



Study on thermal transport behavior of magnesium oxide (MgO) nanostructures as lubricant additives in vegetable oils

Jaime Taha-Tijerina¹ · Kollol Jogesh² · Victoria Padilla-Gainza² · Jefferson Reinoza² · Maysam Pournik²

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Abstract

Due to harmful impact of petroleum-based fluids and lubricants on the environment and Mankind, vegetable oil-based fluids with incorporation of eco-friendly nanostructures have a great potential to be an alternative lubricant if it possesses proper thermal transport and physico-chemical characteristics. In this study, thermal conductivity, and viscosity performance of vegetable nanolubricants, developed from soybean oil and sunflower oil, modified with homogeneous dispersion of magnesium oxide (MgO) nanostructures were evaluated at various filler fractions (0.01, 0.05, 0.10 and 0.25 wt%) over diverse temperatures. For thermal conductivity evaluation, a transient hot wire (THW) methodology was employed. It is observed that for MgO nanolubricants, thermal conductivity increased as a filler fraction and temperature were increased, reaching a maximum of 22% improvement at 0.25 wt% reinforcement at 50 °C. On the other hand, the viscosity showed a consistent behavior as a function of nanostructures filler fraction and decreased significantly in response to increased evaluating temperature.

Introduction

With the increased energy demands, the reduction of fossil resources and reservoirs, fluctuating price of petroleum, rising environmental health concerns, and arising global warming challenges, climate change and having sustainable manufacturing systems researchers and industry have raised interest in searching for alternatives based on eco-friendly fluids and lubricants. For instance, one of the most important breakthroughs occurred in the transportation industry with the development of biodiesel, this material gained attention for being eco-friendly, affordable, and renewable source of fuel [1].

Technological innovations are moving forward with improvements in efficiency, size, new challenges, and requirements. In diverse fields, such as in metal-mechanic industry, among diverse purposes for lubricants, heat dissipation from working surfaces and tooling is a key factor, also

minimizing wear and friction as well as preventing mechanical components from failure. In this sense, the use of fluids and lubricants has been demanding higher performance, which is important for manufacturing processes and more critical is how to properly dispose of these materials once they have been used.

As a result, vegetable lubricants have been evaluated as “green” alternative to substitute petroleum-based fluids. Vegetable lubricants are derived from various types of seeds, nuts, cereal grains, and fruits. These materials are sustainable in nature and may be cultivated in the field without the depletion that petroleum-based lubricants do. They do not contain toluene, xylene, benzene or other toxic compounds which can detriment human health, particularly on respiratory and skin diseases of operators [2–4]. Hence, vegetable lubricants have been widely explored and considered suitable for diverse applications based on their good physico-chemical attributes and characteristics such as low volatility, high viscosity index, high boiling and flash points, greater molecular weight, long and polar fatty acid carbon chains with quick biodegradability, among others [5–8]. Additional benefits have been observed for addition of solid structures with these vegetable fluids and lubricants in many aspects, particularly in thermal transport and tribological characteristics. Lee et al. [9] and Kalantari et al. [10] among other researchers, studied the effects of the particles size within base fluids and lubricants. Results showed a positive effect

✉ Jaime Taha-Tijerina
jose.taha@utrgv.edu

¹ Department of Informatics and Engineering Systems,
The University of Texas Rio Grande Valley, Brownsville,
TX 78520, USA

² Department of Mechanical Engineering, The University
of Texas Rio Grande Valley, 1201 W. University Dr.,
Edinburg, TX 78539, USA

by enhancement of thermal conductivity as particle size decreased [4, 11, 12]

Different methods to improve the characteristics of conventional fluids and lubricants have been explored. Nowadays, with aid of nanotechnology, conventional systems and subsystems have been improved or enhanced in their characteristics and performance. Nanostructures exhibit superb properties due to their small size and good interaction within conventional materials. Diverse kinds of nanostructures have been used as additives and reinforcement agents for preparing nanofluids and nanolubricants. Nevertheless, not all of these nanostructures are environmentally friendly. Hence, even if the base fluid or lubricant is considered as eco-friendly in nature, such as vegetable oils, adding certain nanostructures could harm or contaminate the environment.

