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Research Article

CHARACTERIZATION OF LUBRICANT POLYETHYLENE WAXES

Senem YETGIN[1*]

Polymer processing is become easy while using lubricant in a proper way. Hence viscosity reduction and gelation behavior/release effect of lubricants help the production speed and quality. In this manner by the growing need for lubricant characterization two technical-grade polyethylene (PE) waxes were investigated. PE is one of the most used lubricant and study by characterizing them using Fourier Transform Infrared (FT-IR) spectrophotometry, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) to elucidate their structural, molecular and thermal characteristics in order to evaluate their effectiveness and suitability as lubricants in carpet manufacturing..

Key words*: Lubricant, polymer processing, polyethylene wax*

1. Introduction

Lubricants are extensively used in many industrial applications to increase the general rate of processing of materials, controlling or reducing friction in industrial appliances amongst others. Among its use in various industrial applications, lubricants find use in thermoplastic polymer processes and it functions mainly to advance the surface release properties and/or increase the overall rate of processing. Lubricants are mixed with polymers to modify the apparent viscosity of a polymer melt and it has been reported [1 – 3] that lubricants when compounded in small quantities into a polymer, provides a substantial increase in the movement of the polymer chains during extrusion, injection molding, compression molding, etc., without influencing the polymer properties. Generally, lubricants function internally and/or externally: in polymer processing, they function internally by providing lubrication to the polymer under processing to increase the free flow of the melt bulk polymer by reducing friction between the chain segments and externally by preventing polymers that have the inclination towards tackiness from sticking to metallic parts of the processing equipment [1 – 4]. Figure 1 is a typical example of the mode of action of lubricants in poly (vinyl chloride) (PVC), a typical polymer requiring the use of lubricant additives during processing.

In other words, lubricants aid polymer processing by viscosity reduction and gelation behavior/release effect. These lubricants having high polarities and short C-chains have the ability to penetrate the polymer particles and reduce friction.Polyethylene (PE) wax is a combination of non-polar polymers used in various industrial applications and exhibits waxy properties containing hydrocarbons between C20 and C50 or higher [1]. PE waxes are important materials and have been reported to be synthesized in various ways: direct polymerization of ethylene under defined conditions, separation of high molecular weight polyethylene into lower molecular weight fractions, and separation of low

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[1] Department of Food Engineering, University of Kastamonu , Turkey, (syetgin@kastamonu.edu.tr) https://orcid.org/ 0000-0003-4352-4544

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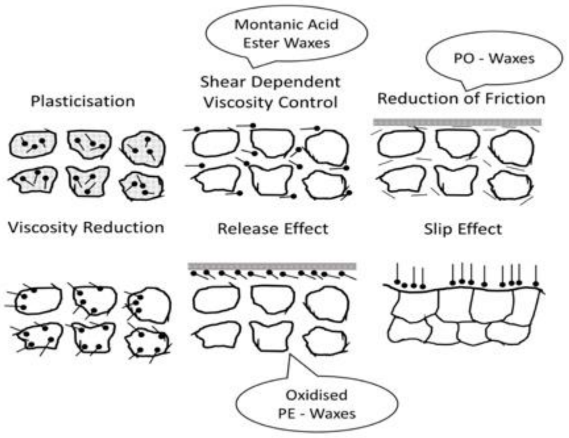


Figure 1 Mode of action of lubricants in PVC adapted by B. Treffler (2005) [2].

molecular weight polyethylene fractions from high molecular weight fractions [5]. PE waxes are commercially used in a variety of plastic / polymer processing applications due to their unique physicochemicals such as high crystallinity and linearity, low solubility in solvents, hardness at high temperatures, and oil thickening abilities. They are increase the lubricity, control set / softening point of hot melt adhesives and broadly used as an additive to provide lubrication in lubricating oils and coatings [5-8] and functions by providing lubrication and / or physical modification in many formulations changing viscosity and / or melting point and they are also used to influence altered chemical properties such as viscosity, temperature, gloss and fusion rate [9]. Reports show that the use of PE waxes as lubricants provides both internal and external lubrication due to reduced friction, and the rubber industry, wiring and electrotechnical industry, PVC processing, dispersing agent for color master batch, carpet manufacturing, printing ink production, paint, lacquer and textile industry. paraffin and bitumen types, fertilizer production, hydrophobic treatment of wooden surfaces, etc. shows that it is used in many industrial applications. [5, 9 - 10]. It has been reported that PE waxes have a self-lubricating performance and can offer lubrication and basic wear resistance in water-lubricated behavior materials [6]. Total degree of purity conditions of these technical-grade lubricants and their fatty acid structure are important factor in determining their suitability for use. In a previous study [11], we reported on the characterization and identification of a commercial PE wax by property comparison with paraffin wax, sorbitan monostearate and myristic acid. This present report aims at examining the morphology and structural characteristics of two different PE waxes to evaluate their feasibility as lubricants for carpet manufacturing and forms part of our studies on the characterization and identification of PE waxes. The data obtained may provide new information on more effective pathways for developing improved PE waxes for use as lubricants in polymer processing as well as other industrial applications.

