

Original Research Article

Multifunctional additive properties of acrylate based ZnO Nano composite for lubricating oil

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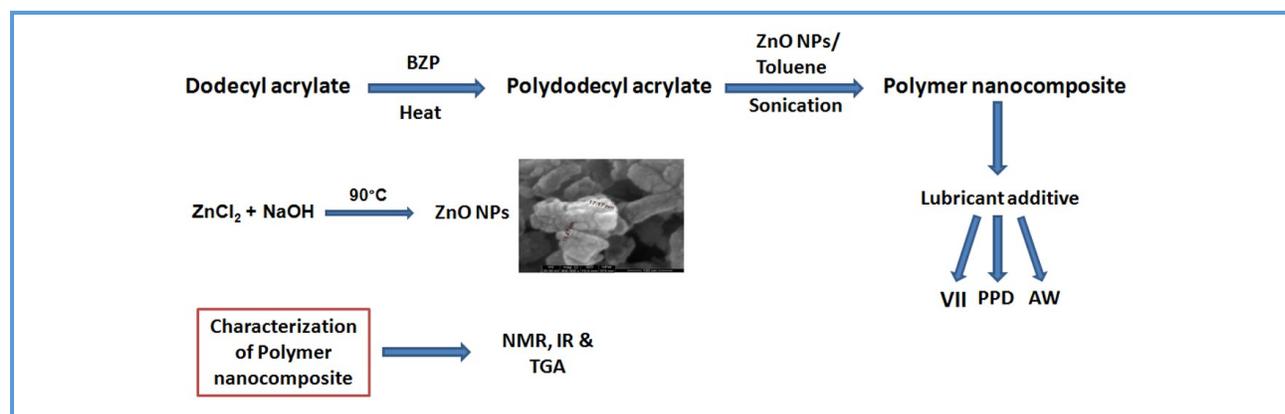
KEYWORDS

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 Rhombohedral
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 Cubic
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ABSTRACT

Recently, polymer nanocomposites have attracted greater interest as lubricant additives compared to pure polymer. In this work, we synthesized ZnO nanoparticles and characterized them using scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis. The synthesized nanoparticles were then incorporated into the poly dodecylacrylate to prepare polymer nanocomposites (PNCs) by sonication. The PNC was characterized using different analytical techniques like FT-IR, NMR, TGA etc. The additive performance of the PNC as viscosity index improver, pour point depressant and anti-wear were evaluated using the standard ASTM methods. The results demonstrated that, the overall performance of the additive was improved by increasing the concentration of PNC in the base stock. It was observed that PNCs have shown good viscosity modifier characteristics as one of the composite having higher nanoparticles content shown viscosity index value of 137, which is higher than neat polymer. Moreover, up to 28% decrease in wear reduction was observed by applying the PNC. © 2021 by SPC (Sami Publishing Company), Asian Journal of Nanoscience and Materials, Reproduction is permitted for noncommercial purposes.

Graphical Abstract



Introduction

The lubricating oil is the blood of the machine's service life. The machine's operation and economic efficiency are relative to the quality, performance and sensible use of the oils [1, 2]. The two major constituents of tribology are friction and wear. Thus when these are controlled and reduced, it automatically increases the service life of the machine. This ultimately saves money. The awareness of the subject, i.e. detection of tribological problems and their solution, can give rise to considerable savings. According to some estimations, losses due to unawareness of tribology are about 6% of its gross national product in the United States. Therefore, the significance of friction reduction and wear management cannot be overemphasized for economic reasons and long term dependability. In these regards people are focused on the application of nanoparticles in lubricating oil. Nanoparticles brought into lubricating oils can boost the properties of anti-wear, extreme pressure and friction reducing competency and thus service life of the machine were also improved [3]. The friction reduction and anti-wear action are relying on the characteristics of nanoparticles, for example size, shape and concentration. One important property that makes nanoparticles dissimilar from other materials is the fact that they have a very large surface area. Due to their very large surface area, nanoparticles are exceptionally reactive compared with that of their bulk form. Nowadays, generally used nanoparticles are oxides based- Al_2O_3 , CuO , ZnO , metals- Al , Cu , nonmetals-graphite, carbon nanotubes, layered composites- $\text{Al-Al}_2\text{O}_3$, Cu+C , and functional nanoparticles. Among these nanoparticles, oxides based nanoparticles such as ZnO has been attracted a great deal of attention due to its unique structure and performance [4-7]. Nano ZnO has huge surface area, high surface

energy, high diffusion, and strong adsorption characteristics. Apart from that, ZnO NPs have attracted increasing attention because these NPs can be easily synthesized and it is a greener material i.e, biocompatible and non-toxic [8]. Base oil additives of nano sized, which is suitable for the high temperature work, heavy load, low speed, have excellent anti-wear resistance, extreme pressure resistance performance and better lubrication properties. In addition, nano- ZnO is a widely used nano oxides and its preparation scheme is simple. Nano- ZnO used as lube oil additive will not only enhance the tribological properties of base oils, but also potentially reduce the cost of lube oil. On the other hand, nano- ZnO is hydrophilic-oleophobic with poor oil solubility. It needs to depend on the role of dispersant, ultrasonic dispersion or strong agitation to disperse nano- ZnO particles in the base oils [9-13]. Again, nano- ZnO particles were not known to show other kind of additive performance other than anti-wear, friction reduction and extreme pressure additive performance. So to disperse nano- ZnO nanoparticle and to meet the purpose of developing multifunctional performance additive, nano- ZnO was dispersed in polymer matrix (acrylate based) by sonication. Since acrylate based polymer were known to perform as good viscosity index improver [14-16] and pour point depressant [17]. The main objective of this research work was to assess the multifunctional additive property of the polymer- ZnO nanocomposites for lube oil. In our previous work we synthesized a polyacrylate-nano magnetite composite [18] and polyacrylate-liquid crystal composite [19] to evaluate the multifunctional additive performance. In continuation of our work, here we have introduced nano ZnO into the polyacrylate system to study the multifunctional additive properties (tribological performance, viscosity index

