

MANDARIN PEEL AS AN AUSPICIOUS FUNCTIONAL FILLER FOR POLYMER COMPOSITES

Aleksander Hejna^{1,*}, Mateusz Barczewski², Paulina Kosmela¹, Joanna Aniśko², Olga Mysiukiewicz², Mariusz Marć³

¹ Department of Polymer Technology, Gdańsk University of Technology, Narutowicza 11/12 80-233 Gdańsk, Poland

² Institute of Materials Technology, Poznań University of Technology, Piotrowo 3, 61-138 Poznań, Poland

³ Department of Analytical Chemistry, Gdańsk University of Technology, Narutowicza 11/12 80-233 Gdańsk, Poland

aleksander.hejna@pg.gda.pl

This work describes the application of mandarin peel (MP) as a waste filler for high-density polyethylene (HDPE) composites. The main goal was to investigate the impact of the filler's essential oils, which include multiple terpenes and terpenoids, on the processing, physicochemical, mechanical, and thermal properties of the composites as a function of different filler content (1 – 10 wt%), as well as its effect on the color and volatile organic compounds emissions of the composites. At small loadings, MP can be considered an efficient filler for wood-polymer composites, enhancing their flowability, tensile strength, and thermal stability. In addition, it may act as a colorant and aroma compound for polymer materials, and can enhance the thermooxidative resistance of composites. The oxidation induction time was increased from 20 min for HDPE up to 62 min for the composites with 10 wt% filler. The research results demonstrate the application of MP not only in the production of highly-filled composites, but also as an additive that significantly enhances the performance of composites at low concentrations.

Keywords: Polymer composites; mandarin peel; recycling; antioxidant activity, volatile organic compounds

КОРА ОД МАНДАРИНА КАКО ПОВОЛНО ФУНКЦИОНАЛНО ПОЛНИЛО ЗА ПОЛИМЕРНИ КОМПОЗИТИ

Овој труд ја опишува примената на кора од мандарина (MP) како полнило од отпад за композити од полиетилен со висока густина (HDPE). Главната цел беше да се истражи влијанието на есенцијалните масла на полнилото, кои вклучуваат повеќе терпени и терпеноиди, врз обработката, физичко-хемиските, механичките и термичките својства на композитите како функција од различната содржина на полнилото (1 - 10% wt), како и неговото влијание врз бојата и емисијата на испарливите органски соединенија на композитите. При мали полнења, MP може да се смета за ефикасно полнило за дрво-полимер композити, зајакнувајќи ја нивната проточност, јачина на истегнување и термичка стабилност. Покрај тоа, може да дејствува како обојувач и соединение за арома на полимерните материјали и може да ја подобри термооксидативната отпорност на композитите. Времето на индукција на оксидација беше зголемено од 20 min за HDPE до 62 min за композитите со 10% wt полнило. Резултатите од истражувањето ја демонстрираат примената на MP не само во производството на високо наполнети композити, туку и како додаток кој значително ги подобрува перформансите на композитите при ниски концентрации.

Клучни зборови: Полимерни композити; кора од мандарина; рециклирање; антиоксидантна активност, испарливи органски соединенија

1. INTRODUCTION

Nowadays, the food industry generates a huge amount of by-products and waste. According to the Food and Agriculture Organization of the United Nations, the global volume of food waste is estimated at 1.6 billion tonnes of "primary product equivalents" [1]. Moreover, a significant amount of non-edible by-products are generated during the processing and manufacturing of various food products. A good representative example is fruit processing aimed at manufacturing juices, jams, or jellies. Depending on the fruit, the share of by-products ranges from 10 to 60 wt%. Processing of dates generates mainly date pits, which account for approximately 10 wt% of the fruit mass [2]. Production of wine, which uses over 80 % of the total grape crop, results in the generation of grape pomace, representing about 20 % of the original fruit mass [3]. The main by-product of apple juice manufacturing is apple pomace, which accounts for approximately 25 % of the processed apples [4]. Banana processing generates higher amounts of by-products because the peel accounts for approximately 30 % of the fruit [5]. The record holder for the amount of by-products generated is mango, whose peel and stones account for 35 to 60 % of the total fruit weight [6].

Considering the global production volume in the food sector, vast amounts of by-products are generated and often not recycled. The share of wasted by-products may even reach 65 % [7]. At the same time, the majority of the food processing by-products, including those from fruits, may be incorporated into polymer technology, mainly as fillers for polymer composites, but also as antioxidants, antimicrobial agents, plasticizers, or colorants [8–10]. Keeping in mind the ongoing trends and law regulations related to the environmental impact of polymer technology [11], the application of food industry by-products may reduce the use of synthetic compounds. Also, the incorporation of raw materials originating from natural sources may enhance the biodegradability of polymer materials [12].

In this paper, we aimed to investigate the potential applications of mandarin peels in polymer technology. This particular by-product was selected because it is generated in very high amounts and shows an exciting chemical composition [13]. It contains noticeable amounts of fiber, mainly cellulose, lignin, and hemicellulose, which makes it relatively similar to conventional materials commonly applied as fillers for wood-polymer composites, e.g., wood flour [14, 15]. Simultaneously, the mandarin peel contains around 4 wt% of com-

pounds often referred to as essential oils [16, 17]. Except for the lipids, essential oils also include chemical compounds, which may provide additional features to the mandarin peel. A significant component of the essential oils is terpenes and terpenoids, mostly D-limonene, γ -terpinene, β -myrcene, linalool, and α -pinene [18]. Except for terpenes and terpenoids, noticeable amounts of octanoic acid, octanal, and decanal were noted. Generally, the composition of mandarin peel oils is affected by the maturity of the fruit [19]. Higher amounts of aromatic compounds have been detected in "green" fruits, while mature fruits contained mainly limonene [20]. These compounds often show antioxidant, antimicrobial, or antifungal activity.

Several studies have discussed the possibility of using dried orange peel waste as a waste filler for manufacturing thermoplastic composites based on polymers, such as low-density polyethylene (LDPE) [21, 22] or poly(vinyl alcohol) (PVA) [23], as well as thermoset polymers [24]. However, there have been no studies on mandarin peels applied as a functional waste filler for polyolefin-based composites. Based on the reported beneficial antioxidant activity of orange peel solid waste on polyethylene films [25], it can be hypothesized that a comparable effect may be achieved in the case of using other dried and ground citrus peels as an additive for polyolefins, especially polyethylene. This polymer was selected for the study due to its many industrial applications. Nevertheless, its use should be reduced, so it is essential to investigate the possibility of its partial replacement by various biodegradable materials from renewable resources, such as fruit waste [26]. Therefore, we decided to examine the mandarin peel as a functional filler for polymer composites. The influence of their incorporation (from 1 to 10 wt%) into a high-density polyethylene matrix on the processing, mechanical, and thermal properties were investigated. Moreover, in addition to the above-mentioned conventional analyses, we also examined the impact of the mandarin peel on the color of the prepared composites and assessed the volatile organic compounds emissions.

2. EXPERIMENTAL SECTION

2.1. Materials

High-density polyethylene (HDPE), type M300054, obtained from SABIC (The Netherlands), was applied as a matrix to prepare the investigated composites. According to producer data, its density is 0.954 g/cm³ and is characterized by a

melt flow rate of 30 g/10 min (190 °C, 2.16 kg). Mandarin peel was generated during the consumption of mandarin oranges, which were acquired from the local market supplier. It was characterized by a density of 1.498 g/cm³ after being subjected to a drying process. Before melt compounding, the

filler was ground using a Retsch GM 200 knife grinder and dried at 80 °C for 24 hours. An image of ground mandarin peel taken with an optical microscope and the particle size distribution evaluated based on the microscopic images are presented in Figure 1.