2. Experimental Procedure

2.1. Materials

Two technical grade PE waxes, Licowax PE 520 P (PE 1) and Luwax® A (PE 2) obtained from Clariant Plastics & Coatings, Deutschland and BASF, Germany respectively, with physical properties as shown in Table 1 were used in this study. These are low-density polyethylene waxes used to improve the gloss, smoothness and water repellency on surfaces, as well as making the plastic easier to process. They have good lubricating effects which allow them to be applied in carpet manufacturing.

2.2. Fourier Transform Infrared (FTIR) Spectroscopy

The characteristic traces of the chemical structures of PE waxes were measured by Fourier transform infrared (FTIR) spectroscopy. For this, Dura Scope (Genesis II) spectrophotometer (Smiths Detection Inc., Danbury, CT, USA) was used in a wavelength range between 400 and 4000cm^{-1}.

2.3. X-ray Diffraction (XRD)

The structure of the powdered PE wax samples was evaluated by X-ray diffraction (XRD). This process practiced with the help of Bruker D8 Advance diffractometer. To be able to define phase structure of the PE Scherer equation was used. Additionaly the crystallite size along the a-axis (La) was calculated from the (110) Bragg peak.

Table 1 Physical properties of PE wax samples

Property	Licowax PE 520 P (PE 1)	Luwax® A (PE 2)
Physical appearance	Off-white waxy granules	Pure white powdery granules
Density, g/cm3	0.930	0.910 – 0.930
Average molecular weight, g/mol	No data available	~ 7000
Melting point, oC	117 – 123	101 – 109
Viscosity, mPa.s	~ 650	600 – 1200

2.4. Scanning Electron Microscope/ Energy Dispersive X-ray (SEM/EDXEDX) Measurements

Scanning electron microscope (SEM) images were taken by Quanta FEG 250, with Energy Dispersive spectroscopy (EDX) analyses was used for the identification of particle size and approximate composition of the PE wax samples.

2.4.1. Particle Size Distribution

The particle size distribution of PE1 and PE2 are determined by measuring the size of the particles in 17 SEM pictures for PE1 and 9 SEM pictures for PE 2 using the software of Qanta FEG 250. The particle size distribution graphs are drawn by using Sigmaplot free software.

2.5. Thermogravimetric Analysis (TGA)

The thermal behavior of the PE wax samples was studied by thermogravimetric (TGA) and differential thermal analyses (DTA) and carried out at using a thermogravimetric analyzer STA7300 (HITACHI) in nitrogen atmosphere of 40mLmin^{-1}. A small amount (≤ 10mg) of each sample was applied to heat energy for the analysis from room temperature up to 1200 ºC at 10 ºC/min.

2.6. Differential Scanning Calorimetry (DSC)

Phase transition temperatures and the associated energy changes in the PE wax samples were performed using DSC 7020 (HITACHI) at a rate of 10 ºC/min from 25 to 400 ºC in nitrogen atmosphere.

3. Results and Discussion

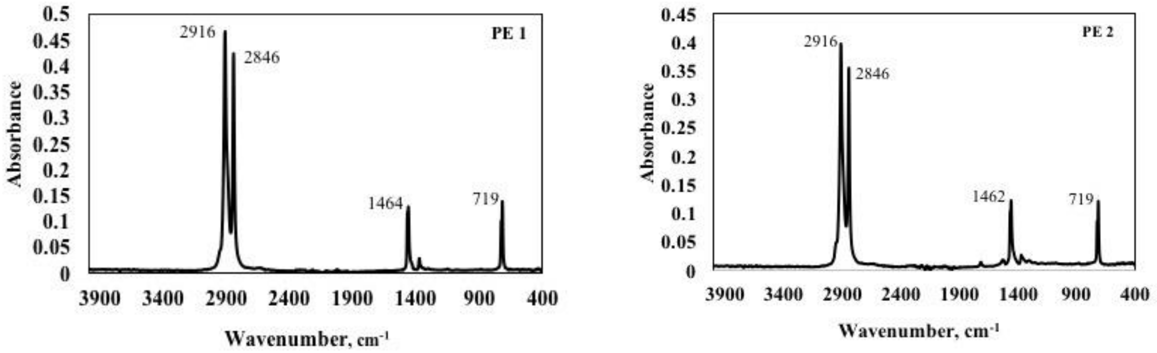
3.1. FTIR study of PE waxes

An IR spectrum provides information by determining the presence of functional groups associated with materials. The fingerprint absorptions of PE in the IR region from previous reports are given in Table 2 [13].

