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Nano-titania and carbon nanotube-filled rubber seed oil as machining fluids

Sunday A. Lawal [a,g], Rasaq O. Medupin [b], Kelvin O. Yoro [c,*], Kingsley O. Ukoba [j], Uzoma G. Okoro [a], Oyewole Adedipe [a], Joseph Abutu [d], Jimoh O. Tijani [e], Ambali S. Abdulkareem [f], Mohammed B. Ndaliman [a], Asipita S. Abdulrahman [h], O. Eterigho-Ikelegbe [i], Tien C. Jen [j]

[a] *Department of Mechanical Engineering, Federal University of Technology, Minna, Nigeria*
[b] *Department of Materials and Metallurgical Engineering, Federal University of Technology, Owerri, Nigeria*
[c] *Energy Technologies Area, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA, 94720, United States*
[d] *Department of Mechanical Engineering, Taraba State University, Jalingo, Nigeria*
[e] *Department of Chemistry, Federal University of Technology Minna, Nigeria*
[f] *Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria*
[g] *Department of Mechanical Engineering, University of Mines and Technology, Tarkwa, Ghana*
[h] *Department of Materials and Metallurgical Engineering, Federal University of Technology, Minna, Nigeria*
[i] *Clean Coal Technology Research Group, School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Private Bag X3, Wits, 2050, Johannesburg, South Africa*
[j] *Department of Mechanical Engineering Science, University of Johannesburg, Auckland Campus, South Africa*

HIGHLIGHTS

- Terminalia cattapa leaves are explored for green synthesis of TiO_2 NPs.
- $nTiO_2$-CNTs (7:3 & 5:5) yields RSO-based fluids with superior viscosity & thermal conductivity.
- Well-dispersed $nTiO_2$/CNTs in RSO as $nTiO_2$ CNTs mitigate clustering of CNTs.
- $nTiO_2$/CNT-RSO ratio of 0.5:100 offers highest thermal conductivity of 0.518 W/m°C.
- Textural properties of $nTiO_2$ & mesoporous nature of the nanocomposites favor easy heat transfer.

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ABSTRACT

Machinists face persistent challenges in managing heat dissipation during cutting operations. To address this issue in an environmentally conscious manner, there is a need for nanofluids crafted from sustainable, eco-friendly materials. This study delves into developing nanocomposites (NCs) of nano-titania ($nTiO_2$) derived from *Terminalia catappa* leaves and carbon nanotubes (CNTs) in varying compositions ($nTiO_2$/CNTs: 90/10, 70/30, and 50/50 wt%). These NCs underwent comprehensive characterization using techniques such as BET, HRSEM/EDX, HRTEM, XRD, and FTIR. The aim was to evaluate their stability as potential fillers in rubber seed oils (RSOs) for machining operations. Furthermore, the homogenous NC samples in RSO revealed distinct polycentric rings, indicating the dispersion of $nTiO_2$ in CNTs, forming Ti–O–C and Ti–O–Ti networks. XRD analysis identified anatase diffraction peaks, though the CNT peaks were less distinct due to overlap with TiO_2 peaks. This successful fusion addresses challenges related to individual fillers, ensuring stable nanosuspension formulation. The TiO_2/CNTs (50/50 wt%) NC emerged as particularly effective in dissipating heat from machining interfaces. The study highlights the nanomaterials' high thermal stability, complementing the abundant unsaturated fatty acids in RSOs to create advanced nanofluids for improved machining. The substantial pore volume and stable nanosuspension formation observed are attributed to the large surface area aiding heat removal. Ultimately, the reinforced RSO with $nTiO_2$/CNTs shows promising potential for safe and efficient machining applications.

* Corresponding author.
E-mail address: kelvin.yoroo@gmail.com (K.O. Yoro).

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1. Introduction

Traditionally, machining operation relies on metalworking fluids (including oils and water) to enhance workpiece surface finishing, prolong tool lifespan, and manage the heat generated by cutting tools. Emulsions combining water and oil have been notably employed as cutting fluids. Metalworking fluid expenditure accounted for around 17% of manufacturing costs, reaching USD 1.1 billion in 2016 and is projected to hit USD 1.5 billion by 2020 [1]. Vegetable oils are fast gaining attention as metal-working fluids [2] and composite reinforced nanofluid is attracting tremendous attention for several machining operations in recent times as it possesses improvement on most demerits of traditional metalworking fluids.

Abbreviation

$nTiO_2$	nano-Titania
CNTs	Carbon nanotubes
NCs	Nanocomposites
NPs	Nanoparticles
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
BET	Brunuer-Emmett-Teller XRD X-ray Diffractometer
FTIR	Fourier transforms infrared spectroscopy
AA2030	Aluminum alloy 2030
nMQL	Nanofluid minimum quantity lubrication
EDX	Energy dispersive spectroscopy
CVD	Chemical vapor deposition
RSO	Rubber seed oil

Vegetable oils, derived from plants, primarily comprise triglycerides composed of glycerol molecules linked to three fatty acid molecules [3]. The triglyceride structure of vegetable oils provides qualities desirable for an ideal cutting fluid. The long, polar fatty acid chains provide high-strength lubricant films that interact effectively with metallic surfaces; thereby offering frictional and wear resistances [4–6]. Furthermore, the triglyceride structure gives the fluid a high natural viscosity and viscosity index and is responsible for its structural stability over a reasonable operating temperature range. According to Chandrakar and Suhane [7], high flash point and its attendant low vapor pressure and volatility make vegetable oils less hazardous during use coupled with their biodegradability, non-toxicity, and renewability which are essential qualities of a sustainable cutting fluid [8].

