Nano-enhanced biolubricant in sustainable manufacturing: From processability to mechanisms

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Abstract: To eliminate the negative effect of traditional metal-working fluids and achieve sustainable manufacturing, the usage of nano-enhanced biolubricant (NEBL) is widely researched in minimum quantity lubrication (MQL) machining. It’s improved tool wear and surface integrity have been preliminarily verified by experimental studies. The previous review papers also concluded the major influencing factors of processability including nano-enhancer and lubricant types, NEBL concentration, micro droplet size, and so on. Nevertheless, the complex action of NEBL, from preparation, atomization, infiltration to heat transfer and anti-friction, is indistinct which limits preparation of process specifications and popularity in factories. Especially in the complex machining process, in-depth understanding is difficult and meaningful. To fill this gap, this paper concentrates on the comprehensive quantitative assessment of processability based on tribological, thermal, and machined surface quality aspects for NEBL application in turning, milling, and grinding. Then it attempts to answer mechanisms systematically considering multi-factor influence of molecular structure, physicochemical properties, concentration, and dispersion. Firstly, this paper reveals advanced lubrication and heat transfer mechanisms of NEBL by quantitative comparison with biolubricant-based MQL machining. Secondly, the distinctive film-formation, atomization, and infiltration mechanisms of NEBL, as distinguished from metal-working fluid, are clarified combining with its unique molecular structure and physical properties. Furtherly, the process optimization strategy is concluded based on the synergistic relationship analysis among process variables, physicochemical properties, machining mechanisms, and performance of NEBL. Finally, the future development directions are put forward aiming at current performance limitations of NEBL, which requires improvement on preparation and jet methods respects. This paper will help scientists deeply understand effective mechanism, formulate process specifications, and find future development trend of this technology.

Keywords: nano-enhanced biolubricant (NEBL); sustainable manufacturing; minimum quantity lubrication (MQL); tribological properties; machining mechanisms

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Nomenclature

NEBL  Nano-enhanced biolubricant  BMQL  Biolubricant-based minimum quantify lubrication
MQL  Minimum quantify lubrication  SDGs  Sustainability development goals
GHG  Greenhouse gas  HBN  Hexagonal boron nitride
PCD  Polycrystalline diamond  GR  Graphene
CNTs  Carbon nanotubes  RSm  Average width of the profile (µm)
CoF  Coefficient of friction  Ra  Arithmetical mean deviation of the profile (µm)
MWFs  Metal-working fluids  Rz  Maximum height of the profile (µm)
VB  Flank wear (µm)  C=C  Carbon–carbon double bond
SEM  Scanning electron microscope  PBLC  Performance between lubrication and cooling
EDS  Energy dispersive spectrometer  APE-10  Alkylphenol polyoxyethylene ether 10
–OH  Hydroxyl group  SDS  Sodium dodecyl sulfate
–COOH  Carboxyl group

1 Introduction

1.1 Background

Limited nature resources and severe environmental issues human beings are facing with at the moment inherently drive the need of sustainable manufacturing in nearly all the industries, from aerospace, marine, automobile engineering, via energy, to optics and electronics. This can not only be clearly evidenced by the emphasized from national strategy of manufacturing industry (e.g., SDGs, Germany Industry 4.0 and Made in China 2025) [1], but also be enforced by carbon emission standards (e.g., ISO 14064 and GHG Protocol). Manufacturers therefore must adapt to existing policies and laws by minimization of machining-induced environmental contamination.

Traditional metal-working fluids (MWFs), which are prepared by non-renewable minerals and scarce water, are necessity in manufacturing industry for hundreds of years [2]. However, it's also the core of machining-induced contamination due to the following environmental, health, and economic issues (Fig. 1): (i) The usage and disposal of non-degradable MWFs would lead to environmental pollution [3], the death of freshwater organisms, and eutrophication of water resources; (ii) compared to with natural environment, more than 150 times concentration of micro particles...
will generate and cause various respiratory diseases [4]; (ii) high cost of traditional MWFs, which is about 2.5 times of the cutter cost, caused by expensive mineral fluid components, inefficient/heavy supply method, and strict requirement of the wastewater disposal. It’s urgent to find a renewable and biodegradable lubricants as substitute for traditional MWFs for sustainable transformation and upgrading of traditional manufacturing industry.

Biolubricant, which is typically produced from raw plant oils and animal fats for industrial application, has already gained importance as alternatives to conventional mineral-based lubricants in various applications, especially the automotive industry [5]. It is undeniable that vegetable oils or animal fats are good alternative lipid sources due to their environmentally friendly, nontoxic, and readily degradable nature. Inspired by the above, scholars have made attempts by using biolubricant in minimum quantity lubrication (MQL) for sustainable manufacturing. Triglycerols of fatty acids are the main ingredients of vegetable oils and animal fats, which usually has poor extreme pressure properties [6]. Especially, biolubricant couldn’t meet anti-friction and heat-transfer requirements of machining, in which working zone characterized by high-temperature and high-pressure. This shortcoming is caused by poor lubrication/cooling performance of biolubricant and can be addressed by introducing nano-enhancer in plant oil to prepare NEBL. NEBL could realize the low cost and sustainable development of industry while realizing the machining performance. By employing only tiny amount of NEBL with the flow rate of 10–100 mL/h [7, 8], MQL can provide similar cooling and lubricating effects in comparison with traditional flood machining processes but with the unique advantages in terms of cost (because of a very small amount of coolant usage and large disposal saving), environmental protection (because plant oils are degradable), and human safety [9].

The employment of NEBL supplying by MQL system has four basic functions of lubrication, cooling, rust prevention, and chip removal, so it is hopeful to replace traditional MWFs: (i) Due to blocking effect of air boundary layer around a rotating tool (especially the grinding wheel) [10], the ‘useful’ flow rate, which is the volume ratio of flow into the cutting zone to total flow, is only 5%–40% [11]. Extra flow rate is wasted. The distribution of airflow field in milling and grinding has been researched by scholars. They found that the airflow field will play a drag role on the entry of micro droplets at a high jet velocity when micro droplets are injected along the ‘entry flow’ in the airflow field (avoiding the ‘return flow’). Iskandar et al. [12] found that the jet velocity researches at 35 m/s when air flow rate is set as 31 L/min. Therefore, although dosage of NEBL is lower than traditional MWFs, the ‘useful’ flow rate is higher thanks to bigger jet speed of NEBL droplets with the help of high pressure gas. Even in high speed machining, NEBL droplets could be fed through air boundary layer into the cutting zone easily; (ii) thanks to favorable physical properties of base oil and high thermal conductivity of nano-enhancers, the usage of NEBL presents better lubrication and cooling performance than traditional MWFs. Moreover, using NEBL to instead water-soluble MWFs is more conducive to the rust prevention of the workpiece; (iii) better than traditional MWFs, the chips will be washing off from cutting zone and maintain cleanliness around cutting zone with combined efforts of lubricants and high pressure gas. Especially for slot parts machining of aerospace structural components, the chips might stay at slot and paly an interference role due to MWFs filling the slot. MQL could solve this problem.

Although substantial efforts have been paid to NEBL application in sustainable machining, the scientific knowledge and understanding in this technology seems still unclear, such as how or why NEBL atomizes, infiltrates, formats film, lubricates and cooling in machining with influence of various molecular structures and physical properties. The present processing couldn’t guide the production practice due to lack of process specifications, such as how to prepare NEBL with suitable plant oil, nano-enhancer, and concentration for multiple processing conditions. In order to fill this literature gap and provide scientific foundation, this paper aims to present a comprehensive review and provide a periodic critical assessment of the existing understandings.

1.2 Paper structure

Figure 2 shows the paper flow. By employing the theoretical and technical bottlenecks of NEBL for
industrial application as the storyline, this review starts with introduction of components of NEBL used in sustainable manufacturing (Section 2), followed by feasibility demonstration of NEBL comparing with biolubricant in MQL application and unique lubrication/cooling mechanisms are revealed in Section 3. Feasibility demonstration is also set furtherly in Section 4 of NEBL comparing with traditional MWFs, in which advanced film-formation, atomization, and infiltration mechanisms are clarified combining with its unique molecular structure and physical properties. The process optimization strategy is concluded based on the synergistic relationship analysis among process variables, physicochemical properties, machining mechanisms, and performance of NEBL (Section 5). Section 6 discusses the contradictory relationship in the coexistence of cooling and lubrication performances of NEBL and proposes the possible solutions. The paper ends with the conclusion and future challenges of sustainable machining processes in Section 7.
2 Characters of nano-enhanced biolubricant

2.1 Biolubricant

Toxic and hazardous contaminants included in mineral oils convey adverse health and environmental effect and heavily influence for the global sustainability. The significant properties of readily biodegradable, low toxicity, and environmental friendliness have attracted manufacturing industries to use plant oils as base oil of NEBL, which could satisfy the higher industrial demand on sustainable lubricants. More significant, plant oil is a renewable resource. Its application in machining avoids overexploitation of nature, which is also an important direction of sustainable development. It's worth noting that biolubricant from animal fats are another main kinds, however, no reference of animal oil application in MQL was published at present. Therefore, the biolubricant as mentioned below in this paper are those derived from vegetable oils.

