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Research Article

A novel compatibilizer obtained from olive pomace oil maleate (OPOMA) and evaluation in PLA composite production

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ABSTRACT

Alternative of using organic and biomass residues as additives or reinforcements in the production of composite materials has attracted great attention since the 2000s. However, when lignocellulosic biomass is used as natural fiber in composite production, it may have some disadvantages such as low interfacial bonding with the matrix phase. The most common methods used to strengthen the bonding between the matrix phase and the additive material is to use maleic anhydride (MA) as a compatibilizer and some chemicals such as dicumyl peroxide (DCP) as reaction initiators to increase the compatibilizing effect of MA. Therefore, in this study, olive pomace oil maleate (OPOMA) was prepared to be used in the production of polylactic acid (PLA) composites. Olive pomace obtained with ionic liquid pretreatment (OP-IL) in the previous studies of the authors and OPOMA were used in composite production with a biodegradable polymer of PLA. The composite was obtained by mixing 95PLA+5OP-IL by weight in twin-screw extruder at 190 °C for 10 minutes. Under the same conditions, the effect of OPOMA was evaluated by adding 0.5%, 1% and 2% ratio to PLA + OP-IL. In FTIR spectrum of OPOMA, a new symmetrical and asymmetric C=O bands were formed differently from olive oil. While the tensile strength of the PLA+OP mixture was approximately 10 MPa; the tensile strength value of PLA+OP-IL and PLA+OP-IL+OPOMA was around 60 MPa. The elasticity modulus showed less change compared to other mechanical properties. To conclude, it can be emphasized that oil maleates of lignocellulosic biomasses can be promising compatibilizer for biodegradable composite matrices.

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INTRODUCTION

Composite materials are formed by mixing two or more materials at the macroscopic level to obtain desirable combination of properties [1]. Mostly two or more distinct phases, namely matrix and reinforcing phases, are used during composite material production. Additionally, a phase called as interfacial phase is formed by creating a bond between matrix and reinforcing phases during the composite production and composite strength is highly depended on interfacial bond as it transmits the force to the reinforcement phase without breaking [2–4]. Composite materials are considered more advantageous compared to known traditional materials. The reasons for this can be listed as the fact that the final product material is versatile in terms of structural design and its unique properties such as high specific strength, hardness, and fatigue.

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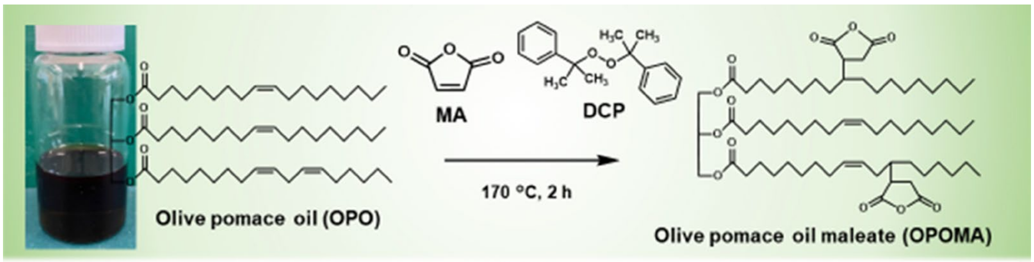

Figure 1. Preparation of olive pomace oil maleate (OPOMA) to apply as compatibilizer (MA: maleic anhydrite; DCP: dicumyl peroxide).

