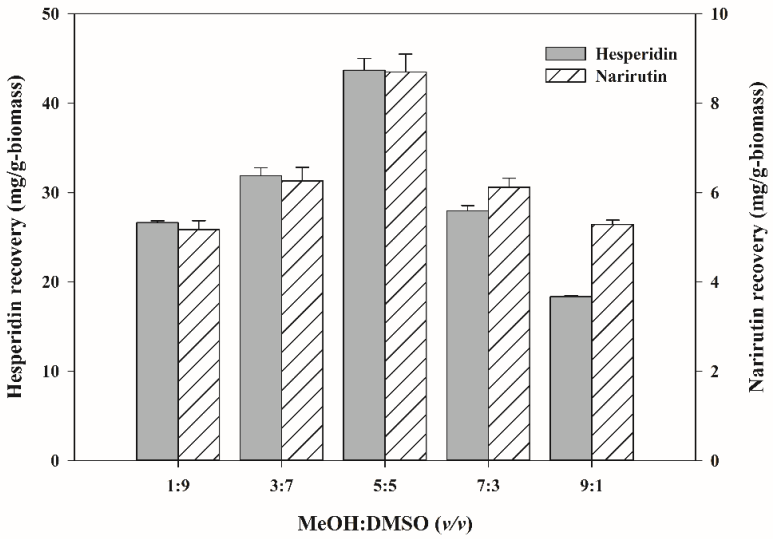
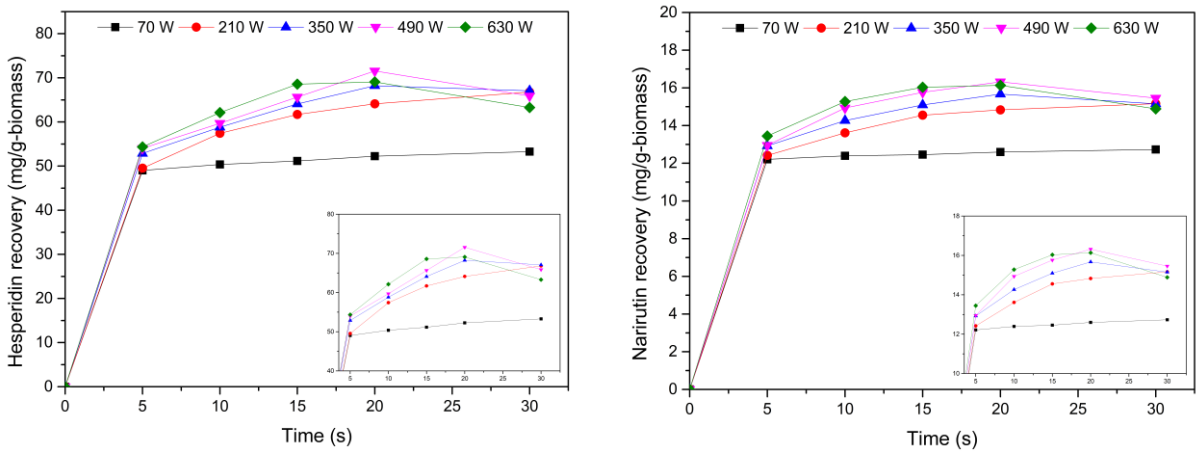


Figure 1. Effects of the mixing ratio of MeOH:DMSO solution on flavanone (hesperidin and narirutin) recovery from MPs.

3.2. Determination of Microwave-Assisted Extraction Conditions

The MAE process was designed to recover high yield of flavanone from MP in a short time. However, high microwave power and extended irradiation time can cause the thermal degradation of these phenolic compounds [47]; extraction conditions should be determined based on the maximum energy that can be input without causing thermal degradation to reduce the consequent loss of bioactive compounds. Therefore, the effects of microwave power and irradiation time on flavanone extraction from MPs were investigated (Figure 2). Figure 2a shows the results of hesperidin recovery from MPs. At a microwave power of 70 W, hesperidin recovery was not significantly affected by irradiation time, and it only slightly increased from 49.0 mg/g-biomass at 5 s to 53.2 mg/g-biomass

at 30 s. At a microwave power of 210 W, hesperidin recovery steadily increased from 49.5 mg/g-biomass at 5 s to 66.8 mg/g-biomass at 30 s, but the maximum recovery was not achieved. At microwave powers of 350, 490, and 630 W, hesperidin recovery steadily increased for 20 s, after which it decreased with increasing irradiation time. The reduction significantly increased as the microwave power increased, which was presumed to be because of thermal degradation caused by excessive energy input. This phenomenon was confirmed by Ahmad and Langrish [48], who extracted phenolic acids from MPs. Finally, the maximum hesperidin recovery was found to be 71.6 mg/g-biomass at 490 W and 20 s. Recovery of narirutin from MPs showed a similar tendency to that of hesperidin (Figure 2b). At microwave powers of 350, 490, and 630 W, narirutin recovery steadily increased for 20 s, after which it decreased with increasing irradiation time. The maximum narirutin recovery was found to be 16.3 mg/g-biomass at 490 W and 20 s. At 490 W and 20 s, the energy input was approximately 9600 J (W × s); as it was estimated that energies higher than 9600 J caused thermal degradation of flavanones, 490 W and 20 s were chosen as the extraction conditions for flavanone recovery from MPs.



(**a**) (**b**)

Figure 2. Effect of microwave power and irradiation time on the hesperidin (**a**) and narirutin (**b**) recovery from MPs.

