

ARKAN JASIM HADI^{1,2}
GHAZI FAISAL
NAJMUDEEN¹
IQBAL AHMED¹

¹Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang, Lebuhraya Tun Razak, Gambang, Kuantan, Pahang, Malaysia

²Department of Chemical Engineering, College of Engineering, University of Tikrit, Tikrit, Salahaldden, Iraq

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QUALITY RESTORATION OF WASTE POLYOLEFIN PLASTIC MATERIAL THROUGH THE DISSOLUTION-REPRECIPITATION TECHNIQUE

Article Highlights

- Dissolution for three types of waste LDPE, HDPE and PP
- Four different pure and mixed organic solvents for solubility with different composition were used
- New dissolution temperature in mixed solvent was obtained
- Excellent recovery with very good mechanical properties for the entire waste sample used

Abstract

This study examines the restoration of waste plastic polymers based on LDPE, HDPE or PP through dissolution/precipitation. Experimental conditions of the recycling process, including type of solvent/non-solvent, original polymer concentration and dissolution temperature were optimized. The results revealed that by using different prepared solvents/non-solvents at various ratios and temperatures, the polymer recovery was always greater than 94%. The FTIR spectra and the thermal properties (melting point and crystallinity) of the polymers before and after recycling were measured using differential scanning calorimetry (DSC). Mechanical properties of the waste polymer before and after recycling were also measured. Besides small occasional deviations, the properties did not change. The tensile strength at maximum load was 7.1, 18.8, and 7.4 MPa for the recycled LDPE, HDPE and PP, respectively, and 7.78, 18.54 and 7.86 MPa for the virgin polymer. For the waste, the strength was 6.2, 15.58 and 6.76 MPa.

Keywords: polymer recycling, waste polyolefins, dissolution/precipitation.

The nearly limitless adaptability of plastics makes them ideal waste materials for all types of commercial and industrial uses. Plastics are primarily used for packaging. Half of the goods in Europe are packaged in plastics, although they contribute only 17% to the weight of all packaging. In the past ten years, the average weight of packaging per product has decreased by 28% [1,2].

The consumption of polymers, plastics in particular, has increased significantly with population

growth. In fact, the average annual consumption in Western Europe has increased from 64 kg per capita in 1993 to 98 kg per capita in 2003. Logically, the 2011 estimate would be 115.2 kg per capita. In Greece alone, consumption went up by 10.9% between 2011 and 2002. Thermoplastics such as polyolefins, high density polyethylene, HDPE - 11%, low density polyethylene, LDPE - 17%, polypropylene and PP - 16% account for more than 78% of the plastics manufactured, the remaining being thermosets such as epoxy resins and polyurethans [3,4].

In Malaysia, the annual plastic consumption rose from 1.1 million tons in 1997 to 1.4 million tons in 2003. The point of concern is the quantity of waste in plastic consumption, which in Malaysia is over 19,000 tons daily. Out of the 230 landfills in Malaysia, a large number have filled to 80% of their capacity. At this

Correspondence: A. Jasim Hadi, Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.

E-mail: arkanaldoury72@gmail.com

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rate, a huge amount of rubble that may become very difficult to manage will accumulate in the coming years [5]. Achilias *et al.* [6] studied deeply the recycling of polymers from plastic packaging materials. The polymer types examined were those normally used in packaging applications, containing LDPE, HDPE, PP, PS, EPS, PET and PVC and their recovery in each sample was recorded. Initially, the method was tested using model polymers of the same type with those used in different plastic packaging applications (polymer from food packaging, pharmaceutical packaging, and detergent packaging). The authors used xylene, toluene, and dichloromethane and benzyl alcohol as solvents, while *n*-hexane and methanol as non-solvent. In almost all waste samples tested, were obtained very good polymer reclamations, however, lower values in some samples, this could have happened because of the removal of additives in the waste polymer before recycling. All the experiments were done at the boiling temperature of the solvents used for the best products recovery.

Polyolefins (LDPE, HDPE and PP) are prominently used thermoplastics for items such as bags, toys, containers, pipes, industrial wrappings, film, house ware, gas pipes (HDPE), battery cases, automotive parts and electric components. In line with the high recent growth in logical polymer synthesis [7], this paper examines the recycling of polymers from waste plastic (LDPE, HDPE and PP) using the dissolution/precipitation method. According to Pappa *et al.* [8], who have investigated this technique using a pilot plan, the cost of the recycled polymer from this method has the same cost of the virgin polymer. The purpose of repeating this investigation is to examine the new solvents and non-solvent with new anti-solvent ratios to reduce the cost of the polymer recycling.