Natural plant oil is composition of various kinds of saturated and unsaturated fatty acids, and can be classified into several types based on carbon chain length (usually varies from 16 to 22), C=C number (usually varies from 0 to 3), and polar group (–OH, –COOH, etc.) (Fig. 3).

2.1.1 Oils with high-content unsaturated fatty-acid

The majority of plant oils has a high content of unsaturated fatty-acid (typical types in Fig. 4(a)). These oils were the most extensively investigated due to the large number of their varieties. These oils have proper viscosity and surface tension, and therefore presents a good balance between cooling and lubrication. However, the problems come from their limited strength and their film instability due to easy-to-oxidise nature of C=C bonds.

2.1.2 Oils with high-content saturated fatty-acid

In comparison, more and more attentions are paid to oils with a high content of saturated fatty-acid (typical types in Fig. 4(b)). These oils have higher viscosity and therefore better lubrication performance. More importantly, these oils have no C=C bonds and molecular chains have straight-line backbones, which are beneficial to lubricating film strength.

2.1.3 Oils with special polar groups

Most oils reviewed above have both –COOH and –COOR polar groups at one carbon chain end. However, there are also some exceptions such as castor oil having –OH at the chain end. The –OH group has

![Fig. 3](https://example.com/fig3.png)  Classification of common fatty acids existed in plant oils.
a very strong adsorption to metallic surface, and therefore provides easy lubricating film formation and desired film properties. However, the existence of –OH increases the viscosity by one order of magnitude (Fig. 4(c)), which degrades the heat exchange performance of NEBL. With this, one big research stream at present is mainly focusing on the optimisation of oils with special polar groups so that the good balance between cooling and lubricating performances can be achieved.

2.2 Nano-enhancers

The purpose of adding nano-enhancer to plant oil aims to further improve the application range of plant oil, which could adapt to high-temperature or high-pressure processing conditions. Thanks to ultra-large specific surface area and various available physicochemical properties of nano-enhancer, NEBL can significantly improve thermal conductivity and tribology behaviors at the tool–workpiece interfaces where intensive friction, high temperature and pressure, and high relative velocity simultaneously exist [13].

2.2.1 Spherical nano-enhancers

There is no surprise that if spherical nano-enhancer can be introduced into NEBL they can act like ‘ball rollers in the bearings’ at nanoscale, significantly reducing friction so as to improve tool life, temperature, and force.

Spherical nano-enhancer (or zero-dimensional nano-enhancer) used in NEBL mainly include Al$_2$O$_3$, SiO$_2$, ZrO$_2$, SiC, and nano diamond (ND) (Fig. 5(a)), where ND and Al$_2$O$_3$ are widely used due to high strength, hardness, and heat resistance. SiO$_2$ nano-enhancer is popular as well due to the three-dimensional reticulated structure containing more unsaturated suspension bonds and therefore high surface activity. The low heat transfer coefficient seems to be the key problem for these nano-enhancer, and therefore many efforts for the moment focused on this field to improve the cooling performances of these particles [14].

2.2.2 Threadiness nano-enhancers

Threadiness nano-enhancers (or one-dimensional nano-enhancers) are also widely used in NEBL.
These nano-enhancers have excellent heat conductivity coefficient, and therefore can largely reduce machining temperature. These nano-enhancers mainly include CuO₂, MnO₂, TiO₂, ZnO, and CNTs (Fig. 5(b)). However, the unwanted aggregation resulted in high modulus and strength, deteriorating the tribological performances of these nano-enhancer at the cutting/grinding zone [15].

2.2.3 Stratiform nano-enhancers

Stratiform nano-enhancers in NEBL (or two-dimensional nano-enhancer) act like sliders at nanoscale thanks to the weak shearing strength between neighboring layers. With this, machined surface quality, process force, and temperature can be improved. In comparison with typical stratiform nano-enhancers such as CBN, MoO₃, HBN, and MoS₂ (Fig. 5(c)), graphene (GR) is the most popular material because of the good combination of excellent heat conductivity coefficient (5,300 (W·m⁻¹·K⁻¹)), high strength, and large Young’s modulus. GR is also the only type stratiform particle whose heat transfer is better than that of CNTs, making GR the most promising materials in terms of both cooling and lubrication. The limitation of GR for wider applications for the moment is the high price.

2.2.4 Composite nano-enhancers

The composite nano-enhancers used in NEBL, which could also be named as mix or hybrid nano-enhancers, are very popular in recent years. The NEBL prepared by composite nano-enhancers may present better lubrication or cooling performance than mono nano-enhancers. Compared with mono nano-enhancers,
composite nano-enhancers have more formulation options, which brings more possibilities for the development of NEBL. This method was first proposed in 2015 by Zhang et al. [15], and then a series of scholars conducted relevant studies. Hemmat et al. [16] and Khan et al. [17] summarized the common tested kinds of composite nano-enhancers in different machining processes. The excellent antifriction mechanisms of composite nano-enhancers have been confirmed in oil film lubrication in tribological tests and strips hot rolling experiment [18]. Du et al. [19] assessed the tribological performance of graphene oxide/TiO\textsubscript{2} composite nano-enhancers. The superior lubricating properties of graphene oxide/TiO\textsubscript{2} nano-composites were attributed to the excellent dispersion stability and the formation of absorption films, carbonaceous protective films, and transfer films. Nevertheless, previous studies did not apply to high temperature, pressure, and speed interface between tool and workpiece, which necessitates in-depth understanding.

3 Advanced mechanisms of NEBL vs. BMQL

The machining performance comparison with BMQL is the most intuitive way to reveal the advanced and unique cooling and lubrication mechanisms of NEBL. Therefore, the feasibility demonstration of NEBL vs. BMQL is naturally the first topic. It should be noted that, the performance evaluation experiments of BMQL or NEBL are carried out with dry machining in the current researches. Therefore, as a comparable method, dry machining is set as common reference of BMQL or NEBL in the evaluation of performance data below.

3.1 Tribological aspect

**Force and torque:** Comparing with dry grinding, the large force reduction (Fig. 6(a)) of 52% in normal and 46%–51% in tangential directions was observed in BMQL for AISI 4140 [20] and 1045 [21–23]. The introduction of nano-enhancer in NEBL further reduced forces, achieving 58%–62% force reduction for AISI 1045 [21–23] and 9%–35% for AISI 52100 [24] in tangential direction. Apart from grinding, the force reduction of 27% in aluminum silicon alloy (AISi5) [25] and 10% in 42CrMo4 BMQL turning [26] were observed in comparison with dry cutting. Except for cutting forces, the torque and thrust force were also reduced by separately 42% and 18% was also obtained in both BMQL drilling of ACP 5080 [27] and BMQL turning of AISI 1040 [28]. However, the negative example obtained by BMQL was the force rise of 20% at the high cutting speed of 800 mm/min in turning of AISI5 [25], which might be due to the cutting instability caused by the intermittent liquid supply and cooling of MQL (chilling effect) under the heavy machining loads.

**CoF:** CoF is the evaluator of lubrication at the tool–workpiece interface and can be calculated based on measured normal and tangential forces. The CoF reduction was observed including 11%–36% in BMQL grinding of AISI 1045 [21–23], 29%–49% using NEBL in grinding of AISI 1045 [21–23], and AISI 52100 [24], and 17% and 38% using BMQL and NEBL in milling of AISI 1045, respectively [31]. These results can be a good indicator of the better lubrication performance induced by NEBL [32].

**Tool wear:** In comparison with dry machining, obviously improved tool wear at the flank surface was observed in BMQL turning of AISI 9310 (Fig. 6(c)) [29], AISI 1060 [33], 39NiCrMo3 alloy steel [34], and AISI 420B [35], where VB values (referring to the principal flank wear, Fig. 6(b)) were separately decreased by 65% [29] and 20% [33]. The tool wear mode was changed from severe adhesive or even corrosive wear in dry machining to abrasive wear in BMQL [36]. The NEBL further extended the tool service life and reduced the VB value by 51% in comparison with BMQL milling and turning of AISI 1045 [37], Ti–6Al–4V [30] (Fig. 6(d)), and alloy 718 [38]. It’s worth noting that the hybrid using of cryogenic and BMQL presents lager VB than BMQL, as shown in Fig. 6(d). The composite usage of cryogenic and BMQL might cause a significant increase in viscosity. Therefore the wetting property and cooling property decreased sharply. Park et al. [30] concluded that tool wear was substantially smaller at the early stage of machining process due to effective cooling action. However, both cutting force and tool wear (adhesion and chipping) increased significantly as the Ti alloy hardens with the application of the liquid nitrogen during the cutting.
3.2 General lubrication mechanism of NEBL

The above improved tribological performance can be explained by the general lubrication mechanism of NEBL. In BMQL machining, micro craters on the workpiece surface and micro pores in grinding wheels acted like ‘capillary tubes’, and were filled with micro plant oil droplet by capillary forces, generating lubricating films at the workpiece–tool interface and improving the tribological behaviors. However, the film locations, sizes, and thicknesses were found random (called boundary lubrication in hydrodynamics [39]), and in most cases resulted in low film strength and instable film performances. This is the drawback of plant oils which limits its application in cleaner processing.

