Study on recycling and characterizationof some waste polymers

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الملخص

تعتبر اعادة تدوير البوليمرات المستهلكة من المواضع الراهنة والمهمة في الاونة الاخيرة وقد تم دراسة عملية اعادة تدوير البولي اثيلين والمتواجد بصيغتين (بولي اثليين واطئ الكثافة والبولي اثيلين عالي الكثافة) بالإضافة الى البولي بروبيلين, بولي ستايرين, والبولي كلوريد الفنيل وذلك بطريقة الاذابة والترسيب .تتضمن الدراسة عملية غسل البوليمرات التالفة ومن ثم طحنها بحجم مليمترات قليلة ثم اجراء الفحوصات الاولية لها من خلال قياس طيف الاشعة تحت الحمراء FT-IR وكذلك بواسطة قياس التحاليل الحرارية لها من خلال المسعر الحراري التفاضلي DSC والتحليل الحراريالوزنيDTG كما تم استخدام مذيبات مختلفة في اعادة تدوير البوليمرات المستهلكة ثم استخدام مرسبات للحصول على وحدات بناء البوليمرات المستهلك بشكل اجزاء بوليمرية وبأوزان جزيئية أوطئ من البوليمر الاصل.

كما تم تطبيق طريقة الاذابة والترسيب باستخدام مذيبات عضوية وفي درجات حرارية مختلفة من اجل الحصول على افضل اعادة تدوير للبوليمر المستهلك بأسهل الطرق وارخص المذيبات والمرسبات حيث اظهرت النتائج اعادة تدوير 90% من البوليمرات المستهلكة تحت ظروف تشغيلية معينة الى قطع بوليمرية وبأوزان جزيئية اوطئ وذلك من خلال تشخيص طيف الاشعة تحت الحمراء وأيضا" من خلال دراسة الثبات الحراري TG-DTA كما تم دراسة معدل الوزن الجزيئي للبوليمرات المستهلة قبل وبعد اعادة تدويرها وكذلك قياس درجات انصهارها.

ABSTRACT

Chemical recycling of waste polymers is one of the important recent objective.The wastepolyethelene that present in two structures (LDPE&HDPE),beside waste polypropylene ,polystyrene and poly(vinyl chloride) were recycled using the dissolution/reprecipitation method. The studied waste polymers were washed and grinded into few millimeter size and then examined by FT-IR spectroscopy and their thermal stability were examined by TG and DTA analysis. Different types of solvents and non-solvents(precipitators) were used for dissolving waste polymers and reprecipitate as polymer segments, respectively, with slight depression in their molecular weight and melting point.

The dissolving method was applied using different organic solvents and at suitable temperature in order to recycle the waste polymers with cheap solvent and non-solvent and using a simplest method.

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This technique provide polymer recovery more than 90%. FT-IR study for recovered polymers was shown no change in polymer structure.TG-DTA investigations were appeared weakness in thermal properties of recovered polymers. The average molecular weights of the studied waste polymers and their recycle precipitate were measured and their melting point also have been examined.

Keywords: Waste plastics,Polymerrecycling,Dissolution /reprecipitation method , Thermal analysis,Viscosity-average moleculer weigh.

Introduction

In the last few years,new disposal plastics waste of the non-biodegradable have been accumulated in the environment, which are very hazardous for the human lives and creating serious environmental problem and if this state is allowed to continued then either we have to stop the uses of polymers or the current non-degradable polymeric systems are either to modified to degradable one, or recycling their wastes as to save the environment from one side and to save the recovery plastics from other side[1,2].

The main important methods used for recycling of plastics waste are: mechanical recycling, burning to generate energy, and chemical recycling to convert them into intermediates,or by converting the plastics waste to their monomers[3], and the reuse of the recycled plastics waste is now adays the main objective[4].

However, the combustion of plastics in incineration process is generate high temperature but on other hand is harmful because of the production of some compounds like carbon dioxide, water and some timesdioxine the poisonous compound.Pyrolysis, which converts waste plastic into fuel or useful hydrocarbons is not favorable technique because of some technical problems[5]. Chemical(tertiary) recycling is an advanced technological processes which convert waste plastics into smaller molecules, usually liquidsor gases, which are suitable primary materials used for production of new plastics[6].