Table 2 Main absorptions of polyethylene in the IR region and their assignment

Absorption band (cm-1)	PE 1	PE 2	Assignment	Intensity
2919	+	+	CH_2 asymmetric stretching	Strong
2851	+	+	CH_2 symmetric stretching	Strong
1768	-	+	C=O stretching	Weak
1594	-	+	COO- stretching	Weak
1473 and 1463	+	+	Bending deformation	Strong
1377	+	+	CH_3 symmetric deformation	Weak
1366 and 1351	+	+	Wagging deformation	Medium
1306	+	+	Twisting deformation	Weak
1176	+	+	Wagging deformation	Very weak
731–720	+	+	Rocking deformation	Medium

The functional groups present in the PE wax samples (PE 1 and PE 2) are shown in Fig. 2



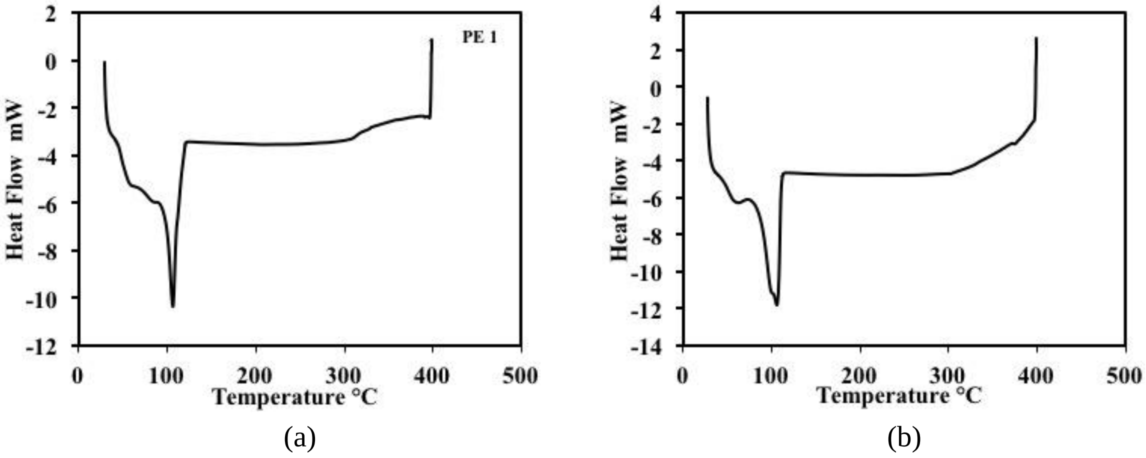
(a) (b)

Figure 2. The IR spectra of PE wax samples a) PE 1 and b) PE 2

PE waxes consists of hydrocarbons containing long –(CH_2)- chains that result in noticeable absorbance belong to methylene asymmetric and symmetric stretching vibration bands in the IR spectra [14]. From the figures above, it can be seen that the distinguishing absorbance frequencies of PE waxes shown in both samples, PE 1 and PE 2. The peaks of 2916 and 2846 cm^{-1} are the asymmetric stretching and symmetric stretching of –CH_2 respectively while the peaks at 1464 and 1462 cm^{-1} represents the bending vibration of –CH [12]. The band at 719 cm-1 can be assigned to the vibration of C-C group [7]. The above results corroborate other findings on commercial PE waxes used in various industrial applications [5, 7, 13]. The intense peaks at 2864 cm-1 for both waxes are a strong indication of a C-H stretch confirming saturated chains [9]. However, PE 2 had weak peaks at 1768 cm^{-1} carbonyl (C=O) stretching and 1594 cm^{-1}(carboxylate stretching).