3.3. Antioxidant Activity of Bioelastomer

Measuring the antioxidant activity of bioelastomers is important for preventing the negative effects of free radicals in biological and food packaging applications [49]. Table 2 shows the radical scavenging activity of the fabricated bioelastomer. The radical scavenging activity of the bioelastomer increased in proportion to the content of MP-derived flavanone extract (MPE). The DPPH radical scavenging activity of the bioelastomer increased sharply by 1.8-fold when 15% MPE was added, but it was still a low 3.3 ± 0.2%. The ABTS radical scavenging activity exceeded 20% at 15% MPE and reached 26.7 ± 1.2% at 20% MPE. The DPPH and ABTS radical scavenging activities of the hesperidin standard (100 ppm) were found to be 3.5 ± 0.4% and 17.8 ± 0.6%, respectively. These results imply that the ABTS assay is more sensitive than the DPPH assay for evaluating the antioxidant activity of the bioelastomers and hesperidin, a major component of MPE. Floegel et al. [50] reported that the DPPH assay is appropriate for hydrophobic systems, and the ABTS assay is suitable for hydrophilic, lipophilic, and highly pigmented systems. Flavonoid glycosides, such as hesperidin, are hydrophilic because the presence of sugars increases their polarity [51]. In addition, MPE recovered using a MeOH:DMSO mixture is hydrophilic and is presumed to contain high amounts of pigments such as flavonoids, carotenoids, and chlorophylls [52].

Table 2. Radical scavenging activity of the fabricated bioelastomer.

Sample	Radical Scavenging Activity (%)	
	DPPH	ABTS
B–MPE 0% (control, PDMS)	0	0
B–MPE 1%	1.0 ± 0.0	13.1 ± 0.3
B–MPE 3%	1.1 ± 0.1	16.8 ± 0.4
B–MPE 5%	1.2 ± 0.1	17.3 ± 0.6
B–MPE 7%	1.5 ± 0.1	18.8 ± 0.3
B–MPE 10%	1.8 ± 0.1	19.8 ± 0.6
B–MPE 15%	3.3 ± 0.2	20.8 ± 0.8
B–MPE 20%	4.8 ± 0.3	26.7 ± 1.2
Hesperidin 100 ppm	3.5 ± 0.4	17.8 ± 0.6

3.4. Antibacterial Activity of Bioelastomer

S. aureus can cause food poisoning and toxic shock syndrome, while *E. coli* can cause septicemia and cholecystitis [53]. In addition, infections of antibiotic-resistant bacteria, such as methicillin-resistant *S. aureus* (MRSA) and vancomycin-resistant *Enterococcus* (VRE), threaten human safety to the extent that the World Health Organization (WHO) has selected it as one of the top 10 threats to global public health [54]. Therefore, bioelastomers that exhibit antibacterial activity are expected to be highly useful in the food packaging, pharmaceutical, and medical fields.

B–MPE 0–10% did not exhibit antibacterial activity against any bacteria (data not shown). However, B–MPE 15% showed antibacterial activity against gram-positive (*S. aureus*), gram-negative (*E. coli*), and antibiotic-resistant bacteria (MRSA and VRE) (Figure 3). The antibacterial zone of B–MPE 15% was determined to be 20.4 ± 1.5 cm^2 for *S. aureus*, 16.0 ± 1.2 cm^2 for *E. coli*, 9.4 ± 0.4 cm^2 for MRSA, and 14.8 ± 1.0 cm^2 for VRE. The antibacterial zone of 50 ppm ampicillin, an antibiotic used as a positive control, was found to be 19.3 ± 0.6 cm^2 for *S. aureus* and 12.5 ± 0.5 cm^2 for *E. coli*. The antibacterial activity of B–MPE 15% was presumed to be due to the flavonoids present in MPE: flavonoids can cause bacterial cell death by inhibiting the metabolism and synthesis of DNA and RNA [55]. The antibacterial effect of B–MPE 15% was more sensitive against gram-positive bacteria (*S. aureus*) than against gram-negative bacteria (*E. coli*). Alexandre et al. [56] reported that gram-positive bacteria are more sensitive to interactions with phenolic compounds because they lack an outer membrane, causing the compounds to diffuse into them more quickly than in gram-negative bacteria. Similarly, Choi et al. [57] demonstrated that hesperidin, a major flavonoid in MPE, has lower values of minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) for *S. aureus* than for *E. coli*.

Therefore, the bioelastomer with antioxidant and antibacterial activity was determined to be B–MPE 15%, and the contents of hesperidin and narirutin added to the bioelastomer were estimated to be 53.7 mg/50 g-B–MPE 15% and 12.2 mg/50 g-B–MPE 15%, respectively.

3.5. IR Analysis of Bioelastomer

The chemical structures of B-MPE 0% (control, PDMS) and B-MPE 15% were measured using FTIR. In the FT-IR spectra (Figure 4), the peak was at 797 cm^{-1}, corresponding to the symmetric stretching of Si–O–Si, the peaks at 1020 cm^{-1} and 1100 cm^{-1} corresponded to the asymmetric stretching of the Si–O–Si of the PDMS backbone, the peak at 1257 cm^{-1} corresponded to the asymmetric stretching of CH_3, and 2926 cm^{-1} corresponded to the symmetric bending of the CH_3 of the PDMS side chain. The same peaks appeared for both PDMS layers, indicating that the PDMS monomers with MPE were completely cured. Furthermore, this proves that there are only physical interactions between the filler and the matrix without the formation of covalent bonds [58]. These results agreed with those of Shivangi et al. [59], who found that the addition of bioactive extracts did not significantly affect the surface chemical properties of the fabricated biofilm.

