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Recycling of polymers from plastic packaging materials using the dissolution–reprecipitation technique

D. S. Achilias · A. Giannoulis · G. Z. Papageorgiou

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Abstract In this work, results are presented on the application of the dissolution/reprecipitation technique in the recycling of polymers from waste plastic packaging materials used in food, pharmaceuticals and detergents. Initially, the type of polymer in each packaging was identified using FT-IR. Furthermore, experimental conditions of the recycling process (including type of solvent/non-solvent, initial polymer concentration and dissolution temperature) were optimized using model polymers. The dissolution/reprecipitation technique was applied in the recycling of a number of plastic materials based on polyethylene (LDPE and HDPE), polypropylene, polystyrene, poly(ethylene terephthalate) and poly(vinyl chloride). The recovery of the polymer was measured and possible structural changes during the recycling procedure were assessed by FT-IR spectroscopy. Potential recycling-based degradation of the polymer was further investigated by measuring the thermal properties (melting point, crystallinity and glass transition temperature), of the polymer before and after recycling, using DSC, their molecular properties (average molecular weight) using viscosimetry, as well as their mechanical tensile properties. High recoveries were recorded in most samples with the properties of the recycled grades not substantially different from the original materials. However, a slight degradation was observed in a few samples. It seems that this method could be beneficial in waste packaging recycling program.

Keywords Polymer recycling · Plastic packaging · Dissolution/reprecipitation technique

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D. S. Achilias (✉) · A. Giannoulis · G. Z. Papageorgiou
Laboratory of Organic Chemical Technology, Department of Chemistry,
Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece
e-mail: axilias@chem.auth.gr

Introduction

Packaging materials are currently considered an important source of environmental waste mainly due to their large fraction by volume in the waste stream. Furthermore, packaging is the economic sector with the highest volume consumption of polymeric materials (mainly plastics). Plastic packaging has several advantages to offer to consumers; it is safe, lightweight, strong, easily processed and stored and economical. Although recycling of materials such as glass, aluminium and paperboard has been rather extensively practiced, recycling of polymeric materials has not reached maturity yet. This is mainly due to the wide variety of different polymers used in packaging, together with the fact that plastics usually used for packaging are not consisted of a single-type polymer but rather of polymer mixtures or copolymers, with sometimes a variety of additives in small amounts. Although, the presence of large quantities of mixed plastic waste, impurities and contamination are the main challenge for the effective recycling of plastics from packaging, during the last decade, effective management of the different waste streams (selective sorting, automatic separation) has allowed the recovery of large volumes of relatively clean and homogeneous polymeric fractions that are viable for mechanical recycling [1]. For the plastic materials the target by 2011 is to recycle at least 22.5% wt. of waste packaging [2, 3].

The predominant method of waste disposal in most countries has been and remains landfill. However, disposing of the waste to landfill is becoming undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used polymers. The approaches that have been proposed for recycling of waste polymers include [4–6]: primary recycling, mechanical recycling, chemical or feedstock recycling and energy recovery. Almost all the above techniques have been used in recycling of polymeric materials used for food packaging [7, 8].

As a continuation of our work on polymer recycling [9–13], in this paper recycling of polymers from packaging materials was examined using the dissolution/reprecipitation method, which belongs to the mechanical recycling techniques. During this technique the polymer can be separated and recycled using a solvent/non-solvent system. Solvent-based processes include stages of treating plastic waste with solvents so that the polymeric materials are dissolved and then recovered by reprecipitation. These processes have the advantage that they are able to deal with mixtures of polymers, based on the principle of the selective dissolution. Moreover, the dissolution/reprecipitation technique seems to comprise a series of advantages, such as: (1) the plastic waste is eventually converted into a form acceptable to fabrication equipment (powder or small grains), (2) additives and insoluble contaminants can be removed by filtration, leaving pure material, (3) except heating for dissolving no further degradation, due to the recycling process itself, is anticipated, (4) the value added during the polymerization stage is maintained intact and the recycled polymers, free of any contaminants, can be used for any kind of application, since the final product is of competitive quality compared with the virgin material. This method has already been studied in the recovery of a variety of mainly model polymers including poly(vinyl chloride) (PVC) [14], polystyrene (PS) [15], low-density polyethylene (LDPE) [16], high-density polyethylene (HDPE) [17], polypropylene (PP) [18], poly(ethylene terephthalate) (PET) [19], the acrylonitrile-butadiene-styrene (ABS) resin [20] and mixtures of polymers [21]. Nowadays, dissolution-based recycling is used in an industrial scale for the recovery of PVC (known as Vinyloop® process) and for expanded polystyrene (EPS) (known as Creasolv® process) [21].