The introduction of nano-enhancer in NEBL stabilized these instable performances [40]. After nano-enhancer were transported into grinding/cutting zone based on capillary forces, these nano-enhancer showed three key functions based on SEM and Energy dispersive spectrometer (EDS) observation [41] (Fig. 7): (i) Nano-enhancer was distributed in the oil film and played a ball-saddle role, which protected oil films from damage due to the high particle strength; (ii) the interactions between the flat facets of abrasive crystals and the workpiece transformed themselves into solid lubricants as the composite tribofilm; and (iii) the composite tribofilms were helpful to avoid not only the bonding between the abrasives and the cutting edges but also the adhesive wear [32].

3.3 Thermal aspect

Temperature: In comparison with dry machining, the employment of BMQL resulted in the temperature
reduction of 14%–52% in AISI 1045 grinding [39, 42, 43], 34% in ductile iron grinding [44], and 18% in AISI 1045 milling [45] (Fig. 8(a)). Even more obvious temperature reduction was achieved by utilizing NEBL, and the examples include: the temperature reduction of 33%–62% in AISI 1045 grinding [39, 42, 43], 22% in AISI 52100 grinding [24], 7% in AISI 1045 turning [46], 13% in AISI 9310 turning [29], 9%–12% in 42CrMo4 steel turning [26], 15% in AISI 1040 turning [28], and 31% in AISI 1045 milling (Fig. 8(b)) [45].

Parameter $R$: Parameter $R$ (the ratio of the energy that transfers into the workpiece to the total energy generated due to the abrasive–workpiece interactions) is a classic thermal evaluator in grinding [39, 47]. Comparing with high-pressure gas where $R$ value was 68%, the smaller $R$ values were obtained, including 54% and 53.5% separately using BMQL and NEBL in grinding of ductile irons [48], and 50% and 41% in using plant oil and NEBL in grinding of AISI 1045 [39, 42].

### 3.4 General heat transfer mechanism of nano-enhanced biolubricant

The above thermal improvement can be explained by general heat transfer mechanism of NEBL. In terms of thermal properties, the heat transfer ability and the specific heat of plant oil were much better and higher than those of flowing gases in dry machining [49], and therefore the increased proportion of machining-generated heat can be transferred away from the cutting or grinding zone. The introduction of nano-enhancer into plant oil further enhanced the thermal conductivity and convective heat transfer capacity of NEBL because solid matters in general have
In terms of heat behaviors, Brownian motion forced nano-enhancer to impact on workpiece and therefore heat would be transferred from workpiece to nano-enhancer (Fig. 9(a)) [51]. Nano-enhancer attracted liquid molecules of plant oil fluids due to high surface energy and formed the adsorption layers on the external surface of nano-enhancer (Fig. 9(b)) [51]. When these layers contacted with each other, heat transfer channels were formed, via which excessive heat was effectively transferred far away from cutting and grinding zone (Fig. 9(c)) [52].

3.5 Machined surface integrity

Machined surface integrity, the most important indicator of the availability of machining, can be considered as the compound result of the above tribological (Section 3.1) and thermal performances (Section 3.3).

In comparison with dry grinding, surface burns were completely avoided by using BMQL and NBEL grinding of AISI 4140 [41], AISI 1045 [21], Ti–6Al–4V [53], and Inconel 600 [54], while the machined surface roughness R_s was reduced by 5% and 11% separately by using BMQL and NBEL grinding of AISI 1045 [23] (Figs. 10(a) and 10(b)). Except for grinding, NBEL milling of AISI 1045 obtained 13% reduction compared with BMQL [31]. The smoother chip back surfaces and better workpiece surfaces were also observed in NEBL machining (Fig. 10(c)) [55, 56].

Fig. 9 General heat transfer mechanism of NEBL. (a) Heat transfer motion of nano-enhancer; (b) nano-enhancer and adsorption layer around them; and (c) heat transfer channels. Reproduced with permission from Ref. [51]. © The Author, 2019.

Fig. 10 Machined surface integrity of BMQL and NEBL compared to dry condition. (a) R_s in AISI 1045 grinding and (b) SEM images of workpiece surface in AISI 1045 grinding. Reproduced with permission from Ref. [23]. © The Authors, 2015. (c) SEM images of chips surfaces in AISI 1045 milling. Reproduced with permission from Ref. [31]. © Springer Nature, 2018.
To summarize this section, it might be concluded that NEBL is the better lubricant, which have improved tribological and thermal properties and extended application scope compared with BMQL. The application of NEBL in MQL shows highly improved performances including force reduction of 9%–62% and temperature reduction of 14%–62%, comparing with dry machining. The application of NEBL also shows machined surface roughness improvement of 5%–13% compared with BMQL. The addition of nano-enhancers changes lubrication performance at tool/workpiece interface by its unique anti-friction and anti-wear behavior due to formation of solid tribofilm. Furthermore, the enhanced heat transfer performance due to Brownian motion of nano-enhancers also significantly reduces the temperature in cutting zone. Because of the above benefits, the machining of difficult-to-cutting materials (e.g. titanium alloy and nickel-based alloy) could be well done, which is a technical bottleneck for BMQL. From the green transformation of the whole industry, therefore, NEBL shows great promise.

4 Distinctive mechanisms of NEBL vs. traditional MWFs

The usage of NEBL meets requirement of sustainable manufacturing from resource sources aspect. Further, no oil mist and waste liquids generation meet requirement of sustainable manufacturing from environmental protection aspect. Therefore, the only question is whether NEBL could provide the same (or better) machining performance compared with heavy usage of traditional MWFs. It might be more interesting to perform the between-group comparison between NEBL and conventional flood machining.

4.1 Tribological aspect

\textbf{Force and CoF:} Comparing with traditional MWFs, the large force reduction was recognised, including 67\% in tangential and 43\% in normal direction in BMQL grinding of AISI 4140 [20], and 7\% in NEBL milling of Ti–6Al–4V [30]. However, the increased force was also observed in BMQL grinding of AISI 1045 [23]. Similar contradictory results were observed as well regarding CoF. The reduction of 38\% and 17\% were separately found in BMQL grinding of cast iron (Fig. 11(a)) and EN24 steel [41] while the increase of 24\% was reported in BMQL grinding of AISI 1045 (Fig. 11(b)) [21]. The general conclusion can be that NEBL can provide either better or worse tribological performances than conventional machining depending on the employed process conditions. Especially in the grinding process with high heat generated and complex geometric interface, the employment of NEBL presents slightly higher CoF than traditional MWFs. Oxidation of plant oil at high temperature is might the reason due to low flash point, therefore their cooling/lubrication properties are lost. This indicates that the preparation method and raw materials of NEBL need to be further optimized before it can completely replace the traditional MWFs in performance.

\textbf{Tool wear:} Compared with traditional MWFs, the VB values of the tool flank surface were largely reduced via BMQL and NEBL turning, including 33\% for 39NiCrMo3 alloy steel [34], 55\% for AISI 1045 [58], 67\% for AISI 9310 [29], and 4.3\% for Inconel 625 [59]. The G-ratio of grinding wheels was increased by 41.9\% for YG8 hard alloy [60]. The flank wear of tool was reduced by 27.1\% for high-speed drilling of Ti–6Al–4V [57]. Furthermore, thermal cracking, adhesion, attrition, and abrasion of tool were fully avoided (Fig. 11(c)) [57].

4.2 Formation mechanism of lubricating film of plant oil

Although the NEBL amount used in MQL is very small comparison with flood machining, improved tribological performances also obtained thanks to excellent film-formation performance of green coolant, which significantly influenced by polar groups, molecular cohesion, and viscosity of NEBL. Mineral oils don’t have these excellent properties.