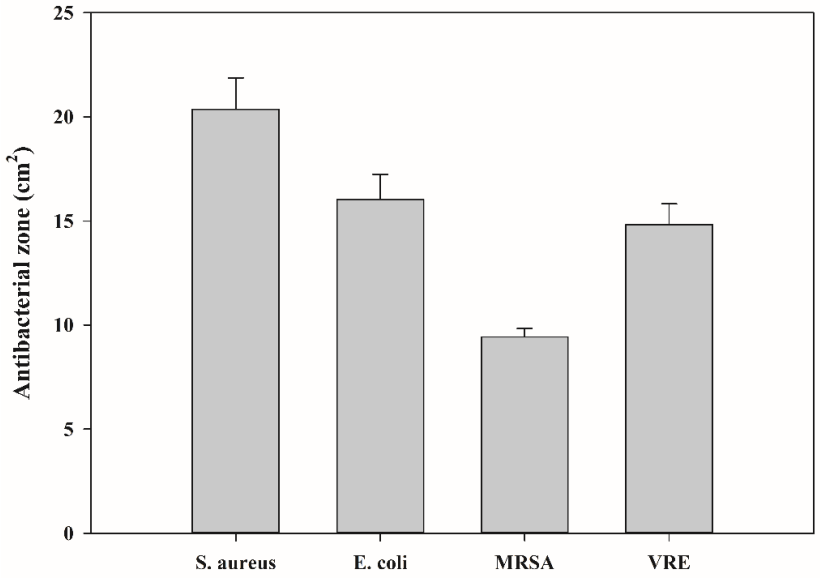


Figure 3. Antibacterial activity of Bioelastomer–MPE 15% against gram-positive (*S. aureus*), Gram-negative (*E. coli*), and antibiotic-resistant bacteria (MRSA and VRE).

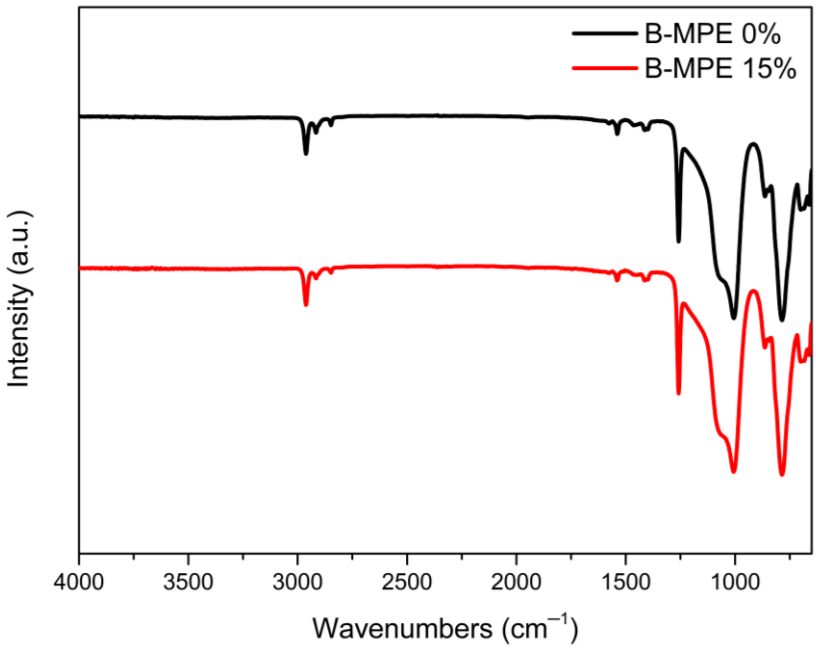
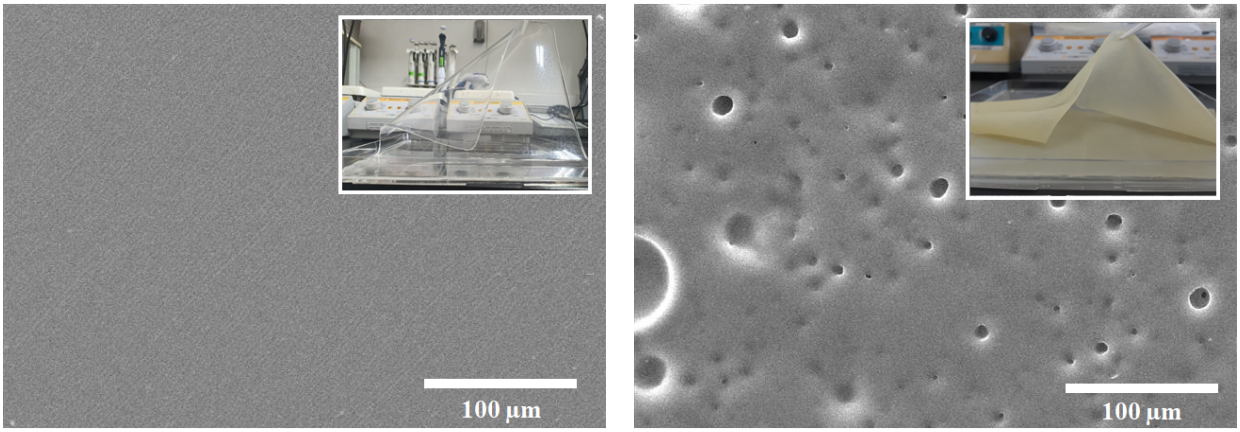


Figure 4. Fourier transform infrared (FT-IR) spectra of the Bioelastomer–MPE 0% (control, PMDS, black) and the Bioelastomer–MPE 15% (red).