The aim of this study is to examine the application of the dissolution/reprecipitation technique in the recycling of different polymers from waste packaging materials used for food, detergent and pharmaceutical products. Initially, different types of polymers in plastic waste packaging materials were identified using Fourier Transform Infrared Spectroscopy (FT-IR) by comparing the spectra of the waste sample to that of different model polymers. The experimental conditions of the recycling process (including type of solvent/non-solvent, initial polymer concentration and dissolution temperature) were optimized using model polymers as raw materials and they were further employed in a number of waste packaging products. The polymer types investigated were those typically employed in packaging applications, including LDPE, HDPE, PP, PS, EPS, PET and PVC and their recovery in each sample was recorded. Possible structural changes during the recycling procedure were assessed by FT-IR spectroscopy, DSC (measurement of the melting point, crystallinity and glass transition temperature), viscosimetry (average molecular weight), as well as by measuring the mechanical tensile properties of the samples.

Experimental

Materials

Model polymers (LDPE, HDPE, PP, PS, PET and PVC) obtained from Aldrich were used in this study together with a number of commercial waste packaging materials (packaging film, bags, cups, glasses, bottles, food retail outlets, miscellaneous pharmaceutical packaging, etc.) made from these polymers. The detergent waste plastic packaging used were bottles under the trade names Viakal™, Soflan™, Karpex™, Overaly™, Merito™, Harpic™ and Bref Power™ and were given the code names D1, D2, D3, D4, D5, D6 and D7, respectively. The solvents used (toluene, xylene, dichloromethane, benzyl alcohol, *n*-hexane, methanol, tetrahydrofuran, D-limonene) were of reagent grade.

Dissolution/reprecipitation technique

The experimental procedure comprised: the polymer (1 g) and the solvent (20 mL) were added into a flask equipped with a vertical condenser and a magnetic stirrer. The system was heated for 30 min to the desired temperature. Then, the flask was cooled and the solution of the polymer was properly poured into the non-solvent. The polymer was re-precipitated, washed, filtrated and dried in an oven at 80 °C for 24 h. The recycled polymer was obtained in the form of powder or grains. Xylene, toluene, dichloromethane and benzyl alcohol were used as solvents, while *n*-hexane and methanol as non-solvent. Some other parameters include solvent/non-solvent volume ratio 1/3, concentration of the polymers 5% w/v; and dissolution temperatures below the boiling point for each solvent. In all commercial waste samples investigated only the plastic part was taken (i.e. without any paper, glue, or other compounds). In order to check the reproducibility of the experiments all runs were replicated twice.

Measurements

Fourier-Transform Infra-Red (FTIR)

The chemical structure of the model polymers and waste plastics, before and after the recycling technique was confirmed by recording their IR spectra. The instrument used was an FTIR spectrophotometer of Perkin–Elmer, Spectrum One. The resolution of the equipment was 4 cm^{-1}. The recorded wavenumber range was from 450 to 4,000 cm^{-1} and 16 spectra were averaged to reduce the noise. A commercial software Spectrum v5.0.1 (Perkin Elmer LLC 1500F2429) was used to process and calculate all the data from the spectra. Thin polymeric films were used in each measurement, formed by a hydraulic press Paul–Otto Weber, at a temperature 20 °C above the melting point of each polymer.

Thermal properties, such as the glass transition temperature T_g, and the melting temperature T_m, of the recycled products were measured using differential scanning calorimetry (DSC) and compared to the original waste samples as well as to the corresponding model polymers. The instrument used was the Pyris-1 DSC from Perkin Elmer. Samples of approximately 10 mg were introduced into the appropriate position of the instrument and the heat released was recorded at a temperature interval 20–200 °C and a scan rate of 10 or 20 °C/min, in N_2 atmosphere. T_g was calculated using the well-known procedure at the point were a change in the slope of the curve was observed.

Molecular properties, such as the average molecular weight of the samples before and after recycling were measured in terms of intrinsic viscosity. Intrinsic viscosity $[\eta]$, measurements of PET based samples were performed using an Ubbelohde viscometer at 25 °C in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40, w/w). The samples were maintained in the above mixture of solvents at 90 °C for some time (ca 15–20 min) to be completely solved and prepare solutions 1 g/dL. These were further cooled to room temperature and filtered through a disposable Teflon membrane filter. Intrinsic viscosity was calculated after the Solomon–Ciuta equation.