3.2. Differential Scanning Calorimetry (DSC) measurements

It is known that, DSC measurements provide information on melting transitions, crystallization temperatures and enthalpies of materials transition. Most hydrocarbon waxes are hydrocarbons, such as paraffin waxes and can be analyzed by DSC analysis. DSC Thermograms of paraffin waxes reported in the literature clearly show that there are two distinct properties for paraffin waxes: a large peak conforming to crystal melt and a small peak comparable to solid-solid transition. The report also shows that hydrocarbons with chain lengths between 21 and 39 carbon atoms reveal the transition from ortho-rhombic to hexagonal crystalline structure upon heating, and that other hydrocarbons with chain lengths outside this range crystallize directly into ortho-rhombic structure and no transition is observed. [15]. On the other hand, PE waxes are hydrocarbon compounds obtained in a controlled thermal decomposition process of polyolefins, usually in the presence of neutral gas. These waxes are reported to be a mixture of higher paraffin hydrocarbons and input materials that may not have decomposed during thermal processing [16]. The DSC thermograms for the PE wax samples (PE 1 and PE 2) used in this study are shown in Figure 3.



(a) (b)

Fig. 3. DSC thermograms for PE wax samples a) PE 1 b) PE 2

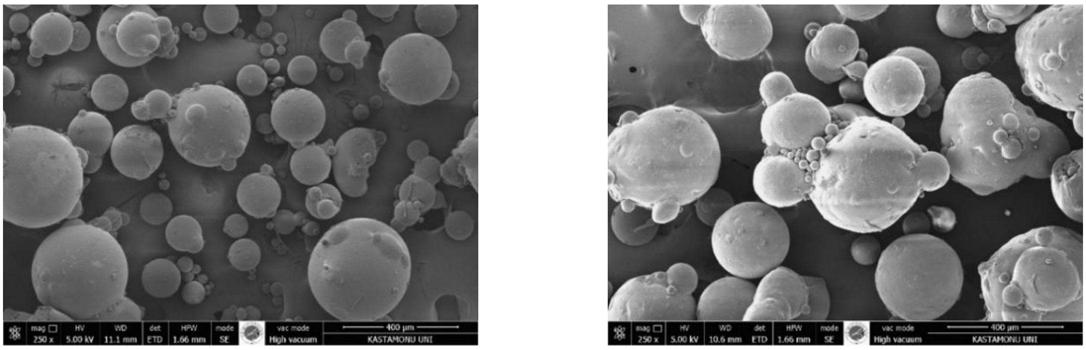
Both thermograms show a large peak occurring around 106 ºC. Another small transition was seen between 55 and 65 ºC for both PE wax samples. These values are somewhat at variance with a recent study on the thermal properties of some PE waxes used for various industrial applications [10]. On the other hand Ciesinska and coworkers reported that fractionated and oxidized PE waxes have the first melting transition temperatures to be between 340 – 350 ºC respect to very low amount heat flow. Lack of the initial temperature range data DSC results around low temperature range could not be compared with our study. Additionally, it is known that lower melting point of PE make it desirable candidate application of natural fiber composite [17, 18]. In another study [8], three defined endothermic peaks were identified for a commercial PE wax at significantly different temperatures indicating phase differentiation in crystalline texture.

As we clearly see at 50C there is a peak emerged by melting of the wax fraction that has specialty of lowest molecular weight; the peak at about 60 ºC aspect to the melting of the wax fraction with the lowest molecular weight and the last peak occurring between 90 – 100 ºC was attiributed to the melting of the low-density polyethylene in the sample. These values corroborate our earlier report on a commercial PE wax [11] whose melting transition temperature was about 50 ºC. Reports indicate that

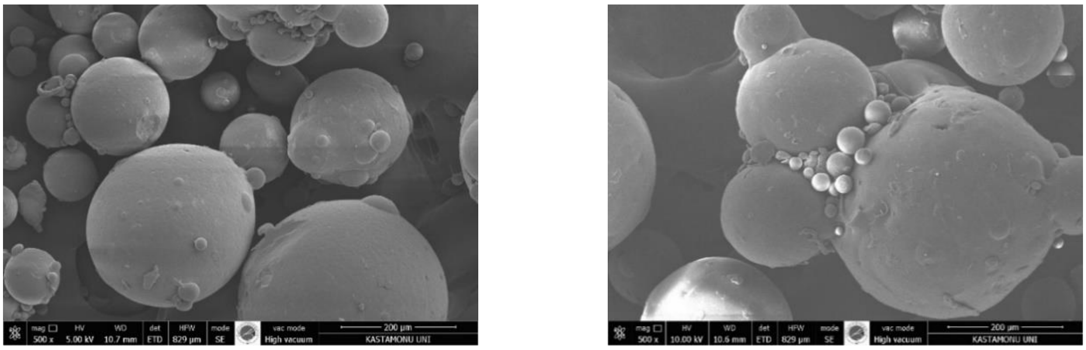
PE waxes that may have been obtained as a result of controlled polymerization of ethylene produce molecules with molecular weight ranging from 1700 to 2500. Such waxes are usually characterized by more homogeneous composition, and so melt in quite a limited temperature range [16].