3.6. SEM Image of Bioelastomer

Scanning electron microscopy (SEM) was used to observe the surface of the fabricated bioelastomer (Figure 5). The B–MPE 0% film was transparent with a smooth surface (Figure 5a). In contrast, the B–MPE 15% film exhibited a yellowish porous surface (Figure 5b). The difference in the morphology of the samples was attributed to the presence of insoluble flavonoid matter that was left behind after the evaporation of the extraction solvent [60]. In addition, the addition of the extracts changed the optical properties of the bioelastomer, resulting in differences in color and transparency.



(**a**) (**b**)

Figure 5. SEM images of B–MPE 0% (**a**) and B–MPE 15% (**b**) (inset: film-type product).

3.7. Mechanical Strength of Bioelastomer

To evaluate the applicability of the selected B–MPE 15%, the mechanical properties of the fabricated bioelastomer, namely its tensility and flexibility, were investigated by measuring its tensile strength and elongation at break, respectively [61]; the results are shown in Table 3. There was no significant difference between the tensile strengths of B–MPE 0% (5.2 N/mm^2) and B–MPE 15% (5.1 N/mm^2). This indicated that the MPEs were uniformly mixed with the well-cured PDMS layer without reducing the mechanical strength of the fabricated bioelastomer. Meanwhile, the elongation at break of B–MPE 15% (694%) was significantly higher than that of B–MPE 0% (551%); these results are consistent with those reported by da Rosa et al. [62], who showed that phenolic compounds, derived from plant extracts, can increase elongation at break.

Table 3. Physical properties of Bioelastomer–MPE 0% (control, PMDS) and Bioelastomer–MPE 15%.

Sample	Tensile Strength (N/mm^2)	Elongation at Break (%)	Water vapor Transmission Rate (g/(m^2 day))
B–MPE 0%	5.2	551	26.6
B–MPE 15%	5.1	649	33.3

3.8. Water Vapor Transmission Rate of Bioelastomer

The water vapor transmission rate (WVTR) refers to the amount of water vapor that can permeate per unit area of a material per unit time. In the food packaging industry, lower values are considered advantageous [63]. Bourakadi et al. [64] reported that barrier properties, including the WVTR, are significantly affected by the chemical properties of the additives. From the WVTRs of B–MPE 0% and 15%, which were found to be 26.6 g/(m^2 day) and 33.3 g/(m^2 day), respectively (Table 3), it can be seen that the addition of MPE slightly increased the WVTR of the bioelastomers. This was probably due to the presence of polar compounds in the MPE: in general, extracts containing polar compounds, such as flavonoids and phenolic acids, improve the hydrophilicity of film materials, leading to an increase in their water vapor permeability [65].

4. Conclusions

Here, we proposed a biorefinery strategy based on the extraction of useful substances prior to the saccharification process of MPs, as well as the utilization of the extracted compounds. In this study, we recovered hesperidin and narirutin from MP and used them to fabricate bioelastomers. These bioelastomers that were fabricated using extracts exhibited significantly improved mechanical strength compared to bioelastomers that directly utilized

biomass in powder form. In addition, the fabricated bioelastomer exhibited significant antioxidant and antibacterial activities and, thus, shows great potential for use in the food packaging, pharmaceutical, and medical industries. Our biorefinery strategy is expected to provide future direction for the realization of a sustainable society and carbon neutrality.

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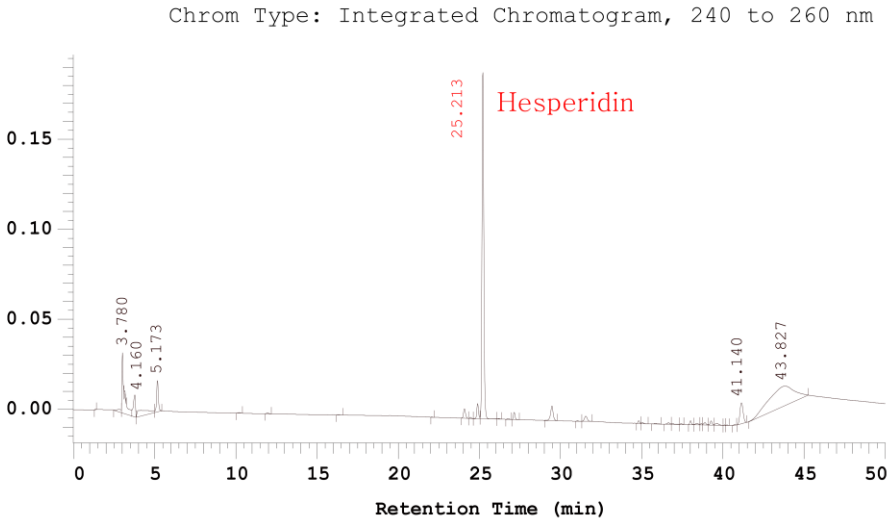
Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A



(**a**)