improver, pour point depressant) of this polymer-ZnO nanocomposite.

Experimental

Materials and methods

Acrylic acid, dodecyl alcohol, BZP and hydroquinone were purchased from Merck specialities Pvt. Ltd. India. Toluene, Methanol, hexane and conc. H_2SO_4 were purchased from Thomas baker Pvt. Ltd. India. BZP was recrystallized from $CHCl_3$ -MeOH. Zinc chloride and sodium hydroxide were purchased from Merck specialities Pvt. Ltd. India. The base oil was collected from IOCL, Dhakuria, Kolkata, India.

Preparation of dodecyl acrylate by esterification

Dodecyl acrylate (DDA) was prepared by esterification process of acrylic acid with dodecyl alcohol in the mole ratio of 1.1:1. The reaction was performed in a resin kettle in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone is added with respect to the reactants as polymerization inhibitor, and toluene used as a solvent. The reaction was performed under the nitrogen atmosphere. The reaction mixture was heated gradually from room temperature to 403 K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of water liberated during reaction to give the ester, dodecyl acrylate (DDA).

Purification of prepared monomer

To purify the product a desired amount of charcoal was added to the ester, followed by reflux for 3 h and then filtered. The filtrate was washed frequently with 0.5 N sodium hydroxide solution to ensure complete removal of unreacted acid. Then to remove traces of sodium hydroxide, purified ester was washed a

number of times with distilled water. The ester was then left on calcium chloride overnight and recollected by distillation under reduced pressure. This purified ester was then used in the polymerization process.

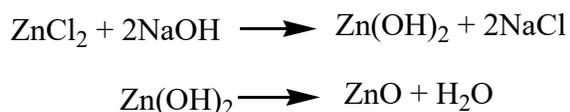
Preparation of homopolymer of dodecyl acrylate

The polymerization was carried out in a four-necked round bottom flask furnished with a condenser, stirrer, thermometer and an inlet for the nitrogen insertion. The required amounts of dodecyl acrylate and benzoyl peroxide (BZP) as initiator were taken in the flask and toluene was also added as solvent. The reaction temperature was controlled at 353 K for 6 hours. Then the reaction mixture was poured into methanol solvent with stirring to cease the polymerization and a precipitate was appeared. The precipitated polydodecyl acrylate (A) (PDDA) was further purified by frequent precipitation of its hexane solution with methanol followed by drying under vacuum at 313 K.

Preparation of ZnO nanoparticle

5.5 g of the zinc chloride was dissolved in 100 mL of distilled water in a beaker. This solution was kept under constant magnetic stirring till zinc chloride totally dissolved in the distilled water. The temperature of the solution was raised to 90 °C by electric hot plate heating. Meanwhile 20 g of sodium hydroxide was dissolved in 100 mL of distilled water in a separate vessel. From the prepared sodium hydroxide solution, 16 mL of sodium hydroxide is added to the beaker with constant stirring, drop by drop touching the walls of the beaker. The aqueous solution turned into a milky white colloid without any precipitation. The reaction was allowed to proceed for 2 h after complete addition of sodium hydroxide. After the complete reaction, the solution was allowed to

settle and the supernatant solution was removed by washing with distilled water for 5 times. After complete washing, the nano-ZnO was dried at 100 °C for 30 min. and then it changed into powder form [20]. The reaction involved is given below.



Preparation of Poly dodecyl acrylate- ZnO nanocomposites

PDDA-ZnO nanocomposites were prepared by mixing the PDDA/toluene solution and nano-ZnO particles. The PDDA- ZnO suspension was prepared as follows: 5 g of PDDA were dissolved in toluene and required amount (0.5, 1, and 1.5 mg) of nano-ZnO particles were added into the PDDA/toluene solution under ultrasonic wave and vigorous stirring to prepare 100, 200 and 300 ppm blend (Table 1). The suspension was then poured into a glass plate and allows the toluene to evaporate naturally and a semi solid mass of polymer-nanocomposites was obtained.

Table 1. Designation and Composition of poly dodecylacrylate-nano ZnO composites

Designation	Composition	
	Polymer in g	Nano (ZnO) in mg
A	5	0
Z-1	5	0.5
Z-2	5	1.0
Z-3	5	1.5

Spectroscopic analysis

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range of 400–4000 cm^{-1} . NMR spectra were recorded in Bruker Advance NEO 400 MHz FT-NMR spectrometer using 5 mm BBO probe using CDCl_3 as solvent and TMS as reference material.