EXPERIMENTAL

Materials

The virgin LDPE, HDPE and PP polymers as standards for the experiments were donated by Polyethylene and Polypropylene Malaysia Sdn Bhd. They were used together with a number of commercial waste materials made from these polymers (bags, caps for water bottle, intravenous fluids containers, some laboratory materials such as pipettes, cleaner packaging, food containers and ice cream packaging). The solvents used (xylene, petroleum ether and *n*-hexane) were of reagent grade purities from Sigma-Aldrich and Merck, Germany. Three types of petroleum ether (PetE) were used, with boiling points

40-60 °C, 60-80 °C and 90-120 °C, and notations A, B, and C, respectively.

Preparation of used polyolefin sample

The waste plastic containers were first rinsed with tap water and then cut with a plastic crusher machine into random pieces of 2-4 cm in size. The pieces were then cleaned with distilled water and placed in simple vacuumed oven for 3-6 h at 50 °C.

Dissolution/precipitation technique

The experimental procedure was performed for several rates ranging from 0.5-25% (weight polymer)/(volume solvent). The solvent and pieces of waste polymer were added to a flask with three necks; the first with a vertical condenser with tap water, the second with a mercury thermometer to measure temperature, and the third with a stirrer. An oil bath was used for heating with the flask immersed and a high speed stirrer doing the mixing. The system was heated for 30 min and brought to the desired temperature. Once the polymer pieces had dissolved completely, the flask was removed from the oil bath and left to cool for 15-30 min, after which the solution was carefully poured into a non-solvent. The precipitate was then washed, filtrated and dried at 70 °C in a vacuumed oven for 10-15 h. The resulting polymer was in granular (powder) form.

Xylene was used as the solvent and *n*-hexane as the non-solvent. The three grades of petroleum ether were used as solvents and non-solvents. Various ratios for xylene/petroleum ether and of the polymer to the solvents were used. Solvent/non-solvent volume ratios of 1:1, 1:2 and 1:3 were applied. The dissolution temperatures were below the boiling point for each solvent and below the melting point of the polymers. Table 1 shows the boiling point temperatures for the solvents and non-solvents used.

Table 1. Boiling temperature of solvents and non-solvents

Type of solvents and non-solvents	Boiling temperature, °C
Xylene	140
<i>n</i> -Hexane	69
Petroleum ether grade A	40-60
Petroleum ether grade B	60-80
Petroleum ether grade C	90-120

Recycling of the solvents

The solvents mixture was separated using a simple distillation process. The purity of the recovered solvents was determined through refractive index (*R*) measurements using an ATAGO digital hand-held "pocket" refractometer PAL. The total amount of the

solvent and non-solvent used in some of the experiments in this study was 800 ml (200 ml xylene and 600 ml *n*-hexane). Approximately 620 ml of the mixture was received from filtration while the remaining 180 ml was obtained from drying.

From 800 ml of mixture used in the process, approximately 750 ml of products (560 ml *n*-hexane, 96 vol.%, and 190 ml xylene, 98 vol.%) were obtained and thus the final recovery was 94%. The solvents, especially petroleum ether, have high vapor pressure and some amount was lost during handling. After separation, the solvents can be reused, although their purity after recovery is not high.

Measurements

Fourier transform infrared (FTIR). FTIR was used to determine the functional group of the product, based on the peak value. The chemical structure of the standard polymers and waste sample plastics, before and after the restoration process was confirmed by recording their IR spectra. The instrument used was a Nicolet (Magna-IR560) FT-IR spectrophotometer with a resolution of 4 cm⁻¹. The recorded wavenumber range was from 400 to 4000 cm⁻¹.

Differential scanning calorimetry (DSC). Thermal properties such as melting temperature (*T_m*) and heat of fusion of the polymer produced after recycling, the waste samples and the model polymers was measured using a DSC Q1000 (V9.6, Build 290) from TA Instruments. 10 mg samples were prefaced onto the instrument and the heat emitted was recorded at a

temperature interval of 20–300 °C and a scan rate of 10 °C/min, in N₂ atmosphere.