Nanostructured oxide materials are one of the most important classes of applied reinforcements. These materials have been widely studied due to their large surface areas, adsorptive characteristics, surface defects and rapid diffusivities. Among diverse metal oxide nanostructures, magnesium oxide (MgO) has been gaining important attention diverse industries due to its unique characteristics. MgO is a basic oxide, it has potential to bind free fatty acids, thus preventing increase of the acid number and to catalyze hydrolysis of the ester groups. In addition to its unique characteristics MgO is non-toxic and easily soluble, it posses a simple stoichiometry, high melting point, low density, recycling activity, high strength to weight ratio, and has good functionality [13–15]. These nanostructures have gained great interest from scientists and researchers due to its environmental friendliness and are promising materials for a broad range of applications and fields such as electronics, biomedical, anti-bacterial and antimicrobial inhibition, lithium ion batteries, catalysis, ceramics, agriculture, energy, petrochemical products, chemical/toxic waste curation, and many others [13–17].

Besides its characteristics, little research of MgO as reinforcing agent of fluids and lubricants for thermal transport and tribological characteristics has been developed. For instance, MgO showed keen performance in a study conducted by Xie et al. [18] while being applied as a reinforcing additive with ethylene glycol (EG) as base material. In their evaluations, thermal conductivity increased 40% at 30 °C, outperforming other oxide-based nanofluids where the nanostructures were coupled within EG. In another investigation, Zyla et al. [19] observed an enhancement of MgO/EG nanofluids of 33% in thermal conductivity with merely 0.20 wt% concentration at room temperature. Also, Anish et al. [20] observed the effects of MgO within heat transfer fluid at diverse concentrations and evaluated temperatures. Results showed thermal conductivity enhancements of 6%, 8% and 11% for 0.10 vol%, 0.20 vol% and 0.30 vol% at 50 °C. Investigation by Esfe et al. on thermal transport of

MgO reinforcing water-EG systems showed that the better fluid mixture was 60:40 water-EG [21]. It is also observed that the temperature effect on the enhancement percentage of the nanofluid is more pronounced as reinforcement filler fraction is greater than 1.0 vol%. Results showed that as MgO concentration is increased and the nanostructures size is minimized will lead to improvement in thermal conductivity. The nanofluid achieve 18% and 34% enhancement for 1.0 vol% and 3.0 vol% at 50 °C, respectively.

On the other hand, in raw material transformation, the generated heat from metal–metal interactions and manufacturing processes such as in stamping, cutting, and machining to mention some of these, is a critical issue to address. Working parts and components quality could be improved as well as tooling deterioration or damage could be prevented or diminished. Padmini et al. [22] identified how the nanostructures tend to modify the vegetable lubricant attributes, this effect was more significant as nanostructures' filler fraction increased. In their study, machining efficiency increased due to the improved attributes and properties of natural nanolubricants, which formed a bulky lubrication tribofilm with higher thermal dissipation and effectively decreases friction and wear. Moreover, Sirin et al. [7] studied the behavior of diverse nanolubricants comparing pure natural oil and dry cutting during machining evaluations of superalloys. It was observed that the machining output was higher when nanolubricant with optimum filler fraction of nanostructures was applied.

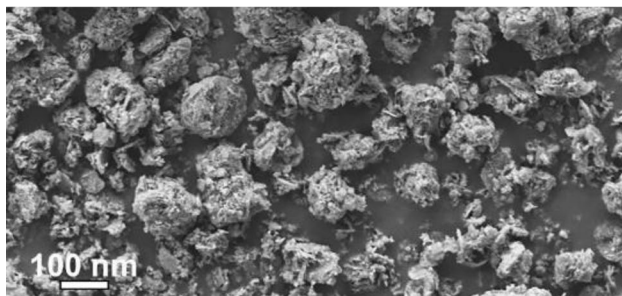
The aim of this study is to determine the benefits of these environmentally friendly nanolubricants, such as improved stability, enhancement in heat transfer, good flow through machinery and device's micro channels without clogging, pumping power is reduced due to the down scaling of systems, improved lubrication stability due to the increased viscosity and thermal conductivity which enhances the performance in plastic deformation manufacturing processes [23, 24]. As MgO has these biocompatible nature and non-harmful properties, herein, we evaluate eco-friendly alternatives for petroleum-based lubricants for diverse manufacturing processes. Nanolubricants at various filler fractions of MgO are prepared and dispersed within soybean oil and sunflower oil. This research will examine thermal conductivity and viscosity of nanolubricants at diverse temperatures to study the behavior and effects of the inclusion of MgO.