Characterization of nano-ZnO by SEM, X-RD and DLS

The synthesized ZnO-nanoparticles were characterized by Field Emission Scanning Microscope (FE-SEM, INSPECT F50, FEI) and XRD analysis are recorded using an Advance D8, Bruker instrument with 2θ angle from the range of 20-90°. The DLS of the suspension was performed on a Malvern Zetasizerver 6.01. For DLS study suspension of NPs in water was prepared by taking concentration of 5 mg/mL.

Determination of molecular weight by GPC

By GPC, the number average molecular weight (M_n) and weight average molecular weight (M_w) were determined. The poly dispersity index was also calculated. In this method HPLC grade THF (0.4%, w/v) was used as mobile phase in the water 2414 GPC system (polystyrene calibration) at 35 °C with a flow rate of 1 mL/min and the injection volumes are set to 20 μL . The data of this study is given in supporting information.

Thermogravimetric analysis (TGA)

The thermal stabilities of the prepared homo polymer and polymer nanocomposites were determined by a thermogravimetric analyzer (Shimadzu TGA-50) using an alumina crucible in air. The system was run at a heating rate of 10 °C/min. The percentage of weight loss (PWL) of the samples with rise in temperature was calculated.

Performance evaluation

Evaluation as viscosity modifier

Viscosity index (VI) of the polymeric additives was determined in paraffinic base oil to evaluate the efficiency of the prepared polymeric additives as viscosity modifier (VM). The viscosity index (VI) of different concentrations of the additives in the base oils was evaluated in two base oils according to the ASTM D2270 method and following the equations as reported by Tanveer and Prasad [21]. Five different concentrations ranging from 1 wt% to 5 wt% of the polymeric sample solutions were used to study the effect of additive concentration on VI.

Evaluation as pour point depressant

The pour point depressant property of the prepared polymeric additives was determined in base oil by the pour point test on a Cloud and Pour Point Tester model WIL-471 (India) according to ASTM D97 method. In this case also five different concentrations of the additives were used for each sample.

Evaluation of tribological performance of prepared additives

The anti-wear performance of the lubricant compositions was evaluated in terms of wear scar diameter (WSD) by Four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method [22]. In this experiment 392 N (40 kg) load was applied at 75 °C for 30 min. to measure the wear scar diameter (WSD). The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm, respectively. The details procedure is described in our publication elsewhere [23].

Results and Discussion

Spectroscopic analysis

The FT-IR spectrum of homopoly dodecyl acrylate (A) and its nano composites (Z-3) is revealed in Figure 1. The absorption band (Figure 1a) at 1734.56 cm^{-1} indicated the ester stretching vibration along with other peaks at 1458.40, 1169.67, 1070.96, 721.65 cm^{-1} . The Figure 1b of polymer/ZnO nanocomposites showed absorption band for ester carbonyl group at 1728 cm^{-1} along with other peaks at 1465.98, 1167.99, 1070.96, 721.63 cm^{-1} . This shifting of carbonyl stretching frequency may be due to some association of nano magnetite and poly dodecyl acrylate. The peaks in the range at 1458.40, 1465.98 cm^{-1} are for asymmetric and symmetric bending vibrations of C-H bonds of $-\text{CH}_3$ and $-\text{CH}_2-$ groups of polymers and its nanocomposites. Peaks in the range of 1169.67, 1167.99, 1070.96 cm^{-1} are due to C-O stretching vibration of carboxylate ester group. Peaks at about 721 cm^{-1} are for C-H bending vibration of the paraffinic chain. Broad peaks in the range 2924.08 to 2937 cm^{-1} are for stretching vibration of paraffinic C-H bonds of $-\text{CH}_2-$ groups. In the infra-red region, the peaks at 454.6 cm^{-1} corresponds to Zinc oxide nanoparticles which show the stretching vibration of Zn-O bond [24]. There is no significant peak observed in the range of olefinic bonds which supported the formation of the polymer.

The ^1H NMR spectra of A and Z-3 are shown in Figure 2. Figure 2a represents the spectrum of A which showed broad singlet centered at 4.013 to 4.293 ppm due to the protons of $-\text{OCH}_2$ group. Methyl protons of dodecyl chain appeared between 0.866 ppm and 0.878 ppm and the absence of singlet between 5 ppm and 6 ppm implies the absence of any vinylic proton in the polymer. The ^1H NMR of polymer nanocomposites (Figure 2b) showed peak at 4.001 and 3.627 ppm due to the protons of

-OCH₂ group of the acrylate polymer and methyl and methylene protons appeared in the range of 0.851 to 0.884 ppm. In the ¹³C NMR spectrum of A, the carbonyl carbon appeared at 174.3 ppm along with other SP³ carbons appeared in the range of 64.72 to 13.94 ppm and it is showed in [Figure 3](#). The ester carbonyl of the nanocomposite (Z-3) appeared at 174.5 ppm as shown in [Figure 3b](#). Peaks appeared in the

range from 65 to 14.19 ppm are for the SP³ carbons of alkyl chains of PNC. The intensity of peaks decreases compared to pure polymer as depicted in NMR spectra. Hence it can be concluded that, ZnO nanoparticles formed a coordinate type of bond with ester group of A which lower the stretching frequency of ester carbonyl.

