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Effect of Pyrolysis Temperature and Time on Wax Production from Waste Polyethene

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ABSTRACT---- ***Waste polyethene was pyrolysed at two different temperatures. The waste polyethene were pyrolysed at 200°C and 250°C for 1hour, 2hours and 3hours respectively. The melting points of the pyrolysed waxes were obtained within the range of 84-114°C, and the waxes showed a decrease in molecular weight of the waxes as the temperature and time of pyrolysis increased***.

Keywords – molecular weight, polyethene, pyrolysis, temperature.

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1. INTRODUCTION

The wide use of polyethene (PE) makes it an important environmental issue. Though, it can be recycled, most of these wastes end up in landfills (11) and in the streams or rivers. Polyethene is the most commonly used commodity in the environment, such as bread wraps, frozen food bags, dry cleaning bags, shopping bags, detergent bottles, tubs, etc. A resource person at the Global Networks on Environmental Awareness and Protection Initiative stated that polyethene bags are the most outstanding waste product in our homes and environment now and their use is driven by ignorance of the health and environmental dangers they pose (5).

Direct disposal (littering or dumping) and incineration (burning) of these wastes are common practice in our environment. Each of these is harmful to the health of people and the environment. For instance, dumping in rivers, streams and even urban drainage system pollute the water and causes flooding.

Ayansina reported that the Director-General of the National Orientation Agency addressing newsmen on the campaign “Operation rid Nigerian streets of menace of polythene” in Abuja, said that; a lot of hazard is associated with improper disposal of polythene (1). Due to its non-biodegradable nature, it is hard to decompose and as a result it can act as breeding place for many of the diseases which sooner or later cause an epidemic in surrounding environment.

The increasing menace of waste PE littering the environment causes environmental pollution. Based on the report from the Federal Environmental Protection Agency (FEPA); a bulk of the refuse dumps in Nigerian environment are PE bags and other plastics (7). Polyethene products are non-biodegradable and they constitute health and environmental hazards because they encourage the spread of water born diseases, constitutes dirty environment and can cause suffocation to small children and animals (5). Waste polymer recycling has received a great attention due to increasing amounts of waste polymers (6). Control of environmental pollution by waste recycling is the best method of reducing bulk of the residue requiring disposal.

Polyethene takes up a reasonable percentage of the total waste stream, and it is mainly from the non-renewable resource petroleum. This makes it very important to device a means of recycling the waste PE (11). This research work is justified in that it aims at minimizing the amount of waste PE in the environment by adding value to the waste for useful domestic purposes. Pyrolysis process is recognized as a promising route for the converting of PE wastes to usable and energy-dense materials; such as high-valued feedstocks for the chemical industry (10). Hence, waste PE can be recycled to reduce environmental pollution and also produce valuable by-products.

Pyrolysis is a form of thermal treatment where waste materials are heated at high temperatures with limited oxygen under high pressure to convert it to solid, liquid and gas products (10). The solid by-product of PE can be converted into useful domestic products such as wax.

Polyethene variants do not have specific melting point, but gradually soften as the temperature is increased. LDPE may melt at approximately 110^{o}C, while HDPE melts at approximately 130^{o}C. For common commercial grades of medium-and-high-density PE the melting point is typically in the range of 120^{o}C to 130^{o}C (2).

Degradation arises when a polymer is subjected to degradative agencies such as heat, light, ionizing radiation, mechanical agitation and the action of compounds such as oxygen or water. Degradation of a polymer can be defined as the undesirable change that occurs in a polymer affecting its physical and chemical properties (4).

For many polymers, degradation is usually associated with chain cleavage and a drop in molecular mass. However, in some cases, cross-linking reactions do occur which can render a polymer brittle. Colour generation is another phenomenon typical of degradation process (9).

Thermal degradation of polymers is a molecular deterioration as a result of heating. At high temperatures, the components of the long chain backbone of the polymer can begin to separate (molecular scission) and change the properties of the polymer. Thermal degradation generally involves changes in the molecular weight (and molecular weight distribution) of the polymer. Significant thermal degradation can occur at temperatures much lower than those at which mechanical failure occurs. When heat is applied to polymers, they undergo various chemical and physical transformations accompanied by the formation of gases and liquid products, changes in colour, mechanical strength, tensile strength, etc (3, 12, 13).

Polymers thermally degrade under pyrolysis condition (inert atmosphere, high temperature) by a mechanism depending on the type of the polymer. Thermal degradation of organic polymers typically begins around 150-200^{o}C and the rate of degradation increases as the temperature increases (13). PE usually degrades by random scission- that is by random breakage of the linkages (bonds) that hold the atoms of the polymer together.

PE degrades by intra-molecular migration of hydrogen atoms, resulting in two fragments. One with saturated end chain units, and the other with the unsaturated one. This process is referred to as random scission of the main chain (7).