3.3. Scanning Electron Microscope (SEM) Measurements

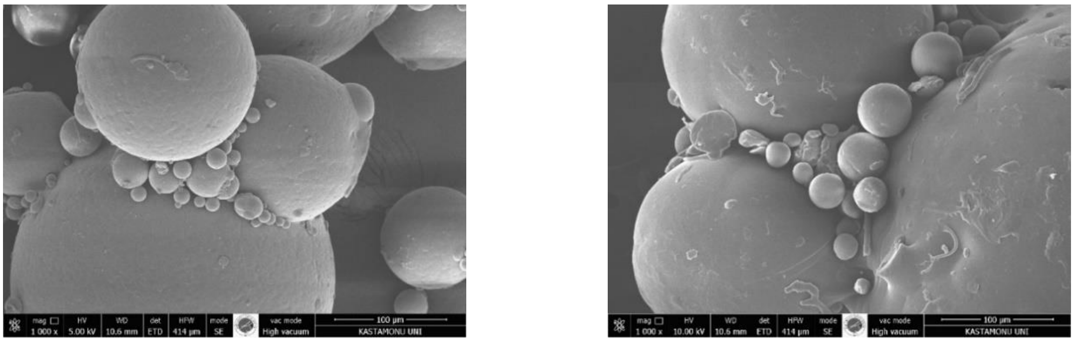
The morphology of the PE wax samples obtained from SEM measurements is shown in Figure 4. The polymer particles are fine and spherical with a clear core-shell structure having a uniform morphology as seen in the micrographs. by the nucleation mechanism during polymerization [12].



PE 1 (x 250) **PE 2 (x 250)**



PE 1 (x 500) **PE 2 (x 500)**



PE 1 (x 1000) **PE 2 (x 1000)**

Figure 4. Micrographs of PE wax samples (PE 1 and PE 2) at different magnifications

It is reported that spherical wax particles could be obtained by spray freezing, dripping molten wax to cold ultrasonic bath, melt emulsification and granulating in a high speed granulator. All them are effective process that have been using already. Among them melt emulsification is the well defined approach to produce paraffin, PE and PP waxes and well explain droplet division in dependency of dispersed phase viscosity as seen in Figure 5 [19]. Viscosity, time, temperature and rotor speed were listed as main parameters [20].

Under reduction of temperature it has been reported that increase of dispersion viscosity, increase the daughter droplets amount and the size of the formed droplets is reduced because the result of drop-size distribution rely on considerably one of the rheological behavior of viscosity of the dispersed phase. Therefore, it can be concluded that PE1 and PE2 have been produced within different viscosity range according to main idea in Figure 5 and results of particle size distribution as seen in Figure 6

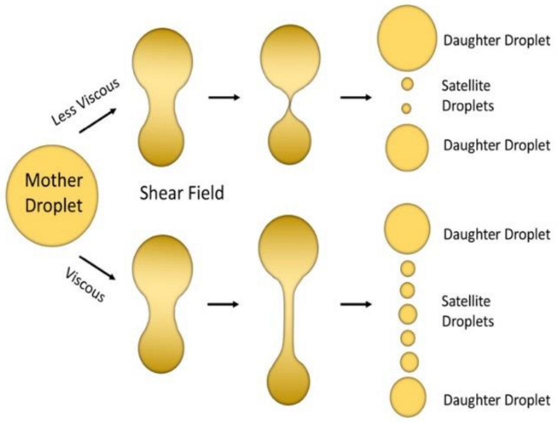
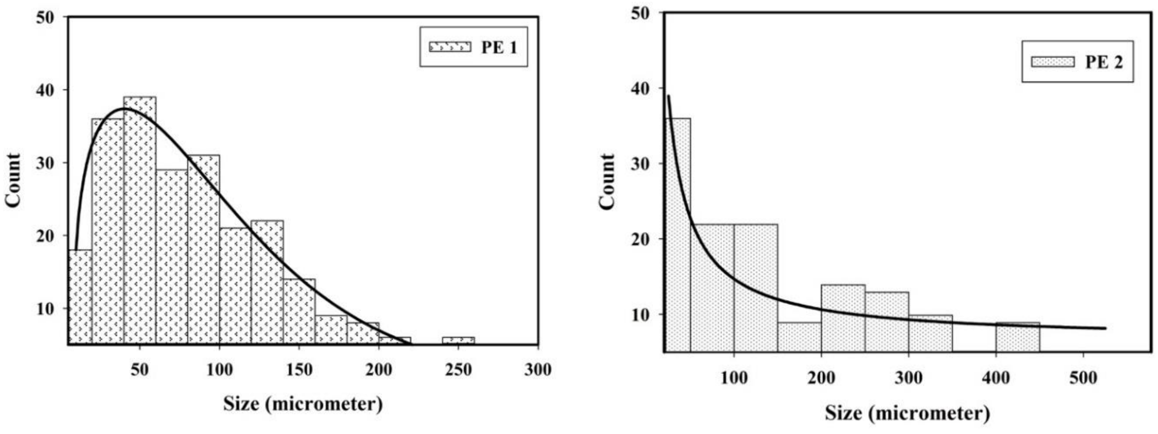


