International Journal of Scientific Research in Chemical Sciences
Vol.**11**, Issue.**6**, pp.**08-12**, December **2024**
E-ISSN: 2455-3174
Available online at: www.isroset.org

Research Article

Preparation of Neem Oil and Acrylonitrile Based Copolymeric Materials as a Potential Bio-Based Additives and Its Effect on Pour Point Depressant of a Lube Oil

Faisal Sanusi[1*], Aminu Musa[2], Auwal Bello[3]

[1,2,3]Dept. of pure and applied chemistry, Umaru Musa Yar'adua University, Katsina, Nigeria

**Corresponding Author: fsanusialiyu@gmail.com.*

Received: 18/Oct/2024; **Accepted**: 20/Nov/2024; **Published**: 31/Dec/2024

Abstract—In other to minimize environmental pollution, green additives prepared from bio-source with low cost and multi-functional applications have driven considerable attention in the field of lube oil industry. In this research, Neem oil was extracted using n-hexane as a solvent and some amount of Neem oil has mixed with turmeric rhizome (Antioxidant) to ascertain its oxidative stability and it was examined by FT-IR analysis. Copolymer derived from Neem oil and acrylonitrile was prepared by direct polymerization through the double bond of the fatty acid chain in the present of free radical initiator led to the formation of environmentally friendly Copolymeric based additives. The prepared Copolymer have been characterized by routine spectroscopic analysis. The rheological behavior and performance evaluation of the lube oil were examined in different concentration of additive Viz. 1% 2% 3% (w/v). However, the green additive act as good pour points depressant improver to the lube oil. The values of pour point for the lube oil blended with different prepared Copolymeric additives ranging from (9 to -11^{0}C). Thus, bio-based oil derived additive can be considered as a good alternative to be used in lube oil formulation.

Keywords —Neem oil, Antioxidant, Copolymeric materials, lube oil, pour point depressant, Biodegradability (green additives).

1. Introduction

Lubes oil are materials (generally a liquid but may be a Solid, semi-solid or gases) [1] that uses to reduce friction and facilitate the relative motion between two surfaces which are in mutual contact to each other [2]. The high level of lube oil performance depends upon collective interaction of the lube oil with the additives present, and the method used during formulation. Without additives, the lube oil may not shield the equipment properly at all operational condition and might lead to rapid contamination, breakdown, overheating and sudden damage of the equipment [2]. Technical equipment requires the uses of lube oil with new performance properties as such, the lube oil can also be improved by adding some additives [3]. Recently, different type of additives used such as pour point depressant and viscosity modifiers. Pour point depressant improver are those additives that effectively improve the fluidity of lube oil at all temperatures much lower than that of the normal pour point [4]. Furthermore, lube oil when formulated with the additives lengthen the lifetime of equipment and reduce environment pollution [5]. But the most of the additives are based upon synthetic acrylate. Due to their toxicity and non-ecofriendly they are not much taking advantage to be used as an additive [6]. As a result, the Preparation of green additives broad our attention to bring out such research output.

2. Related Work

Significant effort has been made in the few years ago to prepare novel multifunctional additives from renewable feedstock as such a bio-based oil is the possible alternative due to their biodegradability, eco-friendly, excellent lubricity and low volatility for improvement, for instance additives prepared from castor oil and acrylate base Copolymer shows much effect on viscosity index and Pour point depressant of a lube oil [7]. Copolymer of stearyl methacrylate co-triglyceride shows better pour point depressant improver and viscosity index modifier [6] sunflower oil and dodecyl acrylate Copolymer behaved as a pour point depressant and viscosity modifier for the lube oil [1]. From the above study, it was found that a lot of works has been done on acrylates, methacrylates with varying structure and morphology for improving the pour point and viscosity index of a lube oils. However, the acrylate and methacrylate based copolymeric additives are among the most widely used commercial additives for the lube oil formulation [1]. Many researchers used edible oil for examples melon and palm oil to prepare green additives but the fluctuating prices of edible oils is

increasing due to its nutritional needs have made Neem Seeds oil to be among the raw materials of choice. Neem plant is an evergreen tree which has been used as lubricant for many years in the past [7],[8]. Thus, Neem seed oil contains high level of unsaturation, making it preparable for additives synthesis [8]. The dominant oleic acid is 60.402%, palmitic acid 23.654%, caprylic acid 5.933%, myristic and steric acid 0.0005% respectively [3]. This present research revealed the Preparation, characteristics and performance evaluation of green additives materials based on neem oil and acrylonitrile copolymer. Their performance assessment as additives has also been studied.