Thermoplastics are represent most of the recycling work,up to 80% of the plastics are concerned with the following polyolefins[7] high density polyethylene (HDPE) used in piping, automotive fuel tanks, bottles, toyes; low density polyethylene (LDPE) used in plastic bags, cling film, flexible containers; polypropylene (PP) used in food containers ,battery cases, bottle crates, automotive parts and fibers; polystyrene(PS) used in dairy product containers, tape cassettes, cups and plates; poly(vinyl chloride) (PVC) used in window frames, flooring, bottles, packaging film, cable insulation ,credit cards and medical products.

Experimental

2.1 Materials

Thepolymer samples(LDPE,HDPE and PP) were obtained in a granule bullet and PVC as ribbon from demostic workshop and polymer mold factories, whereas PS was obtained from BDH,UK(out of stock,25 years back). The solvent used(dimethyl sulfoxide DMSO, toluene, xylene, dioxane, benzene, dimethyl formamide DMF, chloroform, n-hexane, methanol, anisol, ethylbenzene, N,$\overline{\text{N}}$-dimethyl aniline, toluene, aceton, methyl propyl keton) were of reagent grade.

2.2.Waste plastic dissolution method

Cleaned and washed examined waste plastic was grinded, and (1g) of the powder with (20ml) of the selected solvent was added , heated for 30 min to the temperature below the boiling point of the selected solvent where magnetic mantel was used for heating .Then, the dissolution was stopped and the cooled solution was prepared properly in clean beaker for re-precipitation .

2.3.Reprecipitation of dissolved plastic method

The dissolved plastic was re-precipitated in (60ml) suitable solvent (n-hexane, methanol, water).The re-precipitated polymer was filterd, washed and dried in an oven at 80 °c for 24 h.The recycled polymer was obtained in the form of powder or grains.

2.4.Fourier-transforminfra-red(FT-IR) measurement

The specific functional groups of the model waste plastics, before and after the dissolution was investigated by recording their IR spectra. The FT-IR spectra were recordedusing the instrument, Tensor Co. Brucker, 2003, Germany, in the spectral region between 500-4000 cm^{-1}.

2.5.Thermal analysis study

Thermal analysis parameters,such as glass transition temperature Tg(°c) and heat of fusionΔHf (J.mg-1) of the waste plastic before and after the recycling method was studied using differential scanning calorimetry (DSC).

The temperature at maximum decomposition Tm(°c) where 50% of polymer weight is loss, and maximum polymer weight decomposition per minute mg.min-1 were studied using thermogravimetric analysis(TG) and differential thermogravimetric analysis(DTG), respectively.

The measurement analysis was carried at a heating rate of 10°c/ min,under nitrogen atmospheres, using Perken-Elmer Pyris Diamond(USA), model Extra [TG / DTA 6300].

2.6.Moleculer weight and milting point determination

Intrinsic viscosity [ɳ] measurements of HDPE, LDPE,PP PS & PVC waste samples were carried out using Ubbelohde viscometer and at their suitable temperature and in specific solvent as it is illustrate in Table1. The viscosity-average molecular weight($\overline{M}v$) of the samples was carried out from the [ɳ] values, depending on Mark-Houwink equation[8]:

$$[\eta]=K\overline{M}va \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where ,K and a are constant for a given polymer/ solvent/ temperature system [9-11], and it was given in Table 1.

Table 1: Viscosity-molecular weight constants of waste plastic models Measured in specific solvent and temperature.

Waste plastic model	Solvent	Temp(°c)	$kX10^3(ml.g^{-1})$	a
HDPE	Decalin	135	67.7	0.67
LDPE	Decalin	135	67.7	0.67
PP	Benzene	78	27.0	0.71
PS	Toluene	25	38.0	0.63
PVC	THF	25	1.67	0.851

The difference in melting point or decomposition point of the waste plastics and the polymers recovered after the recycling procedure was curried using melter instrument type Electro thermal 9300 engineering LTD.

Results and discussion

The goal of this work is recycling of the most commercially used plastics and reuse the recovered polymers, depending on simple and cheap technique.Dissolutionre-precipitation process isconsider the most acceptable technique in recycling the waste polymer specially when cheap and available solvent /precipitator are use. Simple equipments and technology, low temperature and solvent/precipitator recovery are the essential characters of such technique.

3.1.Recycling of waste plastic models

Different waste plastic models LDPE, HDPE, PP, PSand PVC were studied. Different solvents with a mostly different values of the solubility parameter(δ) were used, and different experimental conditions were applied for each polymer in order to find the optimum conditionsin terms of dissolution temperature, type of solvent, type of precipitator and initial polymer concentration.