Materials and methods

Soybean and sunflower oils (Aceites, Grasas y Derivados, S.A. de C.V., Zapopan, Jal., Mexico) (Table 1) served as base materials to prepare nanolubricants with magnesium oxide (MgO) nanostructures (Sigma-Aldrich Co., St. Louis, MO, USA. CAS #:1309-48-4) at various concentrations,

Table 1 Material characteristics

Materials		Properties and characteristics		
Base lubricant		Density @ 20 °C (g/cm ³)	Viscosity @ 24 °C (mm ² /s)	Viscosity @ 40 °C (mm ² /s)
Soybean oil		0.910	56.7 ± 0.4	31.8 ± 0.5
Sunflower oil		0.921	73.2 ± 0.3	39.1 ± 0.4
Nanostructures	Average size (nm)	Hardness (MPa)	Density (g/cm ³)	Thermal conductivity (W/m K)
MgO	79 ± 38	5000–7000	3600	30–60

**Fig. 1** Morphology of MgO nanostructures at 3 KX magnifications

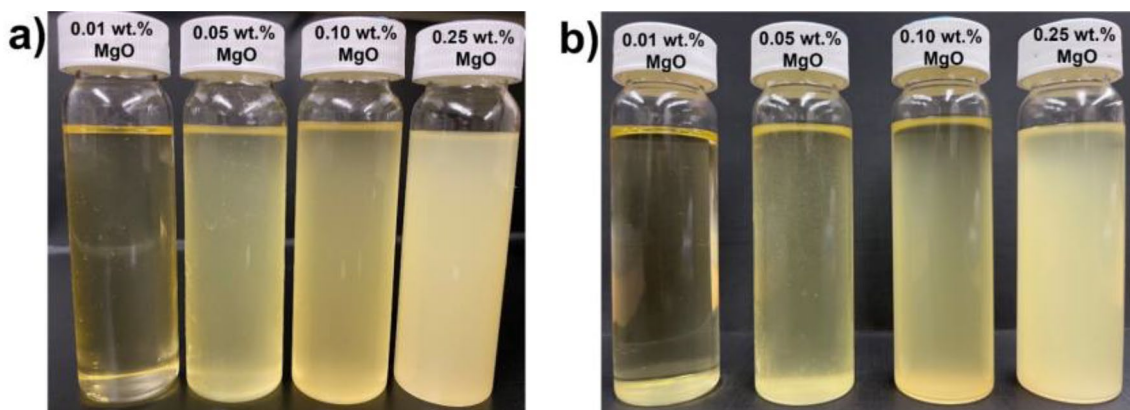
varying from 0.01, 0.05, 0.10 and 0.25 wt%. Morphology and size of MgO nanostructures were examined by scanning electron microscopy (Carl Zeiss, Sigma VP, NY, USA) (Fig. 1). Table 1 shows the characteristics and properties of the vegetable lubricants, and the reinforcing nanostructures.

Nanolubricants preparation

To prepare the samples, the base lubricants (soybean oil and sunflower oil separately) are taken at room temperature in a glass container with the capacity of 120 ml. Then, the

required weight of the nanostructures for 4 different concentrations are obtained and measured in a weight balance machine (Metler Toledo—ME204E). The accuracy of this device is 0.01 mg.

Preparation of homogeneous nanolubricants following a two-step method for dispersing MgO nanostructures within vegetable oils at 0.01 wt%, 0.05 wt%, 0.10 wt% and 0.25 wt% was performed. The prepared mixtures were first manually agitated for 5 to 10 min to guarantee dispersion of the nanostructures within the base lubricant. After this, the glass vials with the samples were homogenized using a Bransonic CPX5800 (Danbury, CT, USA, 40 kHz) water bath sonicator for 8 cycles of 1 h. Fresh water was used in every cycle, maintaining a constant temperature of 24 °C to hinder the nanostructures from quick agglomeration and premature sedimentation. Samples in glass containers were placed on a drawer for 3 weeks with no significant sedimentation of nanostructures (Fig. 2).