$$[\eta] = [2\{t/t_o - \ln(t/t_o) - 1\}]^{1/2}/c \tag{1}$$

where c is the concentration of the solution; t the flow time of solution and t_o the flow time of pure solvent. The number-average molecular weight $(\bar{M}_n)$ of the samples was calculated from intrinsic viscosity $[\eta]$ values, using the Berkowitz equation:

$$\bar{M}_n = 3.29 \times 10^4 [\eta]^{1.54} \tag{2}$$

Additionally, intrinsic viscosity measurements of PS and PVC based samples were performed using an Ubbelohde viscometer at 25 °C in THF solvent and following the usual procedure. The viscosity-average molecular weight ($\bar{M}_v$) was estimated from the [η] values, using the well-known Mark–Houwink–Kuhn–Sakurada equation:

$$[\eta] = \mathrm{K}\bar{M}_v^{\alpha} \tag{3}$$

with the Mark–Houwink constants K and α equal to 11 × 10^{-5} dL/g; 0.725 and 3.63 × 10^{-5} dL/g; 0.92 for PS and PVC, respectively [22].

Tensile measurements

The tensile mechanical properties were studied on relatively thin films of the polymers. Dumbbell-shaped tensile-test specimens (central portions, 5 × 0.5 mm thick, gauge length 22 mm) were cut from the sheets in a Wallace cutting press and conditioned at 23 °C and 55–60% relative humidity for 48 h. The stress–strain data were obtained with an Instron model BlueHill 2 tensile-testing machine, which was maintained under the same conditions and operated at an extension rate of 5 mm/min. The values of the elastic modulus, yield stress, tensile strength, and elongation at break were determined according to ASTM D 1708-66. At least five specimens were tested for each sample, and the average values are reported.

Results and discussion

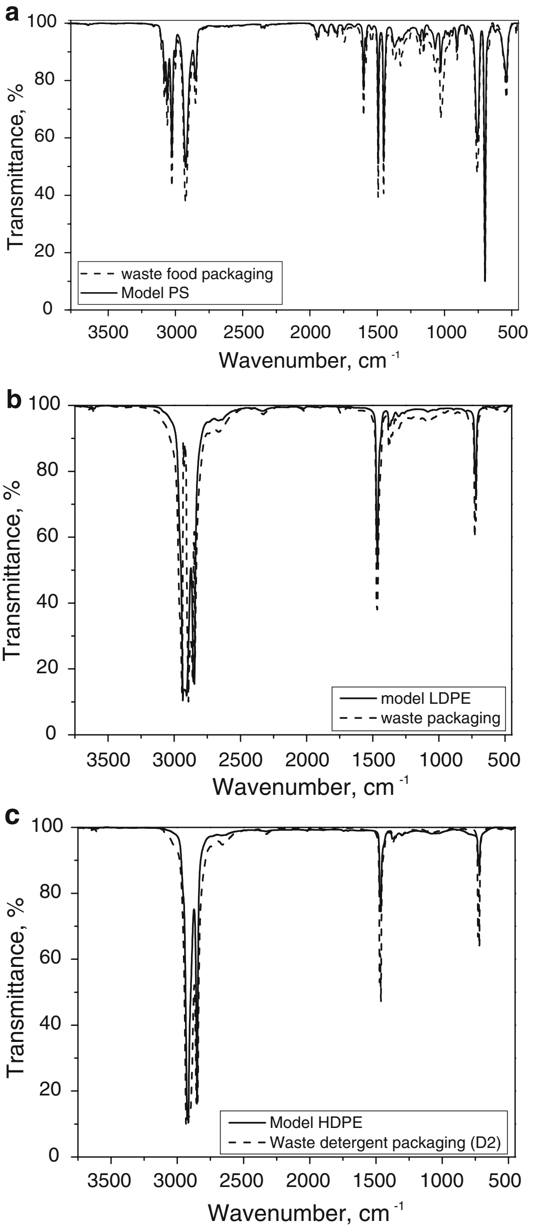
Identification of polymers in plastic packaging materials

In order to identify the polymer from which the selected packaging material was made of, its FTIR spectra was recorded and compared to the corresponding model polymer. Indicative plots are presented in Fig. 1. In all cases the polymer marked with the specific recycling symbol was identified. Minor differences in the recorded spectra in some wavenumbers were attributed to additives present in small amounts in the commercial waste products. As it can be seen in Fig. 1, in all different cases the characteristic peaks of the waste product are almost identical to those of the corresponding model polymer.

Recycling of model polymers

Initially the method was tested using model polymers of the same type with those used in different plastic packaging applications. As it was reported previously the basic polymer types used in different packaging categories are LDPE, HDPE, PP, PS, PVC and PET. Different experimental conditions were employed in each polymer in order to find the optimum conditions in terms of dissolution temperature, type of solvent and/or non-solvent and initial polymer concentration. Detailed results on the effect of polymer concentration, dissolution temperature and type of solvent on the recovery of model polyolefins (i.e. LDPE, HDPE and PP) have been reported in a previous study [12]. It was concluded there that the recovery is promoted by increased temperatures and decreased polymer concentration.