\textit{(i) Polar groups:} Lubricating films were resulted from the co-existence of both physical and chemical absorptions between NEBL and workpiece surface in the cutting/grinding zone [61]. In comparison with traditional MWFs used in flood machining, NEBL can generate much stronger physical absorptions due to the polar atoms or groups such –COOH, –COOR, and –OH (Fig. 12(a)) with the large van der Waals forces. NEBL was also easy to form chemical absorption
Fig. 11  Tribological parameters of BMQL and NEBL compared to traditional MWFs. (a) CoFs in cast iron grinding. Reproduced with permission from Ref. [41]. © Elsevier, 2012. (b) CoFs in AISI 1045 grinding. Reproduced with permission from Ref. [21]. © Springer, 2014. (c) Tool failure modes in Ti–6Al–4V high speed drilling. Reproduced with permission from Ref. [57]. © Elsevier, 2010.

Fig. 12  Schematic diagrams of formation mechanism of NEBL. (a) Polar groups in molecule of NEBL. Reproduced with permission from Ref. [61]. © Elsevier, 2016. (b) Slide of lubrication film; (c) lubrication film on tool surface (PCD); and (d) lubrication film on workpiece surface (titanium alloy). Reproduced with permission from Ref. [64]. © The Author, 2018.
based on the metal saponification effect thanks to –COOH [22].

(ii) Molecular cohesion: NEBL resulted in not only easy formation of lubricating films but also the improvement of lubricating film properties. Fatty acid molecules have the long-chain structure (usually 12–14 carbon atoms), resulting in strong cohesive force within and between NEBL molecules [62]. This cohesive force was much larger than the internal force within traditional MWFs molecules in flood machining, leading the much higher film strength in MQL. Except for cohesion within NEBL molecules, the cohesion between oil molecules and nano-enhancer was also enhanced [63]. Nano-enhancer such as CNTs or SiO2 can either physically or chemically react with fatty acid molecules and become a new part of fatty acid chain, further increasing the film strength (Figs. 12(b)–12(d)) [64].

(iii) Viscosity: The polar atoms or groups (such as –COOH, –COOR, and –OH) in fatty acid molecules can increase the viscosity and therefore plant oil viscosity was much higher than that of traditional MWFs [65]. These viscous NEBL would result in good tribological performances thanks to the strong colloidal force and Brown force in lubricants [66]. This explanation can be experimentally supported by tribological tests [67–70], grinding trials [24, 71, 72], and cutting experiments [73–75].

4.3 Thermal aspect

Temperature and R: In comparison with traditional MWFs, BMQL can effectively lower machining temperature, including the reduction of 10% in AISI 9310 turning [29] and 35% in AISI 1045 milling, while NEBL achieved the temperature reduction of 43% in AISI 1045 milling (Fig. 13) [76]. However, in comparison with traditional MWFs, grinding with NEBL might also generate higher temperature such as temperature increase of 190 °C for ductile iron [44], 100 °C for AISI 1045 [42], and 30 °C for AISI 1045 [42]. Few studies also reported the slightly improved R value of 5.6% in AISI 1045 grinding [39, 42].

4.4 Atomization and infiltration mechanisms of plant oil

In comparison with traditional MWFs, the above thermal improvements can be explained by the excellent atomization and infiltration performances of NEBL [77–79].

(i) Atomization: In MQL, NEBL were mixed with gas and then the mixture was atomized and transformed into either symmetrical or asymmetric waves modes (Fig. 14(a)). This mixture can be smoothly delivered into the cutting/grinding zone by negative pressure via capillary structures [80]. This provided two difference in comparison with traditional MWFs: (i) Atomized coolants delivered with high pressure had a higher passing rate when obstructing air barriers around fast rotating tools; and (ii) atomized coolants enable the generation of fog droplets with much smaller sizes (Fig. 14(b)) [39].

(ii) Infiltration: The above atomization mechanism can result in very fast infiltration (Figs. 14(c) and 14(d)). On the contrary, traditional MWFs in flood machining would experience two stages before they reach cutting/grinding zone: (i) Atomization at high cutting temperature; and (ii) flow into capillary structures.

Fig. 13 Milling temperature of AISI 1045 under (a) traditional MWFs; (b) BMQL; and (c) NEBL. Reproduced with permission from Ref. [76]. © The Authors, 2018.
Therefore, infiltration in flood machining was often slow, providing insufficient cooling performances.

### 4.5 Machined surface integrity

Based on the above tribological and thermal improvement, machined surface integrities were improved by BMQL and NEBL. Compared with traditional MWFs, the $R_a$ was reduced by 37% for Ti–6Al–4V [81], 31.2% for Inconel 718 [82], and by 48% for AISI 9310 [29]. Better surface quality with lower depth of wear scars on the ground surface of AISI 1045 was observed (Fig. 15(a)). The introduction of nano-enhancer in NEBL further optimized plastic flows (Fig. 15(b)) [32], which indicated NEBL produced better surface quality. However, in one exceptional case the increased $R_a$ by 25% was also observed in NEBL in grinding of AISI 4140 [20].

Except for grinding, the employment of BMQL and NEBL in turning reduced the $R_a$ value by 50% for 39NiCrMo3 alloy steel [34], 6.7% for M2 steel [83], 23% for AISI 1045 [76], and 5.2% for Inconel 625 [59] in comparison with traditional MWFs.

Based on above, an encouraging conclusion could be obtained that NEBL is the ideal replacement of traditional MWFs. The application of NEBL in MQL shows highly improved performances including force reduction of 7%–67%, temperature reduction of 5.6%–43%, and surface roughness improvement of 5.2%–48%, comparing with traditional MWFs.

The usage of a small amount of NEBL could obtain comparable processing performance compared with Massive using of traditional MWFs. On one hand, the physicochemical properties of NEBL are more conducive to cooling and lubrication than that of traditional MWFs. On the other hand, the jet supply method of NEBL to cutting zone with help of high-pressure gas results in a higher utilization rate of the trace amount
of lubricant. And unique film-formation, atomization, and infiltration mechanisms of this technology also conducive to better cleaner manufacturing performance. Therefore, both environmental and processing performance could be achieved with employment of NEBL.

5 Multi-factor influence with considering various components and concentrations of NEBL

In order to improve performance stability of current process application and provide a theoretical guidance for sustainable machining of unexplored processing/materials in future, it’s important to understand how to obtain the best machining performance and establish optimization strategy of NEBL. It is closely related both base oils (plant oils) and nano-enhancer in terms of not only types but also volume/mass proportions. With this, this section focuses on understanding the mechanisms and optimization strategy in terms of different (i) base oils, (ii) nano-enhancer, and (iii) concentration of NEBL.

5.1 Processability and mechanisms using different base oils

In application of sustainable manufacturing, many kinds of plant oils are generally used as base oil of NEBL. It’s more important to make clear the influence rule and mechanism of different base oil molecules on the lubrication/cooling performance, which is the theory basis for plant oil application in cleaner machining.

5.1.1 Tribological aspect

Force and CoFs: Based on the NEBL grinding trials of AISI 1045 [39] and Inconel 718 [72], the CoF by using sunflower, maize, and palm oils only showed a slight difference. They believe that the molecular structure of different vegetable oils is responsible for the differences. The application of castor oil in NEBL generated the largest CoF reduction of 50% (Fig. 16), which might be because of the high viscosity and the –OH group contained in fatty acids. In the drilling of Inconel 718 [74] and Ti–6Al–4V [57], the palm oil also outperformed synthetic ester in terms of cutting force, power, and specific cutting energy thanks to higher viscosity and high content of saturated fatty acids.

Tool wear: Tool wear and service life were also varied by using different kinds of plant oils. In NEBL milling of AISI 1045 [84, 85], the obvious tool wear was observed when using canola oil (better lubricity) and cottonseed oil (better cooling ability) (Fig. 17). Moreover, adhesion or attrition (stick-slip phenomenon) was recognised as the dominant wear mechanism for these two oil types. This is due to the different vegetable oils in the tool workpiece interface have relatively large differences in friction reduction and wear resistance.

Based on above experimental results analysis, it could be found that the tribological performance of different base oils are different and certain rules. This is closely related to the composition and molecular structure of the base oil, which will be discussed in-depth in Section 5.1.2.

5.1.2 Varied lubrication performances due to microstructures of base oils

The above varied tribological performances in NEBL can attribute to different microstructures of plant oils in terms of (i) special polar groups, (ii) saturated levels of fatty acids, and (iii) molecular chain length.

(i) Special polar groups: For oils with special polar groups (such as –OH in castor oil [86]), they showed better lubrication performances than other oils because these polar groups significantly improved the formation ability (by stronger adhesion) and strength (by higher viscosity) of lubricating films. Therefore, this kind of oils can achieve much stronger adhesion between the
formed lubricating film and cutting edge/workpiece surfaces [22]. At the meantime, the high viscosity of these oils also enabled the good film strength. However, the excessively high viscosity resulted in poor heat transfer [87].