The experimental results of LDPE, HDPE, and PP have been shown in Table 2. LDPE seems to be dissolve in low dissolution temperature in comparison with HDPE because the last is more compact with slightly high molecular weight and melting point. On other hand PP was partially dissolved in xylene might because the polymer is branched, but it shows complete dissolve in N,N-Dimethylaniline at 184°c and in anisolat 149°c. The best precipitator for LDPE,HDPE&PP was n-hexane which was used as third to one of the used solvent and it gave white precipitate.

PS the hard and solid polymer was shown in Table 2 partial dissolve in p-xylene and toluene at 50 °c but in aceton the polymer was completely dissolved specially when leaved for some time, might for the penetration of solvent molecules between the cross-linked polymer chains.Methanol was used for precipition of dissolved PS and white precipitate was shown.

The most popular waste plastics in the landfill is PVC.Where PVC was shown in Table 2 partial dissolve in xylene ,while it was completely dissolved in chloroform at 70°c ,pyridine at 55-60°c ,DMFat 90 c° and finally in the dioxane at 80 °c.

The polarity of the PVC molecules allow the polar solvents to penetrate easily between the polymer chains.All PVCdissolved solutions were precipitated from H2O and formed white precipitate, except the PVC solution in dioxane ,which was needed methanol and H2O for precipitation.

Table2:Suitable organic dissolution solvents and precipitators used for waste plastic models and their dissolution temperature with weight percentage of polymer recovery.

Waste plastic model	Dissolution solvent	Precipitator	Dissolution temperature(°c)	Weight percentage of recovered polymer(wt%)
HDPE	Xylene	n-hexane	100	99.4
	Xylene	methanol	100	99.1
	Anisol	n-hexane	149	98.5
	Ethylbenzene	n-hexane	115	98.7
	N,N-dimethylaniline	n-hexane	185	97.9
LDPE	Xylene	n-hexane	98	99.6
	Anisol	n-hexane	148	98.2
	Ethylbenzene	n-hexane	110	98.3
	N,N-dimethylaniline	n-hexane	180	96.7
PP	Xylene	n-hexane	140	99.5
	Anisol	n-hexane	149	96.7
	Ethylbenzene	n-hexane	110	96.9
	N,N-dimethylaniline	n-hexane	184	98.8
PS	Xylene	methanol	50	98.9
	Toluene	methanol	50	97.8
	Aceton	methanol	25	99.8
	Dioxane	methanol	40	97.3
	Benzene	methanol	45	97.2

PVC	Pyridine	water	58	99.6
	Chloroform	water	70	98.3
	THF	water	35	99.3
	DMF	water	90	98.8
	DMSO	water	80	97.5
	Dioxane	methanol	80	96.8
	Methyl propyl keton	water	40	96.3

FT-IR characterization of structure changes

FT-IR spectra were measured of waste plastics structures and the possible changes in the chemical structure of their recycled polymers. It was shown clearly in Fig.1 and Table 3 that the characteristic peaks of recycled plastics were almost identical to those of the corresponding model waste plastics. With small differences in some wavenumbers were attributed to two main reasons,first to the additives present in the waste plastic models,and second the dissolution/reprecipitation process would change the geometrical configurations of the polymer chains and many lower molecular weight segments would remain soluble in the solvent leave long polymer chains to precipitate with new molecular weight distribution and with different numbers of end groups.

Table 3:Characteristic IR frequencies of waste plastic models.

Waste plastic model	Characteristic IR Frequencies cm-1			
	γC-Hstr	γC-Hdef	γC-Hdef out of plane	γC=C str
LDPE	2927,2850	1410	980	1630
HDPE	2936,2845	1430	970	1640
PP	2930,2849	1400, 1470	960	1610
PS	3030,2936,2855	----------	700,750,800	1640,1580,1490
PVC	2929,2848	----------	800	1635

Degree of purity and precipitated particles form would have some significant effects on the intensity of characteristic peaks and on some shift in their positions.