Fig. 1 Comparative FT-IR spectra of waste plastic packaging and model polymers. **a** PS and a food packaging, **b** LDPE and a bag for pills, **c** HDPE and a detergent bottle (D2)



Therefore, only optimum results are presented in this paper. For the LDPE and HDPE recovery typical solvents used are toluene and xylene [16, 17]. Two solvents were chosen for the recycling process, based on the fact that plastics can be dissolved in solvents with similar values of the solubility parameter, δ. These solvents were xylene [$\delta = 8.8$ (cal\cm^3)$^{1\backslash 2}$] and toluene [$\delta = 8.9$ (cal\cm^3)$^{1\backslash 2}$].

Polyolefins present, generally, a value of solubility parameter near to 8.0 (cal\cm^3)$^{1\backslash 2}$. According to a previous publication [12] xylene was found to be more effective giving slightly greater polymer recoveries. Therefore, this solvent was also used in this investigation. It was also observed there that polymer recovery was promoted by increased dissolution temperatures near the boiling point of the solvent. Therefore, a temperature of 140 °C was selected as the best value providing almost complete polymer recovery for both polymers. However, since the melting point of LDPE and HDPE is around 120 °C and 130 °C, respectively, it was decided in this investigation to use a temperature below these values and as such 100 °C was employed in all experiments involving LDPE and HDPE. Furthermore, concerning recovery of polymers based on PP, since the melting point of this polymer is around 160 °C, the highest possible temperature of 140 °C was used. The percentage of polymer recovery measured appears in Table 1. A recovery near 99% was measured for all polyolefins examined. In addition the use on methanol instead on *n*-hexane as a non-solvent gave similar results within experimental error.

The recovery of PS was investigated using different conventional solvents at different dissolution temperatures. Again toluene and xylene have been proposed as adequate solvents for this polymer [15, 23]. It was observed that high recovery values were measured at 50 °C not increasing very much with further increase in temperature (near the boiling point of the specific solvent). Therefore, this temperature was employed in all further experiments with commercial waste samples and either toluene/*n*-hexane or xylene/methanol as the solvent/non-solvent system. Particularly, the extent of polymer recovery (i.e. 96%) with the xylene/methanol system was found quite satisfactory. Due to the environmental concern,

Table 1 Experimental conditions and recovery (wt.−%) of model polymers by the dissolution/reprecipitation technique

Sample	Polymer	*T* (°C)	Solvent/non-solvent	Recovery
Model	LDPE	100	Xylene/*n*-hexane	98.9
Model	HDPE	100	Xylene/*n*-hexane	98.6
Model	HDPE	100	Xylene/methanol	97.0
Model	PP	140	Xylene/*n*-hexane	98.7
Model	PS	25	Toluene/*n*-hexane	87.7
Model	PS	50	Toluene/*n*-hexane	92.1
Model	PS	100	Toluene/*n*-hexane	94.5
Model	PS	25	Xylene/methanol	89.2
Model	PS	50	Xylene/methanol	95.8
Model	PS	100	Xylene/methanol	97.9
Model	EPS	25	D-limonene/−	98.1
Model	PVC	25	Dichloromethane/methanol	91.1
Model	PVC	40	Dichloromethane/methanol	98.2
Model	PVC	25	Toluene/methanol	94.1
Model	PVC	50	Toluene/methanol	94.6
Model	PET	180	Benzyl alcohol/methanol	99.0

very recently it has been proposed the use of more environmental-friendly solvents for the recovery of EPS. As such, D-limonene extracted from natural resources (rinds of citrus fruits), has been used with excellent results concerning recovery and polymer properties [24, 25]. Therefore, this solvent was also tested in this investigation for the recovery of EPS. The advantages of using D-limonene besides its natural origin include employment of a low dissolution temperature (ambient conditions), high solubility (almost equal to toluene) need of a low dissolution time (a 5 wt.−% EPS can be dissolved in only 10 min) and high selectivity. As it can be seen in Table 1 the polymer recovery with this solvent was approaching the theoretical value. Recently, this solvent has been also used by Garcia et al. [26] providing excellent results with properties of the polymer recovered similar to the original. In this case use of a non-solvent is not needed, since the solvent can be further removed by vacuum distillation.

Concerning recovery of PVC, two solvents at two dissolution temperatures were employed and results are included in Table 1. It was found that the system dichloromethane/methanol gave excellent recoveries at relative low temperatures (40 °C) and this was further used. Finally, for PET only the system benzyl alcohol/methanol was investigated, which resulted in high recovery values but at a relatively high dissolution temperature (i.e. 180 °C).