3. Experimental Method

3.1. Materials.

Acrylonitrile was purchased and used without additional purification. The initiator (BPO) was purified by Coloum chromatography using a silica gel and refrigerated prior to use. Toluene (GC 99.5%), ethanol (AR 99.9%) and n-hexane were purchased and used as received. The lubricating oil was obtained from AMASCO oil brand.

3.2. Sample Collection and Preparation.

The Neem seeds sample were collected from Arabic teaching college (ATC), Katsina. Subsequently sorted into good and bad ones. The good Neem seeds were washed and dried for about 5 days, later they were deshelled, sundried for two weeks. The kernels, crushed with mortar and pestle and stored in a polythene bag

3.3. Neem Oil Extraction Procedure.

35g of crushed Neem seeds was placed into the thimble and placed in the Soxhlet chamber. 300ml of n-hexane were placed in a round bottom flask, and assemble for Soxhlet extractor. and the distillation process was begun after the completing of the extraction process, the solvent and extractor were placed on water bath to evaporate the solvent and the extracted oil was weighted. However, the procedure repeated severally after each extraction until required Neem oil was collected.

3.4. Formulation Of Neem Oil with Turmeric Rhizome (CURCUMIN).

The turmeric rhizome (curcumin powder) was mixed with Neem oil in 2:5 ratio (w/w) using dispersal tool (stirrer), and heated for about 10minutes. It was then Centrifuged for about 10 minutes at 500 rpm. The supernatant consisting of oil supplement with curcumin powder was recovered, and the exhausted curcumin powder recycled two times following the same enrichment.[9],[10].

3.5. Process Formation of Neem Oil and Acrylonitrile Copolymer

The solution of Neem oil (9.3 g, 10mmol) in toluene (10 mL), an Acrylonitrile (7.6 g, 30mmol) with 1:3 molar ratios was added. The reaction mixture was continuously stirred and preheated at 90oC for 60 minutes. The initiator used as benzoyl peroxide (0.5% w/w, with respect to the total monomers) was then added and continuously heated for 12 hours keeping the temperature constant at 80°C. The reaction was then cooled before being stopped by dumping the reaction mixture into the ethanol. Decantation with ethanol was employed to remove the unreacted starting material. The furnished green viscous copolymer was then obtained [11].

3.6. Formulation Of Additives.

The prepared bio-based copolymer additives were readily soluble in lube oil. The copolymer was mixed in weight/volume ratios of 1%, 2%, and 3%. The copolymeric materials have been tested for performance evaluation after the formulation of the lube oil.

4. Results And Discussion

4.1. Potential of Neem oil.

The renewable raw feedstock such as Neem oil was selected and favoured because, it contains high level of unsaturation, making it preparable for additives synthesis. The Neem oil was extracted from its seeds using a solvent (n-hexane) and the solvent was recovered and the pure Neem oil was obtained.

4.2. Evaluation of Oil yield Content.

A solvent (n-hexane) was used in the extraction of the neem oil from its neem seeds and this gave a maximum yield of 40.20wt%. The extraction was carried out considering factors that affect the yield of oil extracted. These factors are namely Size of the particles, temperature, time taken for the extraction and volume of solvent used. The extracted oil for each factor was then collected and weighed. This shows that Neem is a good source of oil compared to other seeds like cotton seed, water melon seed etc., which contains about (35-40) %, (25-35) %, respectively.

$$\text{Yield (y)} = \frac{weight\ of\ oil\ exracted}{Weight\ of\ seeds} \text{ x } 100$$

$$\frac{19.7\ X}{49}\ 100 = 40.20\%$$

4.3. Evaluation of Turmeric Rhizome (CURCUMIN) As a Potential Anti-Oxidant.

The effects of turmeric rhizome(curcumin) as an antioxidant were used to enhanced Neem oil stability. The mixed Neem oil with curcumin rhizome (turmeric powdered) was furtherly, characterized by FT-IR spectroscopic analysis exactly after 30days intervals. Its effect showed optimum stability of the oil from spectroscopic results obtained. However, Oxygen plays a leading role in the free radical chain reaction of lipid oxidation mechanism that explain through the stage of initiation, propagation and termination. The addition of antioxidant as free radical scavenger before the propagation phase is considered of the volatile compounds which are markers of rancidity [9],[10].