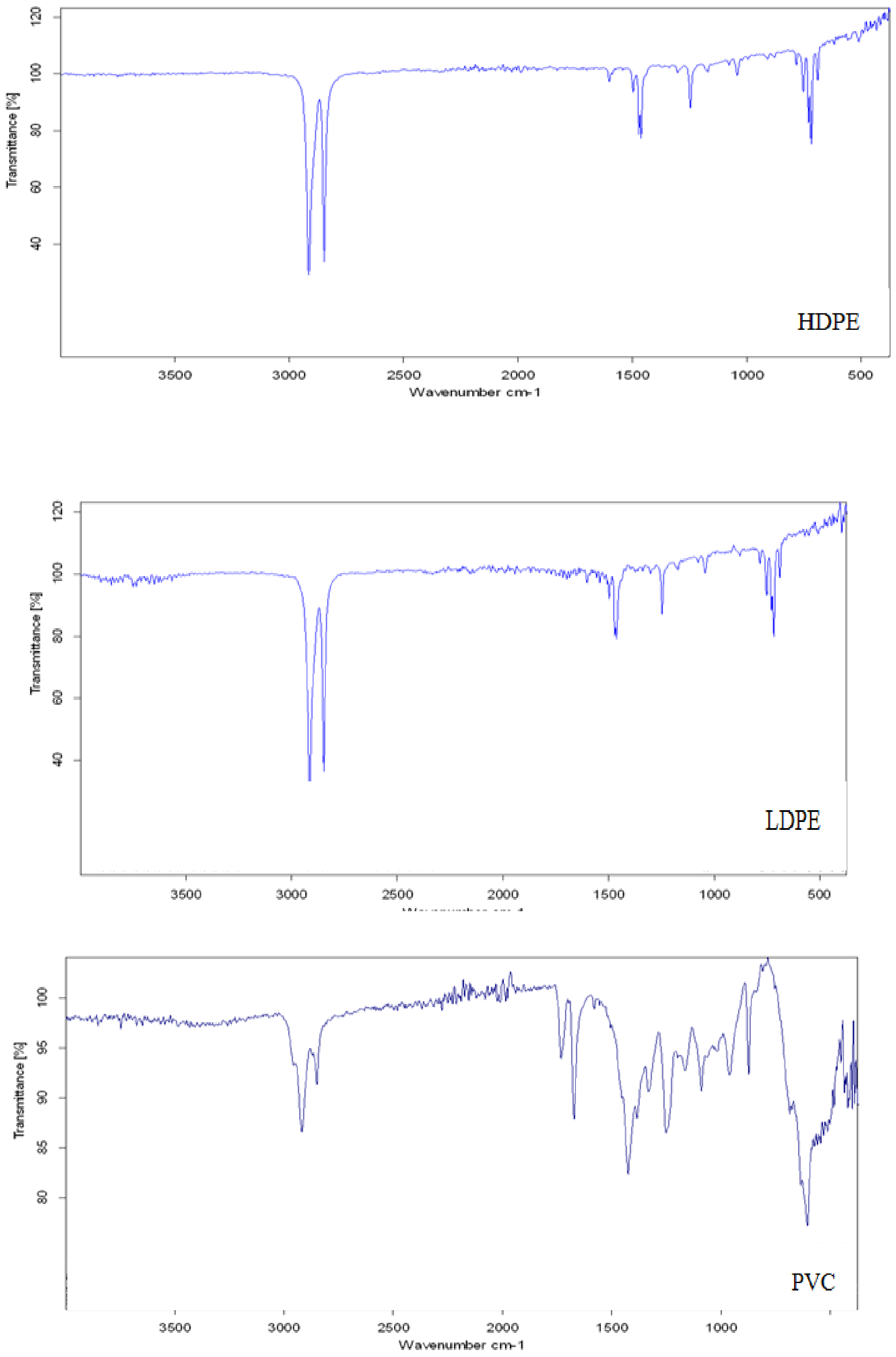


Fig 1:FT-IR spectra of some waste plastic models.

Changes in thermal properties

techniques were used to follow out the thermal properties of the polymer models before and after recycling through dissolution/ reprecipition process.The data taken from the thermograms Figs(2) ,were recorded in details as physical parameters in Table 4. TG,DTG and DTA thermograms of the waste plastic models before the recycled process were studied . It was shown that the heat of fusionΔHf (J g-1) of the polymer at its melting points Tm(ºc), were it is endotherm, and even after the polymer is recover, onlyΔHf become slightly high after recovery[12-14] because the polymer on dissolution and reprecipition only its long chains would precipitate which elevate its ΔHf .The maximum temperature Tmax(ºc)where by the 50% of the polymer weight has be loss is slightly depress after recovery of the polymer means it loss some of its thermal stability and it decompose at lower Tmax(ºc).

