High-Density Polyethylene Waste (HDPE)-Waste-Modified Lube Oil Nanocomposites as Pour Point Depressants

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ABSTRACT: Sustainability metrics have been established that cover the economic, social, and environmental aspects of human activities. Reduce, reuse, and recycle (3R) strategy targets solid waste management in the waste generation sectors. The purpose of this work is to study the possibility of using various plastic wastes containing high-density polyethylene (HDPE) and high-density polyethylene nanoclay (PMON) as polymer additives to modify lubricating oil. The structure of these additives was elucidated by Fourier transform infrared (FTIR) spectra, and the particle size of PMON was determined by dynamic light scattering (DLS). The thermal stability of HDPE and nanoclay HDPE (PMON) was studied, which showed higher thermal stability, and these additives completed degradation above 500 °C. The performance of HDPE and nanoclay HDPE (PMON) in lubricating oil was evaluated as pour point depressants by standard ASTM methods. The results showed that the efficiency of these additives increases with the decrease in the dose of these additives and lubricating oil treated with HDPE at 0.25% dosage lowers PPT to −30 °C, while lubricating oil treated with nanoclay HDPE (PMON7) at 0.25% dosage reduces PPT to −36 °C. Photomicrographic analysis was conducted to study accumulations and modifications in the wax crystal morphology in lube oil without and with HDPE and nanoclay HDPE (PMON). Photomicrographs revealed that wax morphology changes due to effective pour point depressants on crystal growth.

1. INTRODUCTION

Environmental sustainability works wisely to protect the earth’s natural resources and to ensure that future generations do not lose the opportunity to fulfill their needs. Sustainability means using a resource in a way that the resource is not exhausted or damaged permanently. There are several ways to determine levels of sustainability and implementation. Three sustainability strategies (Rs) can be used that represent reduce, reuse, and recycle. This rule is part of the waste hierarchy, which is utilized in the plan of priorities for environmental protection and resource conservation. The purpose is to utilize commodities most practically and produce the least waste. This method also creates other useful externalities, including energy savings, emission reductions, and greenhouse gas emissions reductions, the growth of renewable technology, and job creation. Recycling is a method of treating waste when produced unless it can be reused. It prevents waste from being sent to the sediment and converts waste into new products or commodities. Successful recycling means that waste can be sorted according to different materials for effective recycling. The old material may be turned into a new or completely different version of the same thing. For example, used bottles can be converted into new bottles for construction projects or recycled. Thermoplastic polymer high-density polyethylene (HDPE) is used in a wide range of applications including plastic bottles, milk jugs, shampoo bottles, bottles of bleach, cutting boards, and piping. Plastic material is the most useful. Several researchers have reported the modification of HDPE polymer by various nanoparticles such as CaCO₃, clay, bark fiber, rice husk, Cu-nanofiber, titanium dioxide, and nickel particle. Thermoplastic polymers have become much better than aluminum and other metals due to their ideal properties such as corrosion resistance, low density, and high strength. At very low temperatures, freezing of oil causes damage to machine components (oil cannot pour or flow) and, despite the use of the preheating system, time and energy are wasted. This waxing has long been recognized and is most commonly defined by a point in mineral oils and prepared liquids. The
pour point of lubricating oil is the lowest temperature at which it pours or flows when it is chilled without disturbance under prescribed conditions. Mineral oils do not have a sharp freeze like water because of the complex mixture of mineral oils. Under certain conditions, it depends on the temperature at which the oil begins to flow. Removing the waxy components of the oil can reduce this. Wax removal, however, is costly. Using additives (purpose depressant) to complement the modest dewaxation is another efficient approach to reduce points. At lower temperatures, the crystalline polymer tends to freeze with other types of wax found in lubricants and can greatly exacerbate fluidity difficulties at lower temperatures. All mineral-derived stocks used in lubricants contain waxy carbohydrates, which, when the temperature drops, are released from the solution. They can produce a 3D wax crystal network that can completely immobilize the oil.

Pour point depressants are polymers that can allow oil or lubricants to flow at extremely low temperatures in winter without forming wax and also allow the oil to remain pumpable at this cold temperature (flowable). Typical applications where the extremely low starter temperature of the machine is conceivable are utilized in paraffinic base oils. Point depressants are mostly used in paraffinic engine oils. Therefore, dewaxing could not be used here because the wax is still in oil; however, the main idea is to prevent the accumulation of wax by changing the morphology structure so that the oil can flow at low temperature.

