



## Chemical Recycling of Some Plastic Polymers Wastes to New Oxidize Materials Using Chemical Oxidizing Process

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### Abstract

Chemical oxidization of polymers wastes that manufactured mainly from commodity plastics LDPE, HDPE, PP and PS were applied using different inorganic oxidize agents ( $KMnO_4$ ), ( $K_2Cr_2O_7$ ), ( $H_5IO_6$ ), ( $KIO_3$ ) and  $(NH_4)_2Ce(SO_4)$  in presence of oxalic acid, sulphuric acid, potassium hydroxide and water. The investigated polymers wastes were chemically oxidized either directly from solid or after thermal cracking from oil. Spectrophotometric studies of the polymers wastes and their oxidize materials were investigated. Chemical identification analyses of the produced materials after oxidation have shown appearance of a new functional groups distribute between carbonyl groups and carboxyl or hydroxyl groups. Obvious diminution in the average molecular weights of the polymers wastes and their softening points were recorded for their oxidize materials after oxidation. A comparison study in thermal behaviors of the polymers wastes and their oxidize materials were added another confirmations that the new oxidize materials formed have lowering their thermal stability after oxidation as it was shown along the thermogram scale. The oxidize waste materials were changed completely from elastic compositions to either solid has powder form or liquid with brown oily appearance.

**Keywords:** Recycling of Polymers Wastes, Chemical Oxidizing Process, Oxidizing agents, LDPE, HDPE, PP, PS.

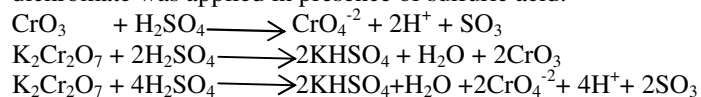
### Introduction

Recycling of consumed and landfill waste polymers is an important economical and environmental issue among different insist matters. Reduction of huge volume of polymer wastes and keeps the polymer raw materials for a long time was the goal<sup>1</sup>. Thermal cracking and thermal degradation are the most known and used processes in which polymer materials are recycle. Commercial Polymers were developed in order to produce original goods have long use life under thermal degradation influence<sup>2</sup>.

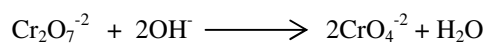
Oxidation of polymers under thermal influence will create new functional groups along the polymer chains<sup>3</sup>. Thermal oxidation of polymers will degraded their chains into short segments beside the functional groups occurrence. Polymer structure has significant influences on chain oxidation and fragmentation processes. No sufficient regions presence for molecular motion of polymer segments, heterogeneity of polymers structures and diminution of oxygen diffusion coefficient will reduce polymer chain oxidation and destructive processes<sup>4</sup>.

Polypropylene PP as a matrix material was treated with oxidizing agent, and its thermal stability and mechanical behavior were increased<sup>5</sup>. The study of oxidation of low-density polyethylene LDPE as commercial polymer using some oxidizing agent solutions have shown some surface changes such as new functional group were added, give good water wettability and adhesion properties<sup>6-10</sup>. The branched structure

of LDPE will allow for the formed functional groups along the polymer chains to appear at different sites like their tertiary carbons also at their backbone methylene groups in addition to their double bonds. While the linear structure of a high-density polyethylene HDPE will not allow after oxidative attacks for the forming of functional groups and are limited only to the methylene groups<sup>11</sup>. Colour removal as well as rigidity and change in polymer surface are yields by oxidative degradation of the polymer according to its structure. The presence of the double bonds in the polymer such as some rubbers will help easily for oxygen attack<sup>12</sup>. Rubber, on oxidation may yields aldehyde and other products such as formic acid, acetic acid and carbon dioxide. In the some time when the double bonds of the rubber are attack by ozone to form an ozonide which hydrolyzed and its double bond will be cleaved to produce ketonic and aldehydic groups<sup>13</sup>. Polyethylene was studied through acid-base catalyzed reaction, where chromic acid and / or potassium dichromate for oxidation were studied. In the case of acid-catalyzed reaction the chromic acid and / or potassium dichromate was applied in presence of sulfuric acid.



while sodium hydroxide, beside potassium dichromate has been used in base-catalyzed reaction.



The functional groups of hydroxyl as polymer side groups were found along the linear chains of polyethylene on initial thermal oxidation of the polymer which leads to ketone- carbonyl groups on further oxidation of the hydroxyl groups followed by chain cleavage with the formation of carboxyl groups (acid and ester)<sup>14</sup>.

Recycling techniques of polymer wastes could be classified according to the type of energy applied to mechanical recycling, chemical recycling, energy recovery and primary recycling. Chemical recycling is considering one of the most popular techniques which are also called feedstock or tertiary recycling<sup>15</sup>.

In the present work, chemical oxidation was carried out on the following polymers LDPE, HDPE, PP and PS. The chemical oxidize process was applied either directly on polymers wastes or it was carried out after thermal crack process of the polymers. For comparison, many oxidize agents have been used such as  $\text{KMnO}_4$ ;  $\text{K}_2\text{Cr}_2\text{O}_7$ ;  $\text{H}_5\text{IO}_6$ ;  $\text{KIO}_3$ ; and  $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_2$  beside oxalic acid, sulphuric acid potassium hydroxide and water. FT-IR spectra, average molecular weights and softening point temperatures of the tested polymers and their oxidized materials were investigated. In addition, chemical identification analyses of important functional groups belong to produced oxidize materials of the examined polymer were carried out for both cracked and un-cracked polymer samples.