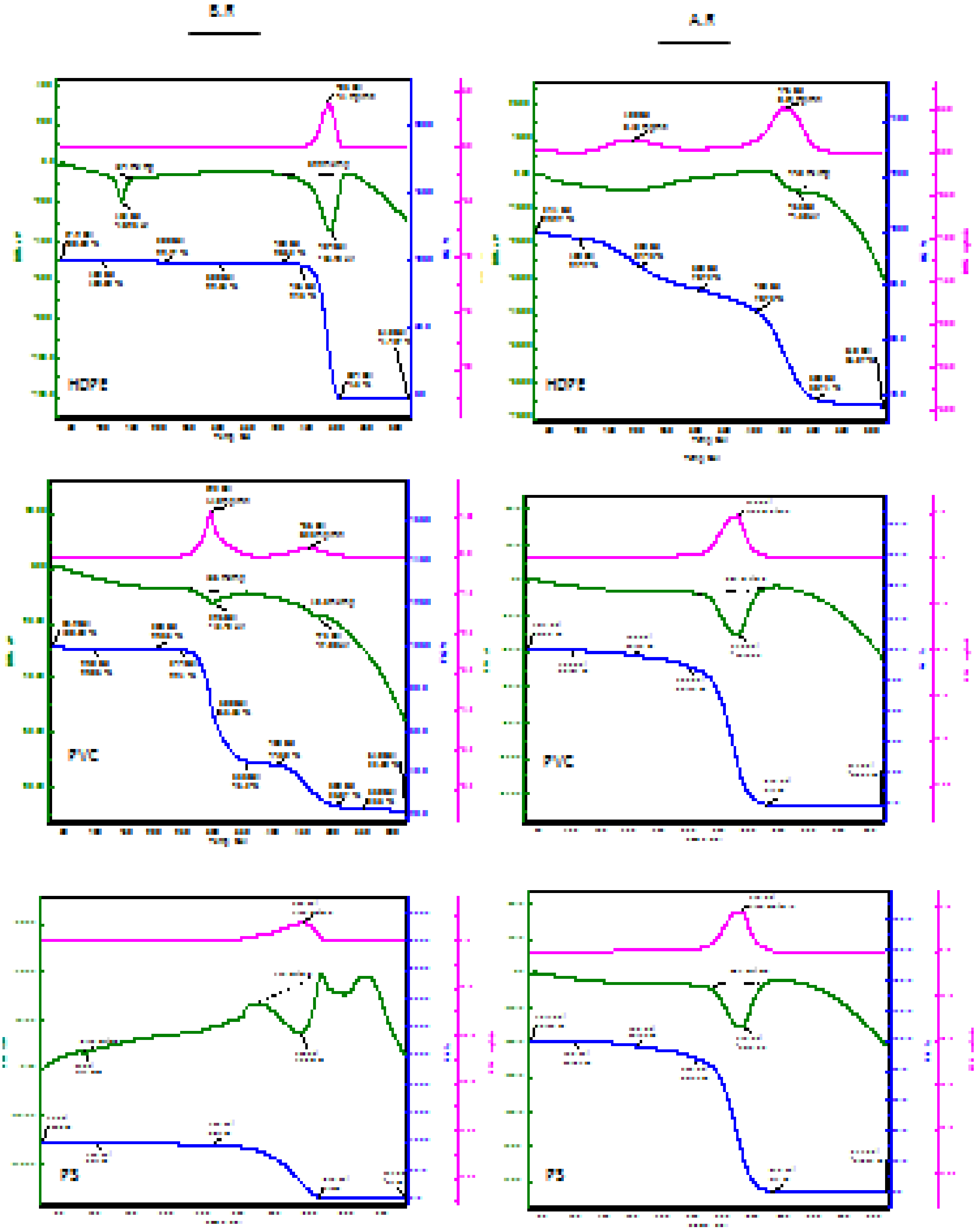
Table 4: Thermo-analysis investigations of waste plastic models before (B.R) and after (A.R) recycling process.