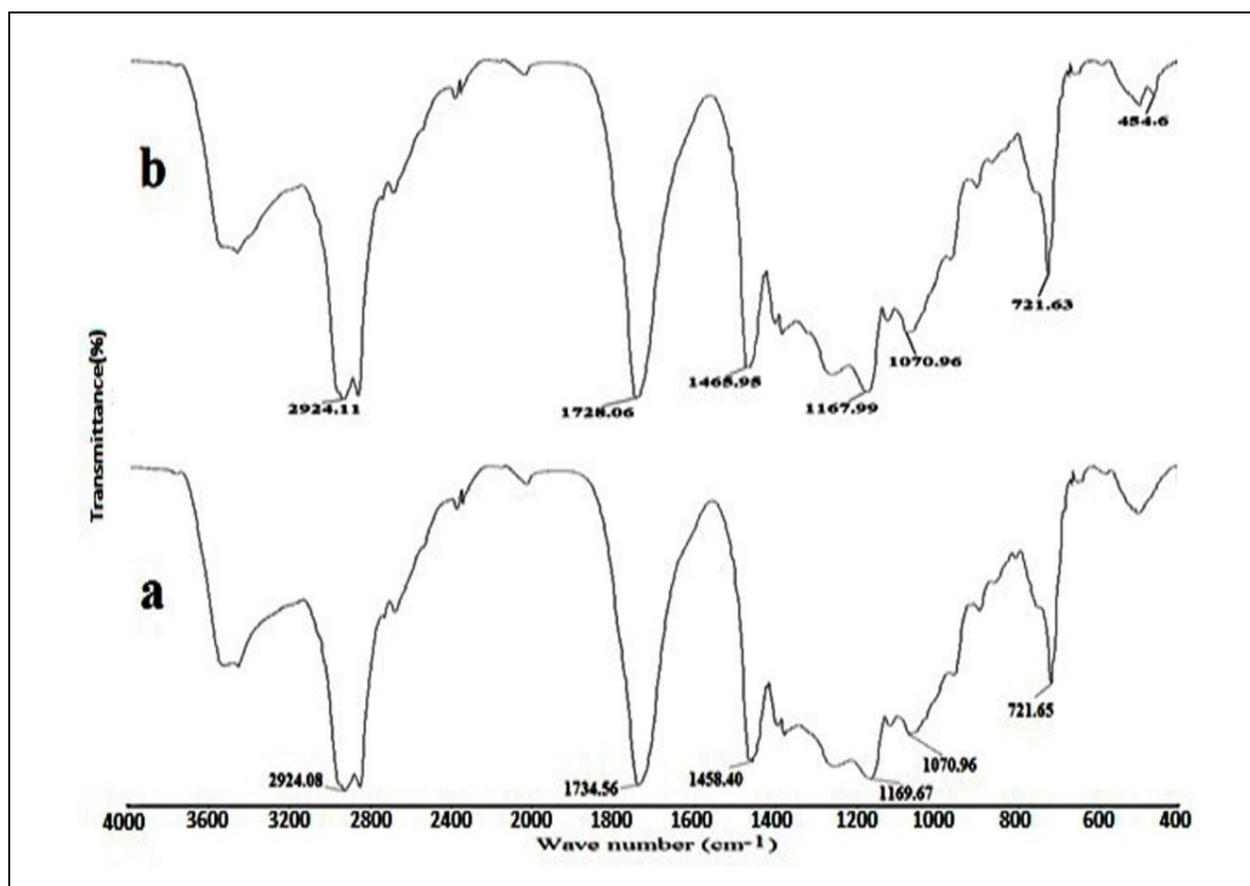


Figure 1. FT-IR spectra of a) polymer and b) polymer/ZnO nanocomposite (Z-3)

Characterization of nano- ZnO (by XRD, SEM and DLS)

[Figure 4](#) demonstrates the X-ray diffraction pattern of the ZnO nanoparticle. The nanoscale range of particles in the prepared materials was indicated by a definite line broadening of the XRD peaks. The eight most intense diffraction peaks located at 31.84°, 34.52°, 36.33°, 47.63°,

56.71°, 62.96°, 68.13° and 69.18° were clearly observed and was in good agreement with a research work published elsewhere [25]. Moreover, it also suggests that the synthesized nanoparticles were free of impurities as it does not show any characteristics XRD peaks other than nano-ZnO peaks.