Universal testing machine (UTM)

A Shimadzu AG-X universal testing machine was used to measure the mechanical properties of the virgin and waste polymers before and after recycling. Stress at maximum load, strain at break, stress at yield and elasticity were noted. Five specimens were examined for each sample and the average values reported. The testing was performed according to the standard method (ASTM D638-03). The speed of the testing was 5 mm/min for LDPE and HDPE, while for PP it was 1 mm/min. The sample was prepared on a hot press. A carbon steel frame (30 cm × 30 cm × 3 mm) was prepared to mold the polymer as a film. Three sheets were prepared from the virgin, waste and recycled polymer, each sheet weighing approximately 240 to 260 g. The molding temperature was fixed at 150, 190, 230 °C, for LDPE, HDPE and PP, respectively. Films were cut and shaped according to ASTM D638-03 by a manual press.

RESULTS AND DISCUSSION

Xylene and the three grades of petroleum ether were tested as solvents using different compositions as shown in Table 2. *n*-Hexane, and petroleum ether in the three grades were used as non-solvents. In order to recognize the polymer class from which the used plastic material was made of, its FTIR spectra

Table 2. Dissolution temperatures and recovery weight percentage of (LDPE/HDPE/PP) polymer in pure and blend solvent at various ratios by dissolution /reprecipitation technique

Composition of the blend solvents as a volume ratio	Dissolution temperature, °C			Recovery percentage		
	LDPE	HDPE	PP	LDPE	HDPE	PP
Xylene	75	100	118	99.4	98	98
Xylene/petroleum ether (A)						
25:75	68	68	68	49	Zero	Zero
50:50	89	89	89	97	40	Zero
75:25	100	100	100	99	92	50
90:10	100	100	108	99	97	85
Xylene/petroleum ether (B)						
25:75	80	80	80	90	Zero	Zero
50:50	67	95	98	99	89	90
75:25	75	100	105	99	93	91
90:10	75	100	105	99	97	97
Xylene/petroleum ether (C)						
25:75	80	100	100	99	89	45
50:50	70	100	108	98	97	94
75:25	70	100	108	98	96.4	94.9
90:10	75	100	118	99	98	98

was recorded and compared to the corresponding virgin polyolefins polymer. Figures 1-3 represent the FTIR graphs of polyolefin classification, which correspond to LDPE, HDPE and PP, respectively. The

distinction between each polymer was made clearly, even though the differences between the characteristic bands are not large.

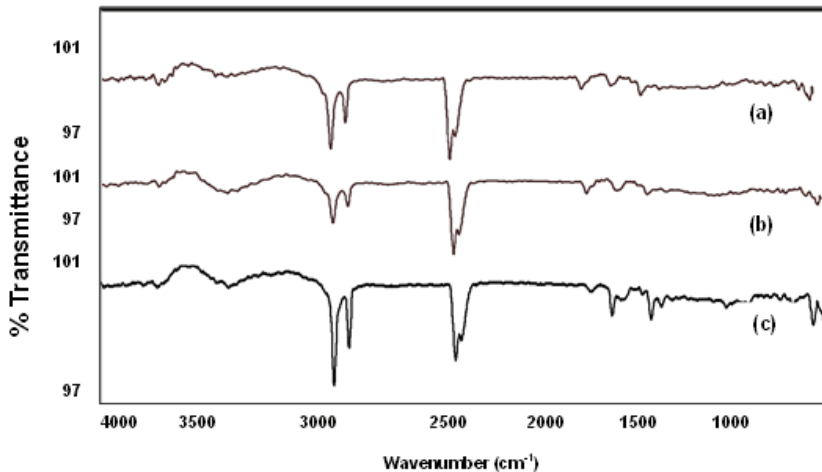


Figure 1. FTIR Spectra for LDPE: a) virgin; b) waste; c) recycled.