**Fig. 2** Images of MgO—soybean nanolubricants: **a** immediately after extensive water bath sonication, and **b** after 21 days placed in a drawer

Experimental details

Thermal conductivity measurements

Measurements of thermal conductivity of MgO nanolubricants are obtained by using a TEMPOS thermal analyzer device (METER GROUP, Inc., Pullman, WA, USA) according to the transient hot-wire (THW) method. A temperature-dependency evaluation from room temperature (24 °C) up to 50 °C was achieved. Prior to each set of thermal evaluation, the sample was manually agitated followed by 20 min ultrasonication. Before evaluation the samples above room temperature, each glass vial was maintained in thermal equilibrium for 15 min, this process was followed to promote uniform temperature in the nanolubricant sample for the evaluations. Thermal conductivity results are compared with the base vegetable lubricants (k_0). The nanolubricants' effective thermal conductivity performance is obtained as k_{eff} . At least six measurements were obtained for each set of specimens, the average thermal conductivity is verified up to 3 decimal points and is reported with error bars as standard deviation.

Viscosity evaluations

The viscosities of the nanolubricants at diverse filler fractions were determined using a Haake Mars 40 Rheometer with a parallel-plate sensor configuration. The gap used between the plates is 0.5 mm. Evaluations were made at various temperatures, starting at room temperature (24 °C), 30 °C, 40 °C and 50 °C for a duration of 10 min per evaluation. Before running our experiments, a calibration of the rheometer was performed according to the suppliers' manual with a standard fluid from Brookfield Engineering Laboratories, Inc.

Results and discussion

Thermal conductivity performance

Thermal conductivity indicates a fluid or lubricant capacity to absorb and dissipate heat to its surroundings. Thermal transport behavior is significantly affected by temperature, this effect promotes the Brownian motion of dispersed nanostructures within the lubricants. Nanolubricants' thermal conductivity improved with an increase of the reinforcing concentration. This is due to the ultrasonication of the nanolubricants; a molecular layering of the lubricant will come into existence. This interfacial layer may allow the ballistic phonons to move easier from one nanostructure to

the neighboring nanostructures; hence, this organized fluid layering acts as an effective thermal transport bridge to carry more heat effectively across the interface and increases the thermal conductivity [5, 23, 24]. As the reinforcing filler fraction increases, these nanostructures come closer, therefore enhancing coherent phonon heat energy distribution inside the nanolubricant due to Brownian motion.

In general, MgO-nanolubricants display good improvements in thermal conductivity, and increase as the evaluation temperature is elevated. Furthermore, unlike the nanolubricants, pure vegetable oils (soybean or sunflower) are not significantly affected by temperature. Since, with the temperature increase, the molecules inside the pure vegetable oils are quickly moving away from each other, thus the mean free path between these molecules of vegetable lubricants is increased. This effect reduces the probability of collisions between molecules in vegetable lubricants, which ultimately does not affect much the thermal conductivity performance.

Shafi et al. [25] explained how the thermal conductivity enhancing performance of a fluid is affected by Brownian motion of the reinforcing nanostructures. Collision of nanostructures creates a solid–solid conduction heat transfer mode (percolation channel formation). Followed by the thermal conductivity enhancement due to a convective heat transfer mode. This result is consistent with the investigations obtained by Taha-Tijerina et al. [4, 23], and Mustafa et al. [26], in which the thermal conductivity of nanolubricants enhances as temperature is increased. Study by Hothar et al. [27] on MgO ionic nanofluids showed a dependence of thermal conductivity on temperature. Additionally, diverse investigations have explored the influence of nanostructures' filler fraction as well as its size and morphology on thermal conductivity.

Figure 3 shows the temperature-dependency results for thermal conductivity of MgO nanolubricants at diverse filler fractions. It is noticeable that base vegetable lubricants did not show significant affectation (only 0.88% increase) in thermal conductivity as evaluation temperature was elevated from room temperature up to 50 °C. Moreover, both vegetable lubricants showed similar thermal conductivity gradual improvement tendency as MgO concentration and temperature were increased. This indicates the contribution of thermal conductivity attributes of the oxide nanostructures. In Fig. 3a, it can be observed a slight increase for the soybean nanolubricants in thermal conductivity at room temperature. Elevating the test temperature, higher thermal conductivity was achieved as filler fraction was also increased, reaching a highest enhancement of 18.60% at 0.25 wt% when measured at 50 °C, compared to pure soybean lubricant. Sunflower lubricant also showed a similar trend (Fig. 3b). Thermal conductivity of pure lubricant did not change significantly in response to increasing the test temperature, just