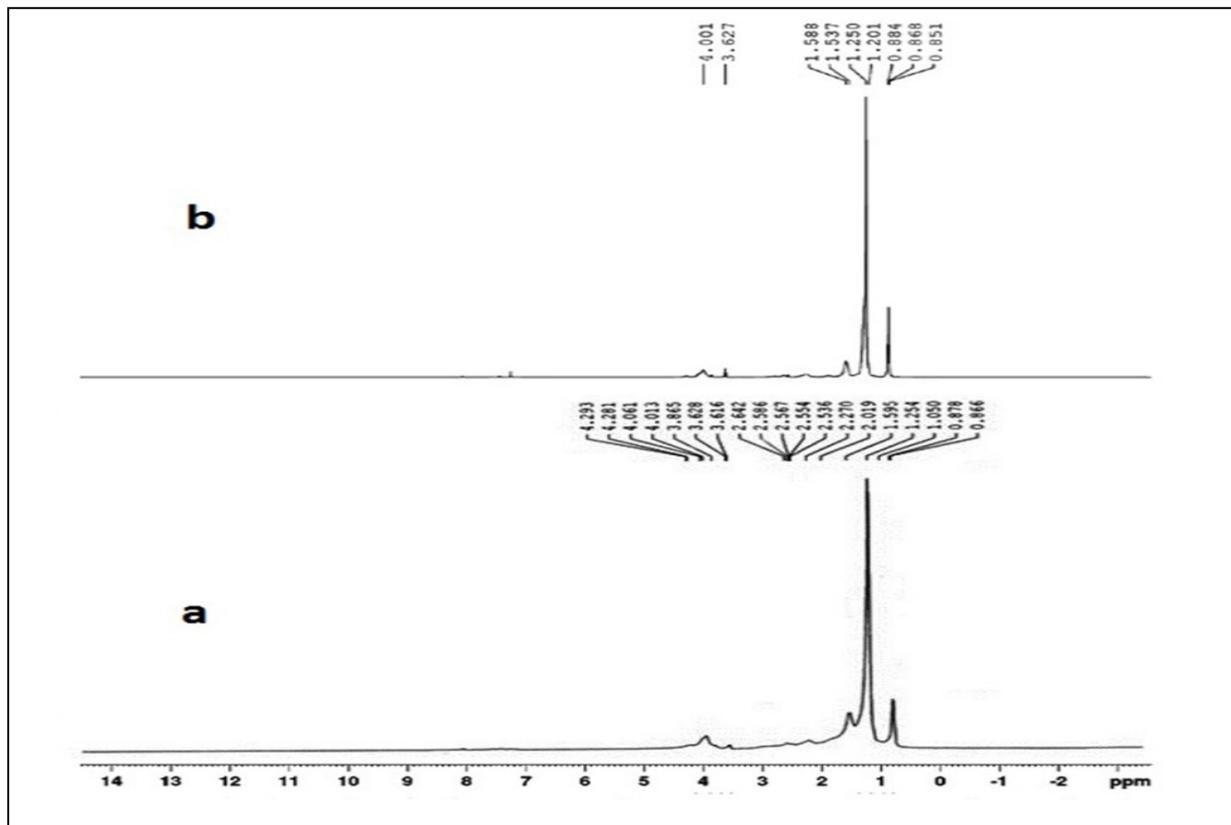


Figure 2. ¹H NMR spectra of a) polymer and the b) PNC (Z-3)

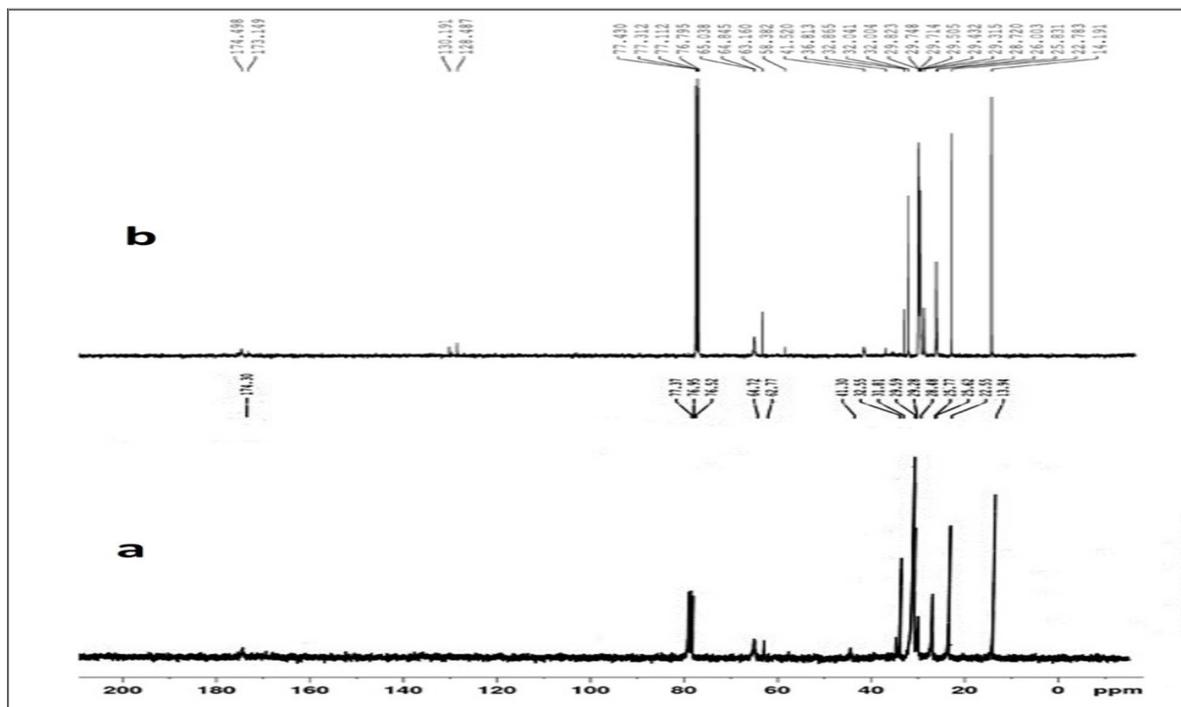


Figure 3. ¹³C NMR spectra of polymer a) and b) the composite (Z-3)