The additives, which are used to improve the flow of lubricating oils, are imported from abroad, or they are prepared in the laboratory from imported chemicals, and this is a major economic problem that is costly to the state. In this research, plastic waste from the hope material found in the empties of shampoos, cosmetics, and washing tools is reused as it is. Then, adding it in different proportions to oils and evaluating its effects the chemistry of point depressants as additives for lubricants, which play an important role in the performance of the oil, but also these types of additives from recycling waste (HDPE) modified using nanoclay. Therefore, this gives a very important role in both economic and environmental directions and because of recycling (it is one of 3Rs of sustainability), which is an important goal in the whole world. In the present work, we use plastic wastes containing high-density polyethylene (HDPE) and high-density polyethylene nanoclay (PMON) as pour point depressants for lubricating oil after studying the characterization of these samples. Furthermore, we conduct a comparative study between the market sample and synthetic and biosynthetic oils.

2. RESULTS AND DISCUSSION

Solid plastic waste continues to be an environmental concern due to its poor handling and disposal. Reusing plastic waste is the perfect key to preserving the environment. Waste thermoplastics such as poly(vinyl chloride) (PVC), polypropylene (PP), and polyethylene (PE) have low melting points and good thermostability. High-density polyethylene (HDPE) offers the advantages of high retraction, easy formation, high melting resistance, and easy processing. In this regard, different concentrations of HDPE waste and 1% wt of oil-based nanoclay were used to modify the lubricating oil to improve its pour point depressant.

2.1. Characterization of the Prepared Additives. 2.1.1. Fourier Transform Infrared (FT-IR) Analysis. The FTIR spectra of high-density polyethylene (HDPE), organoclay montmorillonite (OMMT), lube oil, high-density polyethylene-modified lube oil (PMO1), and nanoclay high-density polyethylene-modified lube oil (PMON7) are shown in Figure 1.

Figure 1. FTIR spectra of high-density polyethylene (HDPE), organoclay montmorillonite (OMMT), lube oil, high-density polyethylene-modified lube oil (PMO1), and nanoclay high-density polyethylene-modified lube oil (PMON7).
1. The characteristic vibrational absorption bands for HDPE are assigned to CH stretching in the range of 2850−2912 cm$^{-1}$ in groups of −CH$_2$; there is a CH$_2$ band at 1470 cm$^{-1}$ and CH$_3$ groups in sequence of the paraffin group with a sequence of 722 cm$^{-1}$.\textsuperscript{13} The adsorption peaks of lube oil are at 2854 and 2923 cm$^{-1}$ assigned to CH stretching in −CH$_2$− groups; at 1460 cm$^{-1}$, there is a C−H bending band of CH$_2$ groups; at 1376 cm$^{-1}$, there is a C−H bending band of CH$_3$ groups; and at 724 cm$^{-1}$, there is a C−H bending band of CH$_3$ groups in the paraffin structure. The intensity bands of a PMO1 polymer composite have the same function groups as shown in Figure 1 except that the intensity of the groups is increased by a very small amount. This happens because of hydrocarbon groups (HDPE) as lube oil indicating physically bonded to lube oil molecules. On the other hand, peaks of organoclay OMMT are at 2852 and 2923 cm$^{-1}$ assigned to CH stretching in −CH$_2$− groups: at 1474 cm$^{-1}$, there is a C−H bending band of CH$_2$ groups; at 1383 cm$^{-1}$, there is a C−H bending band of CH$_3$ groups; at 695 cm$^{-1}$, there is a C−H bending band of CH$_3$ groups in the paraffin structure; and at 526−466 cm$^{-1}$, peaks are assigned to C−Br of organoclay. Finally, the adsorption bands of the PMON7 nanocomposite have the same function groups as those of the PMO1 composite, except that the intensity of the groups is increased by a very small amount. The disappearance of the nanoband proves that OMMT is not bonded to oil but deposited on it.

2.1.2. X-ray Diffraction Analysis of Organo-Nanoclay (OMMT). The organo-nanoclay samples before and after treatment were tested by X-ray diffraction. XRD analysis is used to demonstrate the loading of surfactants in the galleries of the resulting organoclay. Figure 2a,b shows the XRD patterns of unmodified Na-MMT and modified organo-nanoclay (OMMT). From Figure 2a, it is revealed that the typical diffraction peak of water-based Na-MMT is 6.85 corresponding to a basal spacing of 1.29 nm. By comparing the X-ray diffraction graphs of Na-MMT (Figure 2a) and oil-based modified organo nanoclay (OM-MMT) (Figure 2b), it was found that this peak disappeared and a strong shift in the position of 2Θ planes (2Θ changed from 6.85 to 3.63) took place. This means that there is an increase in the basal spacing of these bands. The increase from 1.29 to 2.42 nm is relatively large, confirming the occurrence of interference of organic molecules between the silicate sheets with the CTAB surfactant.\textsuperscript{36}

2.1.3. Dynamic Light Scattering (DLS). Dynamic light scattering (DLS) is a technique that is performed to understand the particle size distribution of the prepared nanoclay high-density polyethylene. DLS images of oil-based organo-nanoclay (OM-MMT) and nanoclay high-density polyethylene (PMON7) are presented in Figure 3a,b. It is evident from Figure 3a,b that the size distribution profiles have particle sizes of 300 and 400 nm, respectively, which confirms the successful formation of the nanocomposite.