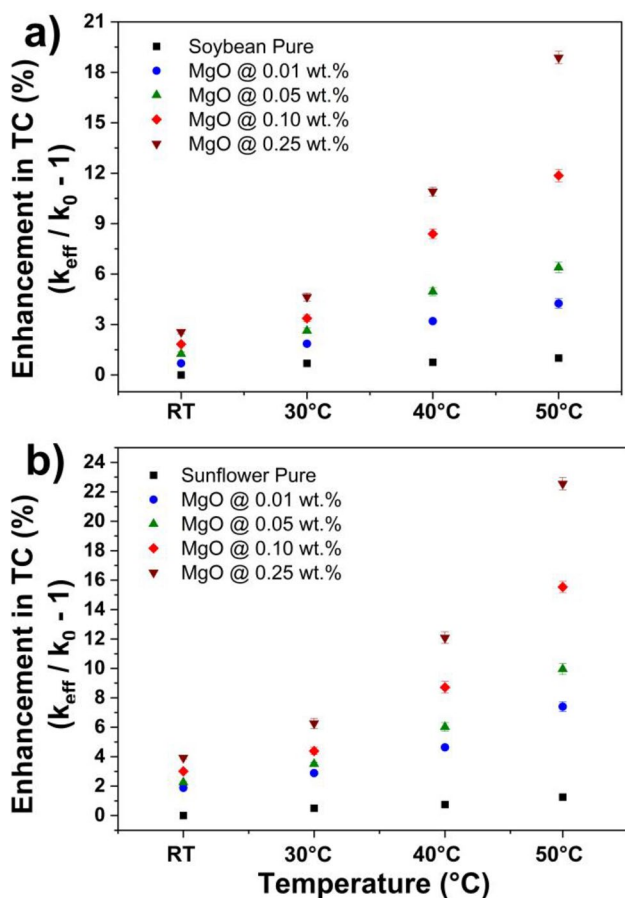


Fig. 3 Thermal conductivity performance of **a** soybean nanolubricants and **b** sunflower nanofluids under temperature-dependence evaluation

like pure soybean lubricant. However, as temperature was raised, thermal conductivity of sunflower-MgO showed better improvement, displaying maximum of 22.65% at 0.25 wt% and 50 °C, compared to pure lubricant.

These improvements as function of increasing the evaluation temperature and increasing the nanostructures concentration can be attributed to the increased Brownian velocity and the surface effects that MgO nanostructures can achieve. Furthermore, the development of thermal bridges among lubricant molecules and nanostructures can also be a potential cause for thermal conductivity enhancement. Additionally, as suggested by Judran et al. [28] due to the amount of filler fraction, the thermal transport effect is generated by molecular interactions, the liquid layering interface, at the vegetable lubricants and the nanostructures. The molecules of the lubricants interact with the MgO nanostructures, being susceptible to create a layered film surrounding the nanostructures, which is related to the enhancement of thermal transport [4, 29].

Viscosity evaluations

Heat transfer performance of nanolubricants depends on the thermos-physical characteristics of both conventional lubricant and reinforcing nanostructures. Experimental studies have shown that the enhancing effects depend on the size, morphology, filler fraction and other attributes of nanostructures [24, 30].

In diverse systems, by increasing the concentration of nanostructures within the vegetable lubricants, the enhancement in thermal conductivity is constrained by the increment in viscosity behavior, which will adversely affect the lubricants' characteristics. Investigation on MgO/EG nanofluids by Xie et al. [18] exhibited a minor enhancement in viscosity with nanostructures filler fraction increase. According to them, nanofluids showed a non-linear relation between the fluid's viscosity and filler fraction. In a similar study by Asadi et al. [31] it was shown a maximum thermal conductivity improvement of 32% for MgO nanolubricant at 1.5 vol% filler fraction. Additionally, a minimum increase in viscosity of the nanolubricant systems, this maximum increase was observed at an elevated temperature of 55 °C.