Recycling of polymers from waste packaging

Food packaging

Eleven different waste packaging products were investigated based on LDPE, HDPE, PP, PS, EPS, PVC and PET. The experimental conditions used and the percentage of polymer recovery appear in Table 2. Using the optimum conditions found in the previous section, it was observed that at all different experimental conditions and for most of the samples examined the polymer recovery was always high and greater than 95%. The rather low temperature used for PVC resulted in a rather low recovery. Higher temperature values for the dissolution of PVC were avoided due to possible polymer degradation and release of toxic degradation products. However, this rather low recovery of the polymer could be also attributed to additives (i.e. plasticizers, etc.) present in the waste packaging which were removed during the recycling procedure. Moreover, concerning the packaging for frozen meat made of EPS it was observed that the polymer recovery using the toluene/*n*-hexane system was clearly lower than that with the D-Limonene, meaning the latter to be a more effective solvent. However, this could not be considered as a rule since for another similar product (single-use glass) almost the same recoveries were measured.

Pharmaceutical packaging

Seven commercial waste packaging products were tested in this category based on LDPE, HDPE, PP and PVC. The percentage of polymer recovery from these pharmaceutical products appears in Table 3. Different types of solvent and

Table 2 Experimental conditions and polymer recovery (wt.−%) from different food packaging polymeric materials by the dissolution/reprecipitation technique

Sample	Polymer	*T* (°C)	Solvent/non-solvent	Recovery
Bag (general use)	LDPE	100	Xylene/*n*-hexane	99.0
Packaging film	LDPE	100	Xylene/*n*-hexane	98.6
Food bag	HDPE	100	Xylene/*n*-hexane	98.3
Bottle	PP	140	Xylene/*n*-hexane	98.9
Cup	PP	140	Xylene/*n*-hexane	99.0
Single-use glass	PP	140	Xylene/*n*-hexane	95.3
Yoghurt bowl	PP	140	Xylene/*n*-hexane	95.7
Yoghurt bowl	PS	50	Xylene/methanol	97.7
Packaging for frozen meat	EPS	50	Xylene/methanol	95.4
Packaging for frozen meat	EPS	25	D-limonene	99.1
Single-use glass	EPS	50	Xylene/methanol	99.3
Single-use glass	EPS	25	D-limonene	99.4
Membrane	PVC	40	Dichloromethane/methanol	82.7
Soft drink bottle	PET	180	Benzyl alcohol/methanol	99.1

Table 3 Polymer recovery (wt.−%) by the dissolution/reprecipitation technique from different pharmaceutical packaging polymeric materials

Sample	Polymer	*T* (°C)	Solvent/non-solvent	Recovery
Bag for pills	LDPE	100	Xylene/methanol	77.2
Syringe cover	HDPE	100	Xylene/methanol	95.0
Bottle for pills	HDPE	100	Xylene/methanol	87.0
Bottle for the liquid of eye lenses	HDPE	100	Xylene/methanol	80.7
Syringe	PP	140	Xylene/methanol	83.7
Blister pack for pills	PVC	40	Dichloromethane/methanol	63.1
Bottle for pills	PVC	40	Dichloromethane/methanol	90.5

temperatures were used depending on polymer type according to the experimental conditions presented earlier. In this packaging category, the amount of polymer recovered was not high enough in some samples, meaning the existence of additives and insoluble contaminants in the packaging product. This was also verified from the FT-IR spectra of the commercial product compared to the model polymer. Again the sample based on PVC gave the lower recovery values.

Detergent packaging

The percentage of polymer recovery from several commercial waste detergent packaging products and model polymers appears in Table 4. As it can be seen almost the same type of polymers are also used. Different types of solvent and temperatures were used depending on polymer type. Again, the existence of several

Table 4 Polymer recovery (wt.−%) by the dissolution/reprecipitation technique from different detergent packaging polymeric materials

Sample	Polymer	*T* (°C)	Solvent/non-solvent	Recovery
D1 (Viakal)	HDPE	100	Xylene/methanol	79.0
D2 (Soflan)	HDPE	100	Xylene/methanol	81.8
D3 (Karpex)	HDPE	100	Xylene/methanol	90.0
D4 (Overlay)	PVC	40	Dichloromethane/methanol	98.1
D5 (Merito)	PP	140	Xylene/methanol	95.3
D6 (Harpic)	HDPE	100	Xylene/methanol	85.0
D7 (Bref power)	PET	180	Benzyl alcohol/methanol	99.0

additives in the plastic packaging material, lead to a not-so-high polymer recovery in some cases, particularly in the HDPE based bottles.