2.1.4. Thermal Analysis of HDPE-modified Lube Oil With and Without Nanocomposites. Both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements provide valuable information that can be used to select materials for a specific end-use application, predict product performance, and improve product quality. This technique is mainly used to estimate the thermal stability and
to estimate the lifetime of the product. \(^{28}\) Thermogravimetric analysis (TGA) of high-density polyethylene-modified lube oil (PMO1) and nanoclay high-density polyethylene-modified lube oil (PMON7) is shown in Figure 4a,b. The graph shows that the initial temperature for degradation of PMO1 or PMON7 is \(\sim 111\) °C, and the thermal stability is increased by incorporating clay nanoparticle contents. The exceptional heat resistance and machinability can be attributed to the PMON7 clay nanoparticles incorporated in the lubricating oil. In addition, the final degradation peaks of PMO1 or PMON7 are obviously determined at 503 or 598 °C, respectively, due to the decomposition of the HDPE waste chains. The initial weight loss of lube oil in both figures is not related to its decomposition but is attributed to evaporation or volatilization of oil. The weight loss that occurs at about 450 °C is the thermal decomposition of the waste polymer. Because of the relatively slow development of oil, its weight loss occurs as polymer degradation. It is difficult to clearly determine the levels of oil and polymer degradations in the modified samples due to the strong overlap between these two degradation peaks.

Differential scanning calorimetry (DSC) of high-density polyethylene-modified lube oil (PMO1) and nanoclay high-density polyethylene-modified lube oil (PMON7) is shown in Figure 5a,b. The DSC curve in Figure 5a shows several endothermic peaks starting from 75 to 500 °C, which relate to the melting and degradation temperatures of the HDPE waste mixture sample. The DSC curve in Figure 5b shows two endothermic peaks at 125 and 500 °C, respectively. The curve shows that the thermal stability of the lubricating oil is increased by the addition of nanoparticles, and this may be due to the interaction between the OMMT particles and the waste HDPE matrix, which is related to the slight coagulation of the surface nanoparticle components on the polymer formation.

### 2.2. Evaluation of the Prepared HDPE and Nanoclay HDPE Samples as Pour Point Depressants (PPDs) for Lubricating Oil

The oil pour point is the temperature at which the oil stops flowing under the influence of gravity. In cold weather, oil with a high pour point makes machinery startup difficult or impossible. The hardness of cold oil is due to paraffin wax, which tends to form a crystalline structure. Pour point depressants reduce the cohesion and size of crystal structures, resulting in reduced pour point and increased flux at lower temperatures. Waxes can cause a lot of trouble in the storage and operability of lubricating oils.\(^{37,38}\)

Figure 6 and Table 1 show the relationship between the various concentrations of the prepared HDPE (PMO1–PMOS) and nanoclay HDPE (PMON7–PMON11) and the pour point depressants (PPDs) for lubricating oil. It is evident from Figure 6 that the prepared HDPE and nanoclay HDPE waste are effective as pour point depressants for lubricating oil.
and the efficiency is reduced by increasing the doses of these prepared additives. It can be attributed to a decrease in the solvation power, and the solvation power of any solvent decreases with decreasing temperature and vice versa.\textsuperscript{26–41} This decrease in solvation power becomes more obvious when the molecular weight of the solute and its concentration increases. The best performance is shown as pour point depressants at a concentration of 0.25%. In comparison between high-density polyethylene waste (PMO1) and nanoclay high-density polyethylene waste (PMON7), the best result is PMON7 because the nanomolecule is more easily adsorbed on the wax crystal to change its morphological structure and prevent the growth of a three-dimensional wax crystal lattice so that the oil can be poured at lower temperatures.\textsuperscript{29,32}

2.3. Effect of Additive Type on Wax Crystal Modification of Lube Oil. Pour point depressants work by adsorption on the surface of wax crystals. The resulting surface layer of the pour point depressants prevents the development of wax crystals and their ability to absorb oil and form gels.\textsuperscript{32–44} Photomicrographic analysis affirms other standard flow experiments, which assess the pour point depressants of treated/unlubricated oil through the crystallization behavior of wax.\textsuperscript{38} It is known that the morphology (shape) of wax crystals is an essential aspect in studying the reaction mechanism of the pour point depressants for lubricating oil.

