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CHARACTERIZATION OF UHMWPE/PEG FILAMENT AND ITS SOLID FORM AFTER 3D-PRINTING WITH FUSED FILAMENT FABRICATION

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Abstract*. In recent decades, ultra-high molecular weight polyethylene (UHMWPE) has gained recognition and widespread utilization as an outstanding polymeric biomaterial for load-bearing components in artificial joints. Despite its promise, this material presents challenges in processing with additive manufacturing techniques. Efforts have been underway to investigate and enhance its printability with the additive manufacturing, aiming to facilitate the production of patient-specific implants. This study aims to prepare UHMWPE-based filament through extrusion and subsequently print it with fused filament fabrication (FFF) 3-dimensional (3D) printer to create a simple rectangular sheet. Characterizations by using Fourier-transform infra-red (FTIR) spectroscopy and differential scanning calorimetry (DSC) were conducted to assess the chemical compositions and thermal properties of the UHMWPE filament and its printed forms. The findings of this research demonstrate the feasibility of printing UHMWPE filament filament within the temperature range of 200 - 240 ℃. Analysis of the FTIR and DSC spectra reveals no evidence of impurities introduced during the preparation and printing processes that could alter its properties.*
Keywords: *UHMWPE/PEG; 3D-printing; fused filament fabrication; DSC; FTIR*

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE) has long been utilized as a polymeric biomaterial due to its biocompatibility and exceptional mechanical and tribological properties [1]. This material is commonly employed as a cushioning material in the acetabular cup of artificial hip joints [2] and as a tibial insert in knee joint prostheses [3]. To achieve the intricate shapes required for these applications, UHMWPE is typically machined [4]. Despite its success, machining processes for such patient-specific devices or products with customized geometries are currently deemed inefficient.

Presently, additive manufacturing (AM) has emerged as a frontier technology with promising prospects for fabricating solid materials with intricate geometries, including patient-

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specific biomedical implants [5], [6]. Among the various AM techniques, fused filament fabrication (FFF), also known as fused deposition modeling (FDM), stands out for its simplicity in producing solid 3D polymeric products [7]. The FFF principle revolves around depositing semi-molten filamentous material layer by layer until a predefined solid three-dimensional (3D) part is realized [7], [8]. Although the FFF technique has been generally used for the rapid prototyping purpose, the demands for functional products, including biomedical implants, fabricated by using this technique have been seen to increase in the recent years [5], [6], [9].

While promising, FFF technology still faces challenges due to the limited availability of raw filament types suitable for product realization. As of now, UHMWPE filament for FFF is scarcely found in the open market, primarily due to its low melt-flow index, making it less extrudable. To address this limitation, previous studies have explored blending UHMWPE with materials like high-density polyethylene (HDPE), polyethylene-glycol (PEG), and polypropylene (PP) to enhance its flowability during extrusion [10], [11]. In addition, PEG and paraffin oil (PO) have been investigated as additives to improve extrudability [12]. While recent efforts have successfully prepared UHMWPE filament [10]-[12], further research is needed to determine an appropriate size for FFF-printer nozzles. Moreover, successful printing of UHMWPE filament remains rarely discussed in the literature.

The aims of this study are to prepare UHMWPE-based filament through extrusion and subsequently print it with fused filament fabrication (FFF) 3-dimensional (3D) printer to create a simple rectangular sheet. Subsequently, a comprehensive set of physical and chemical characterizations was carried out to assess the feasibility of using this filament for FFF printing and to evaluate the properties of the resulting printed forms.

2. Methods

In this research, UHMWPE filament was initially prepared and subsequently printed using an FFF-based 3D printer to create a thin solid material composed of this substance. The UHMWPE filament was produced from chips generated during the turn-machining of this material. To ensure purity, all chips underwent sterilization in a pressurized heating pan at approximately 115°C for 30 minutes. A blend consisting of 5% polyethylene glycol (PEG) (Alphachem Ltd., Canada) with a molecular weight of 400 g·mol-1 and 10 phr paraffin oil (PO) (PT. Brataco, Indonesia) with a density ranging from 0.845 to 0.905 g·ml^{-1} was mixed with the sterilized UHMWPE chips using a BKBM-V0.4 planetary ball mill (Biobase, China) operating at 500 rpm for 30 minutes. The resulting blend was then extruded through a single-screw extruder at a temperature of 180°C and a screw speed of 11 rpm. To achieve a filament diameter close to the standard nozzle size of the FFF machine, which is 1.75 mm, the nozzle diameter of the extruder (D_e) was varied from 1.5 to

1.7 mm. Concurrently, the extruded filament diameter (D_f) was determined by measuring the diameters at 30 locations along the filament using a Vernier caliper (Mitutoyo, Japan).