(ii) Saturated levels of fatty acids: Oils with high saturated levels of fatty acids (i.e. a small number of C=C bonds on molecular chains) have better lubrication performance. This was because (i) no C=C bonds existed and therefore the molecule can align itself as a slim and straight chain [88, 89], which improved the inter-molecular interactions due to the strong packing effect [70, 90] (Fig. 18); and (ii) C=C bonds can be easily oxidized resulting in poor thermal stability of plant oils and consequently physical film failure [73].

(iii) Molecular chain length: Oils with longer molecular chain (i.e. a large number of carbon atoms) had better lubrication performances because absorption capability presented a rise trend with increasing carbon atom number [91, 92]. However, the largest improvement can be reached when carbon atom number was 16 [62].

In fact, lubrication property of plant oils is the comprehensive result of special polar groups, saturated levels of fatty acids, and molecular chain length. The weighted relationship between lubricating properties and molecular structures of plant oils (Fig. 19) can be:

![Fig. 17](https://example.com/fig17.png) The flank wear and tool life in milling of AISI 1045. Reproduced with permission from Ref. [85]. © Elsevier, 2017.

![Fig. 18](https://example.com/fig18.png) Schematic diagrams of lubrication mechanism in NEBL. (a) 3D structure of fatty acid; (b) lubricate with saturated fatty-acid; and (c) lubricate with unsaturated fatty-acid.
(i) plant oils with special polar groups presented the best lubrication performances; (ii) oils with the high content of saturated fatty acids had the second best lubrication performances; (iii) oils with the high content of unsaturated fatty acids had the third best performances because of the long carbon chains and the high-level saturation; and (iv) oils with short carbon chains had the worst lubrication due to the low-level saturation.

Please note superior plant oils in NEBL might require both good cooling and lubrication performances, and these two performances have the opposite relationships with oil viscosity. Although oils with special polar groups had the best lubrication performance, they presented the worst cooling performance.

5.1.3 Thermal aspect

**Temperature:** In comparison with other oils, castor oil resulted in the higher grinding temperature of 176 °C and the larger $R$ value of 69.3% in grinding of Inconel 718 [72, 93]. On the contrary, palm oil based NEBL grinding generated the lowest grinding temperature of 119.6 °C and the smallest $R$ value of 52.3% (Figs. 20(a) and 20(b)). Cottonseed oil and canola oil also resulted in the low temperature and the good convective heat transfer in NEBL milling of AISI 1045 (Figs. 20(c) and 20(d)) due to its good spreadability proved by wettability tests [85]. Surprisingly, the rules obtained for heat transfer performance are different from those obtained for tribological aspect in Section 5.1.1. Castor oil has better tribological performance with lower cutting forces and CoFs, but it is not ideal in thermal aspect. It can be predicted that the viscosity and surface tension of base oil have different influence laws on the heat transfer performance, which belongs to the theory of boundary layer heat transfer.

5.1.4 Heat transfer mechanism of boundary layer

The above varied thermal performances of different plant oils can be explained by the heat transfer mechanism of boundary layer, which was affected by both viscosity and surface tension of NEBL [94].

For viscosity, oils with a lower viscosity can provide better cooling performance. This was because (i) droplets with a lower viscosity generated thinner viscous flows in thermal boundary layer at the tool–workpiece interface (Fig. 21(b)) [39]. The thermal boundary layer contained turbulence and viscous flows [95]. The former transferred more heat than the latter, and therefore the thickness reduction of viscous flows improved the heat transfer efficiency, and (ii) high viscosity in most cases referred to the large intramolecular friction, inactive Brownian movement, and consequently ineffective heat transfer behaviors. Therefore, oils with high viscosity generated small $R$ values.

For surface tension, oils with a lower surface tension can provide better cooling performance. This was because (i) droplets with lower surface tension were small in size but with a high specific surface area [70, 96], covering a large area by a unit volume of lubricant and therefore improving cooling performance [97–100] (Fig. 21(a)); (ii) the thermal boundary layer would be expanded when the surface tension was low (Fig. 21(c)), and improved the cooling efficiency by using a unit volume of lubricant because the thermal
Fig. 20  Thermal parameters of different plant oils. (a) Temperature in Inconel 718 grinding and (b) R in Inconel 718 grinding. Reproduced with permission from Ref. [93]. © The Authors, 2015. (c) Temperature curve in V-AISI 1045 milling and (d) Convection heat transfer coefficient of different plant oil. Reproduced with permission from Ref. [85]. © Elsevier, 2017.

Fig. 21  Schematic diagrams of heat transfer mechanism in NEBL. (a) Oval spray boundary in grinding zone; (b) heat transfer mechanism of thermal boundary layer; and (c) influence mechanism of surface tension on cooling performance. Reproduced with permission from Ref. [39]. © Elsevier, 2016.
boundary layer played the leading role due to the high speed in cutting zone; and (iii) fog droplets with a lower surface tension (i.e., small contact angle) spread out more quickly than those with a large surface tension.

5.1.5 Machined surface integrity

In comparison with other plant oils, the employment of castor oil in NEBL grinding of Inconel 718 [72] resulted in good machined surface morphology and small roughness value (Ra of 0.366 μm and RS_m of 32.4 μm) (Fig. 22(a)). The similar result was also obtained in grinding of H13 hot die steel using castor oil [101]. The average thickness of the deformed layer, which was related to the sticking friction due to elevated temperature [102], was in the range from 122 to 167 μm [74] (Fig. 22(b)).

In the BMQL drilling of AISI 316 using palm oil, olive oil, and sesame oil, however, adhesion was found which indicated the increased friction and flank wear in tool/workpiece interface due to low thermal conductivity of lubricants [103]. Further, the least amount of micro-cracks for coconut oil (lowest viscosity) and the largest amount of micro-cracks for sesame oil (biggest viscosity) were observed (Fig. 22(c)).

It could be obtained that different plant oils have different machining performances, and the varied molecular structure and physicochemical properties (viscosity and surface tension) are the key reason. Higher viscosity of biolubricant benefits lubrication performance, while lower surface tension benefits heat transfer performance. Unfortunately, high viscosity and low surface tension couldn’t co-exist in natural plant oils. This contradiction will be discussed detailly in Section 6.

5.2 Processability and mechanisms using different nano-enhancers

The use of different nano-enhancer are expanding options of plant oil for various processing and materials in cleaner machining system. It’s necessary to understand the effects of micromorphology and physical properties of nano-enhancer on cooling and lubrication performance, which is key reference

![Fig. 22](https://mc03.manuscriptcentral.com/friction)
for cleaner process design based on machining and economic performances.

5.2.1 Tribological aspect

**Force and CoF:** Two or three kinds of nano-enhancers such as Al₂O₃, MoS₂, and CNTs [21, 23, 24, 42] were often used in NEBL grinding and different force and CoF were observed. The CoFs for MoS₂, Al₂O₃, and SiO₂ NEBL were decreased separately by 31.4%, 35.3%, and 34.8% when using traditional MWFs as the reference (Fig. 23(a)) [104], which might be because nano-enhancer (with either spherical and stratiform molecular structure) played a lubricating role in grinding zone. Further, the composite nano-enhancers present better lubrication performance than mono one. In NMQL grinding research of Inconel 718, the CoF for composite MoS₂/CNT NEBL was decreased separately by 8.8% and 15.3% comparing with mono MoS₂ and CNT [15]. The tangential force reduction of 20.9% and 35.0% were obtained by Al₂O₃/SiC comparing with mono Al₂O₃ and SiC [105, 106], respectively. The results of CoFs and specific grinding

![Fig. 23 Tribological parameters in NEBL machining with employment of different nano-enhancers. (a) CoFs in Inconel 718 grinding. Reproduced with permission from Ref. [104]. © Elsevier, 2016. (b) Cutting force in Ti–6Al–4V milling. Reproduced with permission from Ref. [107]. © Springer Nature, 2018. (c) SEM and EDS of the wheel block surface before and after grinding. Reproduced with permission from Ref. [61]. © Elsevier, 2017. (d) Microscopic photographs of tool flank wear with alumina and alumina/MWCNT based NEBL. Reproduced with permission from Ref. [111]. © The author(s), 2018.](image-url)
energy present similar trend. They attribute the improved performance to ‘physical synergistic effect’ of composite nano-enhancers. In further research [106], they found that a composite of large particle size Al₂O₃ and small particle size SiC can increase the grinding efficiency furtherly. It maybe due to the ‘physical coating’ phenomenon of the Al₂O₃/SiC with different particle sizes.

Except for grinding, cutting forces and CoF in NEBL milling of Ti-6Al-4V presented the similar results, where Al₂O₃ NEBL achieved the minimum milling force and CoF compared with another five kinds of nano-enhancers (Fig. 23(b)) [107]. Cutting forces and CoF in NEBL turning of AISI 4340 obtained the lowest value, where CuO NEBL achieved the minimum milling force and CoF compared with Fe₂O₃ and Al₂O₃ nano-enhancers [108, 109].