Figure 7a–c shows the photomicrographs of the prepared high-density polyethylene waste (PMO1) and nanoclay high-density polyethylene waste (PMON7) using 0.25% concentration by weight and lube oil. Figure 7a exhibits the accumulations of wax crystals for the untreated lubricating oil and displays big cyclic crystals, while Figure 7b,c exhibits a big decrease in the size of wax crystals and forms a large number of fine scattered crystals due to the effect of prepared additives.

2.4. Comparative Study Between the Prepared Waste Samples and Other Pour Point Depressant Additives, Commercial Oil, Synthetic Oil, and Bio-Lubricant. Figure 8 shows the comparative study about the pour point depressants between the prepared waste samples and commercial oil, synthetic oil, and bio-lubricant. As shown in Figure 8, the prepared high-density polyethylene waste (PMO1) and nanoclay high-density polyethylene waste (PMON7) samples give a good result as pour point depressants in mineral oils despite the presence of a wax crystal in the oil. However, the commercial Mobil (15W-40), super Mobil (15W-40), synthetic oils, and bio-lubricants give good results as pour point depressants in the absence of waxy crystals because it is not mineral oil. This result for commercial additives is obtained at a very low pour point compared to our prepared waste samples because the commercial additives are measured as pour point depressants in the absence of wax crystals that are not mineral oil.\textsuperscript{35} In addition, our prepared samples give the best pour point depressants in mineral oil and are close to the performance of synthetic oils although our samples are prepared from waste HDPE recycling, so in the economic and environmental aspects, our work provides good sustainability.\textsuperscript{32,45}

3. CONCLUSIONS

The main outputs of the present work can be summarized in the following points:

1. High-density polyethylene waste and nanoclay high-density polyethylene waste samples were successfully prepared and then elucidated by using FTIR, XRD, DLS, and thermal analysis (TGA and DSC).

2. The prepared HDPE and nanoclay HDPE waste samples have high thermal stability and these additives complete degradation above 300 °C.

3. DLS images of organo-nanoclay and nanoclay high-density polyethylene waste revealed that the size distribution profile has a particle size of 300 and 400 nm, respectively, which confirms the successful formation of the nanocomposite.

### Table 1. ID for Waste-Modified Lube Oil Samples

| sample no. | sample ID      | sample description                                      | additions content (%) |
|------------|----------------|---------------------------------------------------------|-----------------------|
| 1          | LO             | virgin lube oil free additive base oil (SAE 30)         |                       |
| 2          | HDPE           | virgin high-density polyethylene waste                  |                       |
| 3          | OMMT           | montmorillonite organo-nanoclay                         |                       |
| 4          | PMO1           | high-density polyethylene waste-modified lube oil       | 0.25% HDPE            |
| 5          | PMO2           | high-density polyethylene waste-modified lube oil       | 0.5% HDPE             |
| 6          | PMO3           | high-density polyethylene waste-modified lube oil       | 0.1% HDPE             |
| 7          | PMO4           | high-density polyethylene waste-modified lube oil       | 0.2% HDPE             |
| 8          | PMO5           | high-density polyethylene waste-modified lube oil       | 0.3% HDPE             |
| 9          | PMON7          | high-density polyethylene waste-modified lube oil       | 0.25% HDPE/0.1% OMMT  |
| 10         | PMON8          | high-density polyethylene waste-modified lube oil       | 0.5% HDPE/0.1% OMMT   |
| 11         | PMON9          | high-density polyethylene waste-modified lube oil       | 0.1% HDPE/0.1% OMMT   |
| 12         | PMON10         | high-density polyethylene waste-modified lube oil       | 0.2% HDPE/0.1% OMMT   |
| 13         | PMON11’        | high-density polyethylene waste-modified lube oil       | 0.3% HDPE/0.1% OMMT   |
(4) The prepared HDPE and nanoclay HDPE waste samples are soluble in lubricating oil (SAE 30) and are effective as pour point depressants for lubricating oil.

(5) The prepared HDPE and nanoclay HDPE waste samples were tested as pour point depressants at different concentrations for lube oil and the obtained result revealed the efficiency of these waste samples as pour point depressants decrease by increasing the concentration of these waste additives.

(6) Photomicrographic analysis indicated that wax modification is affected via the effective pour point depressants on crystal growth.