The FFF printing process of the resulting UHMWPE filament was conducted using the CR-10S Pro V2 3D printer (Creality, China), with printing temperatures ranging from 200 to 240°C. Visual inspection of both the UHMWPE filament and its printed form was performed using the EVO10 electron microscope (Carl Zeiss, Germany). Subsequently, the chemistry and crystallinity of both the filament and its printed form were characterized using differential scanning calorimetry (DSC) in a nitrogen environment and Fourier-transform infrared (FTIR) spectroscopy (IRPrestige-21, Shimadzu Corp., Japan), respectively.

3. Results and Discussion

In this study, a filament composed of UHMWPE was successfully prepared using scrap material obtained from the turning machine of a light green rod material, as depicted in Figure 1(a)-(c). As illustrated in Figure 1(c), the extruded UHMWPE filament appeared solid and exhibited a darker green color compared to its raw material in Figure 1(a) and Figure 1(b). The electron microscopic image of the filament surface in Figure 1(d) revealed minimal defects, aside from some minor scratches likely caused by friction with the inner wall of the nozzle during the extrusion process.

Figure 1. (a) UHMWPE rod as the raw material, (b) UHMWPE scrap obtained from a turn-machining process of its rod shape, (c) the extruded UHMWPE filament and (d) surface morphology of the extruded filament

Table 1 illustrates the relationship between D_e and D_f values of the filament. Generally, Df increased with the use of a larger D_e. The extruder with D_e = 1.6 mm was able to produce filament with a diameter of 1.74 ± 0.13 mm, closely matching the commonly used nozzle size of FFF printers, i.e., 1.75 mm. The die-swell ratios of the extruded filament indicated swelling due to differences in material flow rate distributions inside and outside the nozzle upon extrusion [13]. While summarizing the influence of D_e value on the die-swell ratio of the UHMWPE filament is challenging, the ratios obtained in this study, i.e., 1.08 – 1.15, were notably similar to those of the extruded UHMWPE/HDPE blend, i.e., 1.135 – 1.209 [14]. Previous studies have highlighted the consistency of resulting filament diameter as a common issue during the extrusion process. For example, Chong *et al*. [15] observed swelling in the resulting diameter of filaments produced by extruding high-density polyethylene (HDPE) flakes, i.e., D_e = 3.17 mm compared to its die diameter (D_e) of 3 mm [15].

Table 1. The effect of extruder nozzle sizes on the diameters and the die-swell ratios of extruded UHMWPE filaments

Extruder's nozzle diameter, D_e (mm)	1.5	1.6	1.7
UHMWPE filament diameter, D_f (mm)	1.68 ± 0.18	1.74 ± 0.13	1.96 ± 0.14
Die-swell ratio, D_f/D_e	1.12 ± 0.12	1.08 ± 0.08	1.15 ± 0.08