Fig. 5. Droplet breakup dependency of dispersed viscosity adapted by Tcholakova (2007) [19, 20]

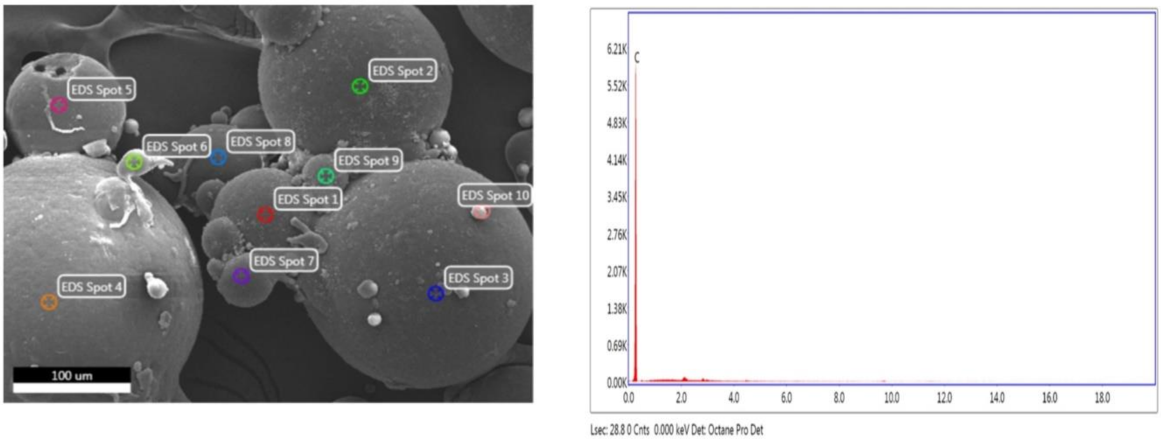


(a) (b)

Fig. 6. Particle size distribution of a. PE 1 and b. PE 2

3.3.1. EDX analysis

EDX analysis which could detect the amount of elements with atomic number higher than four give information about the surface composition of the samples. The surface compositions of the ten points shown in Figure 7 for PE1 are shown in Table 2. Nine out of 10 points were 100 % C since H elements is not seen by EDX analysis. However, there were only one points having oxygen element. EDX spectrum of point 2 in Figure 7 a is shown in Figure 7 b. On the other hand nine out of ten points seen in Figure 8a for PE2 were 100 % C as reported in Table 3. Only one point contained 3.49% O element. The EDX spectrum of point 1 for PE2 is shown in Figure 8b. While the FTIR analysis indicated the presence of carbonyl and carboxylate groups in PE 2. However, they were not detected at the surface of the particles indicating that they can be present in the bulk of the particles.