(7) Comparative study between our prepared HDPE and nanoclay HDPE samples and other commercial pour point depressant additives revealed that our prepared samples give the best pour point depressants in mineral oil and are close to the performance of synthetic oils. Although our samples are prepared from waste HDPE recycling, our work provides good sustainability in the economic and environmental aspects.

4. EXPERIMENTAL SECTION

4.1. Materials. The raw materials used in this study included plastic wastes containing high-density polyethylene (HDPE) and nanoclay. Waste HDPE was collected from some local shops and restaurants in Egypt. The plastic HDPE waste was washed and crushed to obtain fine particles, and then stored before adding to the lube oil. Lube oil (SAE 30) is a free additive base oil obtained from the Petroleum Co-operative Society. Nanoclay was obtained from Sigma-Aldrich. The clay used in this work, which mostly contained montmorillonite, had the following composition: SiO₂ 44.8%, TiO₂ 0.89%, Al₂O₃ 13.6%, Fe₂O₃ 11.5%, FeO 0.07%, MgO 1.97%, CaO 1.69%, Na₂O 3.16, K₂O 0.13%, P₂O 0.24%, and H₂O 21.95% with a cation exchange capacity of 0.8 mequiv/g and surface area as 20−40 m²/g. The intercalating agent (Surfactant) was of type cetyltrimethyl ammonium bromide (CTAB), which was purchased from Sigma-Aldrich, Germany. All solvents were supplied by Sigma-Aldrich and used without purification.

4.2. Preparation of Modified Organoclay Montmorillonite (OMMT). The organoclay montmorillonite (OMMT) was treated to improve the performance of polymer-modified lube oil. The nanoclay was changed to ensure layer separation by surface treatment to make an intensive interaction between the nanoclay and the lubricating oil. Organoclay (OMMT) was prepared by a cationic exchange process in an aqueous solution. In this method, 25 g of Na⁺−MMT dispersed in 800 mL of distilled water at 80 °C with 10 g of cetyltrimethyl...
ammonium bromide (CTAB) for 2 h and stirred vigorously. The precipitate was filtered and rinsed with warm distilled water several times until no chloride ions were detected with 0.1 N AgNO₃ solution. Then, the sample was dried at 60 °C for 24 h. The dried organic montmorillonite was ground to obtain clay particles with a mesh size of more than 75 nm from nanocomposites.

4.3. Preparation of High-Density Polyethylene (HDPE)-Modified Lube Oil. HDPE waste-modified lube oil materials were prepared by mixing lubricating oil samples with nanoclay-modified high-density polyethylene (HDPE). The calculated amount of the lubricating oil sample was heated at a temperature of 90–120 °C. The waste was dissolved in toluene and added slowly to oil samples in percentages of 0.5, 0.5, 1, 2, and 3% by weight of oil and solvent with continuous heating by stirring at a temperature ranging from 110 to 120 ± 1 °C for 1 h. The mixer was a sigma-type blade rotated at 4000 rpm.

4.4. Preparation of High-Density Polyethylene Nanoclay (PMON)-Modified Lube Oil. High-density polyethylene nanoclay-modified lube oil was prepared by adding 1 wt. % surfactant-modified nanoclay and mixed by stirring using a rotating mixer at 4000 rpm for 1 h to ensure that the intercalated OMMT nanoclay was dispersed into the lube oil. All of the prepared HDPE nanocomposites (PMON) were left to cool at room temperature before testing. Table 1 shows the ID for all waste samples prepared for the modified lube oil.

4.5. Characterization. The chemical structures of the prepared high-density polyethylene (HDPE)-modified lube oil samples were determined by Fourier transform infrared (FTIR) spectrometer Model Type Mattson Infinity Series Bench Top 961. The KBr plate method was used to record the IR spectra. The samples were mixed with KBr (sample/KBr ratio was 1:100) and then converted to a disk. IR spectra were recorded in the spectra range of 4000–400 cm⁻¹. In addition, thermal properties of the prepared samples were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA and DSC experiments were performed using a thermo-balance instrument SDT Q-600 (TA Instruments). About 10 mg of the specimen at a heating rate of 10 °C/min from 30 to 800 °C was used in the experiments under a flowing nitrogen atmosphere (50 mL/min). Moreover, XRD analysis was evaluated for HDPE nanoclay samples by using an X-ray diffractometer (X’Pert PRO PANalytical) equipped with Cu Kα radiation (λ = 1.5406 Å). The scattering angle of 2θ ranged from 5 to 80° at a scan rate of 2°/min. Furthermore, dynamic light scattering (DLS) measurements were performed by Malvern Zetasizer, NANO ZS (Malvern Instruments Limited, U.K.) equipped with a He–Ne laser operating at a wavelength of 633 nm. DLS was used to measure the particle size and distribution of HDPE nanoclay samples.