Nowadays, more sustainable approaches needed for producing composites and to this purpose, use of waste materials as additives, environmentally friendly and low-cost solutions become popular. Within environmental friendliness context, this study considered both as biodegradable material and as modifying the waste as next generation raw material to prevent it to be landfilled. In this regard, in many studies, biodegradable plastics (such as polylactic acid (PLA)) are frequently used as matrix in composite production [5, 6]. PLA is a biodegradable polymer can effectively be used for various applications, such as packaging and consumer foods, by virtue of its compostable property, having nontoxic and acceptable mechanical performance. Despite its high price, low thermal stability, brittleness, and crystallinity, which are limiting their applications, PLA is still widely preferred material and improvement of its mechanical properties are still being studied [5–7]. Researchers have been studying some toughening modification methods, such as addition of PBAT, silane and PET-RAN-PLA, however these decrease the biodegradability of the PLA [8]. Therefore, using waste and environmentally friendly materials as reinforcement and filling material while improving and/or keeping the mechanical properties of PLA is critical for maintaining environmentally friendly feature of PLA [6, 8]. However, there are limited studies in the literature about PLA composite material production with environmentally friendly additive materials to enhance and/or change PLA characteristic properties comparing to stated toughening modification methods. Sogut and Seydim [7] studied the effects of kiwi fruit peels (KFP) on the PLA composites, and they emphasized that tensile strength and elastic modulus increased with addition of KFP comparing to PLA control composites. In another study, oat husk and Miscanthus were used as additive materials in PLA matrix composites, and it was emphasized that the additive materials increased the thermal bending temperature, hardness, and strength of the composite material by providing strong interfacial bonding. Moreover, the addition of Miscanthus reduced the water absorption of the polymer matrix [9]. However, the most critical and difficult parts for composites where waste/environmentally friendly materials are used as additive material is to strengthen the interface bonding between the matrix phase and the reinforcement phase. The strength of these bonds affects the mechanical strength of the composites. One of the methods frequently used in the literature to strengthen the bonds between biofiber and PLA is the usage of maleic anhydride (MA)-based compatibilizing agents [10–12]. González-López et al. [13] stated that interfacial adhesion between agave lignocellulosic fiber additive material and PLA composites successfully enhanced with MA addition and 68% increment was obtained in tensile strength of the composite by virtue of MA. Some researchers also use MA and some chemicals such as dicumyl peroxide (DCP) as reaction initiators to increase the compatibilizing effect of MA and matrix phase-additive material bonding. Kiangkitiwan and Srikulkit [14] synthesized soybean oil maleate (SOMA) by reacting soybean oil with maleic anhydride (MA) using dicumyl peroxide (DCP) as the initiator and used the resulting maleate in the production of composites.

These literature findings indicated that biomaterial can successfully be evaluated as additive or functional material in PLA composite mixture. Considering environmental sustainability and carbon footprint, the more valuable solution is to use the waste biomaterial from the closer region. From this point of view, for example, kiwi, or mischanthus, stated above, may not be found in some regions where olive is one of the main agricultural products. Olive (Olea europea) is one of the important food products cultivated for both table olives and oil. Majority of global olive production is in the Mediterranean region, and then in minor quantity in some parts of America and Australia. In olive oil extraction significant amounts of solid and liquid residues become a challenge issue for the olive mill operators from both economic and environmental perspectives. This solid residue is a promising biomass resource because their characteristics provide the opportunity for their potential utilization. In the management of olive pomace new alternative recovery/recycle approaches have been developed for years. Considering the high quantity of yearly residue and well-known valuable properties of the material, alternative evaluation methods have always been studied. Therefore, in this study, olive pomace oil maleate (OPOMA) was produced with a similar approach and tried in PLA: Pretreated Olive Pomace composites as a novel compatibilizer to make contribution of investigation PLA composite material production with environmentally friendly additive materials. Characteristics of OPOMA and mechanical properties of composites were also investigated.