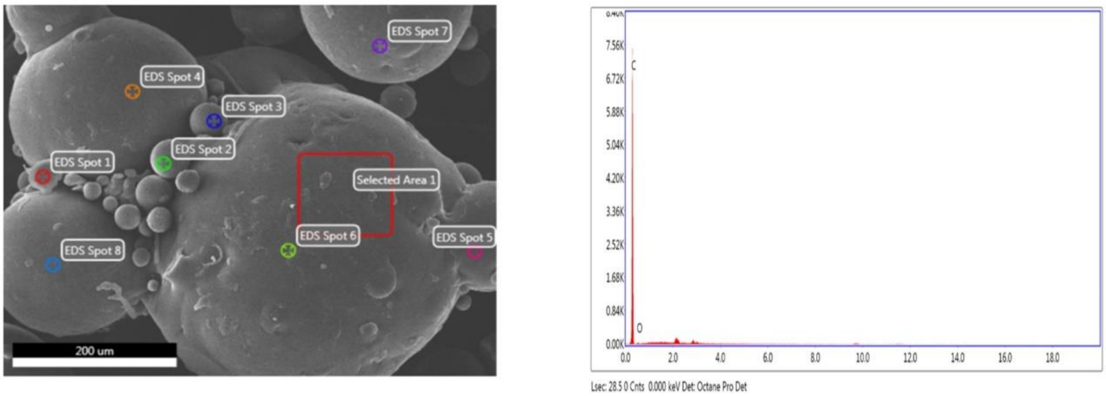


(a) (b)

Figure 7 a. EDX spots of PE 1 in 100 µm scale. EDX spectrum of point 2 in Figure 7

Table 2. Elemental composition of the spots in Figure 7

Element, %	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**	**Point 6**	**Point 7**	**Point 8**	**Point 9**	**Point 10**
C	100	91.35	100	100	100	100	100	100	100	100
O		8.65								



(a) (b)

Figure 8 a).. EDX spots of PE2 in 200 µm scale. b) EDX spectrum of point 1 in Figure 8

Table 3. Elemental composition of the spots in Figure 8

Element, %	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**	**Point 6**	**Point 7**	**Point 8**	**Selected area**
C	**96.51**	**100**	**100**	**100**	**100**	**100**	**100**	**100**	**100**
O	**3.49**								

3.4. Thermogravimetric Studies

Thermal techniques measure the change of mass of a material as a disturbance function of temperature. The degradation curves showing weight loss percent as a function of temperature were plotted for PE 1 and 2 and shown in Figure 9. As shown, the shape of the TG curves is similar. The thermal events occurring show that the two PE wax samples exhibited a two – stage decomposition process at different temperatures: one occurring around 400 °C and the other at about 490 °C for both samples. These transitions varied from those indicated by DSC analysis. These differences has been revealed to arise from the presence of minor amounts of polyethylene polymer existing in the samples which hinders the broad range melting of the crystalline phase [8]. The weight of the materials retained more than 97 % (less than 3% weight loss) before the onset of degradation around 400 °C. The thermal stability of the PE wax samples was characterized in terms of gravimetric analysis method with temperatures at 5%, 10% and remaining mass at 600 °C. The results are summarized in Table 4. PE 1 degraded up to 99% as it had less than 1% remaining mass at this temperature while PE 2 had approximately 16% remaining mass indicating the formation of less volatile substances and carbonization to non-volatile substances [11]. Since PE 2 contains small amount of carbonyl and carboxylate groups that will lead formation of nonvolatile cross linked carbonized materials that will remain at 600°C.

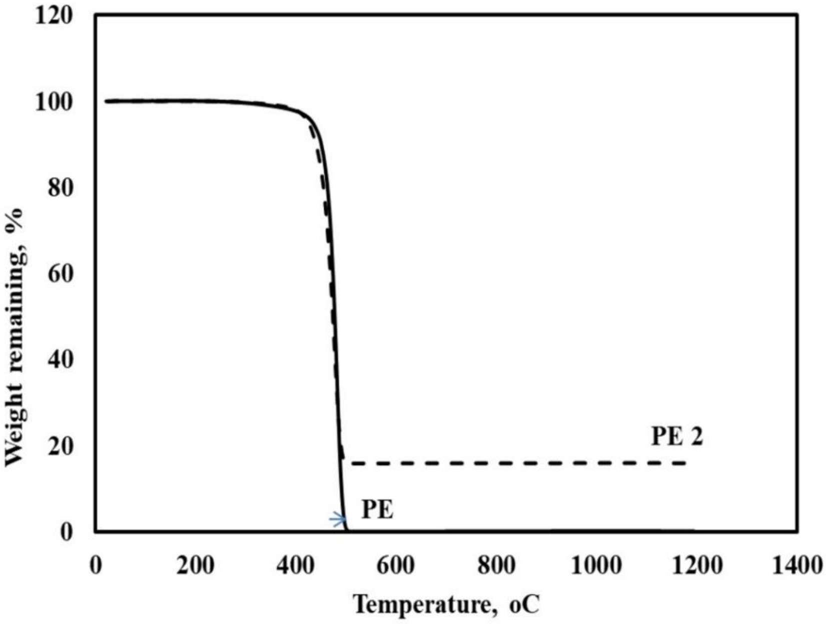


Figure 9. TG curves for PE wax samples (PE 1 and PE 2)