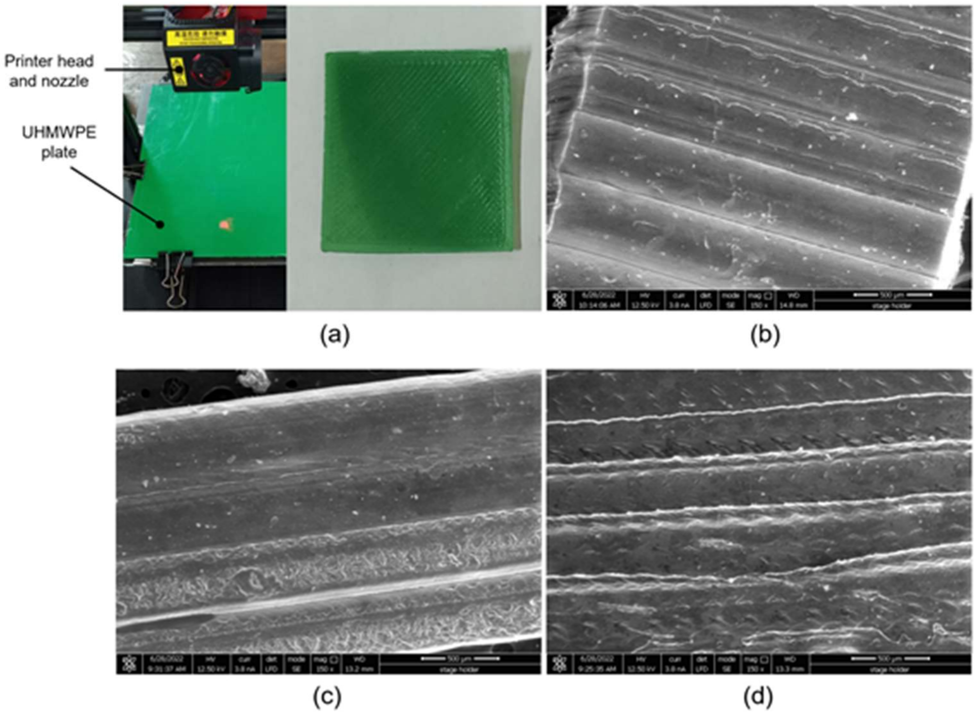

Figure 2. (a) The FFF-printing process of UHMWPE filament and its result, and the micrographs of the printed UHMWPE filament prepared with temperature of (b) 200, (c) 220 and (d) 240 °C

Figure 2(a) depicts the outcome of FFF-based printing using UHMWPE filament. Initially, depositing the first layer of molten filament onto the original glass-made bed of the FFF machine proved challenging. To address this issue, a 5 mm thick plate made of UHMWPE was mounted, as shown in Figure 2(a), serving as a bed onto which the first layer of molten filament could be deposited, forming the foundation of the printed 3D object. As depicted in Figure 2(a), a rectangular object with approximately 3 mm thickness, composed of several deposited layers of UHMWPE, was successfully fabricated in this study. A series of micrographs in Figures 1(b) - (c) clearly illustrates the presence of regular arrays of deposited material without significant defects on the printed UHMWPE object, indicating successful printing with temperatures ranging from 200 to 240°C. Similar findings regarding this physical characteristic can be observed in previous research on FFF printing of HDPE [16] and polyethylene terephthalate (PET) [17]. Nevertheless, further investigation is required to fabricate thicker 3D objects using this UHMWPE filament.

$$X = \frac{\Delta H_{end}}{\Delta H_f} \tag{1}$$

The crystallinity (X) of the UHMWPE rod, its filament, and printed forms can be determined using (1), where ΔH_{end} (shown in Figure 3c) and ΔH_f are the endothermic heat and heat of fusion of UHMWPE, respectively, which is 288 J·g^{-1} [18]. As illustrated in Figure 3(d), the crystallinity of UHMWPE decreased from its raw, rod-shaped material (61.2%), to 55.6% and 46-48% resulting from the extrusion and FFF-printing, respectively. Nonetheless, these values were comparable to the crystallinity values reported in the literature, such as 61.9% [19].