Viscosity measurements were obtained for both vegetable systems with the main purpose of observing the behavior of the nanolubricants with incorporation of MgO nanostructures at various filler fractions as temperature was increased. The viscosity of the nanolubricants is lower as evaluating temperature is raised (Fig. 4). Figure 4a depicts the viscosity behavior for soybean nanolubricants at various concentrations and temperatures. At room temperature, an increase in viscosity was 4.5% at 0.25 wt%. A similar tendency was observed for all the evaluated temperatures. At 50 °C, the viscosity reached a maximum of 5.2% increase, compared to pure soybean lubricant. For sunflower nanolubricants, similar viscosity behavior was observed (Fig. 4b). In this case, at room temperature, viscosity was increased 2.6% at 0.25 wt%, reaching a highest increase of 4.0% at 0.25 wt% filler fraction at 50 °C. Even though, viscosity showed a slight increase with incorporation of the nanostructures, this is attributed to the agglomeration of nanostructures within the vegetable lubricants, inhibiting the easy displacement of adjacent lubrication layers, this effect is consistent with observed results by Kotia et al. [32].

Conclusions

Thermal transport performance and viscosity behavior of vegetable lubricants with incorporation of reinforcing MgO nanostructures were investigated in this work. In general, MgO nanolubricants exhibited significant enhancement in thermal conductivity. A temperature dependency evaluation was performed. Both vegetable lubricants, soybean,

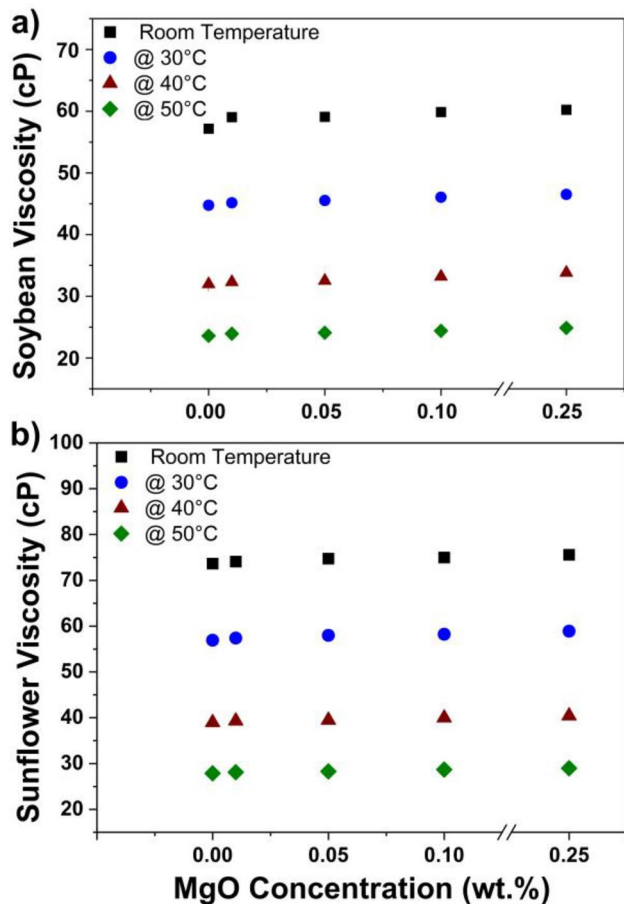


Fig. 4 Viscosity variation of **a** soybean nanofluids and **b** sunflower nanolubricants under temperature-dependence evaluation

and sunflower, showed improvements of 3% and 4.5% at 0.25 wt%, respectively, when compared to pure vegetable lubricants at room temperature. As testing temperature was raised and filler fraction was also increased, the thermal conductivity improved significantly, resulting in a maximum improvement of 18.60% and 22.65%, respectively, at 50 °C. In addition to the Brownian motion effect on the vegetable lubricants, this behavior is attributed to the nano-layering of the base lubricants at liquid/nanostructures interface, evaluation temperature of the nanolubricants, nanostructures size, among others, which contributes to the improvement in thermal transport performance.

In terms of viscosity, the incorporation of MgO nanostructures in the selected filler fraction did not significantly affect this property over the evaluated temperature scan performed, reaching a maximum of 5.2% and 4.0% increase at 0.25 wt% for soybean and sunflower nanolubricants, respectively. This opens a broad area of opportunities as alternative eco-friendly materials for diverse industrial fields and applications where these nanomaterials possess good potential to succeed.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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