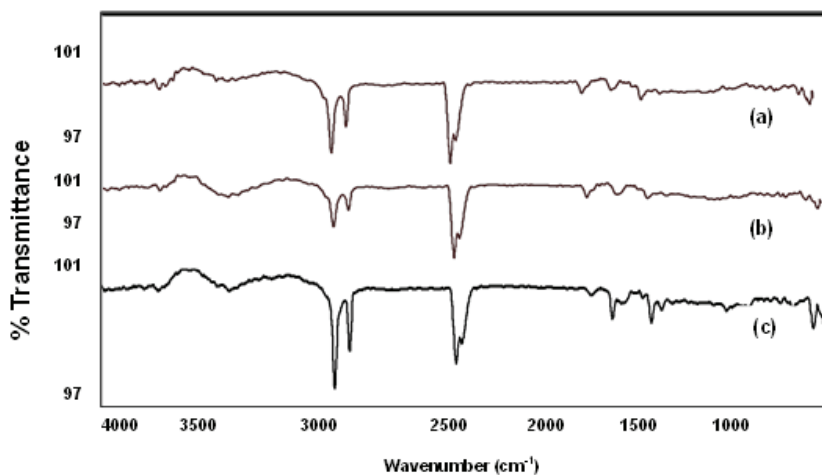


Figure 2. FTIR Spectra for HDPE: a) virgin; b) waste; c) recycled.

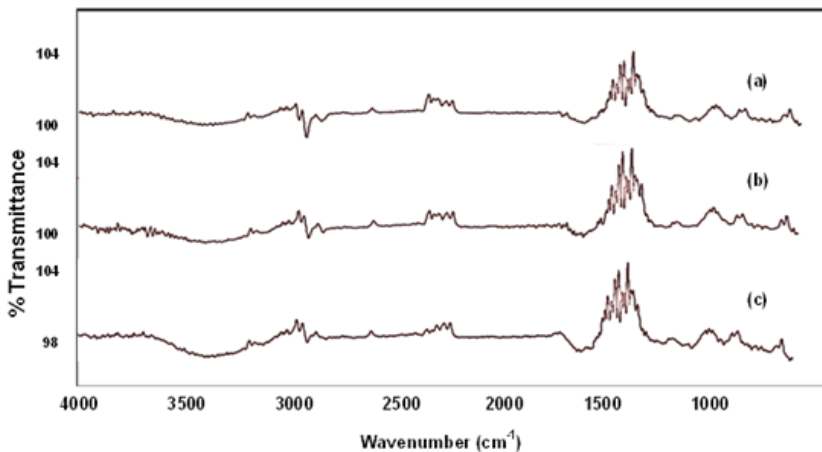


Figure 3. FTIR Spectra for PP: a) virgin; b) waste; c) recycled.

The dissolution temperature and recovery percentage of the polymer after recycling by using xylene and the xylene/petroleum ether blend as solvents in different mixed ratios, along with the non-solvents, are shown in Table 2.

The results in Table 2 correspond to a concentration with 0.5 g polymer and 20 ml solvent. According to the literature [9], the best recovery polymer is obtained at the dissolution temperature that is the boiling point for xylene (140 °C). The mixtures of xylene with petroleum ether were seen to be very good solvents. The dissolution temperatures for the waste polymers with the solvent mixtures containing xylene and petroleum ether were less than with pure xylene. The dissolution temperatures for the mixed solvent xylene and petroleum ether (C) in a 1:1 ratio were 70, 100 and 108 °C for LDPE, HDPE and PP, respectively. The behavior of PP in the solvent containing 1:1 (xylene + petroleum ether (B)) with boiling point 60–80 °C is noteworthy. Small bubbles appeared at 91 °C with some dissolution. Gradually, the temperature reached 98 °C with continued boiling, two minutes into which the pieces started dissolving. After 20–25 min, full dissolution occurred with polymer recovery of about 89–92%. The dissolution temperature for LDPE and HDPE was 67 and 95 °C, respectively. The time for all the experiments was set to 15 min at the required temperature.

The non-solvents used in all the experiments were *n*-hexane and the three grades of petroleum ether. Petroleum ether turned out to be a very good precipitator for all the polymer types, except LDPE in petroleum ether grade (C). The perfect precipitation

occurred with 1:3 ratio solvent/non-solvent. With ratios of 1:1 and 1:2, a delay of 5–15 min was observed before full precipitation, except when the solution was cooled to (50–60 °C). With the blend solvents, the same grade of petroleum ether and a 1:1 solvent/non-solvent ratio yielded good precipitation. With xylene as the solvent and either grade of petroleum ether (B and C) as the non-solvent (in a 1:1 ratio), good precipitation was seen and, without any separation for the filtrated solvent, could be used again directly to another dissolution process.

Effect of polymer concentration with the dissolution temperature on the recovery

Figures 4 and 5 illustrate the effect of the dissolution temperature and the initial concentration of the polymer on the wt.% recovery of the three waste polyolefins (LDPE, HDPE and PP). The polymer recovery remained high at all experimental conditions. High polymer recovery corresponds to high dissolution temperature and low initial polymer concentrations. The recovery of LDPE was higher than HDPE and PP even at low dissolution temperature.