Studies have shown that traditional metalworking fluids can cause corrosion with poor lubrication properties [9]. On the other hand, low oxidation stability is one major factor hampering industry acceptance and application of vegetable-based oils as machining fluids [10,11]. In addition, researchers are unanimous in the admittance of the fact that most vegetable oils undergo precipitation, cloudiness, solidification, and poor flow under severe conditions of temperature and pressure [12]. Hence, chemical modifications of the oxidation stability are often undertaken for improvement. It was argued that reducing the level of unsaturated fatty acids, though positive for oxidation stability, could reduce lubrication effectiveness at low temperatures [13]. Therefore, oils containing a large percentage of mono-unsaturated fatty acids are the most likely candidates for machining lubrication. For example, Jatropha oil is said to perform better in terms of power reduction, lubrication, heat dissipation as well and chip disposal against mineral oil emulsion in the milling of AA2030 and AISI 1050 carbon steel [14]. At a much higher temperature, Palm oil was found to be more stable than rapeseed oil and sunflower oil. In another investigation, palm kernel oil, and cottonseed oil were found to perform better than mineral oil in terms of surface roughness, cutting force, and friction reduction during the turning operation of AISI 4340 steel [15]. Oils from groundnut, shear butter, palm kernel, and coconut are also reported to be effective in reducing cutting force/coefficient of friction and improving product quality during cylindrical machining [16]. More recently, corn oil was used by Arsene et al. [17] as a cutting fluid during the hard turning of AIDI D2 hardened steel with ceramic wiper inserts. Findings from their analyses show that a 17.6% reduction in tool wear was achieved when compared to dry machining.

Stakeholders in the food industry have consistently discouraged the use of edible oils as machining fluids even though researchers see many of them as having potential for such applications [18–20]. Rubber seed oil (RSO) is non-edible and eliminates the possible competition with edible oils as a viable alternative. Mohammed et al. [21], Maliki and Ifijen [22], and Ebelewe et al. [23] reported that rubber seed is rich in oil and a relatively cheap source of vegetable oil. Yet is scarcely put to any major economic use. Recently, Osayi et al. [24] found that RSO performs better in terms of surface roughness reduction than mineral oil-based cutting fluid during a turning operation of mild steel. Its performance was also tested against aluminum alloy 6061 using minimum quantity lubrication in a turning operation with a positive report [25].

Despite volumes of reports in favor of different vegetable oils as a lubricating agent during machining, reinforcement with nanoparticles (NPs) has been researched for a better and safer machining experience [26]. Nanosized MoS_2, Al_2O_3, CuO, ZnO, TiO_2, SiO_2, Fe_3O_4, and CeO_2 are being extensively studied as preferred reinforcing agents for nano-cutting fluid production [27–34]. More recently, a combination of more than one NPs is currently receiving greater attention among researchers having successfully exploited the performance of single NP-reinforced base oils for the production of lubricating nanofluids for machining. Amiri et al. [35] reported on the preference of SiO_2–Cu nanocomposite over the nanofluids prepared with only SiO_2 NPs while Toghraie et al. [36] drew a similar conclusion with ZnO–TiO_2 nanocomposite enhanced ethylene glycol hybrid nanofluid. In another investigation, Anand et al. [37] assessed the rheological and machining properties of TiO_2-enhanced rice bran oil in comparison to the performance of TiO_2-graphene nanocomposite improved rice bran oil. Their conclusion was also in the affirmative; favoring the latter. As far as could be ascertained, the formation of NCs with the combination of nanofibres and NPs is scarcely reported in the literature [38]. Particle-particle reinforcement of base oils is more reported in the literature [38–40]. TiO_2 is a nanoparticle while CNT is fibrous in nature and is more thermally stable than TiO_2 [41,42]. Their relationship at the nano level is as important as their reinforcing capability of the vegetable base oil for any application. Therefore, given the critical role nanofillers play in the attainment of sustainable clean machining through the nanofluid minimum quantity lubrication (nMQL) technique, the processes leading to the production of the fillers as well as the nanofluid deserve all the needed attention. On this note, this study is designed to develop and characterize high-quality hybrid nanofluids for machining applications.

In this study, extracts from three plants (*Terminalia catappa, Plumeria acuminate, and Carica papaya leaves*) were selected and quantitatively screened for flavonoids, total phenols, and tannins. Extract of *Terminalia catappa* leaves was found to contain a higher amount of phytoconstituents than the other two and, on this basis, was selected for the green synthesis of TiO_2 nanoparticles. These phytochemical components in plant extracts can perform the same role as expensive commercial and reducing agents such as $NaBH_4$ and $LiAlH_4$ which release toxic chemicals to the environment and compromise environmental safety [42]. Many researchers have leveraged the mechanical strength of hybrid TiO_2-CNTs as reinforcing fillers in natural rubber for structural application with a high rate of success [43,44]. However, their use as additives in RSO as heat-removing enhancers during machining operations has not been adequately reported. This study explores the high thermal stability of the nanomaterials to complement the large concentration of unsaturated fatty acids in RSOs to develop innovative nanofluids for improved machining experience with difficult-to-machine materials.