## Methodology

**Raw materials:** Waste Samples of LDPE, HDPE, PP and PS polymers were collected from garbage that has been ready to throw out to landfills. Potassium permanganate ( $\text{KMnO}_4$ ), Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), Periodic acid ( $\text{H}_5\text{IO}_6$ ), Potassium iodate ( $\text{KIO}_3$ ), Cerium (IV) ammonium sulfate ( $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_2$ ), Potassium hydroxide ( $\text{NaOH}$ ), Oxalic acid ( $\text{C}_2\text{O}_4\text{H}_2$ ) and sulphuric acid (25-28%) ( $\text{H}_2\text{SO}_4$ ), and the solvents N, N-dimethyl aniline, acetone, benzene, toluene, decaline were supplied by Fluka, Switzerland. The used reagents were applied without further purification.

**Preparation of the polymer waste samples:** The collected waste samples of LDPE, HDPE, PP and PS polymers as empty containers and out of use were washed, shredded then grinded into small particles not more than 5mm size. The polymer waste particles were dried for water removal, and finally prepared for direct chemical oxidation or for thermal cracking and then to chemical oxidation.

**Thermal treatment of the polymer waste samples:** Polyolefin Waste samples were thermally treated alone with no catalyst. Where 5g polymer sample was putted into 100g round bottom flask supplied with a horizontal condenser and stirrer. The polymer samples were distilled at their boiling temperature and the distillate of each was collected into dry flask, closed and kept at  $-10^\circ\text{C}$ .

**Oxidation of the polymers:** Chemical oxidation of LDPE, HDPE, PP and PS waste samples was carried out and for both un-cracked solid and thermally cracked (distillate) samples<sup>16</sup>. Where 2g of each un-cracked teste polymers were dissolved in 5mL N,N-dimethyl aniline except PS sample where dissolved in 5mL acetone. Whereas 4mL of distillate samples after thermal cracking was used directly without solvents. 250mL round bottom flask contain long condenser and stirrer was used for boiling the 100mL solution which prepared from examined polymer and oxidizing agents as shown in Table-1. The flask's content was kept at its boiling temperature for 30 min. Then the flask was cooled.

The oxidizing products for un-cracked samples were consisting of solid and liquid materials. Whereas the cracked samples have shown their products after oxidation as oxidize liquid materials, which divided into two portions. The first product portion was extracted by suitable solvent, then the solvent was evaporated to get pure oxidize oily. And to the second portion a suitable precipitator was added and a pure oxidize white precipitate was produced. Which was washed, filtered and finally dried under vacuum at  $50^\circ\text{C}$  for 8h.

**FT-IR characterization:** The chemical structure and the specific functional groups of the polymer waste samples, before and after oxidation were investigated by recording their characteristic functional groups from FTIR spectra. The applied instrument was an FT-IR spectrophotometer of Tensor Co.Brucker, 2003, Germany. Where the wave number rang was recorded at  $450$  to  $4000\text{cm}^{-1}$ .

**Polymer molecular weight and softening point determination:** The molecular weight of the polymers wastes was determined. The intrinsic viscosity  $[\eta]$  for LDPE, HDPE, PP and PS polymer and their oxidize materials were carried out using Ubblohde viscometer and in specific solvent and temperature as it is shown in Table-2. The intrinsic viscosity  $[\eta]$  of the polymers was drawn for calculation of their viscosity-average molecular weight ( $M_v$ ), depending on Mark-Houwink equation

$$[\eta]=K M_v^a \quad (1)$$

where, K and a are constant for a given polymer at the solvent and the temperature used.

Softening point of the polymer waste samples and their oxidizing materials were carried out using melter instrument type Electro thermal 9300 engineering LTD.

**Thermal analysis measurements:** Thermogravimetric analysis (TGA) of the polymer waste samples and their oxidize products beside their differential scanning calorimetry (DSC) were measured on a TG analyzer (TG / DTA-SDT Q600 V20.9 Build 20), the samples were subjected to heating at a rate of  $10^\circ\text{C}/\text{min}$  and under a nitrogen atmosphere in the temperature range of  $50$ - $600^\circ\text{C}$ .

**Table-1**  
**Oxidizing solution compositions used in chemical oxidation process of polymer samples**

Polymer Sample	Polymer concentration		Oxidizing solution composition				
	Un-crack. %v/v*	Crack. %v/v	KMnO <sub>4</sub> , K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , H <sub>5</sub> IO <sub>6</sub> (NH <sub>4</sub> ) <sub>2</sub> Ce(SO <sub>4</sub> ) or KIO <sub>3</sub> %w/v	Oxalic acid %w/v	Sulphuric acid %v/v	KOH % w/v	H <sub>2</sub> O
LDPE	5.0	4.0	1.8	18	1.4	1.5	Continued to 100mL
HDPE	5.0	4.0	2.5	22	2.3	1.8	
PP	5.0	4.0	2.3	22	2.1	2.0	
PS	5.0	4.0	2.0	20	1.9	1.7	

\*2g Un-crack polymer samples were dissolved in 5mL N,N-dimethyl aniline, except PS sample where dissolved in 5mL acetone.