Recycled polymer properties

Thermal properties

The measurement of the thermal properties of the virgin polymer and waste plastic before and after recycling was done using DSC. The melting points and crystallinities are shown in Table 3. The melting point of the sample based on virgin HDPE and LDPE ranged from 125–140 °C and 105–120 °C, respectively, although a 3% change did occur after recycling.

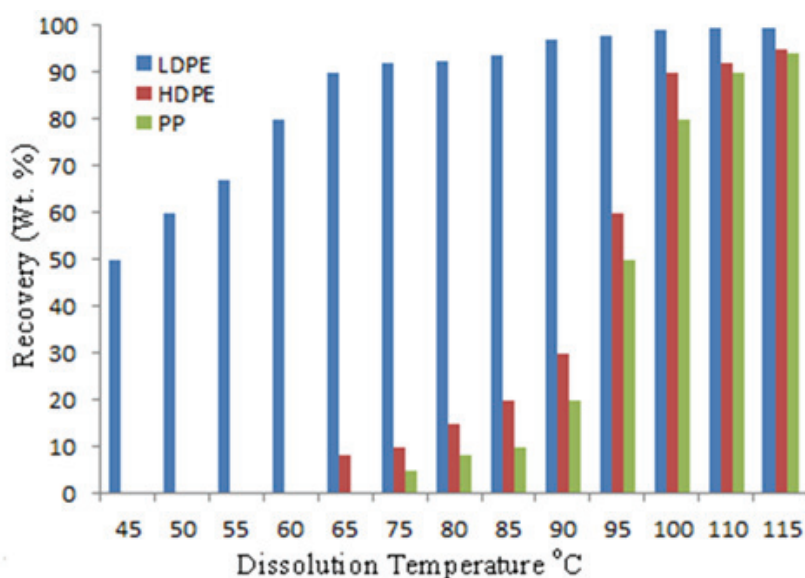


Figure 4. Effect of dissolution temperature on the recovery of polymer from waste polyolefins using xylene + PetE (C)/PetE(A) and 5% w/v sample concentration.

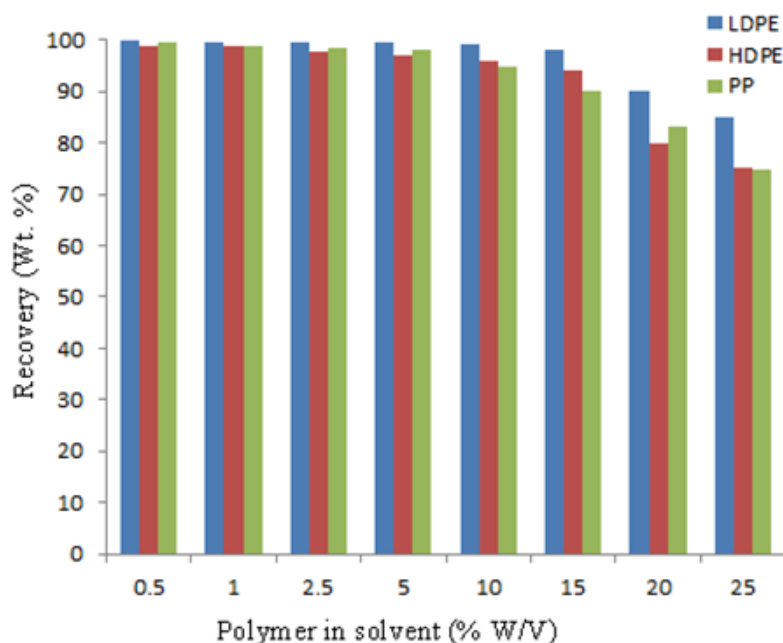


Figure 5. Effect of sample concentration on the recovery of polymer from waste polyolefins using xylene + PetE (C)/ PetE(A) at 115 °C.

The melting point of PP ranged from 160–166 °C and remained practically the same after recycling. The crystallinity of the products was also calculated, by dividing the heat of fusion at the melting point for each polymer by the reference heat of fusion, which was 293 and 207 J/g for PE and PP, respectively [10,11]. A significant difference was observed in the crystallinity after recycling. Compression between the virgin sample and the recycled crystallinity was very good with only small deviation that can be attributed to the experimental conditions and sample preparation. Also, some solvent molecules could have remained with the polymer particles. Nevertheless, after complete dissolution the compression approached the original value.