Properties of the recycled polymers

Chemical structure

The possible changes in the chemical structure of recycled polymers from waste products were studied by FTIR measurements. Figure 2 shows the FTIR spectra of different waste products before and after recycling. Indicative results are presented for HDPE, PET, PVC and PS. As it can be seen all characteristic bands in each polymer type did not change significantly. The differences between peak heights can be a consequence of the somewhat different weight of the samples.

Thermal properties

Thermal properties of the model polymers and waste plastic packaging samples were measured using DSC. The melting temperature and heat of fusion of the samples based on polyolefins (LDPE, HDPE and PP) appear in Table 5. Indicative DSC thermograms for waste packaging based on HDPE, LDPE and PP appear in Fig. 3. The melting point of samples based on PP ranged between 160 and 166 °C and after recycling they either remained unchanged or reduced at most 2.5%. The corresponding melting point of samples based on LDPE ranged between 115 °C and 120 °C and again after recycling they reduced by almost the same percentage (i.e. 2.5%). For the samples based on HDPE the original melting point ranged between 129 °C and 140 °C and they again reduced during recycling by at most 3%. From all these results, it could be concluded that the melting points practically remained unchanged by the recycling procedure. Furthermore, concerning the heat of fusion (ΔH) measured it was observed that in most of the investigated specimens it slightly increases after the recycling, according to literature findings [16–18]. More specifically, in the HDPE based samples a great increase was measured, while a slight decrease was only observed in the syringe made from PP. Furthermore, crystallinity of the samples was calculated by dividing these ΔH values by the heat

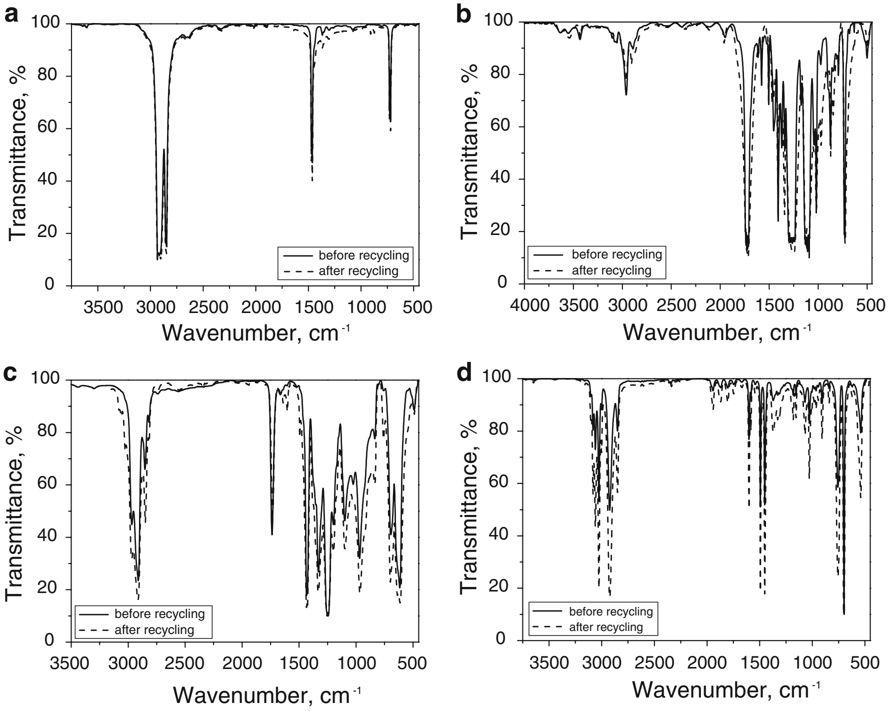


Fig. 2 Comparative FT-IR spectra of waste packaging material before and after recycling **a** waste detergent packaging (D6) based on HDPE, **b** waste detergent packaging (D7) based on PET, **c** waste pharmaceutical packaging (bottle for pills) based on PVC and **d** waste food packaging (plastic yoghurt bowl) based on PS

of fusion of the perfectly crystalline polymer, taken equal to 213.31 and 270.25 J/g for PP and PE, respectively and results are listed in the last two columns of Table 5. Crystallinity of original samples based on LDPE, HDPE and PP ranged in between 29–42, 44–61 and 25–35%, respectively. After the recycling procedure these values increased to 31–43, 50–69 and 27–33% for LDPE, HDPE and PP, respectively. Therefore, it seems that the crystallinity of samples based on LDPE and PP slightly increases after recycling, while a larger variation is observed for the products based on HDPE. According to Papaspyrides et al. [16], this might be attributed to the fact that during the recycling process the polymer is precipitated from the solution under very mild conditions in terms of cooling, which means that the recycling process itself serves as a kind of an annealing treatment.