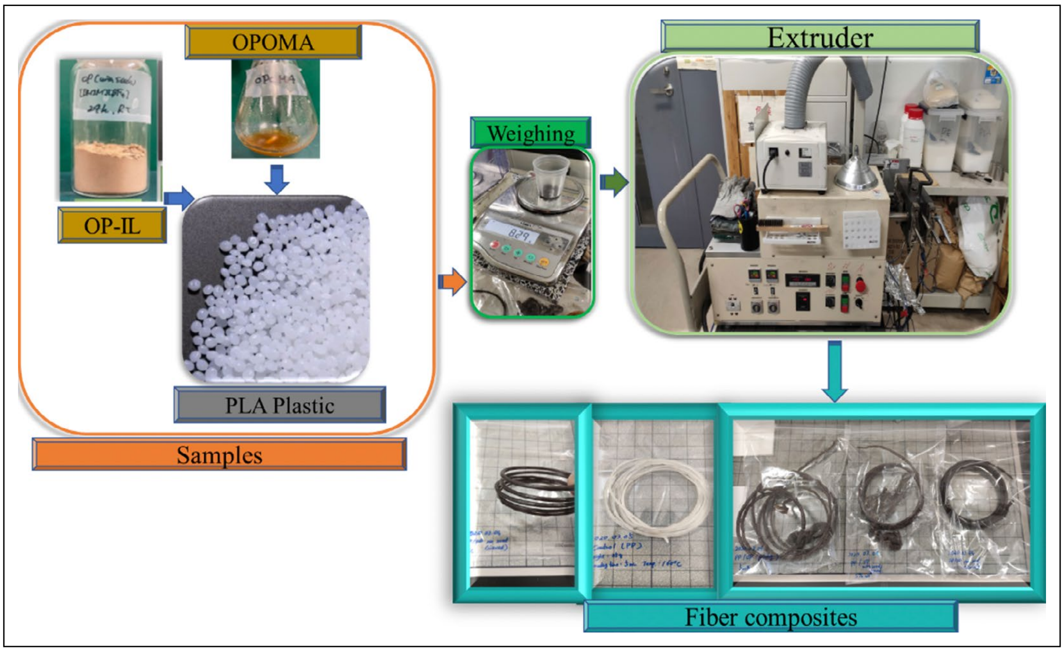

Figure 2. Composite production stages of the study.

MATERIAL AND METHODS

Preparation and Characterization of Olive Pomace Oil Maleate (OPOMA)

Olive pomace oil maleate (OPOMA) was prepared from pomace oil to be used in the production of PLA composites (Fig. 1). In the production of OPOMA, maleic anhydrite (MA) was used as 20% by weight of olive pomace oil and dicumyl peroxide (DCP) was used as 3% by weight of MA. In the study, DCP was used as a free radical initiator. The OPO-MA-DCP mixture of the specified weights was mixed in the mixer at 170 °C for 2 hours to complete the reaction. The experimental conditions for OPOMA preparation were adjusted based on study of Kiangkitiwan and Srikulkit [14].

FTIR analyzes of OPOMA were performed using the ATR method on the Thermo Scientific Nicolet iS5 FT-IR spectrometer. For the ATR method, the monolithic diamond crystal ID 7 module of the FTIR device was used. In the ATR analysis, reading was performed in the computer program after the tip of the ID 7 module was adjusted to completely contact the sample. ^{1}H NMR spectra of OPOMA was conducted with JEOL JNM-ECP500 spectrometer at 500-MHz.

Composite Production and Characterization

Olive pomace obtained with ionic liquid pretreatment (OP-IL) in the previous studies of the authors [3] and OPOMA were used in the production of composites with a biodegradable polymer of PLA. Composites were prepared in a twin-screw extruder using the method shown in Figure 2. Composite production studies started by first producing control composite samples using only PLA plastic. The composite was obtained by mixing 95PLA+5OP-IL by weight in a twin-screw extruder at 190 °C for 10 minutes. Under the same experimental conditions, the effect of OPOMA on mechanical properties of the composite was investigated on the samples produced by adding 0.5%, 1% and 2% ratio to PLA + OP-IL mixtures.

The tensile strength (MPa), modulus of elasticity (GPa), breaking stress and unit elongation values of the produced dumbbell shaped composite samples were measured using the Minebea Mitsumi (Load test standard: 1kNB-S100) brand tensile-compression test device. The test force was set as 1 kN and the tensile speed was set as 10 mm/min. During the test, the elongation in the composites was measured using an extensometer.