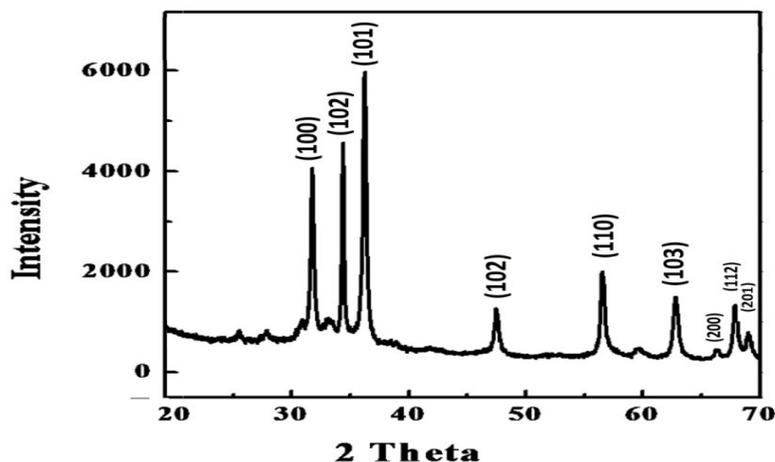


Figure 4. XRD spectra of prepared ZnO nanoparticles

Figure 5 represents the SEM micrographs of the ZnO nanoparticles at different magnifications. These SEM images substantiate the formation of ZnO nanoparticles. These pictures confirm the approximate spherical shape to the ZnO nanoparticles. It also can be seen from the pictures that the size of the nano-ZnO is in the range of 15 to 20 nm.

The intensity plot showed the relative intensity of light scattered by ZnO NPs. DLS

measures the hydrodynamic diameter of the particles. The plot showed only one peak with mean hydrodynamic size (Z-Average) 474.6 nm and Pdl 0.713. The obtained particle sizes are bigger than those shown in the SEM images due to the agglomeration of the particles [26]. The plot of size distribution report by intensity of ZnO NPs as obtained by the experiment was mentioned in the supporting information.

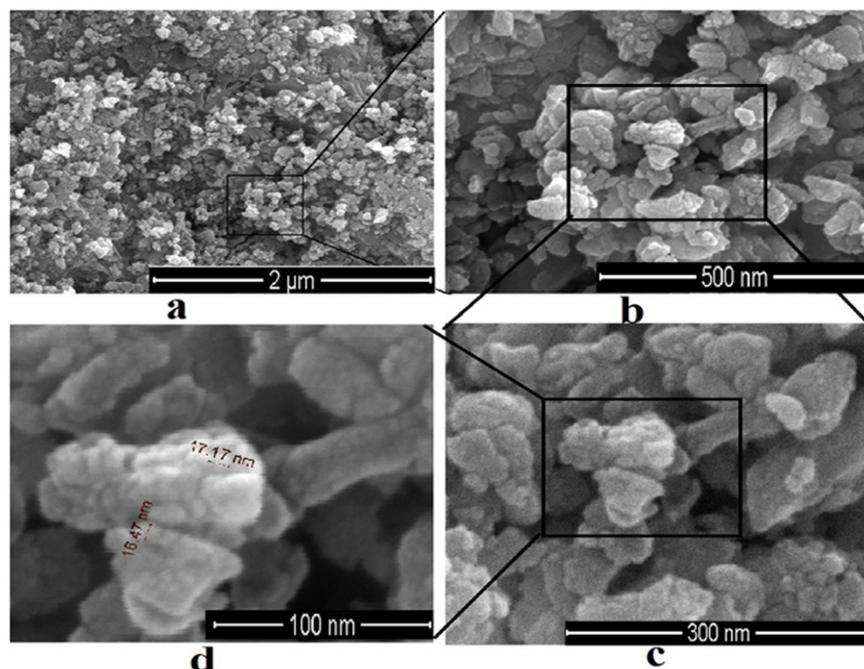


Figure 5. SEM images (a, b, c and d) of prepared ZnO nanoparticle at different magnifications

Thermo gravimetric analysis

The TGA data of the polymer (A) and polymer/ZnO nanocomposites (Z-1, Z-2 and Z-3) are represented in Figure 6. It was seen from the figure that, thermal stability of all nano blended composites is higher than that of A. At 380 °C, the percentage of decomposition of the polymer (A) and nanocomposites from Z-1 to Z-3 were 32.42%, 22.88%, 22.09% and 21.29% respectively, whereas at 490 °C, the percent of weight loss of A, Z-1, Z-2 and Z-3 were 93.71%, 74.86%, 74.08% and 73.27% respectively. Hence thermal stability of the polymer/ZnO nanocomposites (Z-1, Z-2 and Z-3) was improved by dispersion of the nano-ZnO into the A. This enhancement of thermal stability may be due to the reduction of mobility of polymer chain and the tendency of nanoparticles to remove free radicals [27].