Figure A1. *Cont.*

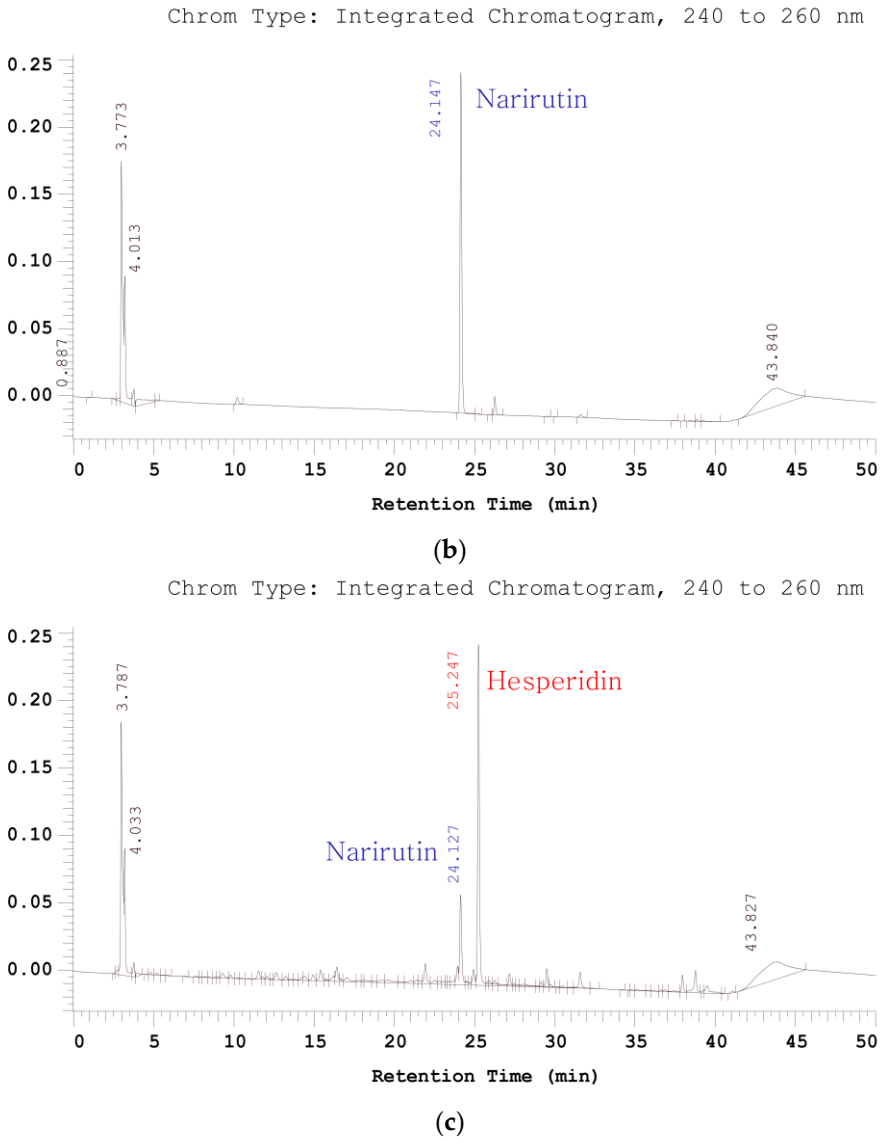


Figure A1. HPLC chromatogram for hesperidin standard (**a**); narirutin standard (**b**); mandarin peel extracts (**c**).

References

1. Jang, S.-K.; Jung, C.-D.; Seong, H.; Myung, S.; Kim, H. An integrated biorefinery process for mandarin peel waste elimination. *J. Clean. Prod.* **2022**, *371*, 133594. [CrossRef]
2. Falcinelli, B.; Famiani, F.; Paoletti, A.; D'Egidio, S.; Stagnari, F.; Galieni, A.; Benincasa, P. Phenolic Compounds and Antioxidant Activity of Sprouts from Seeds of *Citrus* Species. *Agriculture* **2020**, *10*, 33. [CrossRef]
3. Jeju special self-governing province. Citrus Annual Distribution Processing Analysis. Available online: http://citrus.or.kr/board/data/chang/2019.pdf (accessed on 21 March 2021).
4. Lee, H.H.; Heo, D.Y.; Han, H.R.; Park, H.R.; Ruangcharus, C.; Kim, S.U.; Seo, D.C.; Oh, T.-K.; Hong, C.O. Evaluation of the effects of mandarin (*Citrus reticulate*) by-products containing citric acid on immobilization of cadmium in arable soils. *Appl. Biol. Chem.* **2019**, *62*, 45. [CrossRef]
5. Choi, I.S.; Kim, J.-H.; Wi, S.G.; Kim, K.H.; Bae, H.-J. Bioethanol production from mandarin (*Citrus unshiu*) peel waste using popping pretreatment. *Appl. Energy* **2013**, *102*, 204–210. [CrossRef]
6. Shin, D.Y.; Cho, H.U.; Utomo, J.C.; Choi, Y.N.; Xua, X.; Park, J.M. Biodiesel production from *Scenedesmus bijuga* grown in anaerobically digested food wastewater effluent. *Bioresour. Technol.* **2015**, *184*, 215–221. [CrossRef]
7. Kadlimatti, H.M.; Raj Mohan, B.; Saidutta, M.B. Bio-oil from microwave assisted pyrolysis of food waste-optimization using response surface methodology. *Biomass Bioenergy* **2019**, *123*, 25–33. [CrossRef]
8. Jang, Y.W.; Lee, K.H.; Yoo, H.Y. Improved sugar recovery from orange peel by statistical optimization of thermo-alkaline pretreatment. *Processes* **2021**, *9*, 409. [CrossRef]