4.6. Evaluation of the Prepared HDPE and Nanoclay HDPE Samples as Pour Point Depressants (PPDs) for Lube Oil. HDPE and nanoclay HDPE samples were evaluated as pour point depressants for lube oil (SAE30) at various doses (0.25, 0.5, 1, 2, and 3% by weight) according to ASTM D97-87 using Cold Filter Plugging and Pour Point Automatic Tester (CFPPA-T), Model 1 SL CPP 97.2. The effect of additive concentration on pour point was studied by using various doses of the HDPE and nanoclay HDPE samples. Furthermore, we perform a comparative study between the prepared samples, commercial oil, synthetic oil, and bio-lubricants.

4.7. Photomicrographic Analysis. The photomicrographs showing the wax crystal morphology of the untreated and treated lube oil samples with the prepared high-density polyethylene and nanoclay high-density polyethylene at various doses were obtained using an Olympus polarizing microscope Model BHSP fitted with a 35 mm automatic camera. The helium bulb was the illumination source. The temperature of the tested lubricant sample was controlled on the microscope slide by an attached cooling thermostat. All photographs were taken at 100X magnification.

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Notes
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REFERENCES

(1) Goodland, R. The concept of environmental sustainability. Annu. Rev. Ecol. Syst. 1995, 26, 1–24.
(2) Vezzoli, C. Design for Environmental Sustainability: Life Cycle Design of Products; Springer: London, 2018; pp 1–330.
(3) Veiga, L. E.; Magrini, A.; Sziklo, A. S. Eco industrial parks: a tool towards the reduction, reuse and recycling (3Rs) of by-products and wastes: case study in Paracambi EIP, Rio de Janeiro State. WIT Trans. Ecol. Environ. 2008, 109, 395–404.
(4) Mahat, H.; Yussri, M. S.; Ngah, C. 3R Practices Among Moe Preschool Pupils Through the Environmental Education Curriculum, SHS Web of Conferences. EDP Sciences, 2016; p 04002.
(5) Palmeira, M.; Musso, F. 3Rs of Sustainability Values for Retailing Customers as Factors of Influence on Consumer Behavior. In Handbook of Research on Retailing Techniques for Optimal Consumer Engagement and Experiences; IGI Global, 2020; pp 421–444.
(6) Kumar, S.; Panda, A. K.; Singh, R. K. A review on tertiary recycling of high-density polyethylene to fuel. Resour., Conserv. Recycl. 2011, 55, 893–910.
(7) Mayr, L.; Varvakis, G. In 3Rs Principles on the Improvement of Existing Buildings, 2008 World Sustainable Building Conference Proceedings, Melbourne, Australia, 2008.
(8) Yang, R.; Yu, J.; Liu, Y.; Wang, K. Effects of inorganic fillers on the natural photo-oxidation of high-density polyethylene. Polym. Degrad. Stab. 2005, 88, 333–340.
(9) Goma, K.; Hund, M.; Vučak, M.; Gröhn, F.; Wegner, G. Amorphous calcium carbonate in form of spherical nanosized particles and its application as fillers for polymers. Mater. Sci. Eng. A 2008, 477, 217–225.
(10) Sahebians, S.; Zebarjad, S. M.; Khaki, J. V.; Sajjadi, S. A. The effect of nano-sized calcium carbonate on thermodynamic parameters of HDPE. J. Mater. Process. Technol. 2009, 209, 1310–1317.
(11) Yuan, Q.; Yang, Y.; Chen, J.; Ramuni, V.; Misra, R. D. K.; Bertrand, K. J. The effect of crystallization pressure on macro-molecular structure, phase evolution, and fracture resistance of nanocalcium carbonate-reinforced high-density polyethylene. Mater. Sci. Eng. A 2010, 527, 6699–6713.
(12) Mohamed, M. A.; Shaltout, N. A.; El Miligy, A. A. The effect of gamma irradiation and particle size of CaCO3 on the properties of HDPE/EPDM blends. Arab. J. Chem. 2011, 4, 71–77.
(13) Moussa, G. S.; Abdel-Raheem, A.; Abdel-Wahed, T. Effect of Nanoclay Particles on the Performance of High-Density Polyethylene-Modified Asphalt Concrete Mixture. Polymers 2021, 13, No. 434.