RESULTS AND DISCUSSION

The functional groups of both OPO and OPOMA were identified by FTIR and ^{1}H NMR analysis (Fig. 3). Both OPO and OPOMA samples have peaks between 2800–3100 cm^{-1} which represent -C-H, CH_2, CH_3 and cis/trans=C–H stretching bonds. These results also matched up with the olive oil FTIR spectrum given in the literature [14]. Moreover, C=O bonds representing the ester, aldehyde, ketone, anhydride and/or free fatty acids were observed at 1744 cm^{-1} wave number for OPO and OPOMA [15, 16]. Vibration of CO ester bonds and bending vibration of the -OH group were observed at 1160 cm^{-1} and 1033 cm^{-1}, respectively [17]. The different bond observed in OPOMA comparing to the OPO at 1775 cm^{-1} and 1850 cm^{-1} represents the symmetric and asymmetric stretching of C=O in the pendent anhydride group [14]. It was not observed any peak at 3500 cm^{-1} because of the opening anhydride ring, which means that anhydride ring remains intact. This result also can be confirmed by ^{1}H NMR spectra of OPOMA (Fig. 3). Methylene protons of anhydride pendant were observed at 2.60–2.70 and at 2.80–2.90 ppm [14]. Therefore, it can be emphasized that OPOMA were successfully synthesized from OPO.

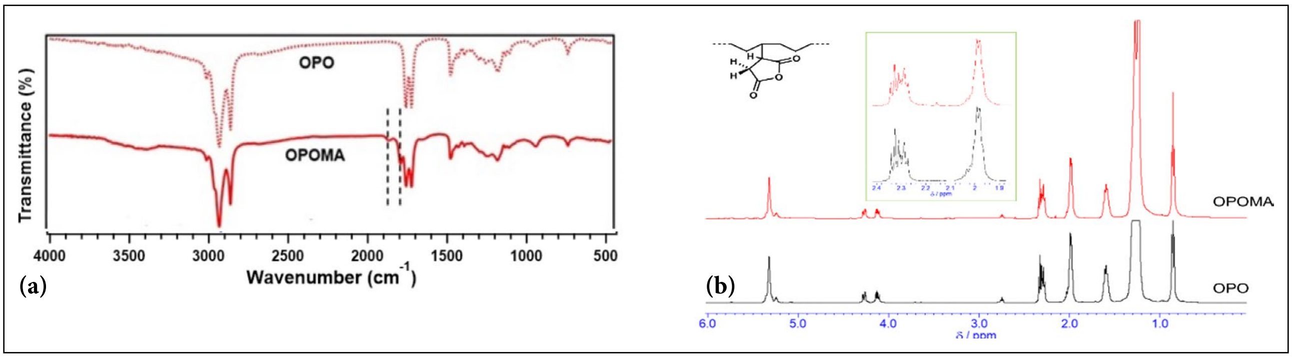

Figure 3. **(a)** FTIR and **(b)** 1H NMR spectra of OPO and OPOMA.