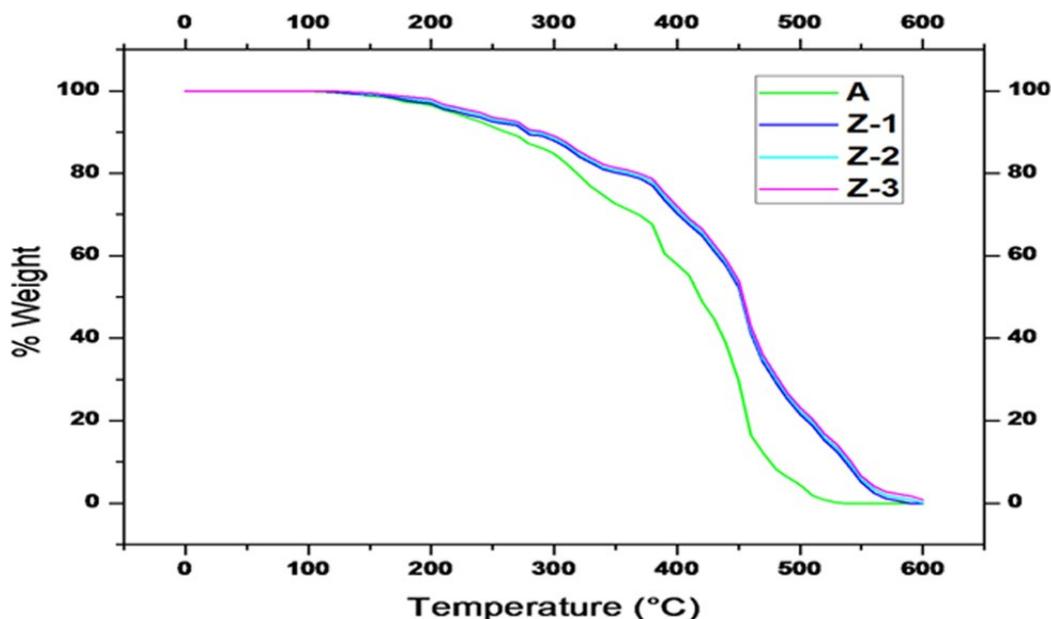


Figure 6. TGA data of polymer (A) and polymer/ZnO nanocomposite (Z-1, Z-2 and Z-3)

Efficiency of additive as viscosity modifier

Figure 7 represents the viscosity index values of the lubricants blended with the additives. It was observed that, the viscosity index (VI) values of the polymer/nano-ZnO composites of different composition (Z-1, Z-2 and Z-3) at different concentration level were better than the pure polymer (A). Again with both type of additives, there is always a steady increase of VI values with the increase in additive concentration. Raising the additives' concentration led to an increase in total volume of polymer micelles in the solutions. The

additional increase of volume compared to pure polymer may be due to the fact that, the nanoparticles present in the polymer matrix leads to the polymer chain separated from each other. For all concentrations, the prepared polyacrylate-ZnO nanocomposites' viscosity index values were higher than polyacrylate-magnetite nanocomposites. The values of viscosity index of polyacrylate-magnetite nanocomposites have been reported in our previous work [18].

Efficiency of additive as pour point depressant

Different level of percentage concentration varying from 1 wt% to 5 wt% of the additives in the base oil was tested as PPD and the results are depicted in Figure 8. The results showed that the additives (A, Z-1, Z-2 and Z-3) are efficient as PPD and the efficiency decreases with increasing additive concentration. The PPD property of all the blended composites is very similar with that of A. That means, incorporation of nanoparticles into the polymer matrix does not affect the PPD property

compared to polymer (A). The decrease of pour point is only significant at low concentration (1%). Battez *et al.*, reported that with higher concentration (more than 0.4 wt%) of the ZnO NPs, no changes in the pour point have been observed [28]. As reported earlier in our previous work, the pour point depressant property of polyacrylate-magnetite nanocomposites is more or less same as studied with polyacrylate-ZnO nanocomposites [18].

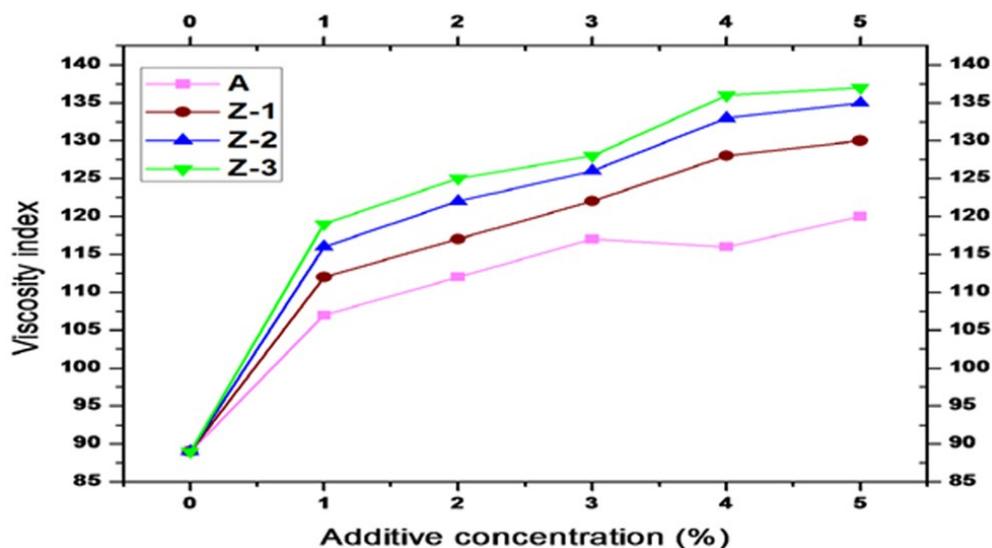


Figure 7. Plot of viscosity index of the lube oil blended with additives at different concentration levels