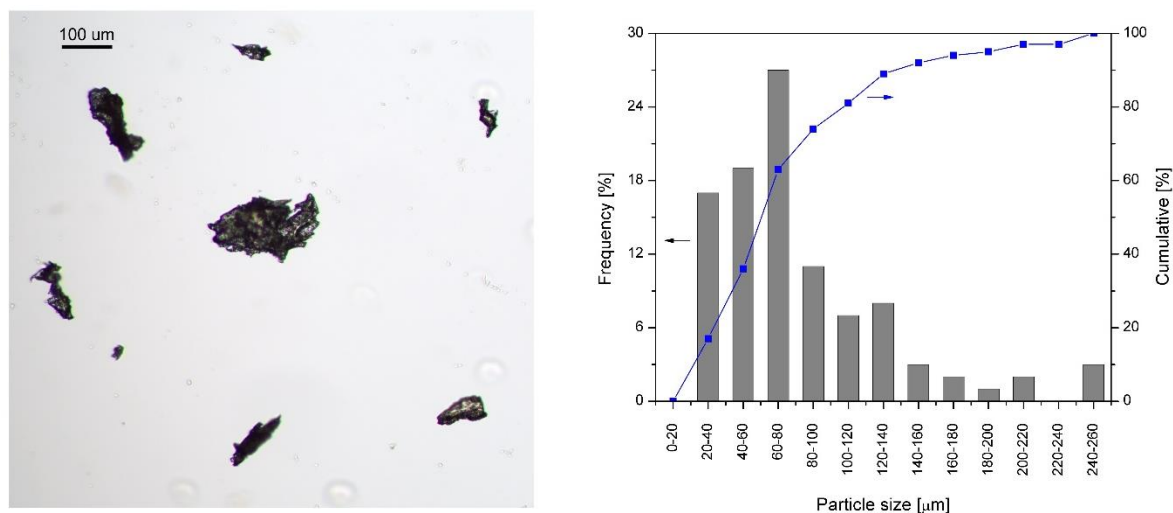


Fig 1. Microscope image of ground mandarin peel and particle size distribution of the filler

2.2. Preparation of polymer composites

The composites were prepared by mixing in a molten state. The HDPE pellets were pulverized into a fine powder using a Tria 25-16/TC-SL high-speed knife grinder to facilitate a more efficient physical mixing process with powdered organic filler. The polymeric powder was then preliminary mixed with 1, 2, 5, or 10 wt% filler. Prior to mixing in a molten state, the compositions were dried in a laboratory cabinet dryer Memmert ULE 500 for 12 h at 70 °C. The mixtures were processed using a ZAMAK EH16.2D co-rotating twin-screw extruder operating at 100 rpm with a maximum processing temperature of 190 °C. The obtained materials were cooled in forced airflow and pelletized. The resulting composites were then compression molded at 170 °C and 4.9 MPa for 2 min and then kept under pressure at room temperature for another 5 min to solidify the material. The unfilled HDPE was processed along with its composites. The specimens were named in reference to their filler content, for example, PE and PE/XMP, where X stands for the filler content.

2.3. Characterization techniques

The presence of the essential oil contained in the mandarin peel was determined by Fourier transform infrared (FT-IR) spectroscopy. First, non-polar

liquid components were extracted from the citrus peel powder by the solvent method. The sample of 2 g of the filler was added to 50 mL of petroleum ether and mixed at 40 °C for 15 min using a magnetic stirrer operating at 300 rpm. The mixture was filtered to remove the solid particles and collect the supernatant, which was dried at 70 °C for 2 hours in a laboratory cabinet dryer so the solvent could evaporate. The obtained extract was characterized using a Jasco 4600 FT/IR apparatus operating in the attenuated total reflection (ATR) mode. A total of 32 scans were collected with a resolution of 4 cm⁻¹.

Melt flow index (MFI) of the composites was investigated using a Zwick mFlow plastometer according to ASTM D1238 standard (190 °C, 2.16 kg).

The specific weight of the prepared composites was determined using an Ultrapycc 5000 Foam gas pycnometer from Anton Paar (Poland). The following measurement settings were applied: gas – helium; target pressure – 18.0 psi; flow direction – sample first; temperature control – on; target temperature – 20.0 °C; flow mode – monolith; cell size – small, 10 cm³; preparation mode – flow, 0.5 min; the number of runs – 5.

Microscopic observations of the filler, as well as polyethylene and its composites, were performed using an optical microscope Opta-Tech SK Series microscope. The obtained pictures were digitally edited and registered using dedicated software.

The tensile strength and elongation at break were estimated following ISO 527 for dumbbell samples type 1BA. Tensile tests were performed on a Zwick/Roell Z020 apparatus with a cell load capacity of 20 kN at a constant speed of 20 mm/min.

To determine the crystallization and melting temperatures, as well as the crystalline structure of the analyzed composites, differential scanning calorimetry (DSC) analysis was applied. The 5 mg samples were placed in aluminum crucibles with pierced lids. They were heated from 20 to 250 °C with a heating rate of 10 °C/min and then cooled back to the initial temperature with a cooling rate of 10 °C/min. The heating/cooling cycle was performed twice in order to erase the thermal history of the polymers during the first heating. The measurements were conducted using a Netzsch 204F1 Phoenix apparatus in an inert atmosphere of nitrogen. The crystallinity degree X_c of the samples was calculated using formula (1):

$$X_c = \frac{\Delta H_m}{(1-\theta) \cdot \Delta H_{m100\%}} \cdot 100\% \quad (1)$$

where: ΔH_m – melting enthalpy of a sample, $\Delta H_{m100\%}$ – melting enthalpy of 100 % crystalline polyethylene, $\Delta H_{m100\%} = 288$ J/g, θ – filler weight fraction.

The thermal properties were determined by thermogravimetric analysis (TGA) with the temperature set between 30 °C and 900 °C at a heating rate of 10 °C/min under a nitrogen atmosphere using a TG 209 F1 Netzsch apparatus. 10 mg \pm 0.1 mg samples were placed in ceramic pans. The initial decomposition temperature T_i was determined as the temperature at which the mass loss was 5 %. The residual mass ($\Delta W\%$) was defined at about 900 °C. Additionally, thermal decomposition was measured at 10 % and 50 % mass losses (W10% and W50%).

According to the Commission Internationale de l'Eclairage (CIE), the color of the prepared composites was evaluated through $L^*a^*b^*$ coordinates [27]. In this system, L^* is the color lightness ($L^*=0$ for black and $L^*=100$ for white), a^* is the green(-) / red(+) axis, and b^* is the blue(-) / yellow(+) axis. Thirty tests of each sample were done and used for the determination of arithmetic mean values. The color was determined by optical spectroscopy using a HunterLab Miniscan MS/S-4000S spectrophotometer that was placed in a specially designed light trap chamber.

The following color parameters were determined based on the obtained results:

- total color difference parameter (ΔE^*) calculated according to the following equation (2) [28]:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (2)$$

- chroma (C) calculated according to equation (3):

$$C = (a^{*2} + b^{*2})^{\frac{1}{2}} \quad (3)$$

- hue (h) calculated according to equation (4):

$$h = \tan^{-1} \left(\frac{b^*}{a^*} \right) \quad (4)$$

Determined color parameters were also converted to the commonly used Adobe RGB color space defined by the three chromaticities of the red, green, and blue additive primaries [29]. Details about the mathematical operations required for conversion were presented in our previous work [30].

The emissions assessment of representative volatile organic compounds (VOCs) as well as the total amount of VOCs (TVOC parameter – the sum of all organic compounds, eluting between n-hexane and n-hexadecane on non-polar or slightly polar stationary phases of a capillary column using gas chromatography/flame ionization detector (GC-FID) and quantifying as toluene equivalents) [31] released to the gaseous phase from the investigated samples of polymer composites was performed by employing a microscale stationary emission chamber - the Micro-Chamber/Thermal Extractor™ (μ -CTE™ 250, Markes International, Inc) [32–34]. The studied polymer composites were weighed on an analytical balance on a glass Petri dish and placed inside a single stainless steel chamber. The average mass of the investigated plastic composite samples was 1.533 ± 0.025 g. Each sample containing a defined wt% of mandarin peel as a filler was investigated two times. The use of Petri dishes allowed potential contamination of the chambers' interior with potential residues of the studied samples to be avoided and the impact of the wall-memory effect on the final result of the determinations to be minimized. Before the emissions assessment studies, chambers were conditioned at 150 °C for 30 min under nitrogen gas flow to remove potential impurities.