(14) Minkova, L.; Filippi, S. Characterization of HDPE-g-MA/clay nanocomposites prepared by different preparation procedures: Effect of the filler dimension on crystallization, microhardness and flameability. Polym. Test. 2011, 30, 1–7.
(15) Yemele, M. C. N.; Koubaa, A.; Cloutier, A.; Soulounganga, P.; Wolcott, M. Effect of bark fiber content and size on the mechanical properties of bark/HDPE composites. Composites, Part A 2010, 41, 131–137.
(16) Ahmad, I.; Lane, C. E.; Mohd, D. H.; Abdullah, I. Electron-beam-irradiated rice husk powder as reinforcing filler in natural rubber/high-density polyethylene (NR/HDPE) composites. Composites, Part B 2012, 43, 3069–3075.
(17) Grigoriadou, I.; Paraskevopoulos, K. M.; Karavasilis, M.; Karagiannis, G.; Vasileiou, A.; Bikiaris, D. HDPE/Cu-nanofiber nanocomposites with enhanced mechanical and UV stability properties. Composites, Part B 2013, 55, 407–420.
(18) Olmos, D.; Dominguez, C.; Castrillo, P. D.; Gonzalez-Benito, J. Crystallization and final morphology of HDPE: Effect of the high energy ball milling and the presence of TiO2 nanoparticles. Polymers 2009, 50, 1732–1742.
(19) Dong, C. X.; Zhu, S. J.; Mizuno, M.; Hashimoto, M. Fatigue behavior of HDPE composite reinforced with silane modified TiO2. J. Mater. Sci. Technol. 2011, 27, 659–667.
(20) Krupa, I.; Cecen, V.; Boudenne, A.; Prokej, J.; Novák, I. The mechanical and adhesive properties of electrically and thermally conductive polymer composites based on high-density polyethylene filled with nickel powder. Mater. Des. 2013, 51, 620–628.
(21) Van Krevelen, D. W.; TeNijenhuis, K. Properties of Polymers: Their Correlation With Chemical Structure; Their Numerical Estimation; Elsevier, 2009.
(22) Schulz, U. Review of modern techniques to generate antireflective properties on thermoplastic polymers. Appl. Opt. 2006, 45, 1608–1618.
(23) Mishra, J. K.; Hwang, K. J.; Ha, C. S. Preparation, mechanical and rheological properties of a thermoplastic polylefin (TPO)/organoclay nanocomposite with reference to the effect of maleic anhydride modified polypropylene as a compatibilizer. Polymer 2005, 46, 1995–2002.
(24) Thermal Characterization of Polymeric Materials; In Turi, E., Ed.; Elsevier, 2012.
(25) Mano, J. F.; Koniarova, D.; Reis, R. L. Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability. J. Mater. Sci.: Mater. Med. 2003, 14, 127–135.
(26) Ahmed, N. S.; Nassar, A. M.; Nasser, R. M.; Khattab, A. F.; Abdel-Azim, A. A. Synthesis and evaluation of some polymeric compounds as pour point depressants and viscosity index improvers for lube oil. Pet. Sci. Technol. 2008, 26, 1390–1402.
(27) Lubricants and Lubrication; In Mang, T.; Dresel, W., Eds.; John Wiley & Sons, 2007.
(28) El-shazly, R. I.; Kamal, R. S.; Nassar, A. M.; Ahmed, N. S.; Sayed, G. H. The behavior of some terpolymers as lubricating oil additives. Appl. Petrochem. Res. 2020, 10, 115–123.
(29) Azim, A. A. A.; Nassar, A. M.; Kamal, R. S.; Preparation and evaluation of acrylate polymers as pour point depressants for lube oil. Pet. Sci. Technol. 2006, 24, 887–894.
(30) Zhang, J.; Wu, C.; Li, W.; Wang, Y.; Cao, H. DFT and MM calculation: the performance mechanism ofpour point depressants study. Fuel 2004, 83, 315–326.
(31) Zhang, J.; Wu, C.; Li, W.; Wang, Y.; Han, Z. Study on performance mechanism of pour point depressants with differential scanning calorimeter and X-ray diffraction methods. Fuel 2003, 82, 1419–1426.
(32) Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Preparation and Evaluation of Some Terpolymers as Lube Oil Additives. J. Dispersion Sci. Technol. 2011, 32, 616–621.
(33) Dimitris, S.; Achillas, L. A. Recent Advances in the Chemical Recycling of Polymers (PP, PS, LDPE, HDPE, PVC, PC, Nylon, PMMA), Material Recycling — Trends and Perspectives; IntechOpen, 2012; pp 1–64.