The molecular backbone will break down randomly, which could occur at any position of the backbone. The molecular weight decreases rapidly, this is because new free radicals with high activity are formed. The free radical thus formed may react and results in chain scission and molecular – weight reductions (12).

$$\sim CH_2CH_2CH_2CH_2CH_2CH_2CH_2^{\cdot} \longrightarrow \sim CH_2CH_2CH{=}CH_2 \quad + \quad CH_3CH_2CH_3$$

Scheme 1

The initiation step is followed by the depropagation step with monomer fragment splitting-off stepwise along the chain.

$$\sim CH_2CH_2CH_2CH_3 \longrightarrow \sim CH_2CH_3 \quad + \quad CH_2{=}CH_2$$

Scheme 2

The next stage is the termination of the chain reaction which may occur by various mechanisms such as unimolecular or bimolecular.

2. MATERIALS AND METHODS

The equipments used in the study include of a NDJ-8S digital rotary viscometer, Nicolet-IR100 FT-IR spectrophotometer, 5-litre four-necked reactor, magnetic stirrer and a reflux condenser.

Unpigmented low density waste polyethene; shopping bags, dry cleaning packaging bags, and pure water bags found littering around Zaria and Kaduna metropolis were collected.

Waste PE was gathered, washed, dried and chopped into small pieces for pyrolysis. Tap water was used in washing the waste PE. For oily samples, caustic soda was used, followed by rinsing with tap water, dried and then further chopped into smaller pieces.

The chopped waste PE; 300g, was placed in a 5-litre, five-necked flask. The flask was then placed onto the heating mantle, and heated in nitrogen atmosphere at temperatures that ranged from 200 ^{o}C to 250 ^{o}C under reflux. The times of the pyrolyses also varied from 1 to 3 hours. The pyrolysis conditions are shown in Table 1. The pyrolysed waxes were purged with nitrogen gas while cooling, then removed and weighed.

Plate 1: Unwashed and washed-chopped PE respectively

3. RESULTS

Generally, the pyrolysed waste polyethene waxes gave light brown coloured solid (Plate2). The samples pyrolyesd at 250^{o}C are softer compared to those pyrolysed at 200^{o}C.

The pyrolysed waxes produced are shown below (Plate 1)

 Unpyrolysed wax	 P250S1N wax	 P250S3N wax
 P200S1N wax	 P200S2N wax	 P200S3N
 P200S1 wax	 P200S2 wax	 P200S3 wax

Plate 1: Unpyrolysed and Pyrolysed Waxes

Table 1: Defination of Codes

Sample	Pyrolysing Temperature (^{o}C)	Pyrolysing Time (Hours)	Condition while cooling
P200S1	200	1	No nitrogen
P200S2	200	2	No nitrogen
P200S3	200	3	No nitrogen
P200S1N	200	1	Nitrogen
P200S2N	200	2	Nitrogen
P200S3N	200	3	Nitrogen
P250S1N	250	1	Nitrogen
P250S3N	250	3	Nitrogen

3.1 Percentage Yields and Melt Viscosities of the Waxes

The percentage yields and melt viscosities of the pyrolysed waxes were presented in Figure1.

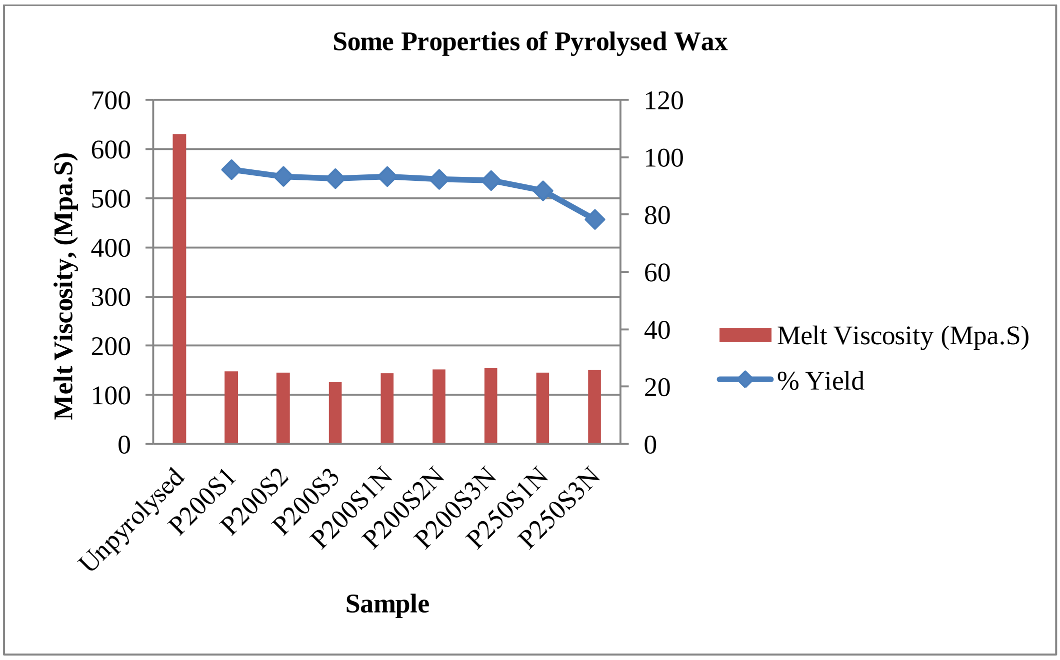

Figure1: Yield and Melt Viscosity of the Pyrolysed Waxes

3.2 Melting Temperatures of Waxes

The results of the melting temperatures of the pyrolysed waxes are shown in Table 2.

