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RESEARCH ARTICLE

Investigation of the ageing behaviour of multiple reused polypropylene binding twines

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Abstract

Climate change is one of the significant challenges of the 21st century. To achieve climate goals a change in plastic waste management needs to be implemented. This research examines the potential of thermo-mechanical recycling of plastic waste, focusing on agricultural binding twines made from polypropylene. Old binding twines from agriculture were collected and recycled with a twin screw extruder. The ageing behaviour of the recyclate in terms of multiple recycling is examined in detail with tensile tests and melt volume rate measurements. The findings indicate a general degradation in mechanical properties and a decrease in viscosity due to molecular chain scission. Despite these degradations, the material remains processable, indicating the potential for continued recycling loops.

KEYWORDS

binding twine, extrusion, polypropylen, PP recycling, thermal ageing, thermo-mechanical recycling

INTRODUCTION

Climate change represents one of the most significant challenges facing humanity in the 21st century. However, measures implemented under public climate protection law alone will not be sufficient to stop global warming and thereby to fulfill the 1.5°C target set out in the Paris climate agreement and achieve climate neutrality by 2050 [1]. Therefore, there is a high need to encourage companies to take action to protect the climate.

A crucial step towards these targets is the sustainable handling of resources and the implementation of closed-loop recycling strategies. Every year 49 million tons of plastics are produced in Europe for further fabrication. Additionally, 25.8 million tons of plastic are newly generated annually [2]. This evidence demonstrates clearly, that the recycling of plastic is a matter of concern, since less than 30% of the plastic waste is currently collected for recycling [2, 3]. Even worse, a major proportion is exported to non-EU countries with lower environmental standards for disposal. Meanwhile, the European Union is increasing the pressure on companies with the objective of achieving a 55% recycling rate for plastic packaging waste by the year 2030 [1, 2].

To achieve the climate targets and stop global warming, it is necessary to conduct a comprehensive survey of all waste producers and investigate their recycling potential, including also smaller, supposedly niche products. One area of significant plastic usage is the agriculture sector. A great advantage of plastic applications in agriculture is often the high level of product purity [4]. Consequently, complex separation processes are not required to separate the individual plastic materials. This also applies to binding twines, which are frequently utilised and mostly disposed after a single use. They are manufactured entirely from the semicrystalline thermoplastic polypropylene (PP) [5].

One common approach to recycling plastic is thermo-mechanical recycling, which involves an extrusion process [6, 7]. This process is in contrast to chemical recycling techniques a cost-effective and solvent-free method, suitable for a wide range of polymers [7]. Moreover, it can be easily extended to larger-scale applications. However, there are also disadvantages, the extruder induces thermo-oxidative and shear-induced chain scission or crosslinking in the polymers, which results in a degradation of the molecules and thus, affects the material properties [8]. A further challenge in thermo-mechanical recycling of twines and yarns relates to the processing of the fibre material. Due to their fine structure and extremely low bulk density, fibres are difficult to feed into the extruder. After recycling, the generated material could also be used in additive manufacturing such as already investigated in several studies [9–14]. This would entail the integration of closed-loop material management with future-oriented manufacturing technologies.

The present study aimed to develop a thermo-mechanical recycling process for old binding twines and to investigate the ageing behaviour of the recyclate in detail. To this end, the recycled material was repeatedly reused (up to 10 times) and the material properties were determined using static tensile tests. Furthermore, potential changes in viscosity were examined through the measurement of the melt volume rate. The outcomes were compared with those of a conventional PP utilized in injection moulding. This research work represents the first study which investigates the recycling potential of single-used agricultural twine made of PP. The novelty and forward-thinking aspect is that this approach might be applied to other perceived niche products and therefore has a far-reaching impact on plastic waste management.

FIGURE 1 Coiled binding twine as raw material.

FIGURE 2 Wool-like granulate after shredding of the binding twine.

METHODOLOGY

To investigate the reusability of binding twine from agriculture, old binding twines were collected from local farmers of the administrative district of Heilbronn (Germany). In their collected status they are dirty and coiled into balls after usage. An example of the raw material as collected is shown in Figure 1. The term 'old' is defined here as no longer in use or discarded. In the case of binder yarns, this is typically the case after a single use. For the sake of completeness and to ensure that the material collected is indeed polypropylene (PP), infrared spectroscopy was carried out on the twine.