9. Kim, M.-H.; Kim, J.-W. Comparison through a LCA evaluation analysis of food waste disposal options from the perspective of global warming and resource recovery. *Sci. Total Environ.* **2010**, *408*, 3998–4006. [CrossRef]
10. Saqib, N.U.; Sharma, H.B.; Baroutian, S.; Dubey, B.; Sarmah, A.K. Valorisation of food waste via hydrothermal carbonisation and techno-economic feasibility assessment. *Sci. Total. Environ.* **2019**, *690*, 261–276. [CrossRef]
11. Wang, Y.; Tang, Y.; Li, M.; Yuan, Z. Aeration rate improves the compost quality of food waste and promotes the decomposition of toxic materials in leachate by changing the bacterial community. *Bioresour. Technol.* **2021**, *340*, 125716. [CrossRef]
12. Ryen, E.G.; Babbitt, C.W. The role of US policy in advancing circular economy solutions for wasted food. *J. Clean. Prod.* **2022**, *369*, 133200. [CrossRef]
13. Joshi, P.; Visvanathan, C. Sustainable management practices of food waste in Asia: Technological and policy drivers. *J. Environ. Manag.* **2019**, *247*, 538–550. [CrossRef] [PubMed]
14. Velvizhi, G.; Balakumar, K.; Shetti, N.P.; Ahmad, E.; Kishore Pant, K.; Aminabhavi, T.M. Integrated biorefinery processes for conversion of lignocellulosic biomass to value added materials: Paving a path towards circular economy. *Bioresour. Technol.* **2022**, *343*, 126151. [CrossRef] [PubMed]
15. Jia, F.R.; Jing, W.T.; Liu, G.X.; Yue, Q.; Wang, H.M.; Shi, L. Paraffin-based crude oil refining process unit-level energy consumption and CO_2 emissions in China. *J. Clean. Prod.* **2020**, *255*, 120347. [CrossRef]
16. Zang, Z. Are China's climate commitments in a post-Paris agreement sufficiently ambitious? *Wiley Interdiscip. Rev. Clim. Change* **2017**, *8*, e443. [CrossRef]
17. Lee, K.H.; Lee, S.K.; Lee, J.; Kim, S.; Kim, S.W.; Park, C.; Yoo, H.Y. Energy-efficient glucose recovery from chestnut shell by optimization of NaOH pretreatment at room temperature and application to bioethanol production. *Environ. Res.* **2022**, *208*, 112710. [CrossRef]
18. Yoo, H.Y.; Kim, S.W. The next-generation biomass for biorefining. *Bioresources* **2021**, *16*, 2188–2191. [CrossRef]
19. Mahato, N.; Sinha, M.; Sharma, K.; Koteswararao, R.; Cho, M.H. Modern extraction and purification techniques for obtaining high purity food-grade bioactive compounds and value-added co-products from citrus wastes. *Foods* **2019**, *8*, 523. [CrossRef]
20. Hiasa, S.; Iwamoto, S.; Endo, T.; Edashige, Y. Isolation of cellulose nanofibrils from mandarin (*Citrus unshiu*) peel waste. *Ind. Crops Prod.* **2014**, *62*, 280–285. [CrossRef]
21. Satari, B.; Karimi, K. Citrus processing wastes: Environmental impacts, recent advances, and future perspectives in total valorization. *Resour. Conserv. Recycl.* **2018**, *129*, 153–167. [CrossRef]
22. John, I.; Pola, J.; Thanabalan, M.; Appusamy, A. Bioethanol production from Musambi peel by acid catalyzed steam pretreatment and enzymatic saccharification: Optimization of delignification using Taguchi design. *Waste Biomass Valorization* **2020**, *11*, 2631–2643. [CrossRef]
23. Patsalou, M.; Samanides, C.G.; Protopapa, E.; Stavrinou, S.; Vyrides, I.; Koutinas, M. A Citrus peel waste biorefinery for ethanol and methane production. *Molecules* **2019**, *24*, 2451. [CrossRef] [PubMed]
24. Manaf, I.S.A.; Embong, N.H.; Khazaai, S.N.M.; Rahim, M.H.A.; Yusoff, M.M.; Lee, K.T.; Maniam, G.P. A review for key challenges of the development of biodiesel industry. *Energy Convers. Manag.* **2019**, *185*, 508–517. [CrossRef]
25. Koutra, E.; Economou, C.N.; Tsafrakidou, P.; Kornaros, M. Bio-based products from microalgae cultivated in digestates. *Trends Biotechnol.* **2018**, *36*, 819–833. [CrossRef]
26. Zhang, H.J.; Cui, J.F.; Tian, G.F.; DiMarco-Crook, C.; Gao, W.; Zhao, C.Y.; Li, G.Y.; Lian, Y.H.; Xiao, H.; Zheng, J.K. Efficiency of four different dietary preparation methods in extracting functional compounds from dried tangerine peel. *Food Chem.* **2019**, *289*, 340–350. [CrossRef]
27. Song, X.; Liu, T.; Wang, L.; Liu, L.; Li, X.; Wu, X. Antibacterial effects and mechanism of mandarin (*Citrus reticulata* L.) essential oil against *Staphylococcus aureus*. *Molecules* **2020**, *25*, 4956. [CrossRef]
28. Khan, M.K.; Zill, E.H.; Dangles, O. A comprehensive review on flavanones, the major citrus polyphenols. *J. Food Compos. Anal.* **2014**, *33*, 85–104. [CrossRef]
29. Smeriglio, A.; Cornara, L.; Denaro, M.; Barreca, D.; Burlando, B.; Xiao, J.; Trombetta, D. Antioxidant and cytoprotective activities of an ancient Mediterranean citrus (*Citrus lumia* Risso) albedo extract: Microscopic observations and polyphenol characterization. *Food Chem.* **2019**, *279*, 347–355. [CrossRef]
30. Ernawita; Wahyuono, R.A.; Hesse, J.; Hipler, U.-C.; Elsner, P.; Böhm, V. In vitro lipophilic antioxidant capacity, antidiabetic and antibacterial activity of citrus fruits extracts from Aceh, Indonesia. *Antioxidants* **2017**, *6*, 11. [CrossRef]
31. Gupta, A.; Jacobson, G.A.; Burgess, J.R.; Jelinek, H.F.; Nichols, D.S.; Narkowicz, C.K.; Al-Aubaidy, H.A. Citrus bioflavonoids dipeptidyl peptidase-4 inhibition compared with gliptin antidiabetic medications. *Biochem. Biophys. Res. Commun.* **2018**, *503*, 21–25. [CrossRef]
32. Chen, X.M.; Tait, A.R.; Kitts, D.D. Flavonoid composition of orange peel and its association with antioxidant and anti-inflammatory activities. *Food Chem.* **2017**, *218*, 15–21. [CrossRef] [PubMed]
33. Bensid, A.; El Abed, N.; Houicher, A.; Regenstein, J.M.; Özogul, F. Antioxidant and antimicrobial preservatives: Properties, mechanism of action and applications in food—A review. *Crit. Rev. Food Sci. Nutr.* **2020**, *32*, 1–17. [CrossRef] [PubMed]
34. Singh, B.; Singh, J.P.; Kaur, A.; Singh, N. Phenolic composition, antioxidant potential and health benefits of citrus peel. *Food Res. Int.* **2020**, *132*, 109114. [CrossRef] [PubMed]
35. Bustamante, J.; Van Stempvoort, S.; García-Gallarreta, M.; Houghton, J.A.; Briers, H.K.; Budarin, V.L.; Matharu, A.S.; Clark, J.H. Microwave assisted hydro-distillation of essential oils from wet citrus peel waste. *J. Clean. Prod.* **2016**, *137*, 598–605. [CrossRef]