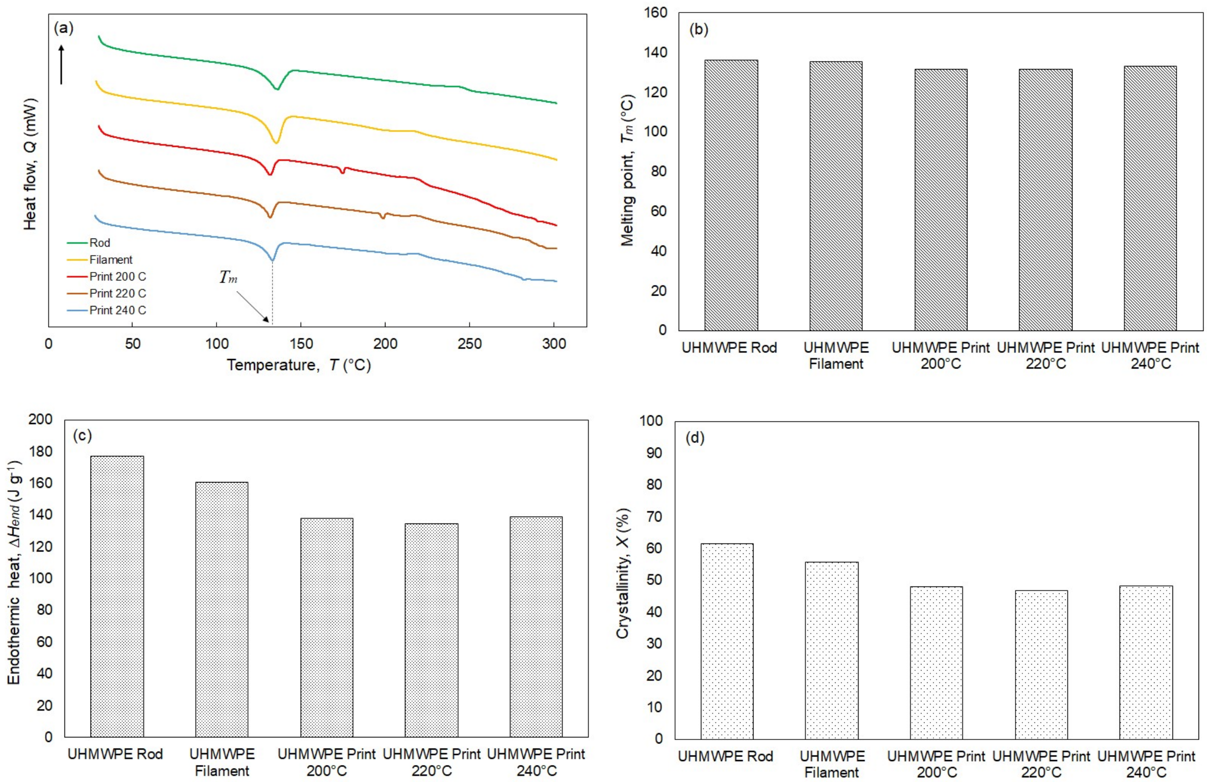

Figure 3. (a) The DSC thermograms, (b) melting points, (c) endothermic heat and (d) crystallinities of UHMWPE rod and its filament and printed forms

Figure 4 displays the FTIR spectra of the UHMWPE rod, its filament, and printed forms. Four principal bands were observed in all specimens: at 717.5 cm^{-1} (A), 1462.1 cm^{-1} (E), and from 2846.9 cm^{-1} (F) to 2912.5 cm^{-1} (G), corresponding to the presence of —(CH2)n— rocking vibrations, —(CH2) deformation vibrations, and —(CH2) stretching vibrations, respectively [20].

The addition of PEG is indicated by bands at wavelengths of 3400 cm cm^{-1} (H), 2900 cm cm^{-1} (G), 1292 –1450 cm^{-1} (B-D), 1250 cm^{-1} (C), and 1100 – 1060 cm^{-1} (B) [21], while the presence of PO is confirmed by bands at 2916 cm cm^{-1} (G), 2848 cm cm^{-1} (F), 1466 cm cm^{-1} (D), and 722 cm^{-1} (A) [22], [23]. Since no bands indicating substances other than UHMWPE, PEG, and PO were observed, this finding demonstrates no chemical reactions among these substances, confirming the excellent stability of UHMWPE [24].

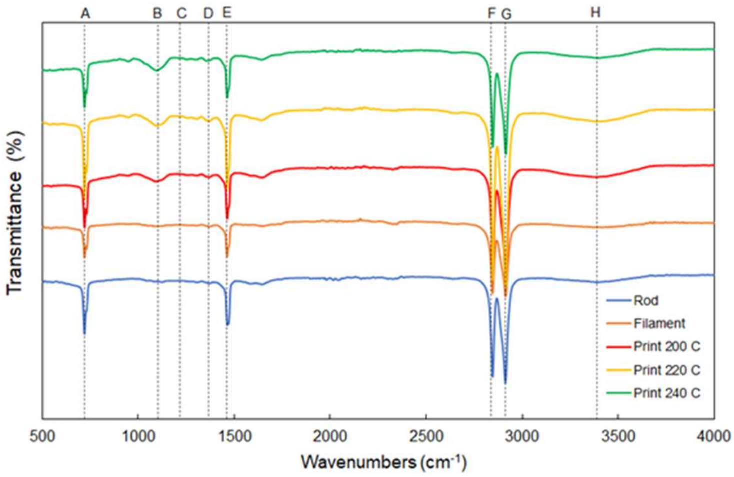

Figure 4. FTIR spectra of UHMWPE rod, its filament and printed forms

4. Conclusions

In this study, a filament composed of UHMWPE blended with PEG and PO was successfully produced and subsequently printed using an FFF-based 3D printer, resulting in the fabrication of thin, solid UHMWPE material that was characterized comprehensively. Based on the findings obtained in this research, it can be concluded that UHMWPE blend with the addition of 5% PEG and 10 phr PO could be extruded and printed effectively using the FFF technique. Printing within temperatures ranging from 200 to 240°C yielded printed forms consisting of several layers with good integrity and without any alterations in chemical composition. Results from FTIR and DSC characterizations revealed that both the UHMWPE filament and its printed forms did not exhibit any chemical impurities.