The material for comparison in this study is Moplen HP500W, a standard PP from the manufacturer LyondellBasell suitable for application in injection moulding and technical compounds as flow modifier. Furthermore, one batch of old binding twines was cleaned by manual washing with soap to investigate whether the cleaning process affects the mechanical or rheological properties. The recycling process itself can be subdivided into two steps. First, the binding twines were shredded since the coiled balls of twine are too long to be properly processed into the twin screw extrusion machine. For this purpose, twine pieces with a length of 20 cm were manually cut and shredded using a colortronic M102L shredder-granulator (Friedrichsdorf). This method has already been proven in previous studies to be sufficient in previous studies producing processable material for the extruder [15, 16]. With the help of the granulator, the binding twine can be processed into a wool-like mass, as shown in Figure 2 that can be fed into the extruder. This constitutes the second step, which involves thermo-mechanical recycling using a twin screw extruder.

Thermo-mechanical recycling

To produce new granulate for further use in injection moulding machines, the shredded twine material was processed with the aid of a Leistritz ZSE 18HP-45D twin screw extruder (Nürnberg). With its nine heating zones, the process can be adjusted on various materials and on the addition of different additives to reach certain material

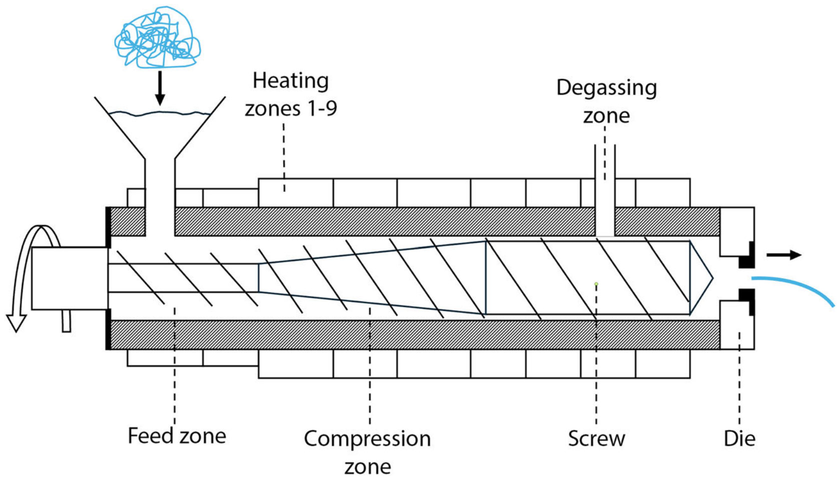

FIGURE 3 Schematic sketch of the extruder used for the recycling process.

FIGURE 4 Recycled granulate after processing with the twin screw extruder.

properties. As this study is focused on the ageing behaviour and not on material development no further additives were used in the compounding process. From previous experiences on the processing of PP the temperatures of the heating zones 3–9 are set to be constant at 220°C. Only the first two heating elements at the feeding zone are set to be 230°C to have a sufficient melting of the inserted material. A schematic sketch of the extruder can be seen in Figure 3.

As the automatic feeder system associated with the extruder only works satisfactorily for granulate but not for the wool-like shredded binding twine, the fibre material was fed into the extruder manually using a plastic stamp as a feeding aid. This allows the fibres to be drawn in quickly through the screw, preventing the material from burning due to prolonged dwell time in the extruder and also minimises thermal degradation during the process. The shredded material begins to plasticise immediately upon emerging from the feeding zone of the extruder. In the subsequent area of the machine, the melt pressure is increased by the geometry of the twin screws, assuring the complete melting of the material. In the degassing zone, any remaining air inclusions are released from the melt before finally being extruded through the circular die outlet. The hot PP melt solidified by passing through a water cooling basin and a compressed air-driven water separator. Finally, the strand was cut into granulate with a size of approximately 1 mm using a Scheer SGS 25-E4 pelletizer (Grossostheim). The produced recyclate as shown in Figure 4 is now ready for further processing in injection moulding machines.