For the samples based on PS, PVC and PET the glass transition temperature was measured using DSC. Results on T_g measurements before and after the recycling procedure appear in Table 6. An increase in the T_g values was observed for the waste packaging samples based on PVC, which was attributed to the removal, during the recycling process of any kind of additives (i.e. plasticizer, etc.) present in the commercial products. In contrast, for all other samples based on PS, or PET a

Table 5 Melting temperature, T_m, heat of fusion, ΔH and crystallinity of waste plastic packaging materials and model polymers measured before and after the recycling procedure

Sample	Polymer	T_m (°C)		ΔH (J/g)		Crystallinity (%)	
		Original	After recycling	Original	After recycling	Original	After recycling
Wastes from food packaging							
Bag	LDPE	115	113	78	85	28.9	31.5
Food bag	HDPE	129	128	121	134	44.8	49.6
Cup	PP	163	163	66	68	30.9	31.9
Wastes from pharmaceutical packaging							
Syringe	PP	165	163	74	71	34.7	33.3
Bottle for eye lenses liquid	HDPE	131	129	153	164	56.6	60.7
Bag for pills	LDPE	120	117	113	116	41.8	42.9
Wastes from detergent packaging							
D3	HDPE	135	134	165	187	61.1	69.2
D5	PP	160	158	53	58	24.8	27.2
Model polymers							
	LDPE	120	118	92	95	34.0	35.1
	HDPE	140	135	118	151	43.7	55.9
	PP	166	163	62	69	29.1	32.3

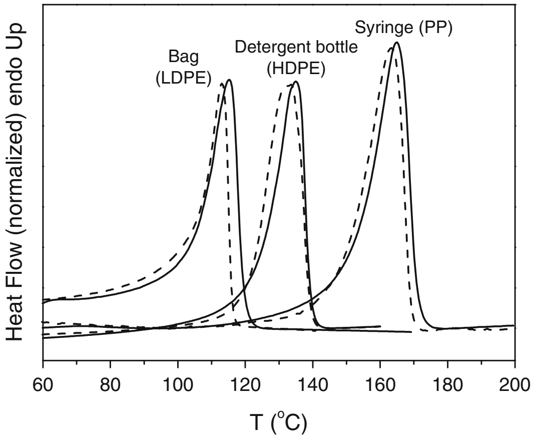


Fig. 3 DSC thermograms of waste plastic packaging before and after recycling based on *LDPE* (bag), *HDPE* (detergent bottle) and *PP* (syringe)

slight decrease was obvious, which in fact was also the case in the model PVC. This might be due to small-scale chain degradation during the dissolution/reprecipitation, but it should be further checked. Therefore, the molecular properties of these samples were further examined.

Table 6 Glass transition temperature of waste plastic packaging materials and model polymers measured before and after the recycling procedure

Sample	Polymer	T_g (°C)	
		Original	After recycling
Wastes from food packaging			
Packaging for frozen meat	EPS	102	99
Yoghurt bowl	PS	99	97
Single-use glass	EPS	101	99
Wastes from pharmaceutical packaging			
Bottle for pills	PVC	82	86
Blister pack	PVC	84	85
Wastes from detergent packaging			
D7	PET	76	74
D4	PVC	80	85
Model polymers			
	PS	100	99
	PET	76	75
	PVC	87	86

Molecular properties

The average molecular weight of the original samples and the polymers recovered after the recycling procedure was obtained using viscosimetry. Intrinsic viscosity was measured in each case, which provided the viscosity average molecular weight for samples based on PS and PVC and the number average molecular weight for PET. The values for all samples before and after recycling are illustrated in Table 7. It can be observed that the average molecular weight of almost all samples, slightly decreased after the recycling procedure, probably due to the beginning of chain degradation. Therefore, it seems that slight polymer thermal degradation occurs even at the soft heating employed and it may be stated that although temperatures above 50 °C facilitate solubility they should be avoided due to possible degradation of polymer chains. A slight decrease in the polymer average molecular weight after this recycling technique has been also observed in literature [26].