References

[1] N. A. Patil, J. Njuguna, and B. Kandasubramanian, “UHMWPE for biomedical applications: Performance and functionalization” *European Polymer Journal*, vol. 125, p. 109529, Feb. 2020, https://doi.org/10.1016/j.eurpolymj.2020.109529.

[2] K. Arora, and A. K. Singh, “Magnetorheological finishing of UHMWPE acetabular cup surface and its performance analysis,” *Materials and Manufacturing Processes*, vol. 35, no.

14, pp. 1631-1649, Jul. 2020, https://doi.org/10.1080/10426914.2020.1784928.

[3] S. Liza, A. S. M. A. Haseeb, A. A. Abbas, and H. H. Masjuki, “Failure analysis of retrieved UHMWPE tibial insert in total knee replacement,” *Engineering Failure Analysis*, vol. 18, no. 6, pp. 1415–1423, Sep. 2011, https://doi.org/10.1016/j.engfailanal.2011.04.001.

[4] M. M. Sava, B. Munteanu, E. Renault, Y. Berthier, and A. M. Trunfio-Sfarghiu, “Tribological analysis of UHMWPE tibial implants in unicompartmental knee replacements: From retrieved to in vitro studies,” *Biotribology*, vol. 13, pp. 1–15, Mar. 2018, https://doi.org/10.1016/j.biotri.2017.11.001.

[5] D. J. Thomas, “3D printing durable patient specific knee implants,” *Journal of Orthopaedics*, vol. 14, no. 1, pp. 182–183, Jan. 2017, https://doi.org/10.1016%2Fj.jor.2016.12.015.

[6] S. Singh and S. Ramakrishna, “Biomedical applications of additive manufacturing: Present and future,” *Current Opinion in Biomedical Engineering*, vol. 2, pp. 105–115, Jun. 2017, https://doi.org/10.1016/j.cobme.2017.05.006.

[7] T. Sathies, P. Senthil, and M. S. Anoop, “A review on advancements in applications of fused deposition modelling process,” *Rapid Prototyping Journal*, vol. 26, no. 4, pp. 669–687, Jan. 2020, https://doi.org/10.1108/RPJ-08-2018-0199.

[8] B. Arifvianto *et al.*, “Tensile properties of the FFF-processed thermoplastic polyurethane (TPU) elastomer,” *International Journal of Advanced Manufacturing Technology*, vol. 117, pp. 1709–1719, Aug. 2021, https://doi.org/10.1007/s00170-021-07712-0.

[9] J. M. Chacon, P. J. Núñez, M. A. Caminero, E. García-Plaza, J. Vallejo, and M. Blanco, “3D printing of patient-specific 316L–stainless–steel medical implants using fused filament fabrication technology: Two veterinary case studies,” *Bio-Design and Manufacturing*, vol. 5, pp. 808–815, Jun. 2022, https://doi.org/10.1007/s42242-022-00200-8.

[10] M. S. Ramli, M. S. Wahab, M. Ahmad, and A. S. Bala, “FDM preparation of bio-compatible UHMWPE polymer for artificial implant,” *ARPN Journal of Engineering and Applied Sciences*, vol. 11, no. 8, pp. 5474-5480, Dec. 2016. http://eprints.uthm.edu.my/3482/

[11] Y. Li, H. He, Y. Ma, Y. Geng, and J. Tan, “Rheological and mechanical properties of ultrahigh molecular weight polyethylene/high density polyethylene/polyethylene glycol blends,” *Advanced Industrial and Engineering Polymer Research*, vol. 2, no. 1, pp. 51–60, Jan. 2019, https://doi.org/10.1016/j.aiepr.2018.08.004.