Ageing process

To completely determine the effects of the ageing mechanisms, 10 different ageing stages of the material were analysed. These different ageing states are referred to as generations (Gen.) in this study, starting with Gen. 1 for the first time recycled material. To demonstrate the ageing process in the laboratory, the granulate is subjected to thermal and mechanical stress once for each ageing generation. The thermal stress is achieved by melting the pellets in the twin-screw extruder and the mechanical stress by chipping the extruded strand in the pelletiser. The loss of material properties due to UV exposure is not described in this research.

In detail, the ageing process is carried out as follows. The binding twines were recycled to granulate (Gen. 1), afterwards the granulate was fed back into the extruder to produce ageing Gen. 2. This process was continuously repeated until the desired ageing state was reached, whereby each generation was completely extruded before the granulate was fed back in to obtain the next generation. In the context of this research, the ageing was performed until generation 10 was reached.

The major advantage of this procedure is that there is no start-up and run-out phase in the extrusion process. However, there is still a certain amount of the last generation in the extruder before the start of a new generation. To remove this portion, the transition material between the generations was removed. To determine the transition material, a test was carried out to measure the duration of the transition from one material to another for the given machine setting.

TABLE 1 Process parameter for the injection moulding process.

Process parameter	Unit	Value
Injection pressure	[bar]	266
Melt cushion	[ccm]	10.45
Holding pressure	[bar]	650
Fill time	[s]	1.04
Dosing time	[s]	7.41
Cycle time	[s]	53.3

FIGURE 5 Produced tensile test specimen from recycled polypropylene with gate.

For this purpose, white granulate was added in between the extrusion of the blue granulate from the binding twine.

A sample of 50 g of granulate was taken from each generation for further rheological testing of the viscosity, that is, the determination of the melt volume rate. Furthermore, tensile test specimens were produced out of Gen. 1, 5 and 10 to determine the mechanical properties. For the production of the specimen, 1.5 kg of granulate is needed for each set, which leads to a total amount of 5 kg of material to be recycled from the binding twine.

Injection moulding process

The granulate obtained from the recycling process was used to fabricate the tensile test specimens by means of a Demag IntElect 80/310 (Wiehe) electrical injection moulding machine with a clamping force of 800 kN. After initial tests and final configuring the machines, the process parameters shown in Table 1 proved to be stable and sufficient for the present material. The tensile test specimens were fabricated with dimensions selected according to DIN EN ISO 527-2 Type 1 A (h = 4 mm, l_2 = 167 mm, b_1 = 10 mm, b_2 = 20mm).

From the 1.5 kg of granulate per material condition, the following number of samples were produced. In the case of Gen. 1, 22 tensile test specimens could be used for later testing. An example of the fabricated tensile test specimen with gate can be seen in Figure 5. The production of the specimen from the Gen. 5 and 6 granulate leads to a total number of 20 samples, ready for testing. Due to some more scrap components only 19 tensile test specimens could be used from virgin PP and only 13 in case of the cleaned material. However, as the sample size is far larger than the five tensile test specimens required by the standard DIN EN ISO 527-1, this is not critical and still results in a statistically reliable test series.

Material testing

Tensile tests were carried out in accordance with DIN EN ISO 527-1 on a Zwick 1445-02, 10 kN universal testing machine (Ulm) at a test rate of 1 mm/min in the linear elastic range and 50 mm/min for the remainder of the test. To obtain more accurate strain values, modular sensor arm extensometers were used to evaluate the elastic modulus. When a strain of 0.25% was reached, the extensometers were removed and further measurements were taken throughout the traverse path. This was done to avoid any damage caused by the specimen suddenly breaking when the ultimate tensile strength (UTS) was reached. To obtain a clear assessment of the mechanical properties and the effects of the ageing processes the number of specimens tested was chosen to be significantly larger than required by the standard. The tests were conducted at room temperature.

Furthermore, melt volume rate (MVR) measurements were carried out in accordance with DIN EN ISO 1133-1 using a Göttfert Model MP-D melt flow index testing device (Buchen, Germany). Although the tensile tests were conducted solely for generations 1, 5 and 10, the melt volume rate was determined for every material condition. For each test, 50 g of granules are melted at 190°C for a predetermined heating time of 3 min using a 2.16 kg weight. To ensure a reliable assessment of the melt volume rate, 30 measurements were taken during the 10 min testing period.