The seasoning conditions of the investigated samples of polymer composites using the μ -CTE™ 250 system mentioned above were as follows: seasoning/conditioning temperature – 40 ± 0.5 °C; seasoning/conditioning time – 30 ± 0.5 min; inert (nitrogen, class 2.2) gas flow rate continually passing through the chamber – 15 ± 0.5 ml/min. At the outlet of each chamber, the stainless steel tube filled with Tenax TA sorption medium (60/80

mesh, Merck KGaA, Darmstadt, Germany) was attached to collect the analyte samples emitted to the gaseous phase from the studied materials. After the sampling stage, collected analytes were analyzed using a two-stage thermal desorption (TD) system (Markes Series 2 Thermal Desorption Systems; UNITY/TD-100 - equipped with multibed microtrap that ensures the determination of terpenes) combined with gas chromatography equipped with a

flame ionization detector (GC-FID). Moreover, in addition to the TD-GC-FID analysis, the samples of analytes emitted from the studied samples collected on the sorption medium were analyzed using the TD-GC system combined with a mass spectrometry detector (MSD). Detailed information about the working parameters of the applied analytical equipment are listed in Table 1.

Table 1

General information about the operating parameters of the applied GC-FID and GC-MSD system

Separation and identification of selected chemical compounds retained on the applied sorption medium		
Type of gas chromatograph	Agilent Technologies 6890	Agilent 7820A GC
Detector	Mass spectrometer (5873 Network Mass Selective Detector) working in a SCAN mode	Flame Ionization Detector Working temperature: 280 °C
Transfer line temperature	GC-MS transfer line: 300 °C TD-GC transfer line: 160 °C Ion source: 230 °C Quadrupole mass analyser: 150 °C	TD-GC transfer line: 180 °C
Type of capillary column	HP-1ms 30 m × 0.25 mm × 1 μm	DB-1 30 m × 0.32 mm × 5 μm
Helium flow rate	1.0 ml/min	2.0 ml/min
Oven temperature	50 °C by 1 min 10 °C/min to 120 °C, hold 2 min 15 °C/min to 280 °C, hold 10 min	45 °C by 1 min 15 °C/min to 120 °C, hold 2 min 10 °C/min to 250 °C, hold 5 min
Data collecting software	CHEMSTATION	OpenLAB CDS ChemStation Workstation VL

The number of chemical compounds, especially the broad spectrum of terpenes emitted from the polymer composite samples, was estimated by using the TD-GC-FID system and the external standard (ESTD) method. The calibration solutions were prepared based on a commercially available reference standard solution containing 20 chemical compounds classified as terpenes (Cannabis Terpene Mix A certified reference material, 2000 μg/ml of each component in methanol, Supelco, USA). Five calibration reference solutions in 1 mL of methanol were prepared containing from 1 ng up to 200 ng of each measured terpene. The calibration process was performed employing the homemade laboratory device, which allows the desired amount of calibration solution to be introduced onto the sorption bed. Detailed information about the device and calibration procedure are listed elsewhere [35,36]. Each point of the calibration curve was repeated three times and analyzed under the same thermal desorption and chromatographic conditions as the real samples. As for the aliphatic hydrocarbons identified on the GC-MS system, the chromatograms that were obtained were compared with chromatograms obtained from the GC-FID system, and their amounts were calculated as a toluene equivalent. The calculated amounts of chemical compounds and the TVOC

parameter were corrected for the blank field value, which was evaluated after every measuring period. The estimated average recovery values of the investigated chemical compounds adsorbed on the Tenax TA do not exceed ± 5 %. The MDLs (method detection limits) were assessed based on the signal-to-noise ratio. The average value of the MQLs (method quantification limits), calculated as 3 × MDL, was 0.10 ng/g.

The oxidation induction time (OIT) of the analyzed composites was determined by differential scanning calorimetry (DSC) analysis. The 5 mg samples were placed in aluminum crucibles with pierced lids. They were heated from 20 to 190 °C with a heating rate of 20 °C/min in nitrogen, kept at 190 °C for 5 min in nitrogen, and then the gas was switched to oxygen and the time required for sample oxidation was measured. The measurements were conducted using a Netzsch 204F1 Phoenix apparatus.

3. RESULTS AND DISCUSSION

3.1. Presence of the essential oil in the mandarin peel

The FT-IR spectrum of the mandarin peel extract is presented in Figure 2. The assignment of the characteristic bands in the spectrum is shown in

Table 2. The mandarin peel extract's chemical composition is complex and is comprised of alkenes, alcohols, and esters, which can be found in citrus peel essential oil [37]. Even though the shape of the spectrum slightly differs from model spectra obtained by Manaila et al. for orange, lemon, grapefruit, or pomelo [37], it can be concluded that the filler used in the study contains small amounts of the natural essential oil, which can have an anti-oxidizing [38] or plasticizing influence on the polymeric matrix [39]. Moreover, the presence of the non-polar organic compounds in the mandarin peel powder is believed to promote its adhesion to the hydrophobic polyethylene.

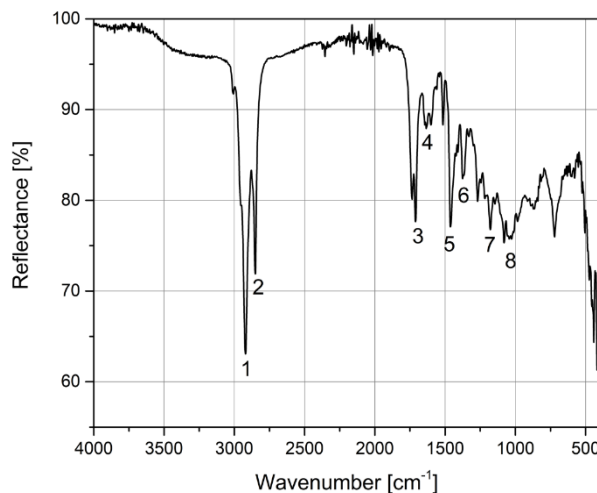


Fig. 2. FT-IR ATR spectrum of the mandarin peel extract

Table 2

Assignment of the characteristic bands observed in the mandarin peel extract

Band number	Wavenumber, cm^{-1}	Assignment
1	2920	CH_2 stretching [37]
2	2850	C-H stretching [37]
3	1710	C=O stretching (aldehyde or ester carbonyl groups) [38]
4	1634	C=C stretching (alkenes) [40]
5	1462	C-H bending (alkenes) [40]
6	1374	C-H bending and OH bending (phenol or tertiary alcohol) [37]
7	1177	C-O stretching (tertiary alcohols) [37]
8	1050	C-O stretching (primary alcohol), C-O-C stretching (alkyl-substituted alcohol) [37]

3.2. Mandarin peel as a conventional filler for wood-polymer composites

Figure 3 presents the influence of the mandarin peel content on the melt flow properties of composites. It can be seen that, for up to 5 wt% loading of the filler, the flowability of the neat matrix was hardly affected. Such an effect is rarely observed when lignocellulose materials, which contain high amounts of fiber, are incorporated [41]. In the case of mandarin peels, it is related to the content of oils in the material, which act as a plasticizer for the polymer matrix. The observed effect can be considered beneficial because incorporating the filler in the analyzed amounts hardly affect the material's flowability. Therefore, it can be efficiently processed without a decrease in process throughput. Similar effects have also been noted in other works related to the use of food waste containing oils, e.g., linseed cake [42].