**Table-2**  
**Mark-Houwink equation constants of the polymer samples at their specific solvent and temperature**

Polymer sample	Solvent	Temp(°c)	Kx10 <sup>3</sup> (ml.g <sup>-1</sup> )	a
LDPE	Decalin	135	67.7	0.67
HDPE	Decalin	135	67.7	0.67
PP	Benzene	78	27.0	0.71
PS	Toluene	25	38.0	0.63

## Results and Discussion

Chemical oxidation of the wastes of the most commercial known polymers LDPE, HDPE, PP and PS has been done using different oxidizing agents. The process leads to a modification and segmentation in polymer chains with addition of new functional groups. The Chemical oxidation process is considered as an acceptable technique in recycling project of polymers wastes. Where the steps of such recycling technique are easy, cheap and use moderate conditions.

**Chemical Oxidation of polymer waste samples:** The chemical oxidation process was mainly used for recycling of the polymers wastes of LDPE, HDPE, PP, and PS because they are aliphatic hydrocarbons have no active functional groups could be used for chemical reactions, means are chemically inactive, while their resulted oxidation products give a new materials have a new functional groups and the process could change the wastes into useful applicable materials. Chemical oxidation of the solid waste samples LDPE, HDPE, PP and PS (un-cracked) have been done directly in presence of different oxidizing solutions. The waste samples after oxidation have been changed completely into another new mixture contain a solid and liquid materials. The first look at oxidize solid product would shows materials completely different have new properties such as a new components and color with a sharp decrease in their elasticity. Functional groups characterizations were applied for

identification of solid and liquid unknown oxidizing produced materials. The identification applied tests, Table-3 and 4 are (2,4-dinitrophenyl hydrazone, Tollens, Iodoform, Lucas, xanthate and iodate-iodide) test, which are used for identification of carbonyl groups of aldehyde and ketone, aldehyde, β-ketone and alcohol, classification of alcohol, hydroxyl group of alcohol and carbonyl group of carboxylic acid, respectively. Those characterization tests have been shown in Table-3, with no doubt, the appearance of new functional groups along the examined polymers such as carbonyl groups and carboxyl or hydroxyl groups which were found clearly in both solid and liquid oxidize products, Table-3.

However, the oxidation of the thermally cracked polymers have been also examined, where the colorless distillate polymer solution became bright, shiny yellow solution immediately after the addition of orange colored oxidize agent solution, which finally changed to yellowish at the end of oxidation process. The yellowish oxidized liquid as mentioned before has been divided into two portions. One portion was extracted with suitable solvent, and separated as oily product, whereas the second portion was precipitated with suitable solvent and the white solid precipitate has been filtered.

Chemical oxidation of the thermally cracked samples have been shown more changes in their physical and chemical properties, especially in case of PP because of its good leaving methyl side

group. Significant changes in the color, form of the solid precipitate polymer, beside large changes in its elasticity were recorded. However, the positive identification tests were proved that changes in chemical compositions of the polymer after oxidation have been occurred through the formation of carbonyl groups along the polymer chains, as it is shown in Table-4. The collected solid precipitates after oxidation of the polymers, whether oxidize directly or after thermal cracking they would give after cooling white crystals with fine particles except HDPE polymer which gave ordinary white powder precipitate, whereas LDPE and PP polymers have shown very fine and strong needle crystals.

original polymer samples at specific bands along the spectra, Figures-1-4 and Table-5. The chemical oxidation of the polymers has shown new FT-IR characteristic peaks. Certainly, an actual changes in the FT-IR spectra after chemical oxidation of LDPE was studied and Figure-1(B) has shown specific bands at frequencies of  $1604\text{cm}^{-1}$  and  $1740\text{cm}^{-1}$  of  $(\nu(\text{C}=\text{O})_{\text{str}})$  are related to enolic  $\beta$ -diketone and  $\alpha$ - $\beta$ -unsaturated ketone respectively. The absorption bands at  $1584\text{cm}^{-1}$  and  $1313\text{cm}^{-1}$  of  $(\nu(\text{C}=\text{O})_{\text{str}})$ , Figure-1(B) are related to carboxylate anion  $(\nu(\text{C}=\text{O})_{\text{str}})$  of antisymmetric and symmetric groups, respectively. In addition, LDPE after oxidation its FT-IR spectra has shown an broad band at  $3245\text{cm}^{-1}$  of  $(\nu(\text{O}-\text{H})_{\text{str}})$  is related to hydroxyl group and two characteristic bands at  $1441\text{cm}^{-1}$  and  $1278\text{cm}^{-1}$  of  $(\nu(\text{C}-\text{OH})_{\text{def}})$  and  $(\nu(\text{C}-\text{O})_{\text{str}})$ .