RESULTS AND DISCUSSION

As the measurement results of the infrared spectroscopy confirmed the assumption of PP and the purity of the material, the study could proceed. Determining the stress-strain curves of the tested samples indicates a general loss in the UTS, as well as a general loss in ductility

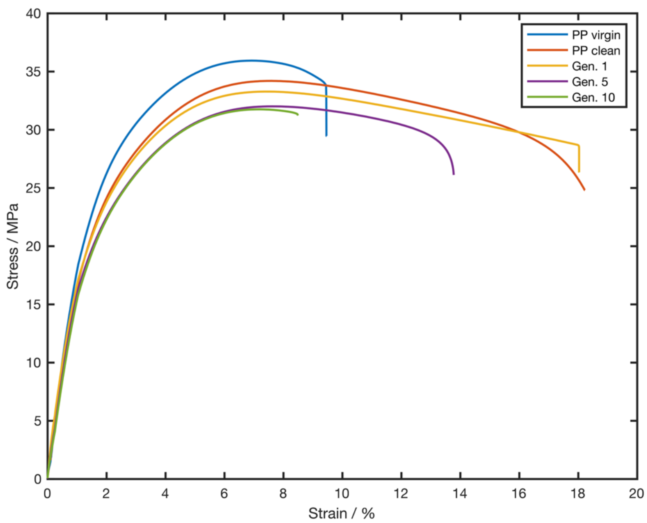

FIGURE 6 Selected stress–strain curves of different ageing stages and material conditions of recycled binding twines.

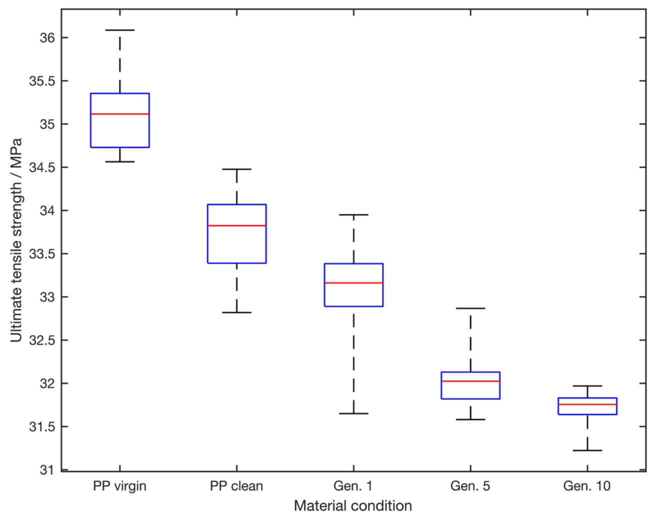

FIGURE 7 Ultimate tensile strength of different ageing stages and material conditions of recycled binding twines.

with increasing ageing state. This can be clearly seen in Figure 6 as the elongation at break decreases significantly in the case of the ageing stages of Gen. 5 and Gen. 10. The stress–strain curves presented here demonstrate the exemplary results obtained from the initial tensile tests.

For a better interpretation, the results from the tensile tests are evaluated and visualised below as boxplot diagrams, in which the measured mechanical properties are plotted on the axis of ordinate and the examined material condition, that is, ageing state on the axis of abscissae. This representation has the advantage of illustrating all important statistical characteristics, including the extreme values of each series of measurements which are shown as whiskers, and the 25% and 75% percentile, displayed by the upper and lower edges of the blue box. Furthermore, the median can be taken from the red central mark.

The resulting values for the UTS are visualised in Figure 7. It can be clearly seen, that the tensile strength is decreasing with increasing ageing stage. It is notable that there is only a marginal discrepancy in the UTS values between the clean and dirty (Gen. 1) material conditions. The average UTS only declines from 33.8 to 33.1 MPa which shows that a cleaning, as performed in this study has proven to be ineffective. There might be the option for extensive and complex cleaning processes to be developed to influence the tensile strength of the recycelt material. In this case, the overall sustainability should be proven. As the cleaning process was not effective, only the soiled twines were analysed further.

Compared to the virgin material, the mean loss in UTS for the ten times recycled material amounts to 9.8%. It is important to note that the comparison material is a standard material and the exact composition of the base material of the binding twines is not known. Consequently, the comparison serves only as a rough indication.

The mean decline in strength from Gen 1. to Gen. 5 (3.2%) is about three times higher than from Gen. 5 to Gen. 10 (0.97%).