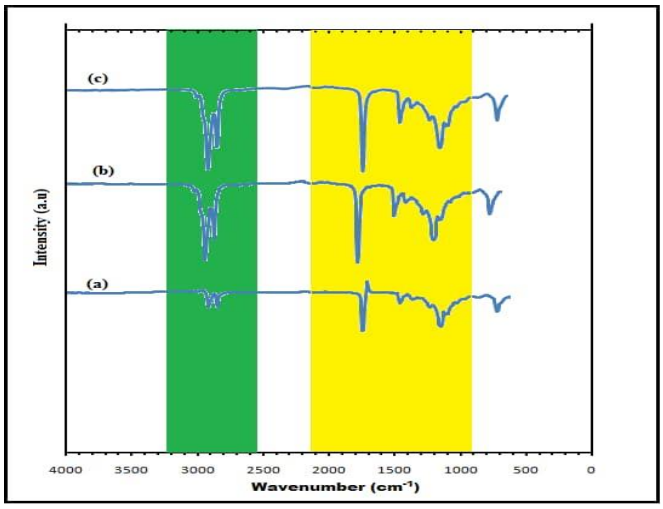


Fig1. FT-IR Spectra of the Neem oil mixed with antioxidant

(a) spectrum of Neem oil, (b) spectrum of mixed Neem oil with turmeric rhizome (curcumin), (c) spectrum of mixed Neem oil with turmeric rhizome (curcumin) after 30 days interval.

4.4. Copolymerization

Free radical polymerization was employed to prepare the green additive (Neem oil and acrylonitrile). It was noted that benzoyl peroxide (BPO) decomposes by heat generate free radical which is responsible to initiate the copolymerization reaction between triglyceride of Neem oil and Acrylonitrile. It was then accompanied by chain propagation and finally, the reaction was terminated by pouring the reaction mixture into an Ethanol solution to obtain new Neem oil copolymeric green additive materials.

4.5. Spectroscopic Data Analysis.

The Neem oil was further characterized by routine spectroscopic analysis. Several peaks were observed, peak around 2855–2922 cm−1; showed the presence of aliphatic C–H stretch present in the oil. The C=O stretch of the triglyceride ester of the oil appeared at 1744 cm−1, and for C–H bending at 1461 cm−1. The presence of the esters was inferred at peaks 1162 cm−1 which was expected for C–O–C stretching vibration and that at 477–566 cm−1 was because of methylene rocking vibration present in the oil. furthermore, the absence of double bond in the prepared Copolymer while present in the respective monomer support the formation of the Copolymer [12].

4.6. Evaluation Of Pour Point Depressant.

The lower temperature was used to determine fluidity of the lube oil by using standard pour point depressant method. The copolymer additive was used to test for its ability to lower the pour Moreover, Copolymer additive on the formulation in lube oil at various concentration i.e 1%, 2%, and 3% shows a Pour point values as -9,10 and -11 respectively.

Table 1: performance properties of base oil and its mixtures with different concentration of additives.

Performance properties	**Base oil**	**Copolymer additives (w/v) %**		
		1%	**2%**	**3%**
Pour point (^{0}C)	-8	-9	-10	-11

Since the base oil Pour point was been observed as -8°C, therefore a sudden drop of pour point was observed as variouscopolymer additive added to the lube oil. A more polar additives fight more efficiently against the creation of wax crystal network and subsequently shows greater flow.

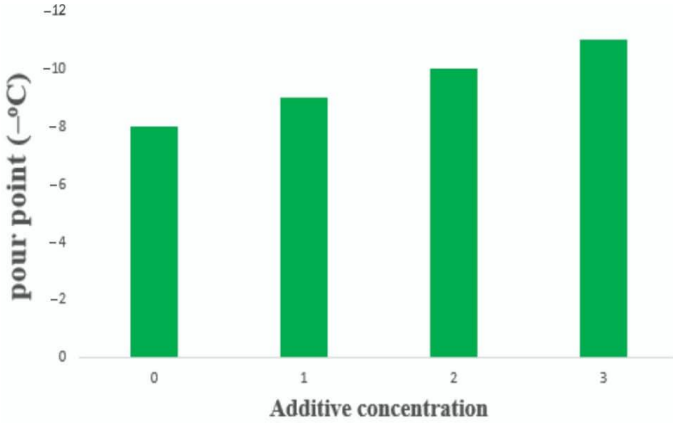


Fig.2 pour point evaluation of the mixed lube oil with Various Concentrations of Additives