Figures 6–8 show the DSC thermograms for the virgin and waste LDPE, HDPE and PP polymers before and after recycling. Small deviations were observed for some HDPE samples, especially in the mixed solvents, but the results for LDPE and PP were good. The HDPE deviation is, as mentioned before, likely due to experimental conditions, sample preparation and the kind of waste materials used. The peak for the waste PP was very small in comparison with

the original and the recycled, as well as for the LDPE and HDPE. The tests were repeated two or three times using a different instrument in more than two places. This situation was accrued due to an initial additive and plasticizers and some more additives in waste polymers, so after the dissolution process using an organic solvent, the additives and the plasticizers were removed from the original polymers molecules. A promising inference from the graphs is that good dissolution and precipitation is achieved after recycling the waste polymers with the proper solvent, besides an almost complete retention of mechanical and thermal properties.

Mechanical properties

This section presents the properties of LDPE, HDPE and PP for the virgin and the waste polymers before and after recycling, recorded using the Shimadzu AG-X universal testing machine (Table 4). The tensile strengths at maximum load levels are very close for the virgin and recycled polymers. The tensile stresses at yield measurement remain the same. The elastic modules seem to decrease after recycling, possibly due to the fractionation phenomena (*i.e.*,

Table 3. Melting temperature, T_m , and crystallinity of virgin polymers and waste polymer materials before and after recycling

Sample	Polymer	T_m / °C			Crystallinity, %		
		Virgin	Waste	Recycled	Virgin	Waste	Recycled
Bags (original use)	LDPE	106	106	110	52	24.3	44.1
Body lotion bottles, shampoo bottles	HDPE	135	130	131	77	32.1	68.2
Transparent food containers	PP	166	165	166	59	20.5	45.7

some lower molecular weight fractions may remain soluble in the solvents/non-solvents phase), as well as the additives initially contained in the starting material [12,13]. Due to the effects of the sample preparation methods, the tensile stress at yield for the recycled polymer fluctuates from the virgin polymer value, as is seen in Table 4.

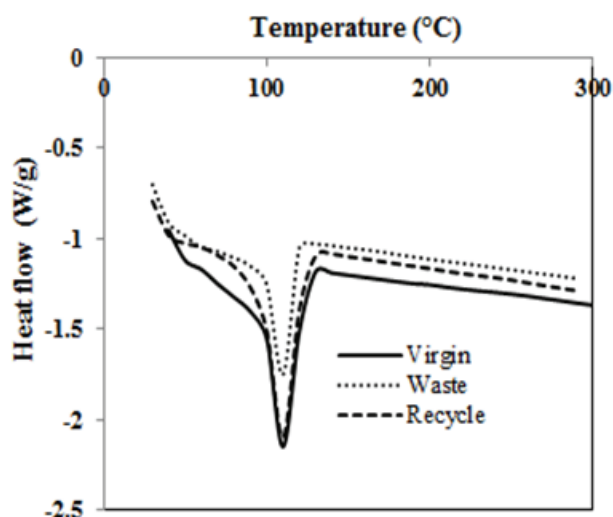


Figure 6. DSC Thermograms of virgin and waste plastic before and after recycling based on LDPE.

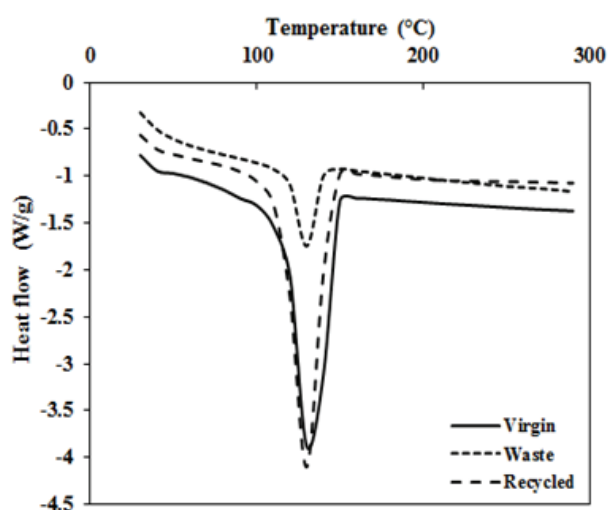


Figure 7. DSC Thermograms of virgin and waste plastic before and after recycling based on HDPE.