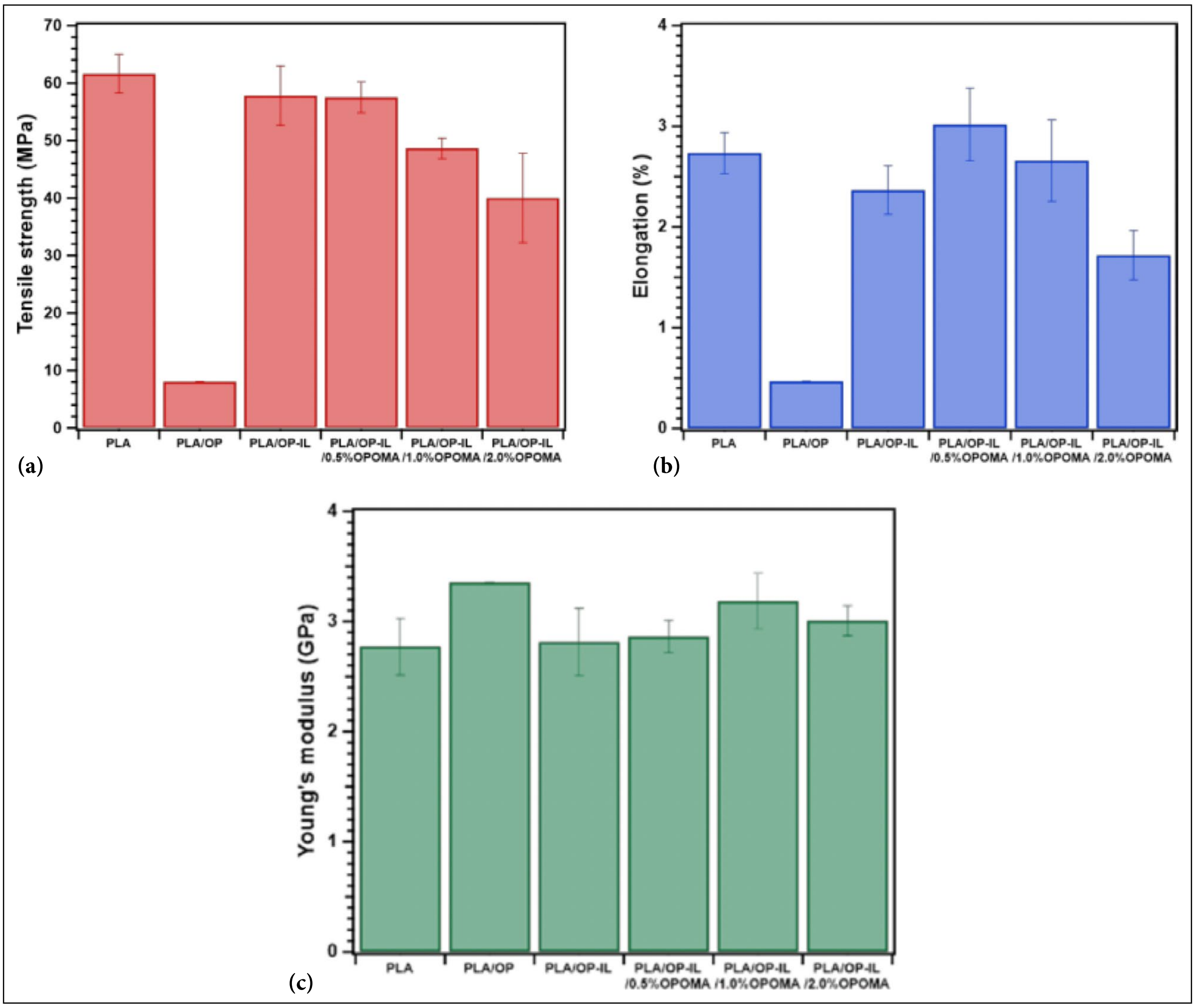

Figure 4. Mechanical properties of PLA+OP composites **(a)** tensile strength **(b)** elongation **(c)** elasticity modulus.

Mechanical properties of the obtained green composites were shown in Figure 4. The tensile strength of the PLA+OP composite increased remarkably with the addition of OP-IL. While the tensile strength of the PLA+OP mixture was approximately 10 MPa; the tensile strength value of PLA+OP-IL was around 60 MPa (Fig. 4a). This shows that the ionic liquid pretreatment applied to the pomace partially removes the hemicellulose and lignin structures in the OP and cellulose in the structure strengthens the interfacial bonding of PLA matrix and OP particles. On the contrary, increment of the OPOMA in the mixture decreased the tensile strength of the composites. Similar to the tensile strength, the elongation value increased with the application of ionic liquid pretreatment to OP. The addition of 0.5% OPOMA had an increasing effect on the elongation value. Increasing the OPOMA percentage in the mixture from 0.5% to 3% caused a decrease in the tensile

Table 1. Mechanical properties of PLA composites with different reinforcement materials