4.7. Pour Point Variation of the Base Oil Blended with Different Concentration of Additives

In addition, it also proved that, concentration of copolymer additive increases the efficiency as a pour point depressant gradually improved. However, the improved pour point depressant related to the change of the stiff network of wax crystal from the dissolved waxy hydrocarbon in mineral oil [1]. Mineral lube oil is always associated with some waxy material (high molecular weight hydrocarbon). At high temperature all the high molecular weight paraffin's remain in dissolved state in the lube oil. But, with lowering the temperature of the oil, some of this waxy hydrocarbon tends to separate as tiny crystal entrapping a substantial amount of oil. thus, inhibit the lube oil flow. Generally, pour point is proportional to the amount of wax present in the oil [2].

5. Conclusion and Future Scope

In this present work, analysis of the prepared Copolymer was carried out to ascertain its performance evaluation as a green additive and pour point depressant improver. The results revealed out that mixing of these additives to the lube oil depressed the pour point under examination. In addition, the study illustrated that the green additives are also environmentally benign. Therefore, the prepared copolymeric additives may be used for designing green bio-lube oil that satisfy the mounting environmental and performance concerns of modern lube oil.

For future research, it is recommended that: -
(i) The test for viscosity index of the prepared copolymer should be carried out to ascertain thickness of the additives as it plays a vital role in ideal lube oil formation.
(ii) The preparation of copolymeric green additives of Neem oil should also carried out using synthetic monomer that have higher molecular weight to evaluated their performance on viscosity index and Pour Point Depressant.
(iii) The comparative Study should also carry out to ascertain the formulated lube oil it's biodegradability rate on the thermal (heat energy)

Data Availability
Because of the technical and time limitations, the raw data required as part of an ongoing study cannot be shared.

Conflict of Interest
The authors have no any potential conflicts of interest to declare.

Funding Source
The authors do not receive any financial assist from any agency or institution for the research, the research was funded from authors.

Authors' Contributions
The author **Faisal Sanusi Aliyu**[1*] carried out the research and drafted the manuscript with the contribution of his friend **Auwal Bello**[3], **Prof. Aminu Musa**[2] supervised the research and edited the manuscript. All authors reviewed and edited the manuscript and approved the final version of the manuscript.

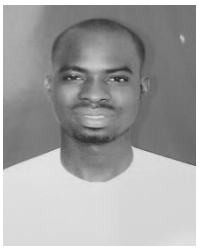
Acknowledgement
The authors also wish to appreciate the support rendered by the Laboratory technicians of the department of pure and applied chemistry, of Umaru Musa Yar'adua University Katsina, Nigeria.