Table 4 Thermal characteristics of PE wax samples

Sample	T5%, (oC)	T10%, (oC)	Remaining mass at 600 oC
PE 1	433.7	450.9	0.07
PE 2	425.0	440.3	15.89

3.5. X-ray Diffraction (XRD) studies

The diffractograms obtained by X-ray diffraction analysis for the PE wax samples are shown in Figure 10. The two PE wax samples exhibited a single well – defined broad peak for the 110 (2θ =

21.3o for PE 1 and 21.25o for PE 2) and 200 (2θ = 23.45o for PE 1 and 23.85o for PE 2) reflection planes. These sharp and intense peaks are indicative of orthorhombic crystallinity and values match the intensity of a commercial PE wax sample in a previous report [5]. The average crystallite size (L) of the PE wax samples was calculated for one prominent peak using the Scherrer equation:

$$L = \frac{K\lambda}{\beta\ Cos\theta} \qquad (1)$$

where β is the observed full-width at half maximum (radians), θ is the Bragg peak angle of the peak, λ is the X-ray diffraction wavelength, L is the effective crystallite size, and K is a constant = 0.9. The values obtained were 21.2 and 32.9 nm for PE 1 and PE 2 wax samples respectively.

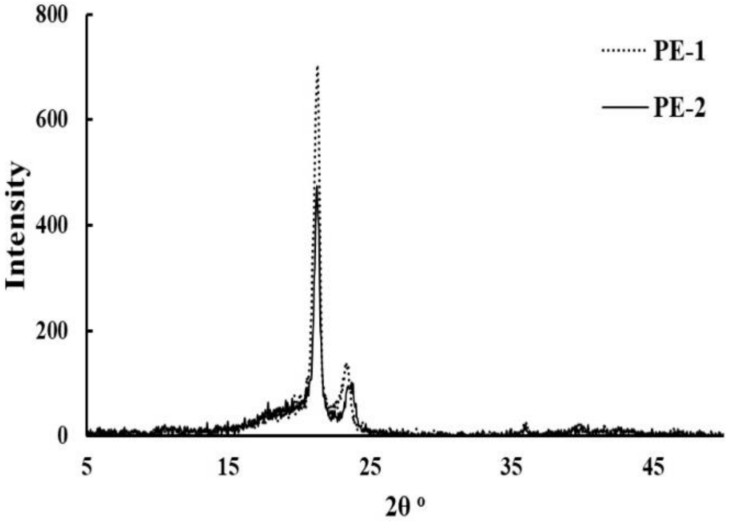


Figure 10. Diffractograms for PE wax samples (PE 1 and PE 2)

The crystallinity (X_c) of the samples can be evaluated by using the intensities of crystalline and amorphous diffraction peaks.

$$X_c = \frac{\text{I crystalline}}{(\text{I crystalline} + \text{I amorphous})} \qquad (2)$$

Considering the area of the crystalline 110 and 200 peaks and the area of the amorphous peak the crystallinities of PE1 and PE2are found as 0.75 and 0.65 respectively. Additionally, crystallinity Xc can be can be calculated below equation [21]

$$X_c = \frac{\Delta H_m}{\Delta H_{100}} \text{x}100\% \qquad (3)$$

where, ΔH_m is the enthalpy value absorbed by the test sample during the heating process and ΔH_{100} is the enthalpy absorbed by the sample during the crystallization-melting process. The ΔH_{100} of polyethylene has been reported as 293 J / g in different studies [22, 23]. According to this formulation, the crystallinity of PE1 and PE2 was found to be 0.54 and 0.43, respectively, with a similar attitude.

4. Conclusion

The focus of this study was to investigate the structural, molecular and thermal characteristics of two commercial PE wax samples used as lubricants in carpet manufacturing. The analytical tools FTIR, SEM/EDX, XRD, DSC and TGA have demonstrated that the commercial PE wax samples had similar properties with characteristic commercial PE wax samples used for various industrial applications. Such as making, water repellent hydrophobic surfaces which is indispensable to avoid moisture absorption to be able to enhanced degradation process especially like in carpet industry, or candles, external lubricant in thermoset and thermoplastic extrusions and other polymers, preparation of pigment masterbatches, as well as phase change materials (PCM) in building industry.

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