[12] S. Yousef, A. Visco, G. Galtieri, D. Nocita, and C. Espro, “Wear behaviour of UHMWPE reinforced by carbon nanofiller and paraffin oil for joint replacement,” *Materials Science and Engineering C*, vol. 73, pp. 234–244, Apr. 2017, https://doi.org/10.1016/j.msec.2016.11.088.

[13] S. P. Sajjadi, “Impact of die materials on the effect of new polymer processing aids for sharkskin properties,” *Journal of Materials Science and Chemical Engineering*, vol. 4, no. 9, pp. 17-27, Sep. 2016, http://dx.doi.org/10.4236/msce.2016.49002.

[14] L. Liu, F. Wang, P. Xue, and S. Wang, “Influence of interfacial condition on rheological instability behavior of UHMWPE/HDPE/Nano-SiO_2 blends in capillary extrusion,” *Rheologica Acta*, vol. 58, pp. 183-192, https://doi.org/10.1007/s00397-019-01139-x.

[15] S. Chong, G.-T. Pan, M. Khalid, T. C.-K. Yang, S.-T. Hung, and C.-M. Huang, "Physical characterization and pre-assessment of recycled high-density polyethylene as 3D printing material," *Journal of Polymers and the Environment*, vol. 25, pp. 136–145, June 2017. https://doi.org/10.1007/s10924-016-0793-4.

[16] C. G. Schirmeister, T. Heesa, E. H. Licht, and R. Mülhaupt, "3D printing of high density polyethylene by fused filament fabrication," *Additive Manufacturing*, vol. 28, pp. 152-159, August 2019. https://doi.org/10.1016/j.addma.2019.05.003.

[17] B. Van de Voorde *et al.*, "Effect of extrusion and fused filament fabrication processing parameters of recycled poly(ethylene terephthalate) on the crystallinity and mechanical properties," *Additive Manufacturing*, vol. 50, p. 102518, February 2022. https://doi.org/10.1016/j.addma.2021.102518.

[18] N. C. Parasnis and K. Ramani, "Analysis of the effect of pressure on compression moulding of UHMWPE," *Journal of Materials Science: Materials in Medicine*, vol. 9, pp. 165-172, Mar. 1998, https://doi.org/10.1023/A:1008871720389.

[19] D. L. P. Macuvele *et al.*, "UHMWPE/HA biocomposite compatibilized by organophilic montmorillonite: An evaluation of the mechanical-tribological properties and its hemocompatibility and performance in simulated blood fluid," *Materials Science and Engineering C*, vol. 100, pp. 411-423. Jul. 2019, https://doi.org/10.1016/j.msec.2019.02.102.

[20] W. Li, R. Li, C. Li, Z.-R. Chen, and L. Zhang, "Mechanical properties of surface-modified ultra-high molecular weight polyethylene fiber reinforced natural rubber composites," *Polymer Composites*, vol. 38, no. 6, pp. 1215-1220. Aug. 2015, https://doi.org/10.1002/pc.23685.

[21] Khairuddin, E. Pramono, S. B. Utomo, V. Wulandari, A. W. Zahrotul, and F. Clegg, "FTIR studies on the effect of concentration of polyethylene glycol on polimerization of Shellac," *Journal of Physics: Conference Series*, vol. 776, p. 012053, Aug. 2016, https://doi.org/10.1088/1742-6596/776/1/012053.

[22] C. O. Chin, X. Yang, S. C. Paul, Susilawati, L. S. Wong, and S. Y. Kong, "Development of thermal energy storage lightweight concrete using paraffin-oil palm kernel shell-activated carbon composite," *Journal of Cleaner Production*, vol. 261, p. 121227, Mar. 2020, https://doi.org/10.1016/j.jclepro.2020.121227.

[23] J. Han, R. Sun, X. Zeng, J. Zhang, R. Xing, C. Sun, and Y. Chen, "Rapid classification and quantification of Camellia (Camellia Oleifera Abel.) oil blended with rapeseed oil using FTIR-ATR spectroscopy," *Molecules*, vol. 25, No. 9, p. 2036, Apr. 2020, https://doi.org/10.3390/molecules25092036.

[24] M. R. Senra and M. D. F. V. Marques, "Thermal and mechanical behavior of ultra-high molecular weight polyethylene/collagen blends," *Journal of Mechanical Behavior of Biomedical Materials*, vol. 103, p. 103577, Mar. 2020, https://doi.org/10.1016/j.jmbbm.2019.103577.