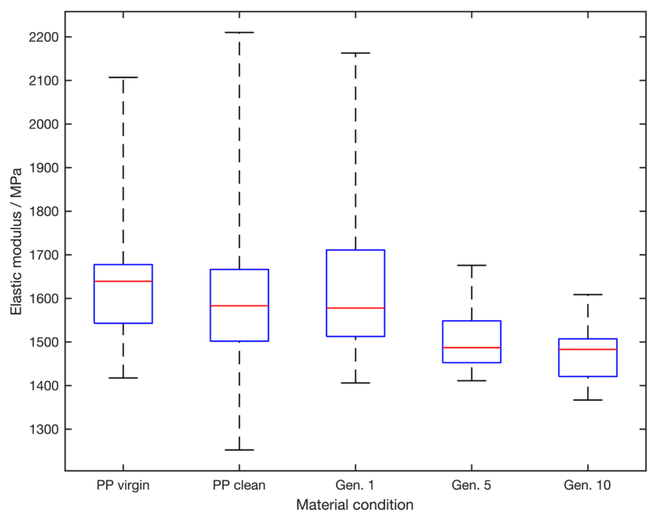

FIGURE 8 Elastic modulus of different ageing stages and material conditions of recycled binding twines.

This indicates that the major degradation occurs in the first recycling loops. Further measurements should be conducted to ascertain whether a strength plateau is developing and the UTS is not declining further. The determined values for the elastic modulus are visualised in Figure 8.

It can be observed that the measured elastic moduli for the virgin PP, the cleaned material and the Gen. 1 recyclate are consistent. The average elastic moduli are between 1630 and 1669 MPa, with the virgin material exhibiting the highest value and the cleaned material the lowest. Similar to the results of the UTS, a decline in elastic modulus can be observed after multiple reuse of the material. Once more, this decline is considerably higher during the initial five recycling loops than between Gen. 5 and Gen. 10. The average decrease in the elastic modulus between Gen. 1 and

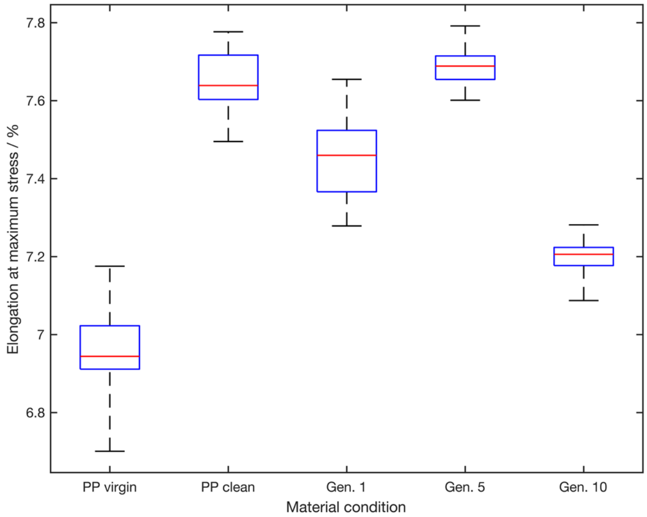

FIGURE 9 Elongation at maximum stress of different ageing stages and material conditions of recycled binding twines.

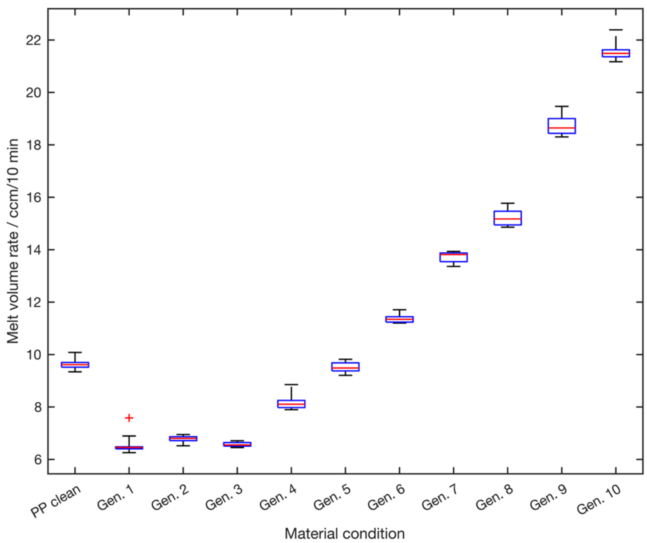

FIGURE 10 Melt volume rate of different ageing stages and material conditions of recycled binding twines, polypropylene virgin: mean melt volume rate of 76.3 ccm (not depicted).