**FT-IR characterization of chemically oxidize polymers:** The examined samples after chemical oxidation have shown different FT-IR characteristic frequencies in comparison with

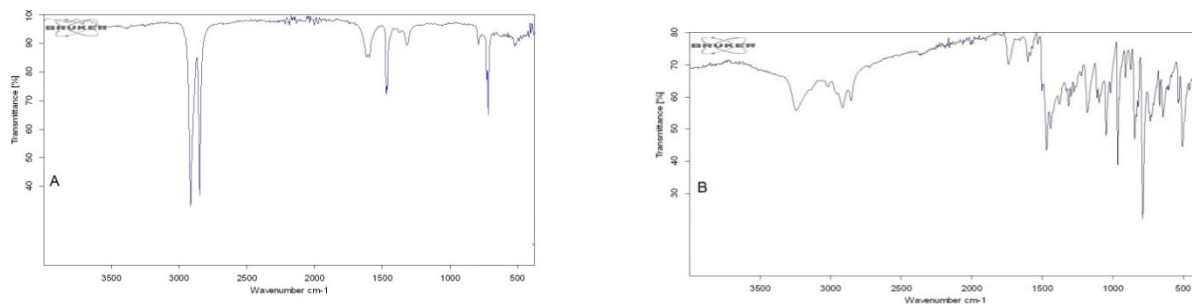
**Table-3**  
**Identification tests applied on un-crack oxidize polymer samples used for functional groups characterization**

Identification Test*	Un-crack oxidize polymer samples							
	LDPE		HDPE		PP		PS	
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
2,4-dinitro phenyl hydrazone	-ve	+ve	-ve	+ve	-ve	+ve	-ve	+ve
Tollens	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Iodoform	weak +ve	+ve	weak +ve	+ve	weak +ve	weak +ve	-ve	-ve
Lucas	-ve	-ve	-ve	-ve	-ve	-ve	-ve	primary +ve
xanthate	-ve	-ve	-ve	-ve	-ve	-ve	-ve	+ve
Iodate-iodide	strong +ve	+ve	strong +ve	+ve	+ve	+ve	-ve	-ve

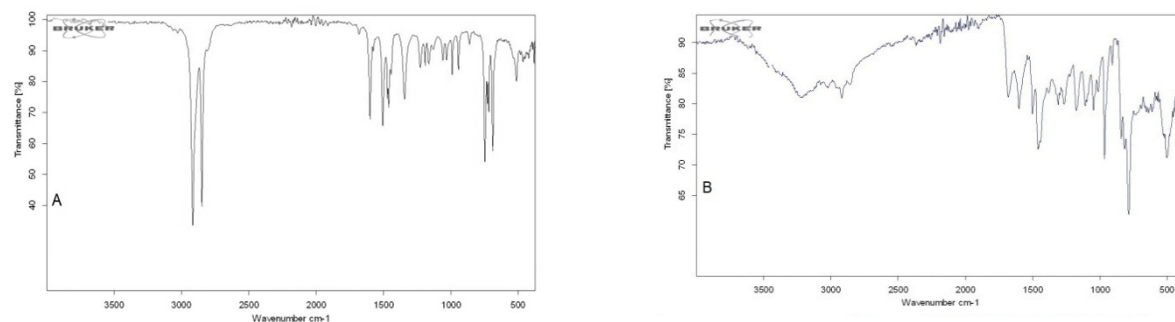
\*2,4-dinitrophenyl hydrazine, Tollens, Iodoform, Lucas, Xanthate and Iodate-iodide tests are used for identification of carbonyl groups of aldehyde and ketone, aldehyde,  $\beta$ -ketone and alcohol, classification of alcohol, hydroxyl group of alcohol and carbonyl group of carboxylic acid, respectively.

**Table-4**  
**Identification tests applied on thermally cracked and oxidizes polymer samples**

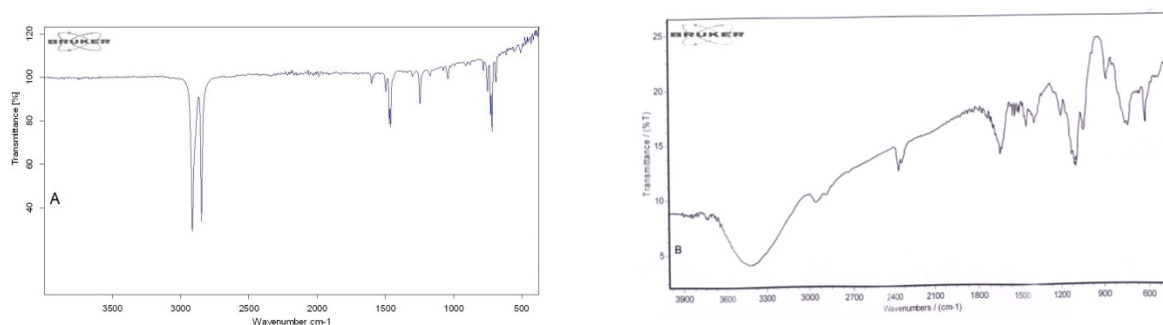
Identification Test	Thermal cracked and oxidize polymer samples							
	LDPE		HDPE		PP		PS	
	Solid	Oily	Solid	Oily	solid	Oily	Solid	Oily
2,4-dinitro phenyl hydrazone	-ve	+ve	-ve	+ve	-ve	+ve	-ve	+ve
Tollens	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Iodoform	-ve	+ve	-ve	+ve	weak +ve	Weak +ve	-ve	-ve
Lucas	-ve	-ve	-ve	-ve	-ve	-ve	-ve	+ve
xanthate	-ve	-ve	-ve	-ve	-ve	-ve	-ve	+ve
Iodate-iodide	-ve	+ve	-ve	+ve	+ve	+ve	-ve	-ve