Tool wear: The G-ratio for MoS₂ and Al₂O₃, SiO₂ NEBL were increased separately by 66.1% and 82.9% compared to traditional MWFs for Inconel 718 [104]. Further observation of the grinding wheel surface showed that oil film existed on the abrasive surface and contained nano-enhancer elements by SEM and EDS analysis (Fig. 23(c)) [61]. It can be inferred that nano-enhancers can form lubricating oil film on the surface of abrasive particles, thus reducing friction coefficient and improving wear resistance of grinding wheel. The average flank wear of AISI 1045 turning also obtained similar results [110].

Compared with mono Al₂O₃, the value VB was reduced by 11% with employment of Al₂O₃/CNT in NEBL turning trials of AISI 304 stainless steel [111]. The worn out cutting edge observed in Al₂O₃ NEBL turning was significant less by composite nano-enhancers (Fig. 23(d)). They ascribe it to ‘synergistic effect’ of Al₂O₃/CNT during relative motion between the sliding surfaces. The usage of GO/SiO₂ also obtained improved tool wear than mono one in NMQL milling, severe chipping and fracture was avoided [112]. In addition, Ali et al. [113] found that the size of nano-enhancer plays a significant role in NMQL turning. The usage of Al₂O₃ with 50 nm particle size in NMQL nanolubricant reduced tool wear by 62.5% compared to that of Al₂O₃ with 600 nm particle size.

Based on above researches, it could be concluded that the geometries and hybrid use of nano-enhancers are the main factor for tribological aspect. Although particle size also plays a role, it is only mentioned as the influencing factor in references of application of composite nano-enhancers. It’s difficult to find a universal law for different kinds of hybrid nano-enhancers. Therefore, the various anti-friction mechanisms due to geometries and combination modes of nano-enhancer will be discussed in detailly in Section 5.2.2.

5.2.2 Various anti-friction mechanisms due to geometries and combination modes of nano-enhancers

(i) Effect of nano-enhancer shape on lubrication performance. The above varied tribological performances in NEBL are related with anti-friction mechanism of nano-enhancers thanks to spherical, threadiness, and stratiform nano-enhancers geometries.

Spherical nano-enhancer with high hardness and strength (such as Al₂O₃ and SiO₂) showed remarkable diffusivity and lubrication property in cutting zone. They changed the friction condition from sliding to rolling friction. The lubricating behaviors can be featured by rolling (Fig. 24(a)), protective film forming (Fig. 24(b)), wear restoration (Fig. 24(c)), and polishing (Fig. 24(d)) [114, 115] so that tool life, temperature, and force can be largely improved.

Threadiness nano-enhancer showed good lubrication performance but the performance was limited by nano-enhancer concentration in NEBL. When threadiness nano-enhancer with a low concentration was introduced in cutting zone, threadiness nano-enhancer can act as ‘cylindrical bearing’ therefore significantly reduce friction. However, when threadiness nano-enhancer with a high concentration was introduced in cutting zone, the formation of cluster would lead to poor friction lubricating performance [15].

Stratiform nano-enhancer can act as a good solid lubricant in tool/workpiece interface (Figs. 24(e) and 24(f)) [116]. The low shearing strength between neighboring layers in nano-enhancer microstructure allowed the smooth sliding at the interface [118]. Different stratiform nano-enhancer presented different lubrication performances due to varied intermolecular force, and in most cases the performance was positively related with relative molecular mass [116].

(ii) Performance gain of composite nano-enhancers. It has been verified by above researches that composite
Nano-enhancers present better tribological property than mono nano-enhancers, especially in the uneven tool workpiece interface. This effect was named as ‘physical synergistic effect’ by researchers. The essence of this phenomenon is that the hybrid use of nano-enhancer with different shapes could change the anti-friction behavior of NEBL.

As seen in Figs. 24(g) and 24(h), stratiform nano-enhancer are distributed in parallel in the interface of the tool workpiece, which divides the uneven lubrication zone into regular shear-sliding interface. On this basis, the spherical or tubular nano-enhancers play a rolling role in reducing friction between the shear interfaces, and play a filling role on the surface of the workpiece and the tool. There are the following advantages: on the one hand, this mode of composite use increases the bearing capacity of NEBL at the high pressure interface, avoiding congestion and interference of nanoparticles between each other caused by the use of single shape nano-enhancers, thus significantly reducing the coefficient of friction. On the other hand, the stratiform nano-enhancer with excellent lubrication performance and the tubular/spherical nanoparticles with high thermal conductivity could act at the same time, which is expected to improve the lubrication performance and increase the thermal conductivity. As seen in Fig. 24(i), the particle size is also the main factor of ‘physical coating’ phenomenon of the Al₂O₃/SiC with different particle sizes. Reproduced with permission from Ref. [106]. © Elsevier, 2016.
composite nano-enhancers increases the viscosity of nanofluids and the oil film to avoid the direct contact tribopair during hot rolling, thus reducing the friction coefficient and roll wear.

5.2.3 Thermal aspect

Temperature and R: Based on the NEBL grinding trials of Inconel718, the application of CNTs NEBL obtained the lowest grinding temperature of 110.7 °C and R value of 40.1% compared to other five typical kinds of nano-enhancers (Fig. 25) [120]. In another research of turning, MoS\textsubscript{2} based NEBL showed thermal conductivity, specific heat, and viscosity than CaF\textsubscript{2} based NEBL [79].

Based on the NEBL turning trials of AISI 304 stainless steel [111], the application of Al\textsubscript{2}O\textsubscript{3}/CNT improved thermal conductivity of 2.6% compared with mono NEBL. A significant reduction of 27.36% in the nodal temperature was achieved for Al\textsubscript{2}O\textsubscript{3}/CNT hybrid nano-enhancer compared to Al\textsubscript{2}O\textsubscript{3}. There were 16.6% and 10.25% decrease in cutting temperature when turning of EN-24 steel under Al\textsubscript{2}O\textsubscript{3}/CuO NEBL as compared to Al\textsubscript{2}O\textsubscript{3} and CuO NEBL [121]. They suggesting that the mixing of CNT with Al\textsubscript{2}O\textsubscript{3} improves the spreadability, thanks to its smallest contact angle. In another researches, although lubrication performance was improved by composite of MoS\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} [122], CNT/Al\textsubscript{2}O\textsubscript{3} [123] and graphene/Al\textsubscript{2}O\textsubscript{3} [124–126], they found that it also affects the thermal conductivity negatively. This phenomenon maybe caused by increased viscosity of composite NEBL compared with mono NEBL, which weakens cooling performance.

It could be concluded that the heat conductivity coefficient, shape, and particle size of nano-enhancers are the main influence factors for thermal aspect, which will be discussed in Section 5.2.4.

5.2.4 Various heat transfer mechanisms of different nano-enhancers

The above varied cooling performances in NEBL are related with heat transfer mechanism of nano-enhancers, which could be understood from three aspects.

(i) Heat conductivity coefficient of nano-enhancer: The introduction of nano-enhancer significantly improved heat transfer ability of NEBL because the heat conductivity coefficient of nano-enhancer is much higher than that of plant oils (Table 1) [127]. This explained why CNTs NEBL presented the best cooling performance.

(ii) Effect of nano-enhancers shape on heat transfer: Except for Brownian motion, self-rotational of nano-enhancer was another key heat transfer behavior between nano-enhancers and plant oil. Nonspherical nano-enhancer had a higher rotational speed than spherical ones in NEBL, and therefore generated a larger disturbance region. Hence, the local micro-

![Fig. 25](Thermal parameters in Inconel718 NEBL grinding with employment of different nano-enhancers. (a) Temperatures and (b) R. Reproduced with permission from Ref. [120]. © Elsevier, 2017.)

| Nano-enhancers | ZrO\textsubscript{2} | SiO\textsubscript{2} | HBN | Al\textsubscript{2}O\textsubscript{3} | MoS\textsubscript{2} | ND | CNT | GR |
|----------------|-----------------|-----------------|-----|-----------------|-----------------|----|-----|----|
| Heat conductivity coefficient (W·m\textsuperscript{-1}·K\textsuperscript{-1}) | < 2 | 7.6 | 33 | 40 | 138 | 2300 | 3000 | 5300 |
convection and energy transmission can be enhanced between the nano-enhancer surface and the liquid (Fig. 26) [47].

(iii) Effect of particle size of nano-enhancers on heat transfer: Particle size of nano-enhancers play an important role in increasing thermal conductivity of NEBL. On the one hand, the thermal conductivity will be increased by smaller size of nano-enhancers, due to the active Brownian motion. This can also be verified by classical equation of thermal conductivity of nanofluids, as studied in Ref. [128]. On the other hand, at the same dosage, smaller particles have larger specific surface area, which is more conducive to improving the heat transfer efficiency of nanoparticles in the base oil.