Table 2: Melting Temperatures of the Waxes

Sample	Pyrolysed waxes (^{o}C
P200S1	110-114
P200S2	106-112
P200S3	105-110
P200S1N	108-114
P200S2N	106-114
P200S3N	108-114
P250S1N	95-100
P250S3N	84-88

3.3 Infrared Spectra

The functional groups of the waxes were identified from their infrared spectra. The summary of the functional groups of the waxes are presented on Table 3.

Table 3: Infrared Spectra analysis of the Waxes

Sample	IR Bands (cm^{-1})	Functional groups
Unpyrolysed	2918	C-H aliphatic stretch
	1459	C-H aliphatic stretch
	723	C-H out-of-plane bending
Pyrolysed waxes	Above 3000	C=C stretch
	2853-2924	C-H aliphatic stretch
	1518-2357	C=C stretch (confirmed alkenes)
	1438-1459	C-H aliphatic stretch
	Around 1040	C-C stretch
	Around 671	C-H bend (alkene)

4. DISCUSSION OF RESULTS

The yields of the pyrolysed polyethene at 200°C are higher than those pyrolysed at 250°C. Also, Figure 1 shows decrease in yields of the pyrolysed polyethene as the time of pyrolysis increased. The higher the pyrolysing temperature and time respectively, the less the yields of the pyrolysed products or the more the waste polyethene substances vaporized during pyrolysis. This agrees with Lichtenberg et al that the distribution of pyrolysis products obtained from a polymer varies predictably as a function of temperature (8). The pyrolysed products agreed with the basis of thermal degradation of polymers that when heat is applied to them, they undergo various chemical and physical transformations accompanied by the formation of gases and liquid products, change in colour, etc. (3, 12, 13).

The results given in Figure 1 for the melt viscosity of the pyrolysed waxes also showed decrease in viscosity as the temperature and time of pyrolysis increased. The decrease in viscosity of the pyrolysed waxes with increase in temperature and time of pyrolysis indicated degradation had taken place, which consequently, lead to the decrease in molecular weight of the polymer (12).

The polyethene structure is a long chain polymer which when pyrolysed, breaks down randomly at any position, and formed fragments of the polymer chain i.e,

$$(\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\sim) \xrightarrow[\triangle]{}$$

$$\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2 \quad + \quad \sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

Scheme 3

When the temperature and/or time of pyrolysis increased, the fragments further break and form lower molecular weights polymers as follows:

$$\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow \sim CH_2\text{-}CH_2\text{-}CH{=}CH_2 \; + \; \sim CH_2\text{-}CH_2\text{-}CH_3$$

Scheme 4

This molecular breakdown continues with increase in temperature and/or time of pyrolysis until a fragment is formed which has a boiling temperature of equal to or less than the pyrolysing temperature. At that instance, the product will volatilise gradually.

This is the reason for the decrease in yields of the pyrolysed waxes and it indicated loss of substances during the reaction, with the increase in temperature and/or time of pyrolysis.

The melting temperature range for the unpyrolysed waxes is 105-115 °C. The pyrolysed products pyrolysed at 200 °C for all the timings had their melting temperatures also within 105-115 °C. The products pyrolysed at 250 °C, however, indicated melting temperatures in the range of 84-100 °C. This shows that the polymer chains had broken down into smaller fragments in agreement with Scheme 2.

The infrared spectra are used to identify the functional groups in a compound. The technique is capable of detecting specific functional groups in polymers thereby helping in their identification and characterization (6). Table 3 presented the functional groups of the waxes. Unpyrolysed wax presents C-H aliphatic stretch and bends only. The pyrolysed waxes showed C-H aliphatic stretch, C-H aliphatic bend, C-C stretch and C-H bend (alkene) and bands for C=C stretch. Bands above 1518 cm^{-1} were also observed which confirmed the presence of C=C stretch (alkene). The presence of double bonds indicated that degradation had taken place in the pyrolysed waxes.

5. CONCLUSION

Waste polyethene was pyrolysed at two different temperatures, It was observed that waste polyethene pyrolysed at 200°C and 250°C produced waxes for domestic purposes with a melting points range of 84 to 114 °C. Thus, the pyrolysed waste PE can be useful for the production of domestic products which will reduces environmental pollution and recovers valuable by-products. It also serves as a means of creating job opportunities for the people.

6. ACKNOWLEDGEMENT

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