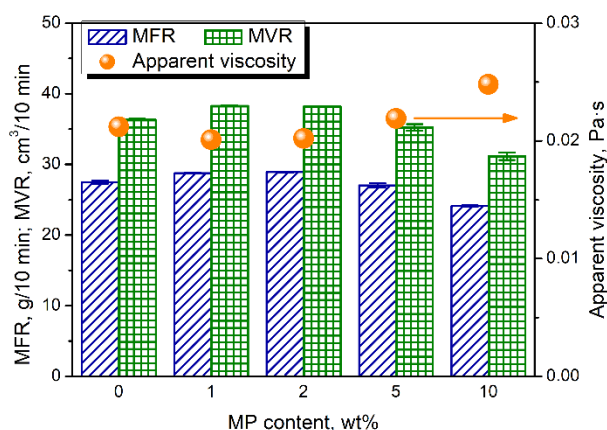


Fig. 3. Melt flow properties of prepared composites

Figure 4 presents the values of the experimental and theoretical values of composites density based on the density of neat matrix and mandarin peel applied as a filler. Theoretical values were calculated according to formula (5):

$$\rho_{theo} = \rho_m \cdot (1 - \varphi) + \rho_f \cdot \varphi \quad (5)$$

where: ρ_{theo} – theoretical density of the composite, g/cm³; ρ_m – density of the matrix, g/cm³; ρ_f – density of the filler, g/cm³; φ – a volume fraction of the filler.

Using obtained values of the density, the composite's porosity was calculated using equation (6):

$$p = \frac{\rho_{theo} - \rho_{exp}}{\rho_{theo}} \cdot 100\% \quad (6)$$

where: p – porosity of the material, % and ρ_{exp} – an experimental value of density of composite, g/cm³.

The increasing values of the composite density are related to the higher density of the filler (1.498 g/cm³) compared to the polyethylene matrix (0.945 g/cm³). This effect is commonly observed for polymer composites because the densities of most polymer matrices are often noticeably lower than most natural and mineral fillers [43]. Nevertheless, despite the increase in density, the incorporation of up to 10 wt% mandarin peel did not exceed 0.997 g/cm³, which means that the prepared materials exhibit a lower density than water. Such an effect is essential during the recycling of plastics because it enables easy separation of polyethylene and polypropylene from other higher-density polymers [44].

Differences between the theoretical and measured values of the composite density lead to the porosity of the structure. Such an effect is associated with the air inclusions during processing and points to imperfect interfacial adhesion. The presented case can be associated with the hydrophilic character of the fiber-part of the mandarin peel and the polyethylene matrix's hydrophobic character. Generally, porosity may noticeably affect the performance of composite materials, but for the discussed materials, its values are relatively low [45].

Figure 5 presents the optical microscope images of composite samples using two techniques. To determine the dispersion of the filler in the polymer matrix, photographs were taken in transmitted light (top photos) on compression molded samples with a thickness of 1 mm, and photos of composite cross-section fractures were taken in reflected light. Based on the analyses performed, no macroscopic porosity was noted in the composite structure, which is in line with the density-based porosity evaluation. Rather, the calculated amount of

composite porosity may result from the structure of the lignocellulosic filler in its internal porosity [46]. The microstructure analysis also confirms the correct distribution of the filler in the polyethylene matrix.

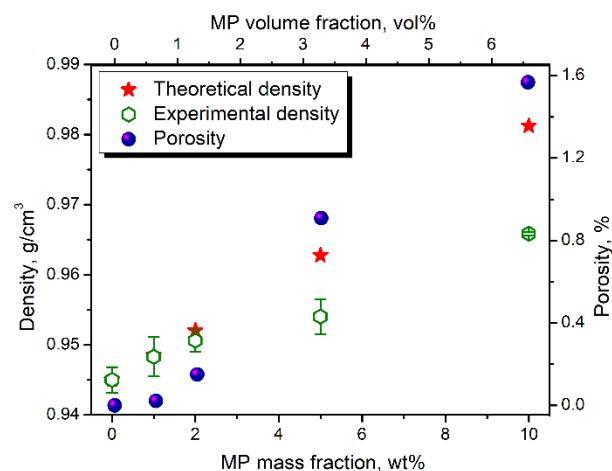


Fig. 4. Theoretical and experimental density and porosity values of prepared composites.

Figure 6 presents the impact of mandarin peel content on the mechanical performance of the prepared composites. It can be seen that the introduction of analyzed filler into a polyethylene matrix did not cause a very significant drop in the tensile performance. The increase in composite stiffness caused by the filler's higher share results in the reinforcing effect of rigid lignocellulosic particles on the polymeric matrix [47]. Moreover, as mentioned above, many natural fillers containing noticeable amounts of cellulose and lignin often show low compatibility with non-polar PE matrix, leading to the deterioration in the composite strength [48]. The presence of filler particles causes stress accumulation during the transfer of mechanical loads by the material. As a result of this phenomenon, the dispersed micrometric ground mandarin peel particles become micro notches due to polymer-filler interphase imperfections. It induces the phenomenon of composite fracture at much lower strain values during the mechanical load compared to unmodified polyethylene [49]. Similar effects have also been observed for similar composites, i.e., LLDPE filled with recycled wood, described by Moreno and Saron [50].

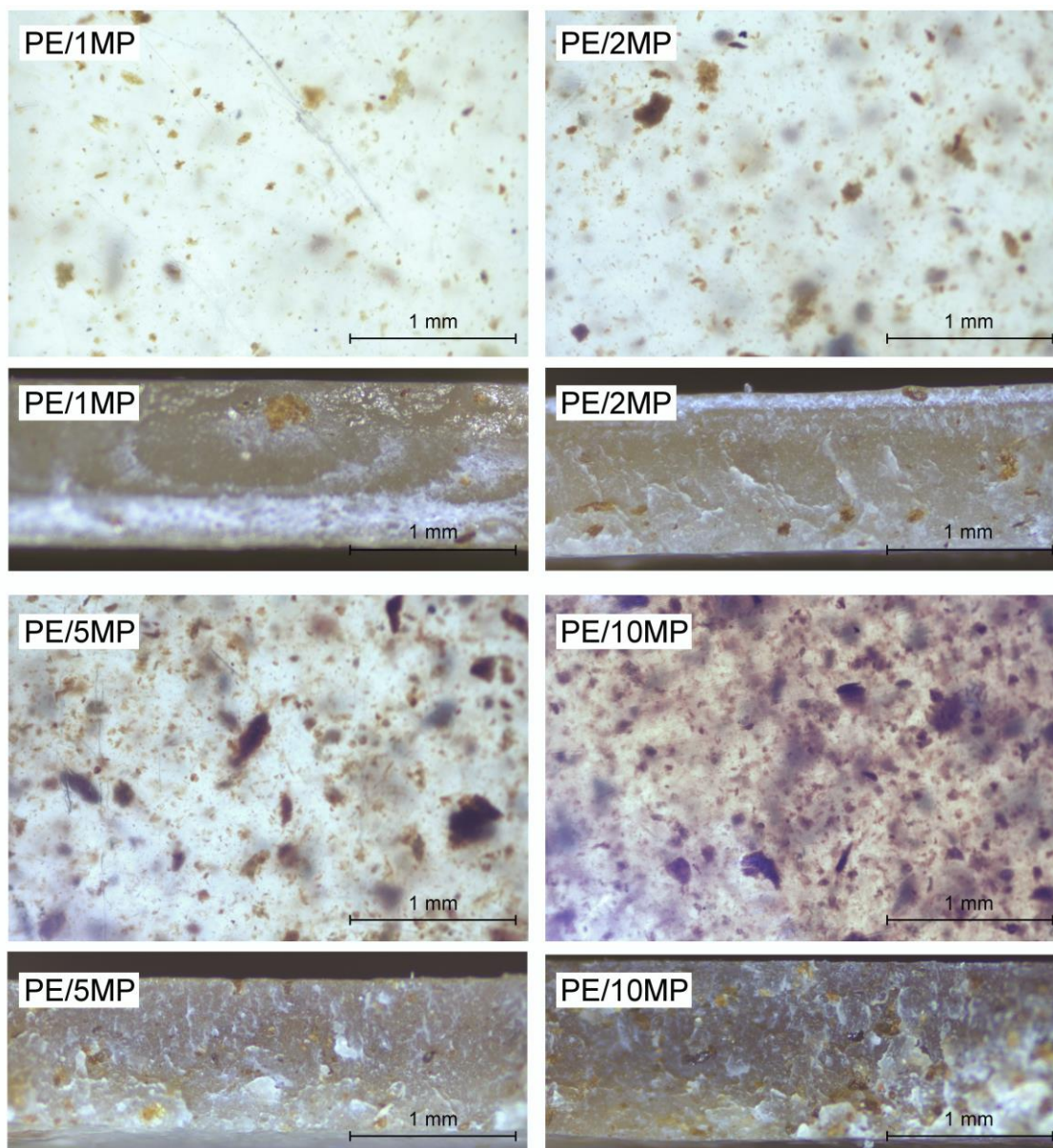


Fig. 5. Images of PE/MP composites taken using optical microscopy with transmitted (filler dispersion) and reflected light (fractured cross-section of the sample).