Tensile mechanical properties

In advance, the tensile mechanical properties of the waste plastic packaging before and after recycling were investigated. Results from tensile breaking measurements for pharmaceutical and detergent packaging based on HDPE and PP are presented in Tables 8 and 9, respectively. For HDPE based samples, the data suggest that the recycled grades (from either pharmaceutical or detergent packaging products) exhibit break strength and tensile stress at yield measurements competent to those of the virgin polymers, while the elongation at break levels are slightly lower. Even

Table 7 Average molecular weight of waste plastic packaging materials and model polymers measured before and after the recycling procedure

Sample	Polymer	Average molecular weight[a]	
		Original	After recycling
Wastes from food packaging			
Packaging for frozen meat	EPS	2.25×10^5	2.20×10^5
Yoghurt bowl	PS	1.83×10^5	1.60×10^5
Single-use glass	EPS	2.74×10^5	2.70×10^5
Wastes from pharmaceutical packaging			
Bottle for pills	PVC	31,870	31,090
Blister pack	PVC	30,320	27,880
Wastes from detergent packaging			
D7	PET	17,830	16,330
D4	PVC	32,920	31,550
Model			
	PS	2.33×10^5	2.30×10^5
	PET	17,080	16,360
	PVC	33,400	31,730

[a] All values refer to viscosity average molecular weight except for PET which is number average molecular weight

more, there is a clear indication that after recycling the elastic modulus increases possibly due to the influence of the fractionation phenomena encountered during the dissolution/reprecipitation process (i.e. some lower molecular weight fractions may remain soluble in the solvent/non-solvent phase), as well as to the role of the additives initially contained in the starting material [16–18]. The same results for the tensile stress at yield and elongation at break hold also for the PP based materials (Table 9). Even more, the break strength showed a clear tendency to increase after recycling, which was also the case for the elastic modulus in the detergent packaging material. However, the elastic modulus of the pharmaceutical product (i.e. of a syringe) exhibited slightly lower values after recycling. In general, the same trends were also observed in literature, as well as in a previous publication

Table 8 Tensile mechanical properties of waste pharmaceutical and detergent plastic packaging based on HDPE before and after the recycling technique

	Waste pharmaceutical sample (bottle for eye lenses liquid)		Waste detergent sample (D3)	
	Before recycling	After recycling	Before recycling	After recycling
Elastic modulus (MPa)	608 ± 23	640 ± 32	609 ± 27	641 ± 32
Tensile stress at yield (MPa)	15.1 ± 0.3	15.1 ± 0.4	15.5 ± 0.6	15.7 ± 0.7
Elongation at break (%)	658 ± 28	606 ± 22	705 ± 34	669 ± 29
Break strength (MPa)	21.5 ± 1.7	21.7 ± 1.3	21.9 ± 1.3	22.2 ± 1.6

Table 9 Tensile mechanical properties of waste pharmaceutical and detergent plastic packaging based on PP before and after the recycling technique

	Waste pharmaceutical sample (syringe)		Waste detergent sample (D5)	
	Before recycling	After recycling	Before recycling	After recycling
Elastic modulus (MPa)	537 ± 14	505 ± 12	467 ± 15	518 ± 12
Tensile stress at yield (MPa)	20.8 ± 0.6	20.4 ± 0.5	13.0 ± 0.7	13.9 ± 0.4
Elongation at break (%)	521 ± 24	498 ± 21	511 ± 23	502 ± 19
Break strength (MPa)	18.9 ± 1.4	20.9 ± 1.2	20.6 ± 1.7	21.8 ± 1.6

Table 10 Tensile mechanical properties of waste pharmaceutical and detergent plastic packaging based on PVC before and after the recycling technique

	Waste pharmaceutical sample (bottle for pills)		Waste detergent sample (D4)	
	Before recycling	After recycling	Before recycling	After recycling
Elastic modulus (MPa)	1601 ± 34	1845 ± 31	1977 ± 35	1969 ± 32
Break strength (MPa)	36.3 ± 2.1	39.2 ± 2.2	36.1 ± 1.9	33.8 ± 1.6

from our group during recycling of waste food packaging materials and model polymers based on LDPE, PP and HDPE [12, 13, 16–18].

Finally, during recycling of PVC based packaging products, similar results (i.e. an in increase in the elastic modulus and break strength) were observed when pharmaceutical products were investigated, while from the detergent bottle both measurements were slightly lower after recycling (Table 10). The first observation could be probably attributed to the removal of any plasticizer included in the original waste product.

Conclusions

In this investigation the dissolution/reprecipitation technique was used as an effective process in recycling waste plastic packaging material. A number of materials were investigated used in food, pharmaceutical and detergent packaging. The polymers identified and investigated were LDPE, HDPE, PP, PS, PVC and PET. The proper experimental conditions (including type of solvent/non solvent, polymer concentration, dissolution temperature) were selected on the basis of the corresponding model polymers. Very good polymer recoveries were obtained in almost all waste samples examined, while lower values in some samples were attributed to the removal of additives present in the original waste products. From FTIR measurements it was revealed that the chemical structure was not significantly altered. Also the process did not seem to modify much the thermal, molecular and mechanical properties of the polymers recovered. However, slight chain degradation was observed in some cases. It could be postulated that the method could be beneficial in waste packaging recycling program.

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