36. Drinić, Z.; Vladić, J.; Koren, A.; Zeremski, T.; Stojanov, N.; Kiprovski, B.; Vidović, S. Microwave-assisted extraction of cannabinoids and antioxidants from *Cannabis sativa* aerial parts and process modeling. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 831–839. [CrossRef]
37. de Oliveira Filho, J.G.; Braga, A.R.C.; de Oliveira, B.R.; Gomes, F.P.; Moreira, V.L.; Pereira, V.A.C.; Egea, M.B. The potential of anthocyanins in smart, active, and bioactive eco-friendly polymer-based films: A review. *Food Res. Int.* **2021**, *142*, 110202. [CrossRef]
38. Dordevic, S.; Dordevic, D.; Sedlacek, P.; Kalina, M.; Tesikova, K.; Antonic, B.; Tremlova, B.; Treml, J.; Nejezchlebova, M.; Vapenka, L.; et al. Incorporation of Natural Blueberry, Red Grapes and Parsley Extract By-Products into the Production of Chitosan Edible Films. *Polymers* **2021**, *13*, 3388. [CrossRef]
39. Magaña, I.; López, R.; Enríquez-Medrano, F.J.; Kumar, S.; Aguilar-Sanchez, A.; Handa, R.; de León, R.D.; Valencia, L. Bioelastomers: Current state of development. *J. Mater. Chem. A* **2022**, *10*, 5019–5043. [CrossRef]
40. Lee, K.H.; Chun, Y.; Jang, Y.W.; Lee, S.K.; Kim, H.R.; Lee, J.H.; Kim, S.W.; Park, C.; Yoo, H.Y. Fabrication of functional bioelastomer for food packaging from Aronia (*Aronia melanocarpa*) juice processing by-products. *Foods* **2020**, *9*, 1565. [CrossRef]
41. Liu, J.; Cheng, Y.; Xu, K.; An, L.; Su, Y.; Li, X.; Zhang, Z. Effect of nano-silica filler on microstructure and mechanical properties of polydimethylsiloxane-based nanocomposites prepared by "inhibition-grafting" method. *Compos. Sci. Technol.* **2018**, *167*, 355–363. [CrossRef]
42. Huang, N.; Zang, J.; Zhang, G.; Guan, L.; Li, S.; Zhao, L.; Tang, L. Efficient interfacial interaction for improving mechanical properties of polydimethylsiloxane nanocomposites filled with low content of graphene oxide nanoribbons. *RSC Adv.* **2017**, *7*, 22045–22053. [CrossRef]
43. Periakaruppan, R.; Li, J.; Mei, H.; Yu, Y.; Hu, S.; Chen, X.; Li, X.; Guo, G. Agro–waste mediated biopolymer for production of biogenic nano iron oxide with superparamagnetic power and antioxidant strength. *J. Clean. Prod.* **2021**, *311*, 127512. [CrossRef]
44. Lee, K.H.; Jang, Y.W.; Kim, H.; Ki, J.-S.; Yoo, H.Y. Optimization of lutein recovery from *Tetraselmis suecica* by response surface methodology. *Biomolecules* **2021**, *11*, 182. [CrossRef] [PubMed]
45. Inoue, T.; Tsubaki, S.; Ogawa, K.; Onishi, K.; Azuma, J.I. Isolation of hesperidin from peels of thinned *Citrus unshiu* fruits by microwave-assisted extraction. *Food Chem.* **2010**, *123*, 542–547. [CrossRef]
46. Magwaza, L.S.; Oara, U.L.; Cronje, P.J.R.; Landahl, S.; Ortiz, J.O.; Terry, L.A. Rapid methods for extracting and quantifying phenolic compounds in citrus rinds. *Food Sci. Nutr.* **2016**, *4*, 4–10. [CrossRef]
47. Ballard, T.S.; Mallikarjunan, P.; Zhou, K.; O'Keefe, S. Microwave-assisted extraction of phenolic antioxidant compounds from peanut skins. *Food Chem.* **2010**, *120*, 1185–1192. [CrossRef]
48. Ahmad, J.; Langrish, T.A.G. Optimisation of total phenolic acids extraction from mandarin peels using microwave energy: The importance of the Maillard reaction. *J. Food Eng.* **2012**, *109*, 162–174. [CrossRef]
49. Chen, C.-W.; Xie, J.; Yang, F.-X.; Zhang, H.-L.; Xu, Z.-W.; Liu, J.-L.; Chen, Y.-J. Development of moisture-absorbing and antioxidant active packaging film based on poly (vinyl alcohol) incorporated with green tea extract and its effect on the quality of dried eel. *J. Food Process. Preserv.* **2018**, *42*, e13374. [CrossRef]
50. Floegel, A.; Kim, D.-O.; Chung, S.-J.; Koo, S.I.; Chun, O.K. Comparison of ABTS/DPPH assays to measure antioxidant capacity in popular antioxidant-rich US foods. *J. Food Compos. Anal.* **2011**, *24*, 1043–1048. [CrossRef]
51. Karaçelik, A.A.; Küçük, M.; Iskefiyeli, Z.; Aydemir, S.; De Smet, S.; Miserez, B.; Sandra, P. Antioxidant components of *Viburnum opulus* L. determined by on-line HPLC–UV–ABTS radical scavenging and LC–UV–ESI-MS methods. *Food Chem.* **2015**, *175*, 106–114. [CrossRef]
52. Rodrigo, M.J.; Alquézar, B.; Alós, E.; Lado, J.; Zacarías, L. Biochemical bases and molecular regulation of pigmentation in the peel of *Citrus* fruit. *Sci. Hortic.* **2013**, *163*, 46–62. [CrossRef]
53. Zhang, Y.; Liu, X.; Wang, Y.; Jiang, P.; Quek, S. Antibacterial activity and mechanism of cinnamon essential oil against *Escherichia coli* and *Staphylococcus aureus*. *Food Control* **2016**, *59*, 282–289. [CrossRef]
54. Herraiz-Carboné, M.; Cotillas, S.; Lacasa, E.; Sainz de Baranda, C.; Riquelme, E.; Cañizares, P.; Rodrigo, M.; Sáez, C. Are We Correctly Targeting the Research on Disinfection of Antibiotic-Resistant Bacteria (ARB)? *J. Clean. Prod.* **2021**, *320*, 128865. [CrossRef]
55. Shehata, M.G.; Awad, T.S.; Asker, D.H.; Abd El-Aziz, N.M.; Youssef, M.M. Antioxidant and antimicrobial activities and UPLC-ESI-MS/MS polyphenolic profile of sweet orange peel extracts. *Curr. Res. Food Sci.* **2021**, *4*, 326–335. [CrossRef] [PubMed]
56. Alexandre, E.M.; Silva, S.; Santos, S.A.; Silvestre, A.J.; Duarte, M.F.; Saraiva, J.A.; Pintado, M. Antimicrobial activity of pomegranate peel extracts performed by high pressure and enzymatic assisted extraction. *Food Res. Int.* **2019**, *115*, 167–176. [CrossRef]
57. Choi, S.-S.; Lee, S.-H.; Lee, K.-A. A comparative study of hesperetin, hesperidin and hesperidin glucoside: Antioxidant, anti-inflammatory, and antibacterial activities in vitro. *Antioxidants* **2022**, *11*, 1618. [CrossRef]
58. Riaz, A.; Lagnika, C.; Luo, H.; Dai, Z.; Nie, M.; Hashim, M.M.; Liu, C.; Song, J.; Li, D. Chitosan-based biodegradable active food packaging film containing Chinese chive (*Allium tuberosum*) root extract for food application. *Int. J. Biol. Macromol.* **2020**, *150*, 595–604. [CrossRef]
59. Shivangi, S.; Dorairaj, D.; Negi, P.S.; Shetty, N.P. Development and characterisation of a pectin-based edible film that contains mulberry leaf extract and its bio-active components. *Food Hydrocoll.* **2021**, *121*, 107046. [CrossRef]
60. Abshirini, M.; Saha, M.C.; Altan, M.C.; Liu, Y. Synthesis and characterization of hierarchical porous structure of polydimethylsiloxane (PDMS) sheets via two-step phase separation method. *Mater. Des.* **2021**, *212*, 110194. [CrossRef]