Reinforcement material (wt%)	PLA matrix (wt%)	Treatments for biomass	Tensile strength (MPa)	Elongation (%)	Young's modulus (GPa)
5% Pine [21]	95%	–	56.0±1	1.9±0.2	4.3±0.3
5% Cellulose [22]	95%	–	63.4±1.1	N/A	3.9±0.1
5% Rapeseed straw [23]	95%	–	50.9±0.6	3.1±0.31	2.8±0.06
10% Rapeseed straw [23]	90%	–	48.3±1.4	2.35±0.15	4.08±0.02
15% Banana-15% Sisal [24]	70%	Chemical treatments with NaOH for 2 hours	40.0	N/A	4.1
20% Jute–20% Coir [25]	60%	Silane and NaOH treatments	65.0	N/A	3.2
2% Algae [26]	98%	–	58.0±1	3.5 0±0.3	4.0±0.1

elongation value (Fig. 4b). This decrement observed in elongation value with the increment of OPOMA percentage shows that a phase separation occurs in the composite mixture when a high proportion of OPOMA is used. Similar to the presented study result, Lv et al. [18] emphasized that mechanical properties can be increased up to 144% with reactive compatibilizing agent at optimum dosage. However, it was reported in the same study that excess dosage can result in the staying compatibilizing agent at interface phase and thereby, decrement of the tensile strength because of the increment of the distance between chains. Similarly, Poletto [19] reported that mechanical, thermal and/or morphology of composite can successfully be enhanced with maleated soybean oil (MASO) produced with soybean oil and MA at optimum dosages. Elastic modulus showed less change compared to other mechanical properties. The highest elastic modulus value was observed in the PLA+OP mixture (Fig. 4c). These results indicated that, when the raw OP itself is intended to be used as additive in PLA composites, it is not feasible in terms of mechanical properties. However, when the modification proposed in this study was applied, then the mechanical properties that are comparable to the neat PLA can be achieved. When some part of the matrix polymer could be replaced with such a modified waste material, this would help to reduce the consumption of raw polymer material, to increase the use waste material in circular economy and to reduce its discharge into the environment.

Mechanical properties of PLA composites obtained with different reinforcement materials were presented in Table 1. While tensile strength of composites produced with untreated biomasses were between 50–63 MPa, tensile strength of composites addition with treated and/or combination of different biomasses were 40–65 MPa. As seen in Figure 4, tensile strength of PLA+OP-IL+OPOMA composites coincided with the literature values. Moreover, higher mechanical properties, especially for 0.5% OPOMA condition, were obtained in presented study as compared to PLA composites produced with treated reinforcement materials (Table 1). Similar to the presented study, Arbelaiz et al. [20] modified PLA-sisal and flax fiber filler interface with MA in the presence of DCM and it was stated that higher tensile strength was obtained at lower ratios of compatibilizer such as 1%. This can be attributed to degradation of matrix in the case of over the optimum dosage of the reactive compatibilizing agent [19, 20]. Therefore, it can be emphasized that synthesized compatibilizer, namely OPOMA, can be effectively used in PLA-OP composite.

CONCLUSION

In this study, a novel compatibilizer (OPOMA) was produced from olive pomace oil for the first time and used in the production of composites with a biodegradable polymer of PLA. New symmetric and asymmetric C=O bands in the FTIR spectrum of OPOMA, unlike olive oil, show that OPOMA has been synthesized successfully. While the addition of low doses of OPOMA to PLA+OP-IL composites increased the tensile elongation value, tensile strength did not change. The elasticity modulus showed less change compared to other mechanical properties. When the mechanical properties of the composites obtained within the scope of the study were evaluated, it was observed that they matched up with the studies in the literature and more successful results were obtained compared to some pre-treated biomass. Therefore, it can be emphasized that oil maleates of lignocellulosic biomasses can be promising compatibilizer for biodegradable composite matrices and OPOMA can be used as compatibilizer in biodegradable polymer matrixes. Moreover, mechanical properties of PLA-OP composites were successfully enhanced with the addition of both OP-IL and OPOMA. Thereby, with these investigated mechanical properties, the produced composites can be good alternative for specially building-construction and automotive sectors in which composite materials are commonly used in the world. These composite materials can also be preferable to these sectors since the additive material is sustainable, low-cost, easily available, environmentally friendly as it is produced in high quantities, and thus contributes to low-carbon composite production and to the circular economy.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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