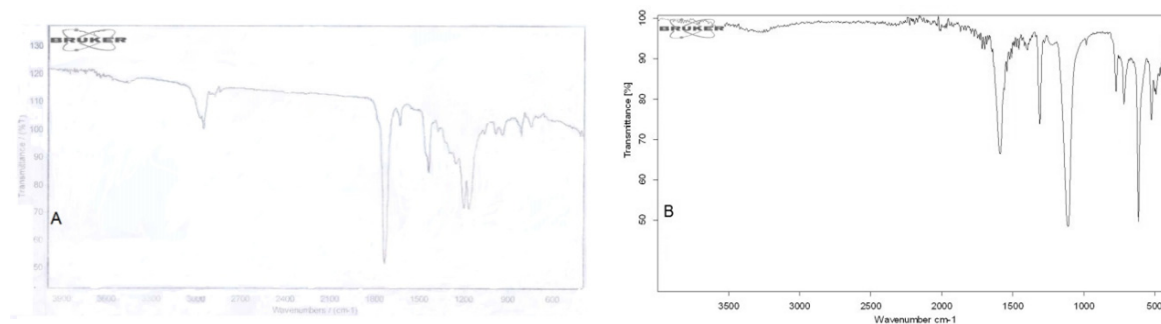
**Figure-1**  
FTIR spectra of LDPE original waste polymer (A), and LDPE oxidized materials after chemical oxidation (B)



**Figure-2**  
FTIR spectra of HDPE original waste polymer (A), and HDPE oxidized materials after chemical oxidation (B)



**Figure-3**  
FTIR spectra of PP original waste polymer (A), and PP oxidized materials after chemical oxidation (B)



**Figure-4**  
FTIR spectra of PS original waste polymer (A), and PS oxidized materials after chemical oxidation (B)

DPE after oxidation has been shown different absorption band at  $1682\text{ cm}^{-1}$  of  $(\nu(\text{C}=\text{O})_{\text{str}})$ , Figure-2(B) Table-5, is related to  $\alpha$ - $\beta$ -unsaturated ketone. The new absorption bands that appeared at  $1602\text{ cm}^{-1}$  and  $1384\text{ cm}^{-1}$  of  $(\nu(\text{C}=\text{O})_{\text{str}})$  are related to antisymmetric and symmetric groups of carboxylate anion, respectively, and  $3227\text{ cm}^{-1}$ ,  $1462\text{ cm}^{-1}$  and  $1267\text{ cm}^{-1}$  of  $(\nu(\text{O}-\text{H})_{\text{str}})$ ,  $(\nu(\text{C}-\text{OH})_{\text{def}})$  and  $(\nu(\text{C}-\text{O})_{\text{str}})$  respectively, are related to carboxylic group, Figure-2(B), Table-5.

The absorption bands appeared at  $1651\text{ cm}^{-1}$  of  $(\nu(\text{C}=\text{O})_{\text{str}})$  Figure-3(B), Table 5, is related to enolic  $\beta$ -diketone of PP polymer waste after chemical oxidation. In addition, the bands which are appeared at  $1598\text{ cm}^{-1}$  and  $1396\text{ cm}^{-1}$  of  $(\nu(\text{C}=\text{O})_{\text{str}})$  are related to the antisymmetric and symmetric groups of carboxylate anion, respectively. Moreover, the absorption bands that appeared at  $3421\text{ cm}^{-1}$ ,  $1458\text{ cm}^{-1}$  and  $1260\text{ cm}^{-1}$  of  $(\nu(\text{O}-\text{H})_{\text{str}})$ ,  $(\nu(\text{C}-\text{OH})_{\text{def}})$  and  $(\nu(\text{C}-\text{O})_{\text{str}})$  respectively, are related to carboxylic group, Figure-3(B), Table-5.

Finally, the FT-IR spectra of PS polymer after chemical oxidation has been shown Figure-4(B), Table-5, disappear of absorption bands at  $(2936\text{ and }2841)\text{ cm}^{-1}$  of  $(\nu(\text{C}-\text{H})_{\text{str}})$  which are related to the methyl groups in the vinyl polymer, and appear of new absorption band at  $3260\text{ cm}^{-1}$  of  $(\nu(\text{O}-\text{H})_{\text{str}})$  and at  $1113\text{ cm}^{-1}$  of  $(\nu(\text{C}-\text{O})_{\text{str}})$  which are related to hydroxyl group, and at  $1591\text{ cm}^{-1}$  and  $1310\text{ cm}^{-1}$  of  $(\nu(\text{C}=\text{O})_{\text{str}})$  which are related to antisymmetric and symmetric carbonyl group respectively,

Generally, the FT-IR absorption spectra of the polymers wastes after chemical oxidation have been shown with no doubt the appearance of carbonyl, hydroxyl and even carboxyl groups along the polymer chains and their fragments or as polymer chains end groups.