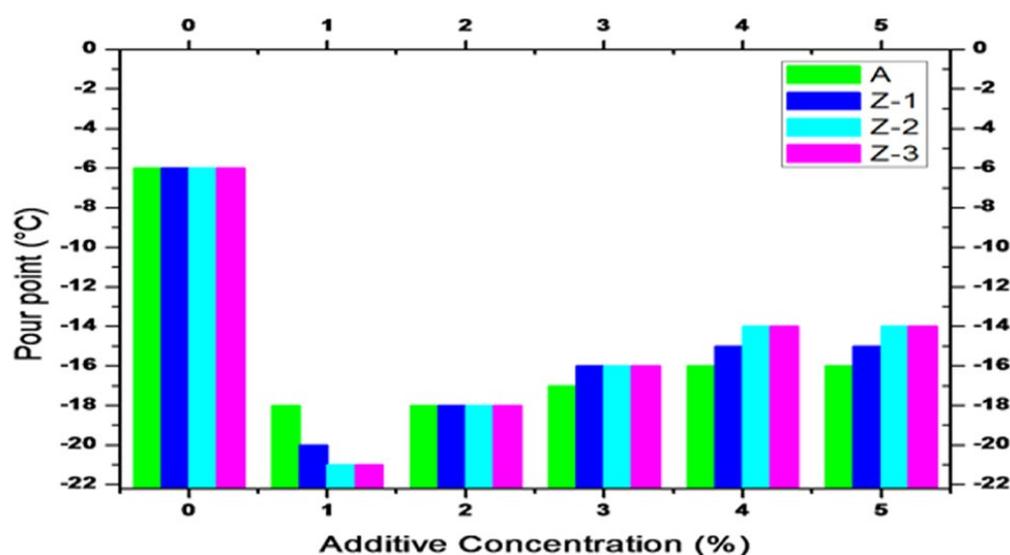


Figure 8. Plot of pour point of the lube oil blended with additives at different concentration levels

Tribological performance

The tribological properties of all the lubricant compositions (A, Z-1, Z-2 and Z-3) were determined by measuring WSD by FBWT apparatus employing 40 kg load (Figure 9). The AW performance of the base oil is significantly enhanced when the additives are blended with it and is indicated by the lower WSD values of the lubricant compositions. The nano-ZnO

blended composites exhibited better anti-wear performance compared to only polymer (A) and the performance becomes increasingly better with increasing the amount of nanoparticles in the polymer matrix as is shown in the Figure 9. The tribological performance of all the lubricant compositions was excellent but less significant than polyacrylate-magnetite nanocomposites as reported in our previous work [18].

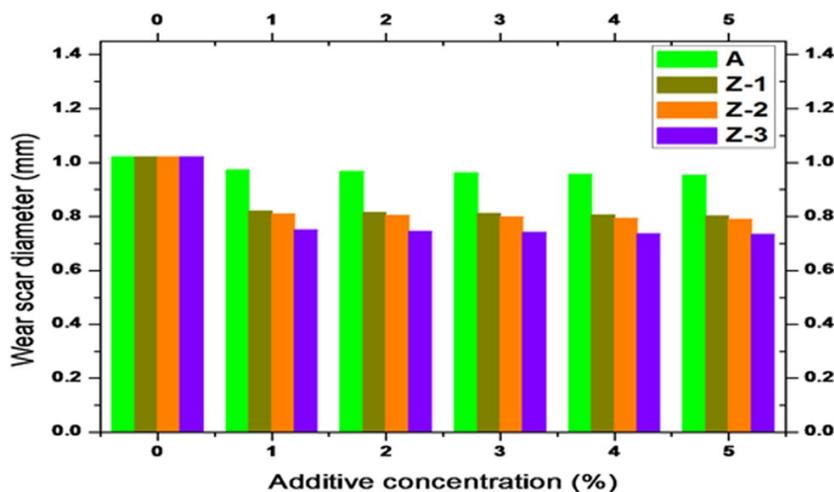


Figure 9. Wear scar diameter (WSD) of the lube oil blended with additives at different percentage (w/w)

Conclusions

In this research study, nano-ZnO was synthesized with a great size distribution (15–20 nm), and was characterized using the SEM, XRD, and DLS analysis. The interaction of nano-ZnO with PDDA was studied using FT-IR analysis and suggested that there was definite interaction between them. All the nano blended composites showed excellent performance as viscosity modifier and anti-wear additives for lube oil. The viscosity index value of one of the composite (Z-3) has shown 137 at 5% concentration in base oil, that is higher than neat polymer and up to 28% decrease in wear reduction was observed. Moreover, the thermal stability of the polymer was also improved by the incorporation of nano ZnO into the polymer

matrix as is evident from thermogravimetric analysis. This change in polymer properties was also an indication of nano-polymer interaction in the blended composites. This study clearly put more insight in the formulation of nano based multifunctional lubricating oil additives. Therefore, the above study is definitely a potential approach to design multifunctional additives for lubricating oil with better thermal stability.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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