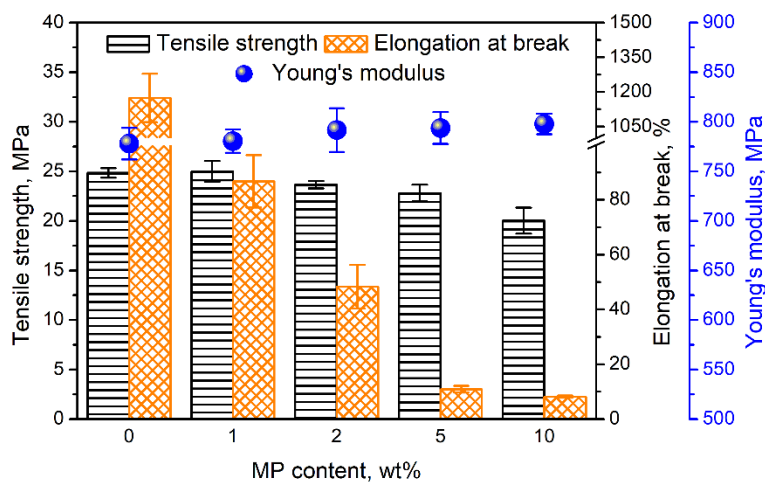


Fig. 6. Mechanical performance of prepared PE/MP composites

3.3. Thermal properties of PE-MP composites

Figure 7 shows DSC thermograms obtained from DSC experiments during the first cooling and second heating of polyethylene and its composites. Additional detailed thermal properties, such as the temperature of crystallization (T_c) and melting (T_m), melting enthalpy (ΔH_m), and crystallinity (X_c), are collectively presented in Table 2. The addition of MP did not cause significant changes in the melting temperature, while a slight upward trend was noted in the case of the crystallization temperature. For all tested samples, a second almost negligible exothermic peak at 76 °C was observed. A similar effect was observed in other studies [51, 52]. According to Mohammadi [51], the separate second crystallization broad peak at a lower temperature suggests the presence of crystallites with various thicknesses. The double crystallization peaks in polyethylene usually indicate the effect of chain branches in their structure, which form less stable crystals at lower temperature values. The DSC cooling curve in the case of the

composite containing 10 wt% of the MP showed a different shape, with a visible change in the thermogram slope after reaching the peak. Despite changes in the signal intensity and peak shift to higher temperature values, composite materials did not broaden the exothermic peaks. The higher the MP content, the higher the T_c value. This may indicate the nucleating effect of the ground mandarin peel. Due to the increased ability of HDPE to form a crystalline structure compared to polyethylene grades with lower density resulting from a higher number of side branches, the incorporation of fillers does not usually lead to significant heterogeneous nucleation effects [53]. Therefore, a lack of significant changes in the composite's crystallinity compared to the unmodified polymer is understandable. Simultaneously, it should be emphasized that the reduction of the melting enthalpy of the composite can be interpreted as a beneficial effect of the modification because it may be translated to power and money savings during melt processing by extrusion or injection molding processes [54].

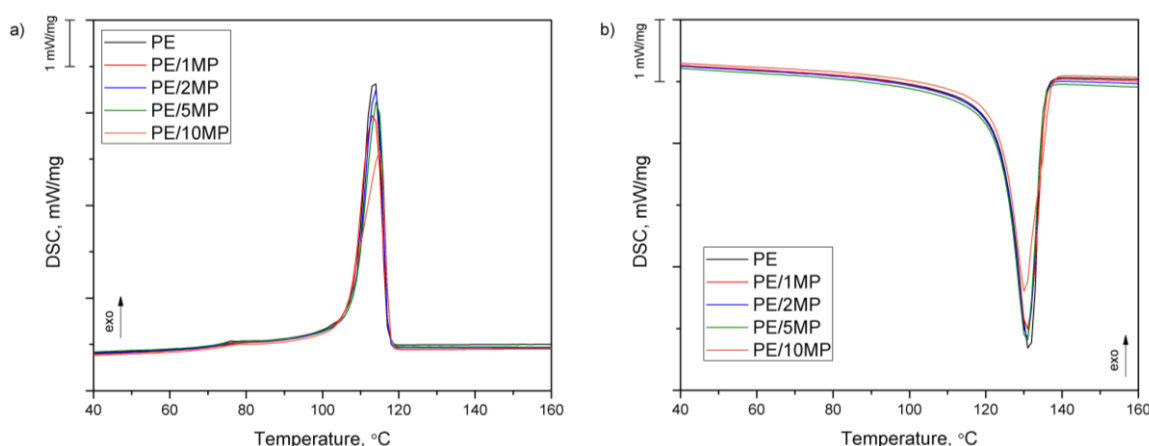


Fig. 7. DSC curves obtained during first cooling (a) and second heating (b) of PE and PE-MP composites

Table 3

Thermal parameters from DSC experiments

Sample	T_c , °C	T_m , °C	ΔH_m , J/g	X_c , %
PE	113.4	131.3	227.1	78.8
PE/1MP	113.3	130.8	226.3	79.4
PE/2MP	113.9	130.8	216.7	76.8
PE/5MP	114.3	130.6	217.0	79.3
PE/10MP	114.9	130.3	201.4	77.7

Figure 8 shows TG and DTG curves for PE and PE-MP composites. The curve representing the mandarin peel's thermal degradation process shows

three stages of decomposition, which lead to three peaks in the DTG curve. The first one is at a temperature of 61.5 °C, the second at 203.1 °C, and the third at 327.3 °C. They correspond to water vaporization and the decomposition of pectin, hemicelluloses, and cellulose, respectively [55]. The addition of mandarin peels to PE did not affect any changes in decomposition temperatures. All temperatures of 5, 10, and 50 % mass losses of PE with mandarin peels did not change in comparison to PE. The same relationship occurs in the DTG maximum peaks. All data are collectively presented in Table 4, including the initial decomposition temperature T_i , thermal decomposition at 10 % and 50 % mass

losses ($W_{10\%}$, $W_{50\%}$), and residual mass ($\Delta W_{\%}$) DTG peak value. Residual mass of HDPE/mandarine composites increases with increasing mandarin peel content. The residual mass of mandarin peel is 22.14 %. Adding up to 5 wt% of mandarin peel did not cause a significant decrease in thermal stability of the composites with a matrix of high-density polyethylene. The weight loss of about 200 °C, characteristic for MP, was recorded only for the material containing the high-

est natural filler concentration. However, it should be emphasized that, assuming a 5 % mass loss as a criterion for thermal degradation, all composite samples showed comparable properties to the unmodified polymer. The presented values of residual mass, averaged from three measurements, differ from the expected values, mainly due to the nature of the measurement and the research sample's small volume.