5.2.5 Machined surface quality

In comparison with other kinds of nano-enhancer, the employment of Al2O3 in NEBL grinding of Inconel718 resulted in good machined surface morphology with neither obvious ductile plowing nor adhesion phenomena [104]. The Ra was reduced to 0.30 \( \mu m \) while RS_m was reduced to 38 \( \mu m \) (Fig. 27(a)).

Fig. 26 Schematic diagrams of self-rotational motion of nano-enhancer. (a) Spherical nano-enhancer; (b) irregular nano-enhancer; and (c) tubular nano-enhancer. Reproduced with permission from Ref. [47]. © Taylor & Francis, 2017.

In comparison with mono nano-enhancer, the employment of MoS2/CNT in NEBL grinding of Inconel 718 resulted in good machined surface morphology with no workpiece burns phenomena [15]. When the mix ratio of MoS2 and CNT is 2:1, the Ra was reduced to 0.294 \( \mu m \), 13% and 38.9% lower than that of mono MoS2 and CNT, respectively. Compared with mono MoS2 in NMQL grinding, subsurface damage layer of Si3N4 was significantly reduced with employment of MoS2/WS2 [129].

Similar result was obtained in NEBL milling of Ti–6Al–4V (Figs. 27(b)–27(e)) [107] . Spherical Al2O3 achieved the minimum roughness value (Ra of 0.633 \( \mu m \) and RS_m of 95 \( \mu m \)). Good machined surface morphology and higher Al atom content were also observed on workpiece surface by SEM and EDS. Spherical SiO2 nano-enhancer also had good machined surface topographies and morphologies containing the biggest profile supporting length rate (R_m) of workpiece, and shallow scratches. In addition, the usage of Al2O3/CuO obtained lower Ra than mono Al2O3 in turning of EN-24 steel [121].

Based on above, it might be concluded that different nano-enhancers have different machining performances, and the varied microstructure and heat conductivity coefficient are the key reason. Threadiness CNTs presents better cooling performance, however, its lubrication performance is worse than stratiform and spherical nano-enhancers. This contradiction might be solved by composite using of different kinds of nano-enhancers. Because there are many more

Fig. 27 Machined surface integrity of NEBL with employment of different nano-enhancer. (a) Ra in Inconel718 grinding. Reproduced with permission from Ref. [104]. © Elsevier, 2016. SEM images in Ti–6Al–4V milling with employment of (b) Al2O3; (c) MoS2; (d) SiO2; and (e) CNTs. Reproduced with permission from Ref. [107]. © Springer Nature, 2018.
possibilities for composite nano-enhancers, it is hard to predict a best mixing scheme from the limited literature.

5.3 Processability and mechanisms using different concentration of NEBL

It’s no doubt that increasing the concentration of NEBL could improve the processing performance. However, it’s also one of the most important contents that obtained appropriate concentration to not only realize machining performance but also avoid waste after excessive use. Therefore, the mechanism understanding of concentration on tribological and thermal performance is the major content in sustainable machining.

In the early studies, pioneers employed two or three concentration values for NEBL in research such as MoS$_2$–Soybean oil (5 wt%, 20 wt%) [130], EP additive–coconut oil (8%, 12%) [131], diamond NEBL (1 vol%, 2 vol%) [132], MoS$_2$–Soybean oil (2 wt%, 8 wt%) [41], exfoliated graphite NEBL (0.1 vol%, 1 vol%) [37], and Al / MoS$_2$ NEBL (0.25 vol%, 0.75 vol%, and 1.25 vol%) [122]. However, few studies discussed the accurate relation between machining performances and concentration.

5.3.1 Tribological aspect

Force and CoF: Based on the comprehensive NEBL grinding trials of Inconel718 [133], the employment of 1.5 vol% Al$_2$O$_3$–palm oil NEBL obtained the larger CoF reduction of 29.7% (Fig. 28(a)) and the larger specific grinding energy reduction of 34.4% compared to palm oil. With the concentration increasing from 0 to 4.0 vol%, CoF and specific grinding energy presented first falling and then rising trend, which might be due to aggregation effect of nano-enhancer. The similar result was obtained for Ti–6Al–4V–ELI. The employment of concentration 1.5 wt% graphene NEBL obtained the larger CoF reduction of 17.3% and the larger force reduction of 25% compared to BMQL [134].

Except for grinding, NEBL milling force of TC4 [135] and Inconel 690 [136] presented the similar results.

![Fig. 28](https://mc03.manuscriptcentral.com/friction) Tribological parameters in machining with employment of different concentrations of NEBL. (a) CoFs in Inconel718 grinding of with employment of Al$_2$O$_3$–palm oil NEBL. Reproduced with permission from Ref. [133]. © Elsevier, 2017. Tool wear in AISI 1040 turning with employment of (b) MoS$_2$–sesame oil NEBL; (c) MoS$_2$–coconut oil NEBL; and (d) MoS$_2$–canola oil NEBL. Reproduced with permission from Ref. [137]. © Elsevier, 2016.
The employment of concentration 0.1 wt% graphene NEBL obtained the larger CoF reduction of 26.3% and the larger force reduction of 42.7% compared to BMQL [135].

**Tool wear:** Tool wear was also varied by using different concentration of NEBL. Based on the comprehensive NEBL grinding trials of Inconel718 [133], the employment of 2.5 vol% Al2O3–palm NEBL obtained the larger G-ratio increase of 50% compared to palm oil based BMQL. In NEBL turning of AISI 1040 [137], the smallest tool wear was respectively observed when using 0.5 vol% for MoS2–sesame oil NEBL (Fig. 28(b)), 0.25 vol% for MoS2–coconut oil (Fig. 28(c)), and MoS2–canola oil NEBL (Fig. 28(d)). The curve of tool wear also showed a change trend of first falling and then rising.

### 5.3.2 Thermal aspect

**Temperature and R:** Temperature presented a similar variation trend with the increasing concentration of CNTs–palm oil NEBL in grinding of Inconel718 [138]. The employment of concentration 2 vol% NEBL obtained the lowest grinding temperature of 108.9 °C and R value of 42.7%. The thermal conductivity of different concentration NEBL presented the increasing trend as concentration rising because the increasing amount of nano-enhancer improved heat transfer ability. However, the growth curve of thermal conductivity presented a sharp increasing first and then a slow increasing due to ‘aggregation effect’, which is explained in Section 5.3.3 (Fig. 29).

Except for grinding, temperature of NEBL turning presented the similar results [131]. In turning of AISI 1040 [137, 139], thermal conductivity presented a rising trend and obtained the highest value for NEBL with 1 vol% concentration due to the increased effective number and specific area of nano-enhancer [140, 141].

### 5.3.3 Aggregation mechanism optimum concentration of NEBL

The above varied tribological and thermal performances in NEBL are related with aggregation mechanism of nano-enhancer.

When an excessive particle number of nano-enhancer were introduced into NEBL, the inter-molecular forces would lead to the formation of micro clusters and reduce nano-enhancer dispersibility (Fig. 30) [142, 143].

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**Fig. 29** Cooling-performance parameters of NEBL with different concentrations. (a) Thermal conductivity and (b) growth rate of thermal conductivity. Reproduced with permission from Ref. [138]. © Springer Nature, 2017.

**Fig. 30** Schematic diagrams of aggregation mechanism of nano-enhancer. (a) Good dispersibility with proper concentration and (b) bad dispersibility with exorbitant concentration. Reproduced with permission from Ref. [43]. © Elsevier, 2016.

Based on the measurement test of NEBL with different concentrations, viscosity presented the increasing trend with the reduced increasing rate (Figs. 31(a) and 31(b)). The curve of contact angle first fell and then rose (Figs. 31(c) and 31(d)) [65, 144, 145].
The machining performances reached top at the inflection points for curves of viscosity and contact angle.

5.3.4 Machined surface quality

In comparison with other concentration values, the employment of 2.0% NEBL in NEBL grinding of Inconel718 resulted in good machined surface morphology with the small roughness value $R_a$ of 0.301 $\mu$m (Figs. 32(a)–32(d)) [133]. The excessively high or low concentrations led to poor lubrication performances (Figs. 32(e) and 32(f)). The concentration of 8 wt% was confirmed as the best for MoS$_2$–CNTs NEBL [43].

Except for grinding, $R_a$ showed a change trend of first falling and then rising in turning of AISI 1040 [137]. The employment of concentration 0.5 vol% MoS$_2$–coconut NEBL obtained the most obvious reduction of surface roughness when compared with other NEBL with varied concentrations.