**Molecular weight and softening point determination:** The polymer waste samples were investigated for their viscosity-average molecular weight (Mv) and compared with their (Mv) after oxidation, Table-6. The intrinsic viscosity of their solution was determined according to Mark-Houwink equation, in a suitable solvent and at a fixed temperature, using the correct equation constants (K and a).

The final results have been shown obvious decline in Mv of all examined samples after oxidation, which give indication that the polymer chains were became short under the effect of chemical oxidation reaction, means a new backbone carbonyl functionality were established<sup>16</sup>, and some polymer chain segments were drop off as carboxylic segments from the polymer main chains as the FT-IR investigations were shown. For comparison, the decline in Mv of LDPE and PS samples after oxidation was higher than that of HDPE and PP samples, and that means LDPE and PS were oxidized chemically to the higher extent and their main chains diminish more carbon atoms.

The liquid or oily state of solid polymer samples after oxidation give another prove that the decline was occurred in their molecular weights. Similarly, the decline in the softening point temperature ( $T_s$  °C) of the waste polymers after oxidation would enhance the previous conclusions.

**Thermal studies of the polymers wastes:** Thermal cracking and/ or chemical oxidation applied on the polymers wastes samples would produce new materials having totally different thermal behaviors. However, glass transition temperature  $T_g$ , fusion enthalpy  $\Delta H_f$ , weight loss percentages and other thermal variables were calculated from TGA, DTG and DSC thermograms of the polymers wastes. The thermograms of some polymers wastes Figure-5 and 6, in addition to the thermal parameters shown in Table-7 and 8, where clear a great changes after chemical oxidation in their thermal properties from stable polymers at high temperatures to decomposed materials but furthermore unstable even at lower temperatures. Where the weight loss percentages (Wt%) of the waste polymers after oxidation have been shown increase starting from initial decompose temperature IDT to final decompose temperature FDT and even at  $T_{300}^{\circ}\text{C}$ ,  $T_{400}^{\circ}\text{C}$  and  $T_{500}^{\circ}\text{C}$  in comparison with the polymer sample before oxidation Figure-5 and 6, Table-7. The high architectural structure of the polymer with its compact chains would collapse after oxidation, and give thermally unstable short oxidized segments most probably was in liquid to oil form and rarely are solid with powder form.

The DTG-thermograms of the measured polymers Figure-5 and 6, Table-8, have shown one peak at certain high temperature along the thermogram before oxidation represent maximum rate of weight loss as a function of time which means the polymers have thermal stability to their certain high temperature and after that decomposed sharply and loss maximum of their weights per minute. Whereas their DTG-thermograms after oxidation Figure-5 and 6, Table-8, have been shown different shapes and numbers of peaks represent a mixture of different oxidized materials.

The DSC-thermograms studies of the examined polymers Figure-5 and 6, Table-8, have been shown change in their heat of fusion  $\Delta H_f$  from endothermic behavior before oxidation to exothermic materials after oxidation except PS which shift to a higher exothermic materials. Normally, the explanations of their behavior are the formations of oxidized materials after chemical oxidation have potential energy release to the calorimeter on heating.

**Effect of type of oxidize agent on oxidation process:** The chemical oxidation processes of the polymers wastes have been carried out by different types of oxidize agents for comparison to select the best agents. Practically, Cerium (IV) ammonium sulfate  $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_2$  has been shown chemically more oxidation effects among all used oxidize agents and potassium permanganate  $(\text{KMnO}_4)$  was considered the second in its sequence according to their oxidizing products. Where most of

the characterized or identifiably tested polymer samples and their oxidized products previously mentioned is oxidized by either Cerium (IV) ammonium sulfate or potassium permanganate. Where Cerium (IV) ammonium sulfate is a powerful oxidant even higher potential in HClO<sub>4</sub> than is K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or KMnO<sub>4</sub>.

**Table-5**  
**FT-IR characteristic frequencies of main functional groups of polymer samples and their oxidize materials**

Polymer Sample	FT-IR main functional groups									
	Before oxidation					After oxidation				
	Wave number (cm <sup>-1</sup> )									
	$\nu$ C-H <sub>str</sub> strong	$\nu$ C-H <sub>def</sub>	$\nu$ C-H <sub>def</sub> out of plane	$\nu$ C=O <sub>str</sub>	$\nu$ C-H <sub>str</sub> weak	$\nu$ C-O		$\nu$ C-O <sub>str</sub>	$\nu$ O-H <sub>str</sub>	$\nu$ C-OH <sub>def</sub>
Anti-symm.						Symm				
LDPE	2915 2848	1471	718	1740	2916 2858	1584	1313	1278	3245	1441
HDPE	2916 2849	1462	749	1682	2919 2856	1602	1384	1267	3227	1462
PP	2914 2847	1472	719	1651	2951 2885	1598	1396	1260	3421	1458
PS	2954 2879	1437	748	1684 1669	-----	1591	1310	1113	3260	-----