61. Abdelwahab, M.A.; Jacob, S.; Misra, M.; Mohanty, A.K. Super-tough sustainable biobased composites from polylactide bioplastic and lignin for bio-elastomer application. *Polymer* **2021**, *212*, 123153. [CrossRef]
62. da Rosa, G.S.; Vanga, S.K.; Gariepy, Y.; Raghavan, V. Development of Biodegradable Films with Improved Antioxidant Properties Based on the Addition of Carrageenan Containing Olive Leaf Extract for Food Packaging Applications. *J. Polym. Environ.* **2020**, *28*, 123–130. [CrossRef]
63. Song, Z.; Xiao, H.; Zhao, Y. Hydrophobic-modified nano-cellulose fiber/PLA biodegradable composites for lowering water vapor transmission rate (WVTR) of paper. *Carbohydr. Polym.* **2014**, *111*, 442–448. [CrossRef] [PubMed]
64. El Bourakadi, K.; el Kacem Qaiss, A.; Bouhfid, R. Bio-films based on alginate/modified clay through spray drying: Mechanical, rheological, morphological, and transport properties for potential use as active food packaging. *Int. J. Biol. Macromol.* **2022**, *210*, 663–668. [CrossRef] [PubMed]
65. Cerqueira, M.A.; Souza, B.; Martins, J.T.; Teixeira, J.A.; Vicente, A.A. Seed extracts of *Gleditsia triacanthos*: Functional properties evaluation and incorporation into galactomannan films. *Food Res. Int.* **2010**, *43*, 2031–2038. [CrossRef]