Although the machining performance could be improved obviously by increasing concentration of NEBL, there is an inflection point for concentration value. Before the inflection point, the heat transfer coefficient, viscosity, and surface tension of NEBL will change in a favorable direction. Instead, after the inflection point, the physical and chemical properties will get worse due to aggregation effect of nano-enhancers. It might become a puzzle for processing occasions with higher requirements of cooling and lubrication. This contradiction will be discussed detailly in Section 6.

6 The limitation in coexistence between cooling and lubrication of NEBL

Most of the current researches are focused on the application of natural plant oil and individual nano-enhancer, which exists limitation in coexistence between cooling and lubrication. Therefore, in order to improve application range for industrial application, the contradiction between good cooling and effective
Friction should be analyzed in-depth and possible solutions should be put forward by changing oil viscosity, nano-enhancer types, and nano-enhancer concentration.

6.1 From base oil aspect

The oils with a high viscosity have a strong absorption between molecules, and therefore the generated oil film has a high strength and good lubrication performance. However, the excessive molecule absorption would lead to less active Brownian motion, showing a reduced cooling performance.

Temperature can be considered as the compound result of both cooling and lubrication performance, because the cutting/grinding zone temperature is determined by the difference between the total generated heat and the heat cooled by NEBL. If the oil with a high viscosity is used, the lubrication performance would be enhanced and therefore less heat is generated. However, the cooling performance would be weakened as well. Therefore, there should be an optimum viscosity value to achieve a balance between cooling and lubrication performance. Especially for aerospace difficult-to-cutting materials, which requires high surface quality and no thermal damage at the same time, the coexistence between cooling and lubrication caused by viscosity must be solved in the future.

For nature plant oil, higher viscosity value is usually caused by polar groups (e.g., –OH). There is no doubt that the existence of polar groups is beneficial to film formation and lubrication behavior. In order to avoid lower heat transfer performance due to high viscosity, with this, oils with a high viscosity was mixed with oils with a low viscosity so that not only the cooling can be improved but also the special polar groups can guarantee the good lubrication performance [147, 148]. Besides, chemical modification was also suggested to improve the viscosity [149–151].

6.2 From nano-enhancer aspect

The shape and thermal conductivity of nano-enhancers

Fig. 32 SEM of debris; workpiece; and $R_a$ in Inconel718 NEBL grinding with employment of different concentrations of (a) 0.0 vol%; (b) 1.0 vol%; (c) 2.0 vol%; and (d) 3.0 vol%. Reproduced with permission from Ref. [133]. © Elsevier, 2017. Autocorrelation curve of workpiece surface profile under (e) 2 wt% and (f) 8 wt%. Reproduced with permission from Ref. [43]. © Elsevier, 2016.
are the main factors affecting the processing performance. Spherical or stratiform geometries of nano-enhancer can provide good lubrication, thanks to regular shape and stable lubrication behavior. In contrast, the lubrication performance of tubular nano-enhancers (e.g., CNTs) is fluctuating due to the shape of CNTs is not the standard linear, which feature causes the CNTs to stumble on each other when act as a roller. Even so, CNTs have promising applications because of their thermal conductivity, which is much higher than that of other nano-enhancers.

Therefore, there is a contradiction between cooling and lubrication performance in selection of nano-enhancer. The following are several potential solutions that may become future research directions.

i) If we want to choose a single nano-enhancers with excellent cooling and lubrication properties, the stratiform graphene is the ideal choice. Layer structure of graphene is good for lubrication, while the higher thermal conductivity (higher than CNTs) is conducive to heat transfer. There have been attempts to study graphene based NEBL application in MQL and better processing property is also obtained [152]. However, its price is too high to apply in real industries [153]. Perhaps in the future, when the preparation process of graphene is improved and the production cost is significantly reduced, the application of graphene in NEBL will be broadened.

ii) The composite usage of different kind of nano-enhancers is a more economical and effective way at present. It seems like a compromise when this method was proposed, cooling and lubrication performance could be maintained at a certain level simultaneously, but not the best. What is exciting is that the lubrication mechanism has changed significantly after the mixed using and the improvement of machining performance was far greater than expected [154]. However, because there are many more possibilities for composite nano-enhancers, it is hard to predict a best mixing scheme from the limited literature.

6.3 From concentration of NEBL aspect

As the concentration increases, a large nano-enhancer number will participate in lubrication and cooling process therefore improves the tribological and thermal properties. However, the dispersity of nano-enhancer in plant oils is a limitation. Excessive nano-enhancer would lead to a largely increased number of nanoparticle collision during the Brownian motion, leading to cluster. Some nanoparticles deposit at surface of workpiece or tool due to cluster. Although these deposited nano-enhancer can have the lubrication function, the nano-enhancer in the base oil would be reduced. Therefore the cooling performance is weakened. With this, there should be an optimum concentration for a certain type of nano-enhancers and base oils.

Compared with the selection of base oil and the type of nano-enhancers, increasing the concentration of NEBL to improve the heat transfer performance is a more effective method. Therefore, how to improve the optimum concentration value is the focus of current and future research. To solve this, increasing the concentration and simultaneously improving the cooling performance via adding dispersants is the solution. Regarding this, alkylphenol polyoxyethylene ether 10 (APE-10) (Fig. 34) and sodium dodecyl sulfate (SDS) were found as good dispersants for CNT-based NEBL, while oleic acid is a good dispersant for ZnO and WS2 mixed NEBL [155–157]. More efforts are needed to find best dispersants for other NEBL.

7 Conclusions and future challenges

This paper comprehensively reviewed the advances of minimum quantify lubrication (MQL) technologies using nano-enhanced biolubricant (NEBL). The biodegradability of NEBL, harmlessness to nature, and more than 95% of coolant consumption save establish itself as a promising sustainable manufacturing solution with largely reduced cost and specific energy.

The key findings and possible future research can be identified as follows:

(i) The application of NEBL in MQL is an effective cleaner machining technology, showing highly improved performances including force reduction of 9%–62%, temperature reduction of 7%–62%, and machined surface roughness improvement of 5%–50%, comparing with dry machining. Based on the comprehensive summaries given in this paper, this improved performances can be explained by two theories:

(a) the introduction of nano-enhancer to biolubricant
completely changed the friction state of tool–workpiece interface based on general lubrication mechanism, and (b) the Brownian motion and heat transfer channels of nano-enhancers greatly improved heat transfer performance based on general heat transfer mechanism.

However, the future research might focus on: (a) By understanding of MQL mechanism using NEBL in basic machining processing, this sustainable method could be promoted wider application to other industries such as automobile, aerospace, and ship building industries; (b) the MQL equipment relies on high pressure gas to supply micro droplets of NEBL, which may be scattered floated into the air. The cleanliness of this method is not optimal at present due to the appearance of a certain amount of oil mist in processing environment and the impact on environment and human health of nano-enhancer with small size is still a possible threat, which must be solved to realize cleaner machining. Electrostatic atomization assisted MQL maybe the possible solution in the near future, in which way oil mist dispersion may be reduced under the constraint of electric field force.

(ii) Compared with traditional metal-working fluids, NEBL can provide equal machining performance and pronounce environmental protection because the employed NBEL amount is only 1%-5% thanks to the improved coolant behaviors including atomization, infiltration, and film-formation performances due to unique polar groups, bigger molecular cohesion, and viscosity.

However, this green machining method is limited to conventional process parameters according to current researches. The above conclusions can provide guidance for the extended application. The future research might focus on: (a) The extended application and in-depth analysis in high-efficiency machining, which characterized by machining with extreme processing parameters; (b) solving the issues such as insufficient infiltration performance for high efficiency deep grinding, the insufficient cooling performance for material removal with high strain rate, and difficult-to-machine materials machining. The hybridization between NEBL and cryogenic air, ultrasonic vibration, electrostatic atomization, atmospheric pressure plasma jet, and textured tool might be the possible solutions.

(iii) Diverse plant oil types, nano-enhancer types, and different oil–particle combination and concentration would lead to varied machining performances. Special polar groups, saturated levels of fatty acids and molecular chain length for plant oils, and microscopic shape and heat conductivity coefficient for nano-enhancers would influence machining performances as well.

However, the quick optimisation of the above elements is still based on the trial and error principle, and therefore is limited by (a) the data volume is not enough to form a robust database, (b) the current mechanism analysis is qualitative, and (c) there is no economic analysis. The establishment of the cloud case library by intelligent technology might be the future solution.

(iv) Although various kinds of nano-enhancer and plant oils were attempted in preparation of NEBL, it seems difficult to find the best one which can well balance between good cooling and superior lubrication. In this paper, this bottleneck has been analyzed in-depth, which could be used as guidance for further research in sustainable manufacturing. The future solutions/research directions might include biolubricant from animal fats (come from a wide range of sources and present good thermal stability), mixed plant oils (different kinds of plant oil were mixed together to prepare new oil), and chemical-modified of plant oil (chemical-modified of C=C bond to improve thermostability and oxidation resistance).

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