**Table-6**  
**Average molecular weight (M<sub>v</sub>) and softening point temperature of polymer samples**

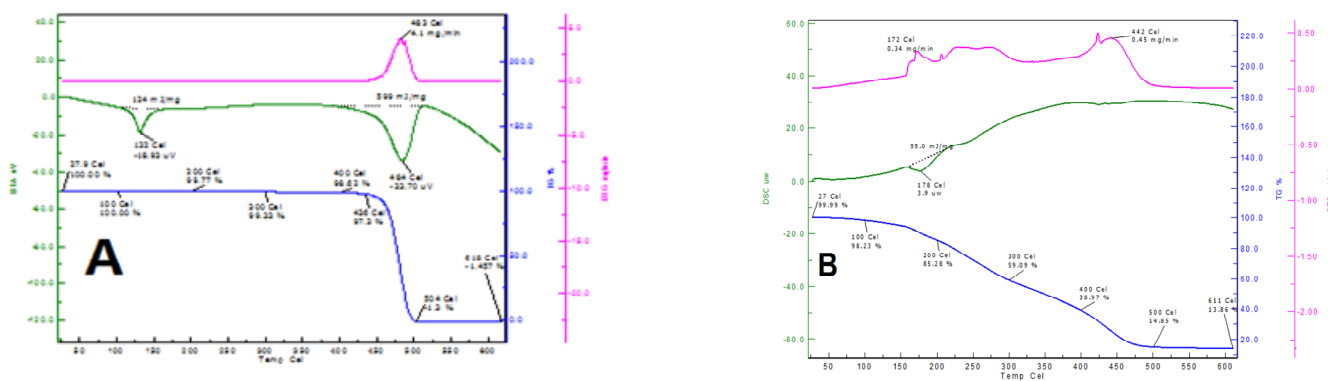
Polymer sample	Viscosity-average molecular weight(M <sub>v</sub> ) g.mol <sup>-1</sup>		Softening point temperature (T <sub>s</sub> ) °c	
	Before oxidation	After oxidation	Before oxidation	After oxidation
LDPE	22,026	8,913	119-121	80-82
HDPE	25,081	11,219	132-134	93-97
PP	27,407	18,743	155-165	110-120
PS	157,276	55,877	183-188	160-165

**Table-7**  
**Thermogravimetric analysis (TGA) of the of the polymer samples**

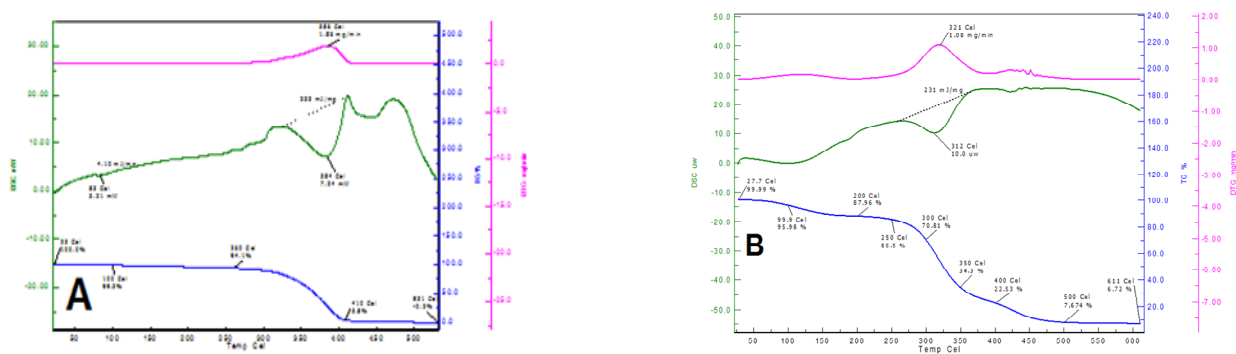
Polymer sample	TG-thermogram (weight loss %)									
	Before oxidation					After oxidation				
	IDT	FDT	T <sub>300</sub> °C	T <sub>400</sub> °C	T <sub>500</sub> °C	IDT	FDT	T <sub>300</sub> °C	T <sub>400</sub> °C	T <sub>500</sub> °C
LDPE	6.0	99.2	1.6	5.6	98.5	11.4	88.6	46.4	62.5	83.5
HDPE	5.7	100.0	0.7	1.4	100.0	10.5	86.1	41.0	61.0	85.2
PP	7.2	98.3	2.0	4.7	68.0	13.5	80.9	44.4	59.0	78.9
PS	4.8	100.0	28.5	94.7	100.0	8.8	93.3	29.2	77.5	92.3

**Table-8**  
**DTG and DSC data of the polymer samples**

Polymer sample	DTG-thermogram(mg min <sup>-1</sup> ) at decomposition temperatures (°C)		DSC-thermogram (mW)			
	Before oxidation	After oxidation	Before oxidation		After oxidation	
			Tg °C	ΔH <sub>f</sub> J mg <sup>-1</sup>	Tg °C	ΔH <sub>f</sub> J mg <sup>-1</sup>
LDPE	3.56(481°C)	0.41(155°C), 0.46(220°C) 0.67(450°C)	110	0.870	59	-1.10
HDPE	4.10(483°C)	0.34(172°C), 0.32(250°C) 0.45(442°C)	123	0.930	68	-1.23
PP	2.86(384°C)	0.11(166°C), 1.2(227°C) 0.87(325°C)	130	0.566	64	-0.84
PS	1.86(386°C)	0.14(128°C), 1.08(321°C) 0.29(430°C)	100	-0.853	33	-0.91