Waste plastic model	TG-thermogram				DTG-thermogram		DTA-thermogram[DSC]			
	ΔHf Jg-1 at Tm(ºc)		Tmax(ºc) at 50%wight loss		Maximum weight decomposition per minute (mg min-1)		Tg(ºc)		ΔHf Jg-1 at complete decomposition	
	B.R	A.R	B.R	A.R	B.R	A.R	B.R	A.R	B.R	A.R
LDPE	98.5(129ºc)	131(121ºc)	481	486	3.56	4.5	/	/	582	478
HDPE	124(132ºc)	146(131ºc)	484	482	4.1	3.83	/	/	599	597
PP	55.2(153ºc)	61.6(125ºc)	495	485	3.92	3.68	/	/	566	550
PS	60(185 ºc)	25(155 ºc)	384	377	2.86	1.89	100	97	680	647
PVC	50(210 ºc)	30 (150 ºc)	292,456	188,446	1.18,0.25	0.18,0.54	82	85	136(296ºc) 18.5(473 ºc)	44.8(465ºc)

The DTG-thermogram is shows a depression in maximum weight decomposition per minute (mg min-1), Figs(2), Table 4, after recovery of the most plastic models, which may because original polymers loss larg segments from their chains and leave the test polymers as the thermogram temperature is rise.

Glass transition temperatureTg(ºc)was measured for the samples PS and PVC using DSC, in addition to the heat of fusionΔHf (J g-1) at complete decomposition of the polymers. The results on Tg measurements before and after the recycling process appear in Figs. (2), Table 4, an slight decrease in the Tg values was observed for PS and an increase for PVC and this might be due to the increase in the linearity of their chains with some loss in PS chains compactness and rearrangement of PVCchains after the recovery process.

The heat of fusion ΔHf (J g-1) needed for complete decomposition of the studied polymer chains was appeared endotherm process at Tmax (ºc).The DTA-thermogramFig(2), Table 4, shows slight decrease in ΔHf (J g-1) after the recovery of polymer with slight decrease in Tmax(ºc).which means, after recovery the polymer its chains may loss some of their strength. The sample PVC polymer Table 4, was shown in general slight increase[15] in its thermal properties after recovery inverse all other studied models. This might due to the chains rearrangement of PVC after reprecipitation.



Fig(2): Thermal analysis diagrams of some waste plastic models before and after recycling process.

Molecular weight and melting point change evidence

The viscosity-average molecular weight($\overline{Mv}$) of the waste plastic models and their recovered polymers after the recycling process was investigated. The limiting viscosity number (intrinsic viscosity) was measured (eq.1) for each studied model in suitable solvent and at fixed temperature using the perfect constants K and a Table 1. The molecular weight and melting point values for allsample before and after recycling are illustrated in Table 5.

Table 5: Melting point temperatures Tm(°c) and viscosity-average molecular weights (Mv)(g.mol-1) of waste plastic models before and after the recycling process.

Waste plastic model	Melting point(Tm)(°c)		Viscosity-average molecular weight (Mv) g.mol-1	
	B.R	A.R	B.R	A.R
HDPE	130	128	649208	645863
LDPE	120	118	529354	523887
PP	160	157	27407	27206
PS	185	183	157276	154881
PVC	212	210	71555	71036

The melting point (Tm) of all the samples was shown slight reduce after reprecipitation[16]. This might due to the change in their average molecular weight which was shown a slight decrease after the recycling process Table 5, for might be two reasons . first the polymer long chains probably undergo degradation during the dissolution process even at low heating temperature. The second reason is concern in the precipitation process of the polymer, where different solvents have been used for dissolving certain polymer ,and that polymer would recover but withalmostly low molecular weight (Mv) in each solvent.The used solvents may have different solubility parameter(δ)which may could keep some polymer chains and allow for others to precipitate .

4.Conclusions

The dissolution /reprecipitation process was used as an effect technique in chemical recycling of waste plastic material. The investigation was include the most popular waste plastics LDPE,HDPE, PP, PS and PVC.The study was search for proper chemical recycling condition, including different types of organic solvents used for dissolution under different dissolution temperatures.The dissolved polymers were recovered using different precipitators and their weight percent of recovery was recorded.FT-IR measurements was shown small differences in some wavenumbers due to the change in the geometrical configurations of the polymer chains. Thermal analysis depending on TG, DTG and DTA, wasconcluded aslight decrease a mostly in all the thermal parameters after recovery of the polymers .However a slight decrease in the average molecular weight of some recovered samples could be considered that the waste plastic recycling process according to dissolution /reprecipition technique is an useful method for recycling waste plastics.

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