References

[1] Mohammed, A., Dhedan, R. M., Mahmood, W. A., & Musa, A."Copolymers of Castor and Corn Oils with Lauryl Methacrylate as Green Lubricating Additives. *Egyptian Journal of Chemistry*, 64(8) pp. **4271-4276, 2021.**
[2] Kumar, D., S. "Modification of lube oil properties by addition of organic polymeric additives". North Bengal university, India- 3(6) pp. **734013, 2018**
[3] Musak, Y., Kovalenko, T., Serdiuk, V., Kravets, T., &Martynyak-Andrushko, M. "Obtaining of polymethacrylate additives and study in operational properties of an alloyed industrial Oil". Eastern-*European Journal of Enterprise Tecnologies*, pp. **9-15, 2016.**
[4] Saha, D.K., &Ghosh,P. "Synthesis, characterization and performance evaluation of Long chain methacrylate-octene copolymer for Lubricant formulation". *Journal Macromolecular Science,* Part A, 56(11) pp. **1050-1059, 2019.**
[5] Karmakar. G., Dey, K., Ghosh, P., Sharma, B.K., &Erhan,S Z. "A short review on polymeric biomaterials as additives for lubricants". *Polymers*, pp. **1333, 2021.**
[6] Agarwal, p., S., Portal, J., Singh, R. K., &Portal, S. K. "Evaluation of renewable feedstock-derived Copolymer of stearyl methacrylate-co-triglyceride as multifunctional green additives in lubricant". *Polymer Bulletin*, pp. **1-16, 2021**
[7] Liao, Y. H., Su, Y. L., & Chen, Y. C. "The Influence of Neem Oil and Its Glyceride on the Structure and Characterization of Castor Oil-Based Polyurethane Foam. Polymers". Vol 13(12) Pp.**103-106,2020**.
[8] Bhan, U., Singh, D., & Ranganathan, A. "Effect of different loads on the friction and wear characteristics of material lubricated with neem oil". *Materials Today: Proceedings* vol. 46 pp. **10113-10116, 2021**
[9] Ghosh, P., Hoque, M., Roy, D. "Castor oil and acrylate-based copolymer as a green additive for lubricating oil". *Polymer* pp. **734-737, 2020**
[11] Quinchia, L. A., Delgado, M. A., Valencia, C., Franco, J. M., & Gallegos, C. "Natural and synthetic antioxidant additives for improving the performance of new biolubricant formulations". *Journal of agricultural and food chemistry*, 59(24) pp. **12917-12924, 2011**
[12] Nandiyanto, A. B. D., Oktiani, R., & Ragadhita, R. "How to read and interpret FTIR spectroscope of organic material". *Indonesian Journal of Science and Technology*, 4(1) pp. **97-118, 2019**
[13] Mohammed, A. H., Mahmood, T. A., Yousif, S. A., & Musa, A. "Sunflower and Linseed Oils with Decyl Methacrylate Based Copolymers as Green Lubricating Additives". *In Materials Science Forum* (Vol. 1045), **pp. 109–116, 2021.**

AUTHORS PROFILE

Assoc. Prof. Aminu Musa received his first degree; Bachelor of Science (B.Sc.) in Applied Chemistry from Usmanu Danfodiyo University, Sokoto. Nigeria, in the year 2004, Master's degree (M.Sc) in Applied Chemistry from Usmanu Danfodiyo University, Nigeria in the year 2012 and Doctor of Philosophy (Ph.D) in Polymer Chemistry from Universiti Putra Malaysia in the year 2017. He has 18 years of working (teaching) experience and 16 years of research experience. His highly esteemed research interests are in the field of polymer and material chemistry, He is currently working as a Senior Lecturer in the Department of Pure and Industrial Chemistry, Umaru Musa Yaradua University Katsina, Nigeria.



Mr. Faisal Sanusi Aliyu earned his B.Sc. with first-class honor from Umaru Musa Yaradua University Katsina, Nigeria in the year 2021, During his undergraduate studies, he worked and gained experience with Ajiwa water treatment plant in the year 2019-2020 as a part of the Students Industrial Work Experience Scheme (SIWES). He did his 1-year National Youth Service Corps (NYSC) program in Kano of Nigeria, working as a research assistant at Yusuf Mai Tama Sule University. He is a member of Chemical Society of Nigeria (CSN) and a member of professional bodies which includes African Science frontier initiatives (ASFI), USA education fund Nigeria, and North-East scholars' mentorship (NES). He has 3 years of research experience, and has research interests in polymer chemistry, bio-based materials, Environmental chemistry, Renewable energy/Sustainable energy, materials science and food chemistry.

Mr. Auwal Bello earned his B.Sc. degree with first-class in industrial chemistry from Umaru Musa Yaradua University Katsina, Nigeria in the year 2023. During his undergraduate studies, he served as two-time academic secretary for the Students' Chemical Society of Nigeria UMYUK Chapter, and he gained valuable industrial experience as a Quality Control Assistant with Maidabino Investment Limited in the year 2019. Additionally, he served as Graduate Assistant at School of Technology, Kano State Polytechnic, during his National Youth Service Corps (NYSC) program from 2023-2024. He is a Proud member of Chemical Society of Nigeria (CSN) and a member of professional bodies which include International Society of Environmental Relationship and Sustainability (ISERS), Community Clean-Up Coalition (CCC), Society of Chemical Industry SCI, International Young Chemists Network (IYCN), Young African Leaders initiative network (YALI), Chemicals and Waste Youth Platform. He has 2-year research experience and developed a strong interest in green and sustainable chemistry, focusing on innovative materials synthesis and recycling technologies that contribute and promote environmental sustainability and climate change mitigation.