**Figure-5**  
**Thermal analysis of HDPE Original waste sample (A), and HDPE product materials after oxidation (B)**



**Figure-6**  
**Thermal analysis of PS original waste sample (A), and PS product materials after oxidation (B)**

## Conclusion

The wastes of LDPE, HDPE, PP, PS plastic, the most popular plastics that collected from household commodities were treated chemically for recycling. The polymer recycling technique by chemical oxidation was found to be completely changes in plastic wastes from polymers into new non-polymeric materials

having different chemical and physical properties. The technical characterizations occurred by chemical identification analysis of plastic waste materials after oxidation were shows appear of new functional groups in the non- polymeric products such as carbonyl group and carboxyl or hydroxyl groups. The decline in molecular weight of the polymers samples after oxidation and



softening point temperatures of their solid residual was another proves for cleavages in the polymer chains. The change in thermal characterizations of the polymers wastes after oxidation was indicated that these polymers were lost their compactness and chains entanglements. In addition, their oxidized products were behaved exothermally with more than one decomposition temperatures peaks which prove that each polymer sample after oxidation give different oxidized materials. Cerium (IV) ammonium sulfate in addition to the potassium permanganate were gave the best oxidizing actions for LDPE, HDPE, PP and PS polymer among all used oxidize agents.

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## References

1. Fried J.R. (2005). Polymer Science and Technology. Prentice – Hall of India Private limited, 2nd Ed., 274 – 277.
2. Chan J.H. and Balke S.T. (1997). The Thermal Degradation kinetic of Polypropylene: Part III. Thermogravimetric analyses. *Polym. Degrad. Stabile*, 57 (2), 135-149.
3. Dogan F. (2012). Polypropylene. *In Tec*, 63-86.
4. Nakatani H., Suzuki S. and Tanaka T. (2005). New kinetic Aspects on the Mechanism of Thermal Oxidative Degradation of Polypropylenes with Various Tacticities. *Polymer*, 46(11), 12366 – 12371.
5. Khan J.A., Khan M.A. and Islam R. (2012). Effect of Potassium Permanganate on Mechanical, Thermal and Degradation Characteristics of Jute Fabric- reinforced Polypropylene Composite. *J. Reinfor. Plast. Compost.*, 31(24), 1725-1736.
6. Gerenser L.J., Elman J.F., Mason M.G. and Pochan J.M. E.S.C.a. (1985). Studies of Corona –Discharge-Treated Polyethylene Surfaces by Use of Gas-Phase Derivatization. *Polymer*, 26, 1162.
7. Gerenser L.J.J. (1987). X-ray Photoemission Study of Plasma Modified Polyethylene Surfaces. *Adhes. Sci. Tech.*, 1(4), 303-318.
8. Briggs D., Zichy V.J.I., Brewis D.M., Comyn J., Dahm R.H., Gree M.A. and Konieczk M.B. (1980). X-ray Photoelectron Spectroscopy Studies of Polymer Surfaces, 4-Further Studies of the Chromic Acid Etching of Low Density Polyethylene. *Surf. Interface Anal.*, 2(3), 107.
9. Holmes Farley S.R., Reamey R.H., Mc carthy T.J., Deutch J. and Whitesides G.M. (1985). Acid-base Behavior of Carboxylic Acid Groups Covalently Attached at the Surface of Polyethylene: The Usefulness of Contact Angle in Following the Ionization of Surface Functionality. *Langmuir*, 1,725-740.
10. Briggs D., Brewis D.M. and Konieczko M.B. (1976). X-ray Photo Electron Spectroscopy Studies of Polymer Surfaces. *Mater. Sci.*, 1270.
11. Nardin M. and Ward I.M. (1987). Influence of Surface Treatment on Adhesion of Polyethylene Fibres. *Mater. Sci. Technol*, 3, 814.
12. Jellinek H.H.G. Ed. (1978). Aspect of Degradation and Stabilisation of Polymer. Elsevier, Amsterdam.
13. Gowarikar V.R., Viswanathan N.V. and Sreedhar J. (1986). Polymer Science. New Age International (p) Ltd., New Delhi, 264.
14. Hsieh Y.L., Barrall G. and Xu S. (1992). Effects of Oxidation on Mechanical and Physical Properties of Ultra-High-Modulus and Ultra-High-Molecular-Weight Polyethylene Fibers. *Polymer*, 33(3), 536-545.
15. Chalias D.S.A, Roupakias C., Megalokononimos P., Lappas A.A. and Antonoakou E.V. (2007). Chemical Recycling of Plastic Wastes, Made from Polyethylene (LDPE and HDPE) and Poly propylene (PP). *J.Hazarad.Mater.*, 149(3), 536-542.
16. Khan J.A., Khan M.A. and Islam R. (2013). Mechanical, Thermal and Degradation Properties of Jute Fabric-reinforced Polypropylene Composites: Effect of Potassium Permanganate as Oxidizing. *Agent, Polym. Compost.* 34(5), 671- 680.