(34) Weber, R.; Gaus, C.; Tysklind, M.; Johnston, P.; Forter, M.; Hollert, H. I.; Lloyd-Smith, M.; Masunaga, S.; Moccarelli, P.; Santillo, D.; Seike, N.; Symons, R.; Torres, J. P. M.; Verta, M.; Varbelow, G.; Vigen, J.; Watson, A.; Costner, P.; Woelz, J.; Wyczisk, P.; Zennegg, M.; et al. Dioxidin- and POP-contaminated sites—contemporary and future relevance and challenges. Environ. Sci. Pollut. Res. 2008, 15, 363–393.
(35) Abdel-Hameed, H. S.; Ahmed, N. S.; Nassar, A. M.; El-Saeed, S. M.; El-Kafrawy, A. F.; Hashem, A. I. Studies on the rheological and tribological properties of acylated derivatives of castor oil and their application as bio-lubricants. Pet. Coal 2018, 60, 1265–1274.
(36) Sabatzedeh, M.; Bagheri, R.; Masoomi, M. Effect of nanoclay on the properties of low-density polyethylene/linear low-density polyethylene/thermoplastic starch blend films. Carbohydr. Polym. 2016, 141, 75–81.
(37) Anwar, M.; Khan, H. U.; Nautiyal, S. P.; Agrawal, K. M.; Rawat, B. S. Solubilized waxes and their influence on the flow properties of lube oil base stocks. Pet. Sci. Technol. 1999, 17, 491–501.
(38) Nassar, A. M.; Ahmed, N. S. Study the influence of some polymeric additives as viscosity index improvers, pour point depressants and dispersants for lube oil. Pet. Sci. Technol. 2010, 28, 13–26.
(39) Abdel-Azim, A. A. A.; Nasser, A. M.; Ahmed, N. S.; El-Kafrawy, A. S.; Kamal, R. S. Multifunctional additives for viscosity index improver, pour point depressants and dispersants for lube oil. Pet. Sci. Technol. 2009, 27, 20–32.
(40) Ghosh, P.; Hoque, M. Synthesis and performance evaluation of vinyl acetate-maleic anhydride based polymeric additives for lubricating oil. Pet. Sci. Technol. 2015, 33, 1182–1189.
(41) Chen, W.; Zhao, Z.; Yin, C. The interaction of waxes with pour point depressants. Fuel 2010, 89, 1127–1132.
(42) Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khdir, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. Egypt. J. Pet. 2012, 21, 19–30.
(43) Nassar, A. M.; Ahmed, N. S.; Haseeb, M. E.; Abdel-Rahman, A. A. H.; Nasser, R. M. Synthesis and evaluation of terpolymers as viscosity index improvers and pour point depressants. Pet. Coal 2017, 59, 442–451.
(44) Elbanna, S. A.; Abd El Rhman, A. M. Al.; Al-Hussaini, A. S.; Khalil, S. A. Synthesis and characterization of polymeric additives based on α-Olefin as pour point depressant for Egyptian waxy crude oil. Pet. Sci. Technol. 2017, 35, 1047–1054.
(45) Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Study the efficiency of some esters as synthetic lubricating oil. Pet. Coal 2018, 60, 520–541.
(46) Iskender, E. Evaluation of mechanical properties of nano-clay modified asphalt mixtures. *Measurement* **2016**, 93, 359−371.

(47) Guo, F.; Aryana, S.; Han, Y.; Jiao, Y. A review of the synthesis and applications of polymer–nanoclay composites. *Appl. Sci.* **2018**, 8, No. 1696.

(48) Innovative Developments of Advanced Multifunctional Nano-composites in Civil and Structural Engineering; In Loh, K.; Nagarajaiah, S., Eds.; Woodhead Publishing, 2016.

(49) Ahmed, N. S.; Nassar, A. M.; Nasser, R. M.; Khattab, A. F.; Abdel-Azim, A. A. A. Synthesis and evaluation of some polymers as lubricating oil additives. *J. Dispersion Sci. Technol.* **2012**, 33, 668−675.

(50) Khidr, T. T. Pour point depressant additives for waxy gas oil. *Pet. Sci. Technol.* **2011**, 29, 19−28.

(51) Shishkin, Y. L.; Yazynina, I. V.; Ovchar, E. V. Study of crystallization and melting of solid waxes by photometric and thermal methods. *Chem. Technol. Fuels Oils* **2008**, 44, 65−70.

(52) Khidr, A.; Taha, T. Alternating Copolymerized Derivative as a Pour Point Depressant for Gas Oil. *Pet. Coal* **2020**, 62, 1420−1426.