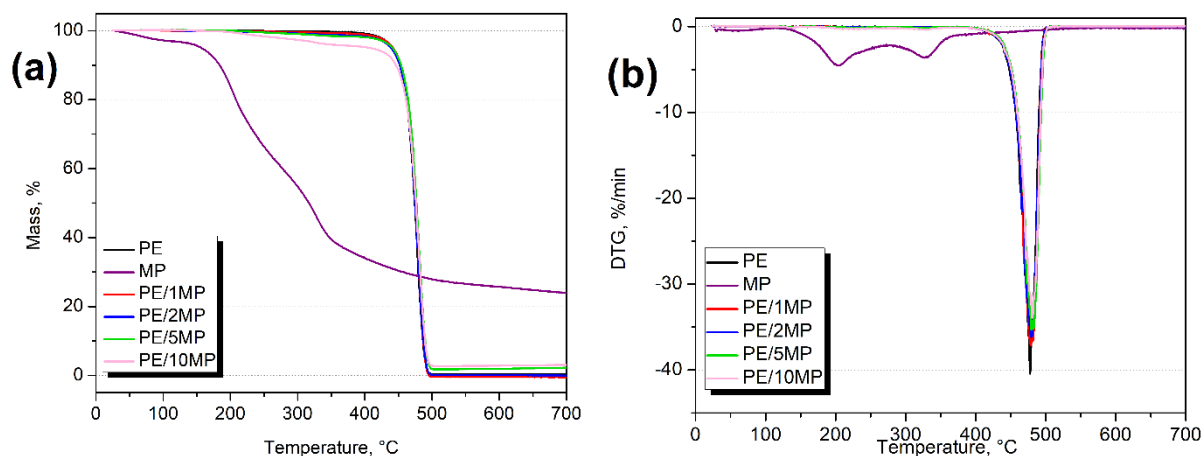


Fig. 8. TGA (a) and DTG (b) curves of HDPE/mandarin peel composites

Table 4

Thermal properties of PE and PE/MP composites from TGA

Sample	$T_i(W_{5\%})$, °C	$W_{10\%}$, °C	$W_{50\%}$, °C	$\Delta W_{\%}$, %	DTG
PE	441.6	452.2	474.3	0.32 (0.09)	478.0 °C; -40.91 %/min
MP	157.1	183.9	316.8	22.14 (0.44)	1) 61.5 °C; -0.51 %/min 2) 203.1 °C; -4.55 %/min 3) 327.3 °C; -3.65 %/min
PE/1MP	442.4	453.3	475.0	0.61 (0.12)	478.8 °C; -37.19 %/min
PE/2MP	439.2	451.8	474.9	0.92 (0.16)	479.5 °C; -36.17 %/min
PE/5MP	441.3	454.0	476.9	3.07 (0.17)	480.0 °C; -35.69 %/min
PE/10MP	407.4	446.2	476.0	3.81 (0.35)	481.0 °C; -34.07 %/min

(a) Standard deviation

3.4. Mandarin peel as a colorant

Figure 9 presents the impact of mandarin peel content on the color parameters of the prepared composites. The symbol colors represent the colors of the prepared PE/MP composites. The size of the symbols in the bubble charts represents the standard deviation of the particular values.

The incorporation of filler significantly affected the neat polyethylene's lightness, which de-

creased from an initial value of 85.3 to 27.3 for the 10 wt% MP loading. Such an effect is associated with the white color of neat unmodified high-density polyethylene material. Nevertheless, changes in lightness are not proportional to the mandarin peel content, suggesting that samples containing 10 wt% filler were almost saturated with its color.

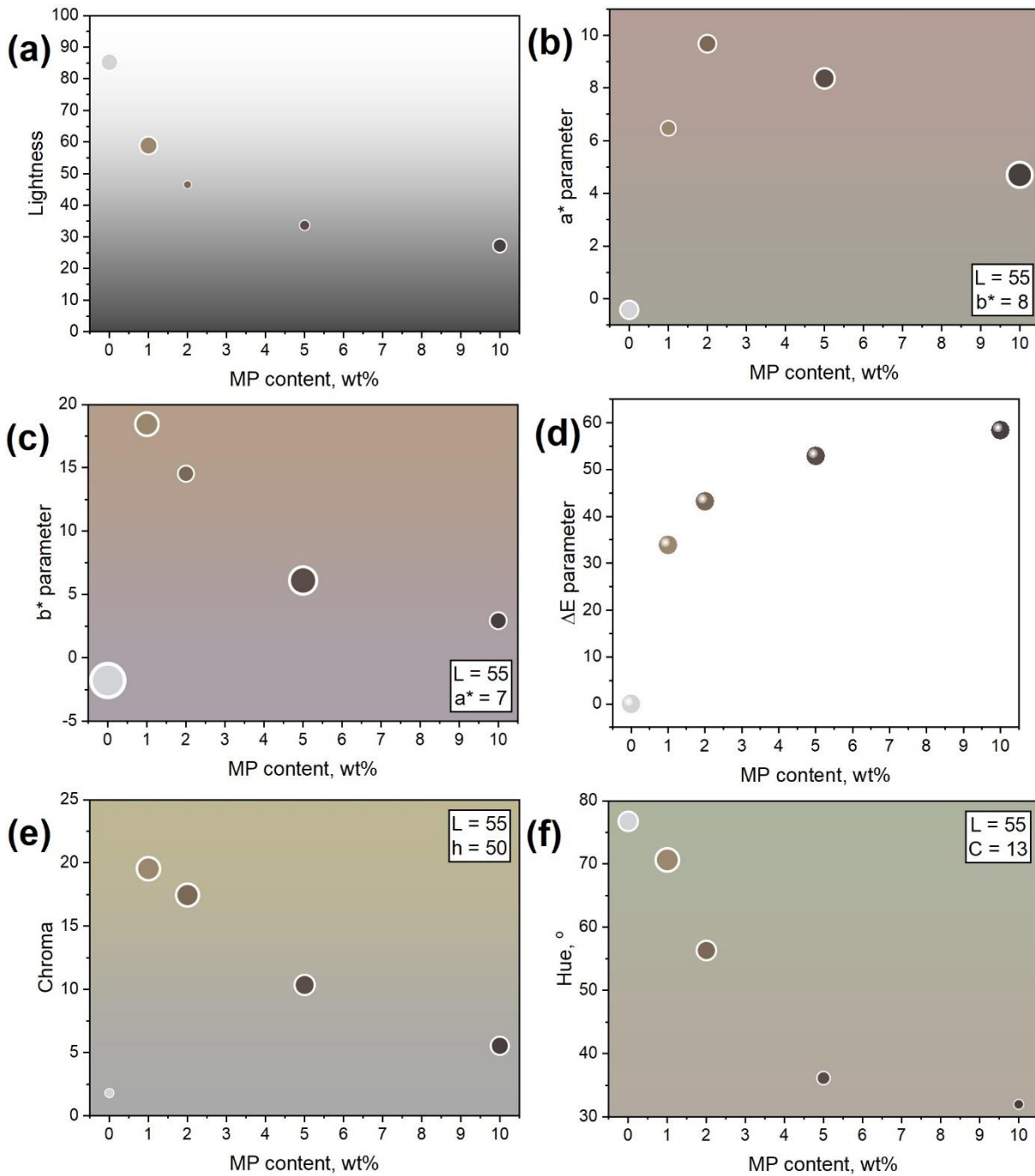


Fig. 9. The impact of MP filler content on (a) lightness, (b) a^* parameter, (c) b^* parameter, (d) ΔE parameter, (e) chroma, and (f) hue of prepared composites

In general, the addition of the mandarin peel caused the browning of the composites. Therefore, changes in the a^* and b^* parameters were noted. Typical brown colors are observed for the positive values of these parameters, mostly in the range of 0–20, but b^* values may be even a little higher [27]. Higher a^* values result in a red and magenta color, while higher b^* values lead to yellow tones. Nevertheless, due to the influence of multiple factors on color perception, e.g., lightness, the chang-

es of a^* and b^* parameters are often not directly proportional to the visible color changes, which can be seen in Fig. 6b and 6c. Moreover, in Fig. 10, there is a presented plot of b^* vs. a^* for prepared composites. It can be seen that there is no simple dependence between the MP loading and the color parameters of the prepared composites. Such an effect is associated with the increasing filler volume content and reduction in the interparticle distance, which impact the light scattering and

color perception. Similar effects related to the complex changes in color parameters were noted by other researchers, who investigated the generation of melanoidins or browning of various food products, e.g., meat or peaches [56–58].