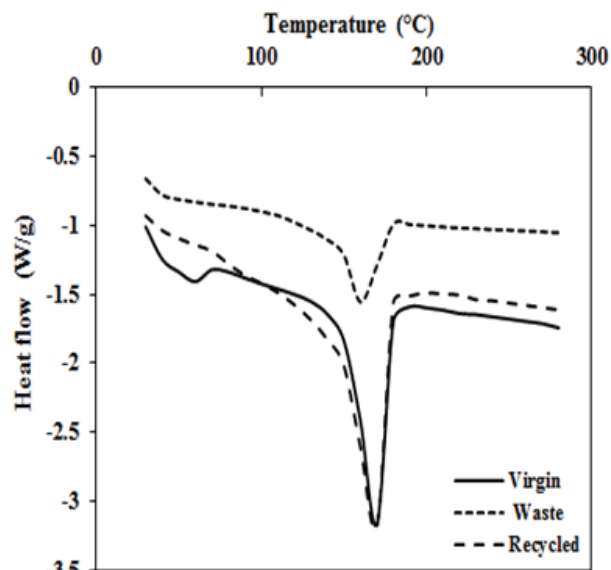


Figure 8. DSC Thermograms of virgin and waste plastic before and after recycling based on PP.

CONCLUSIONS

This study investigated the use of the dissolution/precipitation technique with commercial products from the polymers LDPE, HDPE and PP. A comparison between the properties of the recycled and virgin polymers showed almost no deviation. Pure solvents such as xylene as well as mixtures in different fractions of xylene and three grades of petroleum ether were used. Good recovery was seen for almost all solvents. The chemical structure showed no significant alteration after recycling, after examination by FTIR. The mechanical properties either remained the same or improved after recycling, as was the case with crystallinity. Thus, the technique is quite effective for the recovery of waste polymer.

Acknowledgement

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Table 4. Mechanical properties of virgin and wastes polymers before and after recycling (for same polymer types mentioned in Table 3)

Testing type	LDPE			HDPE			PP		
	Virgin	Waste	Recycled	Virgin	Waste	Recycled	Virgin	Waste	Recycled
Tensile stress at max. load, MPa	7.8	6.2	7.1	18.5	15.6	18.9	7.9	6.8	7.4
Strain at break, %	39.8	97	70.75	58.2	64.2	34.2	2.5	2.27	2.15
Tensile stress at yield, MPa	4.9	4.9	5.3	12.22	9.2	14.7	5.9	4.6	4.3
Elastic modulus, MPa	201	143	174	496	392	453	744	624	717

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ARKAN JASIM HADI^{1,2}
 GHAZI FAISAL NAJMULDEEN¹
 IQBAL AHMED¹

¹Faculty of Chemical and Natural
 Resources Engineering, University
 Malaysia Pahang, Lebuhraya Tun
 Razak, Gambang, Kuantan, Pahang,
 Malaysia

²Department of Chemical Engineering,
 College of Engineering, University of
 Tikrit, Tikrit, Salahaldden, Iraq

NAUČNI RAD

RECIKLAŽA OTPADNE PLASTIKE NA BAZI POLIOLEFINA TEHNIKOM RASTVARANJA I PRECIPITACIJE

U ovom radu ispitivana je reciklaža otpadne plastike zasnovane na LDPE, HDPE i PP putem rastvaranja i precipitacije. Optimizovani su eksperimentalni uslovi procesa recikliranja: vrste rastvarača, koncentracija polimera i temperatura rastvaranja. Rezultati pokazuju da se korišćenjem različitih rastvarača u različitim odnosima i temperaturama uvek postiže reciklaža polimera veća od 94%. Pre i posle recikliranja snimani su FTIR spektri i merena termička svojstva (tačka topljenja i kristalnosti) polimera pomoću diferencijalnog skenirajućeg kalorimetra (DSC). Takođe, određene su mehaničke osobine pre i posle recikliranja. Osim malih povremenih odstupanja, osobine polimera se ne menjaju. Zatezna čvrstoća pri maksimalnom opterećenju za polimere LDPE, HDPE i PP je bila: 7,1; 18,8 i 7,4 MPa za reciklirane, odnosno 7,78; 18,54 i 7,86 MPa za izvorne polimere i 6,2; 15,58 i 6,76 MPa za otpadne polimere.

Ključne reči: recikliranje polimera, otpadni poliolefini, rastvaranje/precipitacija.