Gen. 5 is approximately 8.3%, whereas it is only 2% between Gen. 5 and Gen. 10.

The observed reduction in the elastic modulus indicates a decline in the crystallinity of the recycled material with each reuse cycle [17]. As the crystalline zone acts as cross-linking points that stiffen a polymer, a reduction in the degree of crystallisation and thus, in the cross-linking density, results in a loss of stiffness, namely a decline in the elastic modulus [17–19]. The obtained measurements for the elongation at maximum stress for the different material conditions and ageing stages are shown in Figure 9. It can be seen that the elongation decreases after 10 times reusing the material, indicating a loss in plasticity.

However, the results of Gen. 5 exhibit contradictory behaviour, which precludes the formulation of a definitive conclusion based on the values of the elongation at maximum stress determined here. Nevertheless, as shown in Figure 6, the elongation at break is decreasing significantly for the Gen. 5 and Gen. 10 which clearly indicates a loss of plasticity.

As illustrated in Figure 10, the results of the MVR measurement show a clear trend towards a reduction in viscosity with each generation of ageing. To enhance visual clarity, the measuring results of the virgin PP are not depicted in the diagram, as the values are considerably higher with a mean MVR of 76.3 ccm/10 min. The overall reduction in viscosity is accompanied by an increasing melt volume rate and is attributed to a shortened molecular chain length [17].

Following 10 ageing cycles, the viscosity has decreased by a factor of greater than three from an average MVR of 6.49 ccm/10 min in case of the Gen. 1 to 21.56 ccm/10 min for the Gen. 10 granulate.

The changes in viscosity clearly indicate the chemical degradation affecting the microstructure of the polymer in terms of chain scissioning reaction and a decrease in the molecular weight [5, 17, 18, 20, 21].

In contrast to virgin PP, the MVR of the Gen. 10 granulate can still increase by a factor of 3.5 until it reaches a value comparable to that of the reference material. Consequently, further recycling loops are feasible concerning viscosity. It is striking that the viscosity of the clean PP is significantly lower, that is, the MVR is significantly higher compared to the soiled material (Gen. 1), which might be attributed to the impurities present.

Compared to other studies on recycling of PP also the present work showed a degradation of the mechanical and rheological properties [15, 22]. Nevertheless, the results demonstrate that multiple recycling of plastic waste still results in acceptable material properties and that the processability of the recycled granulate was always given.

CONCLUSION

This study addressed the urgent necessity of enhancing recycling practices to mitigate the environmental impact of plastic waste, particularly within the context of agricultural binding twines. The urgency of this endeavour is underscored by the pressing need to stop climate change and achieve sustainability goals outlined in the Paris climate agreement and the European Union's commitment to climate neutrality by 2050.

Used binding twines from agriculture were collected and granulate with different ageing stages was produced by multiple recycling in a twin screw extruder. A comprehensive examination of the mechanical and rheological properties of the recyclate was carried out with the aid of tensile tests and melt volume rate measurements.

- The findings highlight a general degradation in mechanical properties, including UTS and plasticity, with an increasing ageing state. Furthermore, the elongation at break decreases significantly.
- Notably, the most significant deterioration occurs within the initial recycling cycles, emphasizing the importance of early intervention in recycling processes to mitigate strength loss.
- Furthermore, the viscosity analysis through melt volume rate measurements provided information about chemical degradation processes. A clear trend towards reduced viscosity with each ageing stage indicates molecular chain scissioning and a decrease in molecular weight.
- Nevertheless, despite the considerable decrease in viscosity, the material remains processable as the viscosity remains below that of the comparison material. Consequently, the recycling loops may be continued with appropriate adjustments in processing parameters and material handling.

In conclusion, this research emphasises the necessity of developing effective recycling practices. Furthermore, it should demonstrate the recycling potential for small niche products to meet the environmental challenges of the 21st century and pave the way for a greener, more sustainable future for generations to come.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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