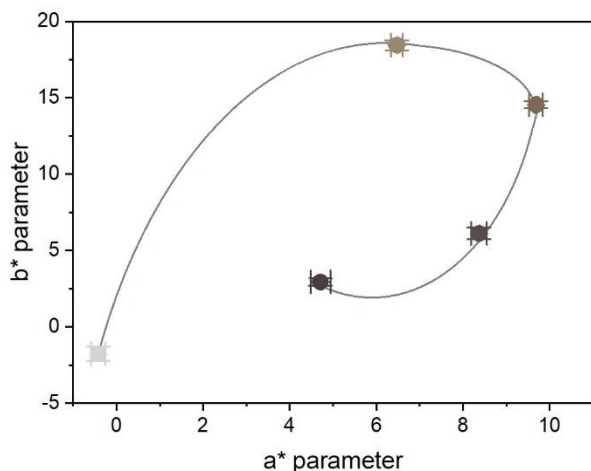


Fig. 10. The dependence between a^* and b^* parameters of prepared PE/MP composites

Values of the ΔE parameter are calculated on the basis of lightness, a^* , and b^* parameters, indicating large color variations resulting from the MP introduction. Similar to the lightness, changes in ΔE were not directly proportional to the filler content, which indicates the saturation of the composite color. Table 5 presents values of the color difference parameter between particular samples. The biggest color change was noted when 1 wt% mandarin peel was introduced into the polyethylene matrix. Quantitatively, a similar level of color difference was noted between PE and PE/1MP as between PE/1MP and PE/10MP samples. Nevertheless, in all cases, values of the ΔE parameter between every two samples were higher than 5.0, which indicates large color variations according to the PN-EN ISO 2813:2001 standard [28].

Table 5

Values of ΔE parameters calculated for prepared composites

Sample	Sample				
	PE	PE/1MP	PE/2MP	PE/5MP	PE/10MP
PE		33.9	43.2	52.9	58.4
PE/1MP	33.9		13.4	28.1	35.3
PE/2MP	43.2	13.4		15.4	23.0
PE/5MP	52.9	28.1	15.4		8.0
PE/10MP	58.4	35.3	23.0	8.0	

Chroma and hue are parameters directly affected by the values of a^* and b^* . Chroma is the measure of color saturation. Fig. 9e points to the low initial value of chroma noted for the neat PE, which is related to its white color. According to CIELab color space, colors from white to black, described as different shades of grey, are characterized by low chroma values. Therefore, the increased loading of mandarin peel resulting in browning and darkening of the composites was associated with an almost linear decrease in chroma from 19.55 (PE/1MP) to 5.55 (PE/10MP). The decrease of chroma resulting from the materials' browning was also noted by other researchers [59]. Similar to chroma, the hue also decreased with the mandarin peel content due to browning. According to the literature data, brown colors are characterized by hue values in the range of 30–70° [60]. Colors with hues close to 70° can already be characterized as orange (see Fig. 9f), while higher values are attributed to yellow colors.

In general, considering the color changes associated with the varying composition of the prepared composites, the mandarin peel can be considered an efficient colorant for polymer materials. Relatively low loadings up to 10 wt% can result in a broad range of colors from light orange to dark brown. Therefore, mandarin peels could be incorporated, e.g., into wood-polymer composites as a partial substitute of conventional fillers to adjust the color of the composites to the recipient's requirements.

3.5. Mandarin peel as an aroma compound

In Table 6, results of the assessment of volatile organic compounds emissions from prepared composites are presented. Except for dodecane and tetradecane, the compounds that were characteristic of the polyethylene applied as a polymer matrix were not included in Table 6. These two compounds were observed in the highest concentrations and accounted for the two most significant signals both in MS and FID analysis, which facilitated the peak assignment. In Fig. 11, a chromatogram obtained for the PE/10MP sample, which indicate powerful signals, is presented. Except for them, analysis with the MS detector revealed the presence of 2,2,4,6,6-pentamethyl heptane, undecane, tridecane, 3-methyltridecane, and hexadecane, which were noted as VOCs emitted from polyolefins by other researchers [51–63]. Peaks attributed to these molecules were characterized by a lower intensity, and their peak area did not exceed 4 %, so we were unable to assign these compounds to the particular signals detected by FID.

Table 6

The average values of the emission rate of selected VOCs released to the gaseous phase from the surface of studied polymer composites samples

Compound	Method	Unit	Sample			
			PE/1MP	PE/2MP	PE/5MP	PE/10MP
Total VOCs		ng/g	470.37±44.69	637.28±60.54	614.68±57.17	616.42±56.71
Dodecane	FID	ng/g	131.67±12.38	165.49±15.39	164.02±15.09	153.29±14.10
		%	27.99	25.97	26.68	24.87
	MS	%	20.06	22.90	20.00	23.93
Tetradecane	FID	ng/g	120.74±11.47	157.12±14.77	144.52±13.44	124.20±11.43
		%	25.67	24.66	23.51	20.15
	MS	%	15.42	16.77	15.65	17.09
α -Pinene		ng/g	0.28±0.027	0.60±0.056	1.45±0.13	3.86±0.36
		%	0.06	0.09	0.24	0.63
β -Pinene		ng/g	<MQL	1.74±0.05	0.55±0.01	2.57±0.13
		%	<MQL	0.27	0.09	0.42
γ -Terpinene		ng/g	14.83±1.41	15.68±1.47	14.43±1.34	18.53±1.70
		%	3.15	2.46	2.35	3.01
L-(-)-Fenchone		ng/g	1.91±0.18	2.67±0.25	2.75±0.26	5.14±0.47
		%	0.41	0.42	0.45	0.83
Fenchol		ng/g	0.63±0.06	1.83±0.17	2.34±0.22	4.20±0.39
		%	0.13	0.29	0.38	0.68
Nerolidol	FID	ng/g	<MQL	5.82±0.55	<MQL	5.62±0.52
		%	<MQL	0.91	<MQL	0.91
α -Cedrene		ng/g	<MQL	<MQL	13.67±1.27	<MQL
		%	<MQL	<MQL	2.22	<MQL
(-)- α -Bisabolol		ng/g	<MQL	<MQL	<MQL	1.53±0.14
		%	<MQL	<MQL	<MQL	0.25
Geranyl acetate		ng/g	5.96 ± 0.57	<MQL	<MQL	<MQL
		%	1.27	<MQL	<MQL	<MQL
Terpenes		ng/g	23.66±2.15	28.34±2.66	35.20±3.27	44.33±4.08
		%	5.03	4.45	5.73	7.19

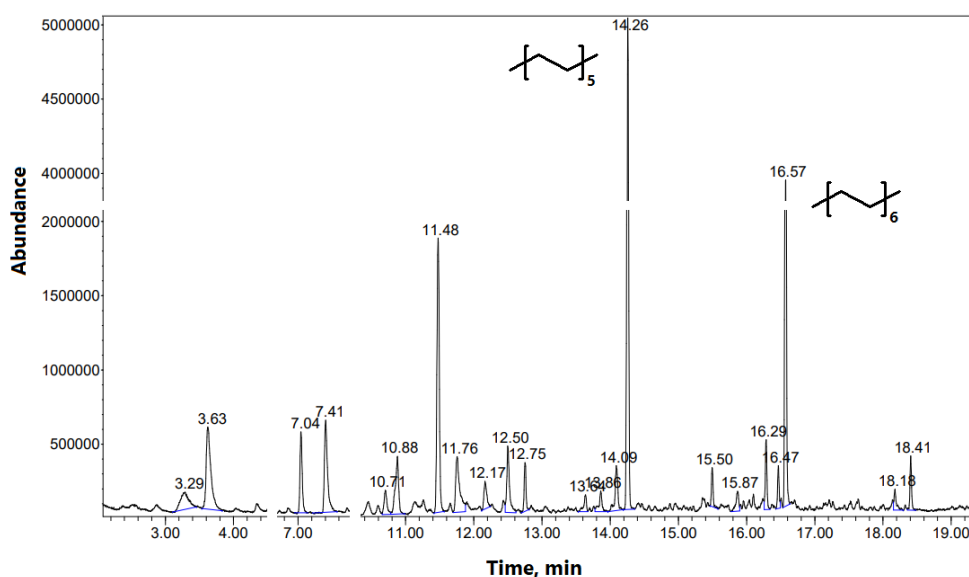


Fig. 11. The chromatogram obtained for the PE/10MP sample

In Table 6, quantitative values of the terpene emissions based on the proper analytical standard are also provided. Terpenes significantly contribute to the aroma and flavor of multiple natural products, e.g., fruits [64]. According to the FID analysis, the primary detected terpene was γ -terpinene, which has been detected in mandarin peel by other researchers [65]. This monoterpene is very popular in various plant materials, and its aroma is described as sweet and citrusy [66]. Such a description corresponds to the actual aroma of prepared granulates. This compound is also characterized by noticeable antioxidant activity [67]. Nevertheless, quantitatively, the amount of detected γ -terpinene was relatively low because of its susceptibility to oxidation [68].

Aside from γ -terpinene, other terpenes were also detected by FID, which also influenced the aroma profile of the prepared materials. Pinenes, fenchol, and L-(-)-fenchone contributed to the piney, herbal, and leafy aromas, while geranyl acetate, nerolidol, and (-)- α -bisabolol raised the sweet, flowery, and fruity notes [69]. It is also worth mentioning that these terpenes and terpenoids may show noticeable antioxidant activity, which may enhance the thermooxidative stability of the prepared composites [70, 71].

The analysis with the MS detector also pointed to the presence of small amounts of nonanal and 2-phenylbutan-2-ol. The nonanal was often detected in orange peels by other researchers [72]. It is characterized by a floral and orange aroma. The other compound belongs to the benzenoids

group, which has also been found in citrus peels [73].

In general, it can be seen that the amount of terpenes detected among VOCs increases with the mandarin peel content in the composites. It indicates that the composition of the composites affects its aroma profile. Such an effect should be considered very important for potential industrial applications of mandarin peels in polymer technology, e.g., as an additive aimed to mask the unpleasant odors in packaging materials or garbage bags. Moreover, after a more in-depth analysis, the prepared composites could be applied as the analytical standards for the particular chemical compounds present in the introduced filler, in this case, the mandarin peel. Nevertheless, this area still requires further research on the dependence of composite composition on released VOCs and the stability of emissions.

3.6. Mandarin peel as an antioxidant filler

As mentioned above, during the analysis of VOC emissions from prepared composites, compounds with reported antioxidant activity were detected [71]. Therefore, it could be presumed that mandarin peels may potentially act as a filler, enhancing the composite's thermooxidative stability. To examine its impact, oxidation induction times were determined. In Fig. 12, thermograms obtained during DSC analysis of composites are presented. Moreover, detailed values of OIT and time of maximum oxidation rate and time of oxidation are summarized in Table 7.

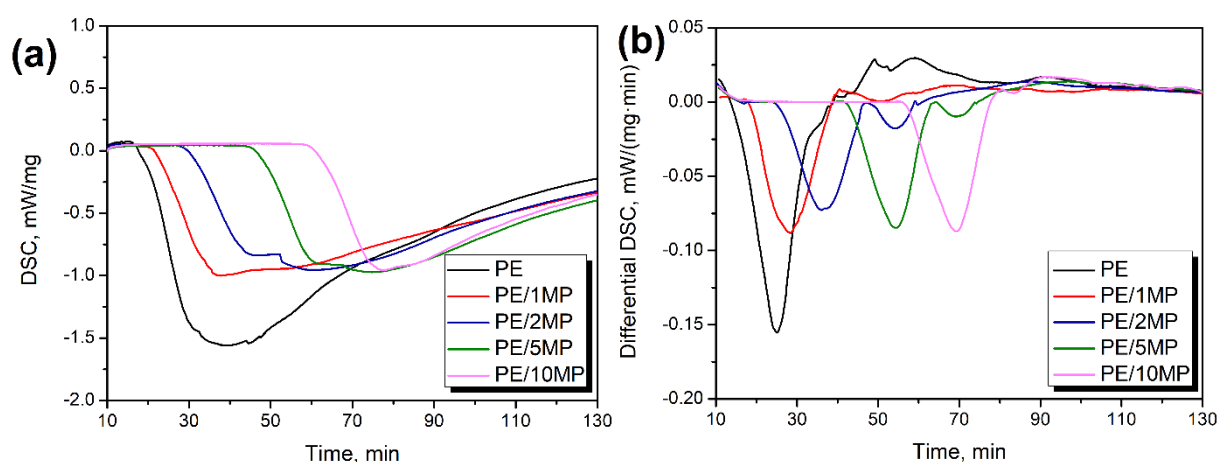


Fig. 12. The results of oxidation induction time analysis of prepared PE/MP composites

It can be seen that the incorporation of mandarin peels noticeably retarded the oxidation process. Even 1 wt% addition of filler caused a > 10

% rise of oxidation induction time. For 10 wt% filler loading, the extension of OIT from an initial 20.0 min to 62.9 min was noted. Simultaneously,

the applied filler acted not only as a retardant but also as an inhibitor of the oxidation process, which was expressed by the extension of the oxidation process.

Table 7

The results of the oxidation induction time analysis.

Sample	OIT, min	t_{\max} , min	Oxidation time, min
PE	20.0	25.0	8.8
PE/1MP	22.3	28.5	10.8
PE/2MP	30.7	36.3	11.8
PE/5MP	46.2	54.3	14.0
PE/10MP	62.9	69.3	11.6

4. CONCLUSIONS

In this paper, we aimed to investigate the impact of mandarin peels on the processing and performance of polyethylene-based composites. A comprehensive analysis of mandarin peel as a "conventional" lignocellulose filler for wood-polymer composites indicated that it could be efficiently applied in amounts up to 5 wt% for slightly enhancing the flowability, tensile strength, and thermal stability of the HDPE matrix. Such effects could be attributed to the presence of the essential oils in the mandarin peels, which include terpenes and terpenoids, mostly D-limonene, γ -terpinene, β -myrcene, linalool, and α -pinene. The essential oils may act as plasticizers, which improve the processing of the prepared composites. Moreover, mandarin peels may act as a natural colorant for polymer materials, whose presence even at low concentrations result in significant color changes of the polymer matrix. This indicates that the mandarin peel could be applied together with traditional lignocellulose fillers to adjust the appearance of the composites. Terpenes and terpenoids also show characteristic aromas, so mandarin peels may provide characteristic aromas for polymer composites, which can be useful in various industrial applications. Probably the most exciting and promising effect of incorporating mandarin peels is related to the enhancement of the thermooxidative resistance of the composites, as evidenced by the extension of the oxidation induction time. The introduction of only 2 wt% of this filler caused the OIT to increase from 20 to almost 31 min. Higher contents of 5 and 10 wt% resulted in OIT values of 46.2 and 62.9 minutes, respectively.

In conclusion, mandarin peels seem to be a very auspicious filler for polymer composites that may be introduced at relatively low loadings, significantly enhancing the thermooxidative stability of the material and providing changes in color and aroma without deteriorating mechanical performance. Further studies associated with this filler should be focused on evaluating changes in processing, structure, and mechanical and thermal properties of the composites subjected to accelerated aging tests. Moreover, combinations of mandarin peels with other fillers, which may provide improved reinforcement effects at higher loadings, appear to be an auspicious research direction.

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